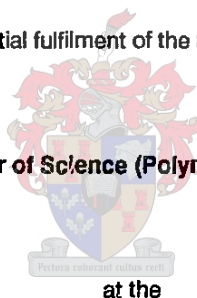# POLYMER SYNTHESIS FROM 3-METHYLBUTENE-1

BY

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Dr. R. D. Sanderson   October 1993

DECLARATION

I, the undersigned hereby declare that the work contained in this thesis is my own original work and has not in its entirety or in part been submitted at any university as a degree.

29/11/93

Date

ABSTRACT

Two homopolymers of 3−methylbutene−1 were synthesized with different cocatalyst/catalyst ratios of the Ziegler-Natta catalyst system. The 3−methylbutene−1 homopolymers were characterized as fully as possible. The stereoregularity of poly(3−methylbutene−1) was determined with three different methods. The thermal and thermo-oxidative stabilities of poly(3−methylbutene−1) were determined by differential scanning calorimetry. A method of stabilizing poly(3−methylbutene−1) with the assistance of an antistatic agent was studied.

Two vinyltrimethylsilane homopolymers were synthesized with a Ziegler-Natta catalyst system and characterized.

A series of 3−methylbutene−1-vinyltrimethylsilane copolymers were synthesized. A correlation was attempted between the amount of vinyltrimethylsilane comonomer incorporated into the copolymer and the properties of the copolymers. All the synthesized copolymers were characterized as fully as possible. The silicon content of the copolymers were determined by elemental analysis and the proton-induced gamma emission technique to give the amount of vinyltrimethylsilane comonomer incorporated into the various copolymers. The monomer reactivity ratios of the copolymers were calculated by the Fineman-Ross method and refined with the Tidwell-Mortimer method.

It was shown that poly(3−methylbutene−1) was a high-melting, highly isotactic, and highly insoluble polymer. Poly(3−methylbutene−1) had a high thermal stability in the absence of air, but a low thermo-oxidative stability in the presence of air. Poly(3−methylbutene−1) could be stabilized with the aid of an antistatic agent, Dehydat 51 Special, and this method also proved to be a way of solubilizing poly(3−methylbutene−1).

Poly(vinyltrimethylsilane) is a very high-melting polymer.

The melting point of poly(3−methylbutene−1) decreased by copolymerization of the compound with vinyltrimethylsilane, but the decrease was not as great as was expected. The isotacticity of poly(3−methylbutene−1) was also lowered through copolymerization with vinyltrimethylsilane. The measuring of the amount of silicon present in the various copolymers with elemental analysis techniques indicated that a small percentage of vinyltrimethylsilane was actually incorporated into the copolymers, although large amounts of it were added to the comonomer feed. The calculation of the monomer reactivity ratios of the copolymers showed that vinyltrimethylsilane had a very low reactivity ratio, namely, 0, compared with that of 3−methylbutene−1, which was on average 19,6.

OPSOMMING

Twee homopolimere van 3-metielbuteen-1 is gesintetiseer met verskillende ko-katalis/katalis verhoudinge van die Ziegler-Natta katalis sisteem. Die 3-metielbuteen-1 homopolimere is so volledig moontlik gekarakteriseer. Die stereoregulariteit van poli(3-metielbuteen-1) is met drie verskillende metodes bepaal. Die termiese en termo-oksidatiewe stabiliteit van poli(3-metielbuteen-1) is bepaal met differensiële skandeer kalorimetrie. 'n Metode om poli(3-metielbuteen-1) te stabiliseer met die hulp van 'n antistatiese middel is bestudeer.

Twee vinieltrimetielsilaan homopolimere is gesintetiseer met 'n Ziegler-Natta katalis sisteem en gekarakteriseer.

'n Reeks 3-metielbuteen-1-vinieltrimetielsilaan kopolimere is gesintetiseer. 'n Poging is aangewend om 'n korrelasie tussen die hoeveelheid vinieltrimetielsilaan komonomeer en die eienskappe van die kopolimere te verkry. Al die gesintetiseerde kopolimere is so volledig as moontlik gekarakteriseer. Die silikon inhoud van die kopolimere is bepaal met 'n element analise metode en die proton-geïnduseerde gamma emissie tegniek om die hoeveelheid vinieltrimetielsilaan komonomeer geïnkorporeer in die verskillende kopolimere te gee. Die monomeer reaktiwiteitsverhoudinge van die kopolimere is bepaal met die Fineman-Ross metode en verfyn met die Tidwell-Mortimer metode.

Daar is getoon dat poli(3-metielbuteen-1) 'n hoë smeltpunt, hoë isotaktisiteit, en hoë onoplosbaarheid besit. Poli(3-metielbuteen-1) besit 'n hoë termiese stabiliteit in die afwesigheid van lug, maar 'n lae termo-oksidatiewe stabiliteit in die teenwoordigheid van lug. Poli(3-metielbuteen-1) kan gestabiliseer word met die hulp van 'n antistatiese middel, Dehydat 51 Special, en hierdie metode is ook bewys as 'n manier om poli(3-metielbuteen-1) op te los.

Poli(vinieltrimetielsilaan) is 'n polimeer met 'n baie hoë smeltpunt.

Die smeltpunt van poli(3-metielbuteen-1) is verlaag deur kopolimerisasie met vinieltrimetielsilaan, maar nie soveel as wat verwag is nie. Die isotaktisiteit van poli(3-metielbuteen-1) is ook verlaag deur kopolimerisasie met vinieltrimetielsilaan. Die hoeveelheid silikon teenwoordig in die verskillende kopolimere het getoon dat slegs 'n klein persentasie van die vinieltrimetielsilaan in die kopolimere geïnkorporeer is, alhoewel groot hoeveelhede daarvan by die komonomeer voer gevoeg is. Die berekening van die monomeer reaktiwiteitsverhoudinge van die kopolimere het getoon dat vinieltrimetielsilaan 'n baie lae reaktiwiteitsverhouding besit, 0, in vergelyking met die reaktiwiteitsverhouding van 3-metielbuteen-1, wat gemiddeld 19,6 is.

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CHAPTER 1

INTRODUCTION AND OBJECTIVES

1.1 GENERAL REVIEW

Isotactic poly(3-methylbutene-1) has been known for a long time to be a high-melting point (about 310 °C), heat-resistant polyolefin, but as yet there are only a few examples of its use as an industrial material **(1-4)**.

The main reasons for the limited industrial applications of isotactic poly(3 – methylbutene – 1) are:

1. The low processability of the polymer because of its high melting point.

2. The poor oxidative stability of the polymer; thermal destruction of the polymer starts only at 300 °C, whereas thermal oxidative destruction of the polymer starts at below 100 °C.

3. The brittleness of the polymer.

This study concerns the synthesis of poly(3 – methylbutene – 1) with improved processability, which may be achieved through copolymerization with an alpha-olefin. The choice of a similar comonomer was limited by a few factors:

1. The comonomer should be compatible with Ziegler-Natta catalysts. It is important that it will not deactivate the catalyst or cause any side reactions.

2. The comonomer should have more or less the same reactivity as 3 – methylbutene – 1 to produce a random copolymer with less perfect crystalline regions relative to the homopolymer and, therefore, a lower melting point than poly(3-methylbutene-1).

Vinyltrimethylsilane was chosen as comonomer, as it has a low reactivity and the silicon atom enabled the amount of incorporation of the comonomer into the 3 – methylbutene – 1 copolymer to be determined.

1.2 OBJECTIVES

The main purpose of this work was to synthesize and characterize a 3 – methylbutene – 1 copolymer with improved processability, that is, a copolymer with a lower melting point than poly(3-methylbutene-1).

In order to achieve this, a study was made of the following:

1) A theoretical study of the homopolymerization of 3 – methylbutene – 1 concerning:
    1.1) Ziegler-Natta polymerization (anionic coordination) polymerization with organometallic catalysts to yield an isotactic homopolymer.

1.2)   Isomerization polymerization (cationic polymerization) with Lewis bases to yield an atactic homopolymer.

2)   The synthesis of isotactic poly(3 – methylbutene – 1) with a Ziegler-Natta catalyst.

3)   The characterization of poly(3 – methylbutene – 1):
   3.1)   Chemical structure identification.
   3.2)   Melting point.
   3.3)   Stereoregularity.
   3.4)   Temperature of the onset of thermal and thermo-oxidative destruction, respectively.
   3.5)   Thermo-oxidative stabilization.

4)   The synthesis of poly(vinyltrimethylsilane) with a Ziegler-Natta catalyst.

5)   The characterization of the vinyltrimethylsilane homopolymer:
   5.1)   Chemical structure identification.
   5.2)   Melting point.

6)   The synthesis of various 3 – methylbutene – 1-vinyltrimethylsilane copolymers with a Ziegler-Natta catalyst.

7)   The characterization of the 3 – methylbutene – 1-vinyltrimethylsilane copolymers:
   7.1)   Chemical structure Identification.
   7.2)   Melting points.
   7.3)   Stereoregularity.
   7.4)   Amount of vinyltrimethylsilane incorporated into the copolymer.
   7.5)   Determination of the reactivity ratios of the two comonomers.

CHAPTER 2

HISTORICAL AND THEORETICAL BACKGROUND

2.1   3-METHYLBUTENE-1

3-Methylbutene-1 is classified as an alpha-olefin; olefins are aliphatic hydrocarbons containing at least one carbon-carbon double bond. The name olefin is derived from the property of these compounds to form oily liquids on reactions with halogens (*gaz oléfiant*, oil-forming gas). The industrial importance of olefins started in the 1950s when the lower olefins became widely available from thermal cracking of wet natural gas and petroleum fractions, displacing ethyne as the dominant commodity chemical.

The importance of alpha-olefins lies in their ability to form chains with asymmetric carbons. By an appropriate choice of a Ziegler-Natta catalyst system, polymers of various degrees of isotacticity can be synthesized.

2.1.1   SYNTHESIS

3-Methylbutene-1 is available as a byproduct from commercial processes such as the refining of petroleum products and as a product of the thermal cracking of hydrocarbons.

Phillips Petroleum Co. developed a chemical process for making the speciality olefin 3-methylbutene-1 **(5)**, used mainly in the synthesis of pyrethroids. The Phillips process involves the catalytic dehydration of 3-methylbutanol-1 using a high surface area, base-treated gamma-alumina (See **Figure 1**). 3-Methylbutene-1 can also be synthesized by the dehydrobromination of 1-bromo-3-methylbutane with alcoholic potassium hydroxide.
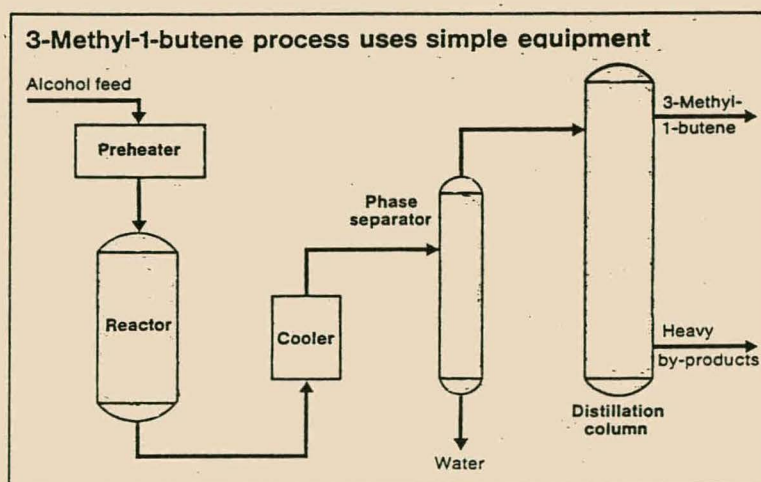
FIGURE 1. The Phillips Petroleum process (5).

3–Methylbutene–1 is produced in pilot plant quantities by Shell from their isoprene by-product streams in the Netherlands. Kararay in Japan uses a process which involves butene and formaldehyde to produce the monomer.

2.1.2   PROPERTIES

3-Methylbutene-1 is a gas at ambient temperature and pressure; boiling point is 20,061 °C (760 mm Hg). It is highly combustible and can form explosive mixtures with air. 3-Methylbutene-1 is highly reactive from a chemical point of view, as the double bond provides the reactive site for catalytic activation and numerous radical reactions. Peroxides are readily formed when 3-methylbutene is exposed to air and they must be removed before polymerization, especially when Ziegler-Natta catalysts are used. (See **Table I** for a summary of the properties of 3–methylbutene–1.)

TABLE I: Properties of 3-methylbutene-1

PHYSICAL DESCRIPTION	Colourless, toxic, flammable gas
HEALTH HAZARDS	Highly toxic and irritating - eye contact, inhalation, skin irritaion and ingestion
BOILING POINT @ 760 mm Hg	20,061 °C
MELTING POINT	-168,49 °C
DENSITY, LIQUID, 20 °C	0,6272 g/ml

2.1.3   MONOMER REACTIVITY

The attachment of a substituent to the double bond in the higher alpha-olefins alters the reactivity of the metal-carbon bond at the Ziegler-Natta centre. A large change in activity occurs when the pendant group is branched. Monomer reactivity decreases notably as the branching site in the pendant group (R in $CH_2 = CHR$) moves closer to the double bond **(6)**, for example, branching at carbons number 3 and 4, and as the size of the alkyl substituent increases. Thus, 3–methylbutene–1 has a very low reactivity, as it contains branching at carbon number 3 and the alkyl substituent is bulky. (See **Figure 2.**)

$$CH_2 = CH$$
$$|$$
$$CH - CH_3$$
$$|$$
$$CH_3$$
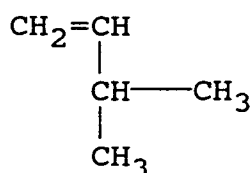
FIGURE 2. 3-Methylbutene-1

2.1.4   USES

3-Methylbutene-1 is used in organic synthesis and in the manufacture of high-octane fuel. It is also used as a raw material for making polymer gasoline, which consists of hydrogenated dimers, with solid phosphoric acid **(7)**.

2.2   HOMOPOLYMERIZATION OF 3 – METHYLBUTENE – 1

3-Methylbutene-1 can be polymerized readily with alkyl metal coordination catalysts of the Ziegler-Natta type **(8)** at ambient temperatures. The product obtained by this process is a highly crystalline isotactic polymer and has conventional 1,2 head-to-tail structure:

$$(-CH_2-CH-)_n$$
$$|$$
$$CH-CH_3$$
$$|$$
$$CH_3$$
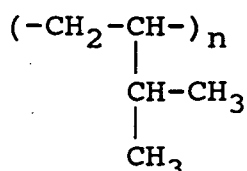
The cationic polymerization of 3-methylbutene-1 at low temperatures has been shown by Kennedy *et al.* **(8)** to yield a product having a structure fundamentally different from that of the vinyl addition polymer obtained with Ziegler-Natta catalysts. NMR data **(9)** indicate that the polymer consists predominantly of repeating units :

$$CH_3$$
$$|$$
$$(-CH_2-CH_2-C-)_n$$
$$|$$
$$CH_3$$
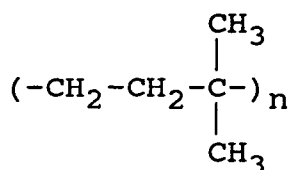
When 3-methylbutene-1 is polymerized with strong Lewis acid catalyst at -130 °C, a crystalline polymer is obtained. This crystalline product is not isotactic.

2.2.1   CATIONIC HOMOPOLYMERIZATION

3-Methylbutene-1 was first polymerized cationically in 1927 by Norris and Joubert **(10)**, who thought that they had obtained dimers and higher polymers with a sulfuric acid catalyst. In 1934 Leendertse *et al.* **(11)** treated the monomer with aluminium chloride at -80 °C, but only oily products were formed, presumably because reaction conditions were unfavorable (solid $AlCl_3$ in bulk). Webb **(12)** mentioned the polymerizability of 3-methylbutene-1 with boron trifluoride in 1937. Thomas and Reynolds **(13)** patented the preparation of poly(3-methylbutene-1) in 1945, using Lewis acid-type catalysts in alkyl chloride diluent at low temperatures (-78 °C). The product they obtained was a colourless, amorphous, tough, semi-solid material with a rather low molecular mass.

2.2.1.1   *INTRAMOLECULAR HYDRIDE SHIFT POLYMERIZATION BY CATIONIC MECHANISM*

The low-temperature cationic polymerization of 3-methylbutene-1 proceeds by an intramolecular hydride-shift mechanism **(8)**. The secondary carbonium ion which is formed by direct interaction between monomer and cationic catalyst during initiation, rearranges to an energetically more favoured

tertiary carbonium ion before it reacts with the next monomer unit in the propagation step as shown below:

Initiation:

$$A^+ \; + \; \underset{\underset{CH_3}{\overset{|}{\underset{|}{CH-CH_3}}}}{\overset{}{CH_2{=}CH}} \qquad \longrightarrow \qquad \underset{\underset{CH_3}{\overset{|}{\underset{|}{CH-CH_3}}}}{\overset{}{A{-}CH_2{-}CH^+}}$$

1,2 Hydride shift:

$$\underset{\underset{CH_3}{\overset{|}{\underset{|}{CH-CH_3}}}}{\overset{}{A{-}CH_2{-}CH^+}} \qquad \longleftrightarrow \qquad \underset{\underset{CH_3}{\overset{|}{\underset{|}{{}^+C{-}CH_3}}}}{\overset{}{A{-}CH_2{-}CH_2}}$$

Propagation:

$$\underset{\underset{CH_3}{\overset{\overset{CH_3}{|}}{\underset{|}{A{-}CH_2{-}CH_2{-}C^+}}}}{} \; + \; \underset{\underset{CH_3}{\overset{\overset{CH_3}{|}}{\underset{|}{CH_2{=}CH}}}}{\underset{CH-CH_3}{}} \qquad \longrightarrow \qquad \underset{}{A{-}CH_2{-}CH_2{-}\overset{\overset{CH_3}{|}}{\underset{\underset{}{CH_3}}{C}}{-}CH_2{-}\overset{}{C^+}}$$
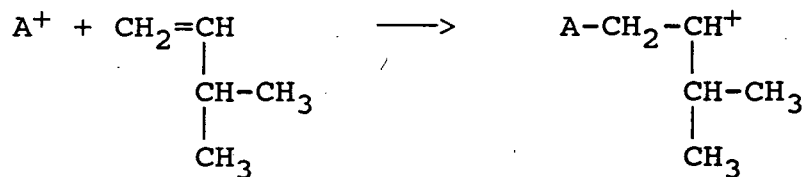
etc.   < ———————— 1,2 hydride shift ————————
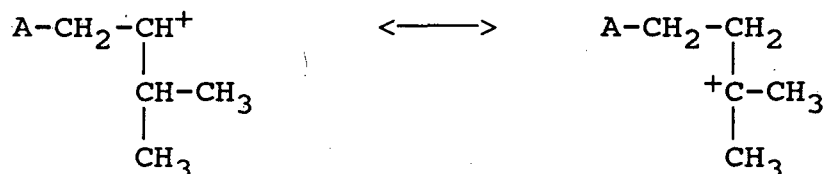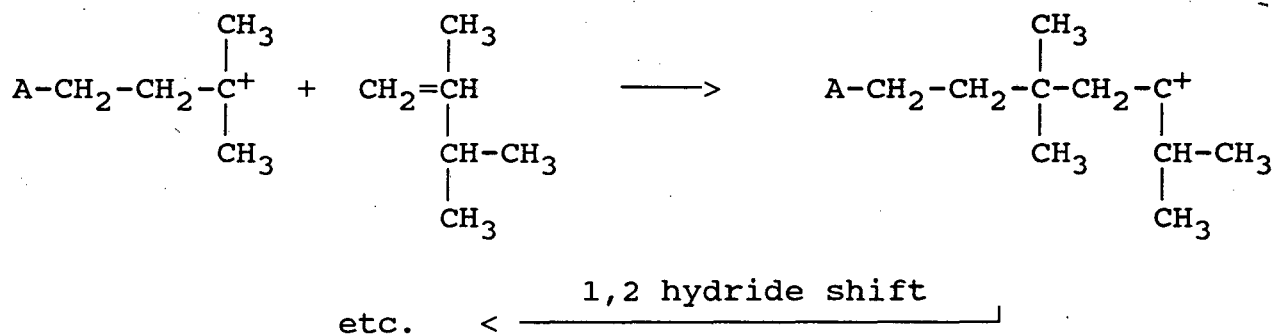
Termination and chain breaking are achieved by conventional cationic mechanisms.

Polymerization at -130 °C produces a crystalline polymer with almost exclusively the 1,1'-dimethylpropane-type 1,3 structure. However, polymerizations at temperatures above -100 °C produces a rubbery polymer which is a mixture of about 30% conventional 1,2 head-to-tail enchainment and 70% 1,3 polymer. The exact nature of the mixture (i.e., block copolymer, physical mixture, etc.) is unknown.

The characterization of cationic poly(3 – methylbutene – 1) is discussed in **Appendix A**.

2.2.2   ZIEGLER-NATTA HOMOPOLYMERIZATION

The Ziegler-Natta catalysts originated from a combination of brilliant science and coincidence in the laboratories of Karl Ziegler **(16, 17)** in the early 1950s. Ziegler discovered that certain combinations of transition metal compounds and organometallic compounds polymerize ethylene at low temperatures and pressures to give polyethylene that has an essentially linear structure.

Guilo Natta **(18, 19)** and co-workers subsequently found that with some of these catalysts, alpha-olefins could, for the first time, be polymerized to stereoregular, crystalline polymers of high molecular mass.

The range of catalysts has since been extended enormously, including both soluble (homogeneous) and insoluble (heterogeneous) catalysts, capable of polymerizing a number of monomers, including those derived from dienes and cycloalkanes. Many of these polymers are now manufactured on a commercial scale.

2.2.2.1   ZIEGLER-NATTA CATALYSTS

Definition of a catalyst: chemical substance that exerts its influence throughout the growth of the chain. A catalyst is also an agent helping to start, maintain and regulate polymerization reactions.

Definition of a Ziegler-Natta catalyst: combination of a transition metal compound, more commonly a halide of an element of groups IV to VIII, such as Ti, V, Cr, *etc.*, and an organometallic compound of a metal from groups I to III, such as reactive metal alkyl, aryl or hydride, from the Periodic Table. The active centre of the catalyst is the transition metal-carbon bond. The transition metal compound is known as the catalyst and the organometallic compound as the cocatalyst. The polymerization reactions are normally carried out in an inert solvent, for example heptane or toluene, under inert conditions, but gas phase reactions are gaining importance.

The organometallic cocatalyst, has the following functions:
- (1)   Alkylates the transition metal compound (site-former).
- (2)   Acts as a transfer agent.
- (3)   Removes the impurities from the reaction medium, acting as a poison scavenger.
- (4)   Reduces the transition metal compound to lower valences.
- (5)   In a supported catalyst system, complexes the electron donors.

Catalysts are usually prepared by mixing the components in a dry, inert solvent at low temperatures and in the absence of oxygen. The catalysts are characterized by having high reactivity towards many nonpolar monomers and are capable of giving polymers with a high degree of stereoregularity. Catalyst activity changes with time, and it is not unusual for maximum activity to be reached after ageing for periods of up to 2 h.

For a given catalyst system, when the activity increases, the control of the stereoregularity of the polymer decreases and *vice versa*. The activity of the catalyst is increased by changing the reaction conditions and the control of the stereoregularity of the polymer is increased by the addition of a third component, such as an electron donor.

A significant key to these catalysts is the observation that systems of different composition produce polymers of widely different structures. The ratio of metal-to-metal from Groups I-III and the valency of the transition metal can affect the rate of polymerization as well as yield, molecular mass and stereoregularity of the polymer. It is therefore possible to vary the molecular mass by changing the catalyst ratio. The Ziegler-Natta catalysts produce polymers with a broad molecular mass distribution, because of the different types of active centres on the catalyst. The molecular mass distribution can

be varied by changes in the catalyst composition and the process conditions. Other additives, for example, electron donors such as amines, also affect the polymerization process and products.

Ziegler-Natta and related catalysts are of four general types: (i) heterogeneous Ziegler-Natta catalysts; (ii) homogeneous Ziegler-Natta catalysts; (iii) modified Ziegler-Natta catalysts; and (iv) transition-metal alkyl catalysts.

2.2.2.1.1 Heterogeneous Ziegler-Natta catalysts

2.2.2.1.1.1   Non-supported heterogeneous catalysts

FIRST GENERATION TITANIUM TRICHLORIDE CATALYSTS

The first generation titanium trichloride catalytic systems consist of preformed solid titanium trichloride, alpha-, gamma-, or delta-form, and an organometallic compound of a metal from Group IA or IIIA in the Periodic Table, for example Li, Be, or Al, in an inert reaction medium. The preformed insoluble titanium trichloride catalysts produce higher yields of isotactic polypropylene than soluble titanium halide catalysts do (20).

The activity and stereospecificity of these catalysts also depend on the type of aluminium alkyl compound used as cocatalyst. Use of triethylaluminium (TEA) gives a much higher activity but much lower stereospecificity, and for this reason diethylaluminiumchloride (DEAC) is used for the polymerization of propylene and other alpha-olefins, while a trialkylaluminium, for example triethylaluminium, tri-isobutylaluminium, is used for ethylene polymerization.

More about the four crystalline modifications of violet crystalline titanium trichloride. The alpha- and gamma-forms have lower activities than the delta-form whereas the beta-form produces polymer which is essentially amorphous. This indicates that the stereoregularity of the polymer is very much dependent on the surface characteristics of the catalyst.

DONOR-MODIFIED TITANIUM TRICHLORIDE CATALYSTS

The addition of certain Lewis base compounds to titanium trichloride or to the catalytic system in appropriate amounts improves the stereospecificity of the catalyst. A very wide range of donors such as ethers, esters, ketones, amines, amides, phosphines, organophosphorous compounds, and polymeric derivatives can be used. The donor-modified Ziegler-Natta catalysts are referred to as second generation catalysts.

Whereas the donors often produce catalysts with higher stereospecificities for alpha-olefin polymerization, they often adversely affect catalyst activity. However, this is not always the case, and catalysts with higher stereospecificities as well as higher activities can be prepared by the judicious addition of an appropriate donor. The mechanism by means of which electron donors may affect activity and stereospecificity are complex. In short, the modifier molecules block the predominant inactive sites, such as impurities, together with most of the atactic sites by complex formation, leaving the isotactic sites free. This increases the stereospecificity of the catalyst. The activity is increased, because of the acceleration of the diffusion of the monomer to the active sites. **Table II** lists some typical examples of the use of electron donors as additives in catalyst preparation.

Table II: Some selected Lewis bases used as catalyst additives.

COMPANY	CATALYST SYSTEM
Montecatini	$TiCl_3/AlEt_3$ + pyridine
Eastman Kodak	$TiCl_3/AlEt_3$ + HMPT
Phillips Petroleum Co.	$TiCl_3.0,33AlCl_3/AlEt_2Cl$ + aromatic esters
Mitsui Petrochem. Ind.	$TiCl_4$ reduced with aluminium alkyl; $TiCl_3$ produced ground with organonitrogen or organophosphorous compound
Plastipolimer Res.	$TiCl_3/AlEt_2Cl$ + diisopropyl ether
BASF AG	$TiCl_3.0,33AlCl_3$ milled with $Bu_3P/AlEt_2Cl$
Shell Int. Res. Mij. BV	-$TiCl_3$ prepared from $TiCl_4$ heated to 120 °C with BuCl to give violet $TiCl_3$
Stauffer Chemical Co.	$TiCl_3.0,33AlCl_3$ milled with Ph_3PO or benzophenone
Mitsubishi Chem. Ind. KK.	$TiCl_3$ treated with thioether as used with *n*-propyl or *n*-hexyl aluminium alkyl
BASF AG	$TiCl_3.nAlCl_3$ (*n* = 0,01-1) ball milled with an ester, $ROCOR_2$ or $R_1OCOCR_2CHR_2$ and reacted with an alcohol, *e.g.* $TiCl_3.0,33AlCl_3$ and ethyl phenyl acetate, ball milled and reacted with *n*-BuOH

2.2.2.1.1.2   Supported Ziegler-Natta catalysts

Natta *et al.* (19) found that only a small percentage of the titanium atoms, < 1%, in first generation, preformed catalysts are active. Higher activities can be achieved through the use of transition metal compounds supported on appropriate matrices. The supported catalyst gives a large increase in the number of accessible active sites (21).

The supported catalysts consist mainly of titanium halides and Lewis bases supported on activated $MgCl_2$ or silica. Trialkylaluminium compounds alone or combined with additional Lewis bases are used as cocatalysts. The presence of a Lewis base is essential for high stereospecificity to be attained. Preferred Lewis bases include esters of aromatic carboxylic acids such as ethyl benzoate and sterically hindered amines like 2,2,6,6-tetramethylpiperidine or alkoxy silanes (22).

The term *supported catalyst* is used in a very wide sense and includes not only systems in which the transition metal compound is linked to the substrate by means of a chemical bond, but also systems in

which the transition metal atom may occupy a position in a lattice structure, or where complexation, absorption, or even occlusion, may take place.

2.2.2.1.2 Homogenous Ziegler-Natta catalysts

Homogeneous Ziegler-Natta catalysts are formed when a transition metal halide and a metal alkyl interact to produce a soluble catalyst. Usually the transition metal halide is itself soluble in the solvent used, but the polymer is, however, very often precipitated as it is formed.

The behaviour of many soluble polymerization systems is very complicated. Complex formation reactions often occur with much of the transition metal being locked up in inactive complexes. In addition, systems may be only colloidally dispersed, whereas in others precipitation of the catalyst as well as the polymer may occur.

Commercial use of soluble catalysts has been limited so far to the field of diene polymerization and ethylene-propylene copolymerization.

2.2.2.2   POLYMERIZATION MECHANISM

The true mechanism of Ziegler-Natta polymerization is still not entirely clear. The general kinetic scheme for polymerization is similar to the other types of addition polymerization in that initiation, propagation, and termination steps are involved, as shown below:

Initiation

$$\text{Cat--R} + \text{CH}_2\text{=CHR} \longrightarrow \text{Cat--CH}_2\underset{R}{\text{CH}}\text{--R'} \tag{1}$$

Propagation

$$\text{Cat--CH}_2\underset{R}{\text{CH}}\text{--R'} + n\text{CH}_2\text{=CHR} \longrightarrow \text{Cat-}\left[\text{-CH}_2\underset{R}{\text{CH-}}\right]_{n+1}\text{-R'} \tag{2}$$
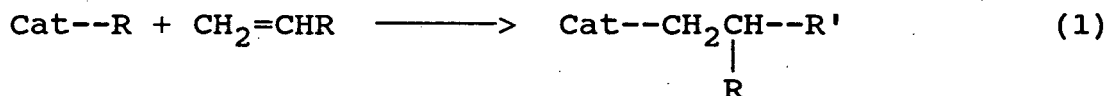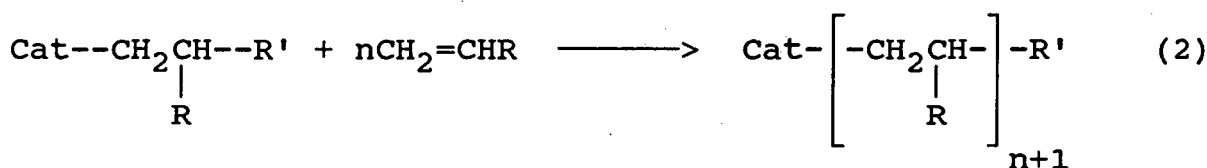
Termination

By an active hydrogen compound:

$$\text{Cat--CH}_2\underset{R}{\text{CH-}}\left[\text{-CH}_2\underset{R}{\text{CH-}}\right]_{n}\text{-R'} + \text{HY}$$

$$\downarrow$$

$$\text{V}$$

$$Cat--Y \; + \; CH_3CH-\left[-CH_2CH-\right]_n-R' \qquad (3)$$
$$\qquad\qquad\quad | \qquad\qquad | \qquad$$
$$\qquad\qquad\quad R \qquad\qquad R$$
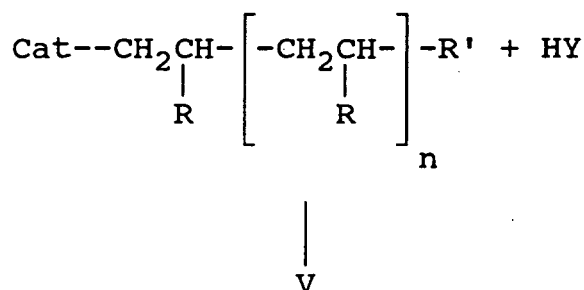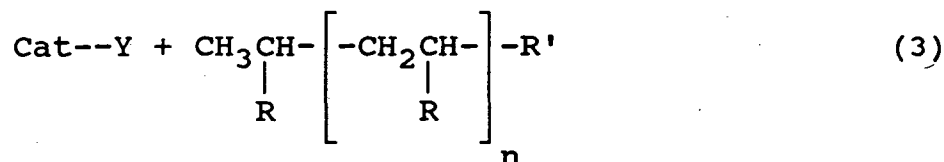
By transfer with monomer:

$$Cat--CH_2CH-\left[-CH_2CH-\right]_n-R' \; + \; CH_2=CHR$$
$$\qquad\qquad | \qquad\qquad |$$
$$\qquad\qquad R \qquad\qquad R$$

$$\downarrow$$
$$V$$

$$Cat--CH_2-CH_2 \; + \; CH_2=C-\left[-CH_2CH-\right]_n-R' \qquad (4)$$
$$\qquad\qquad\quad | \qquad\qquad | \qquad\qquad |$$
$$\qquad\qquad\quad R \qquad\qquad R \qquad\qquad R$$
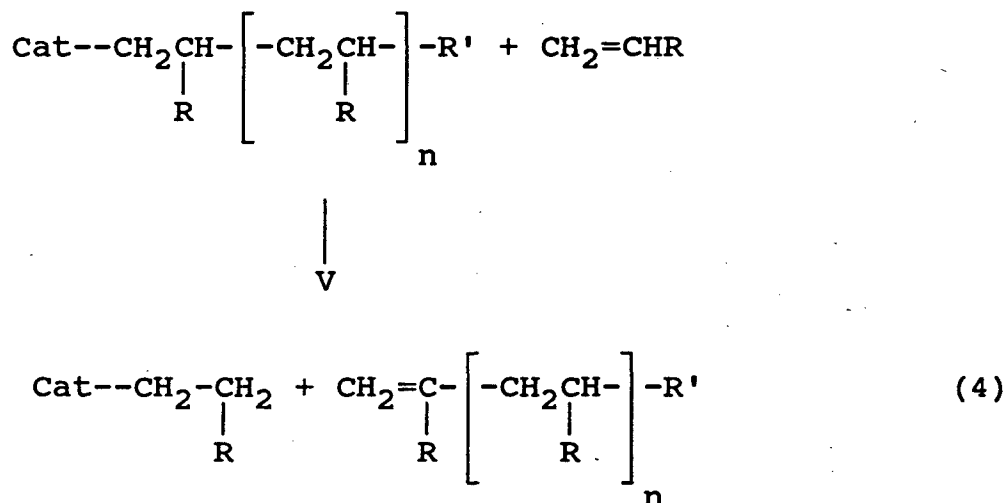
By spontaneous internal hydride transfer:

$$Cat--CH_2CH-\left[-CH_2CH-\right]_n-R'$$
$$\qquad\qquad | \qquad\qquad |$$
$$\qquad\qquad R \qquad\qquad R$$

$$\downarrow$$
$$V$$

$$Cat--H \; + \; CH_2=C-\left[-CH_2CH-\right]_n-R' \qquad\qquad (5)$$
$$\qquad\qquad\qquad | \qquad\qquad |$$
$$\qquad\qquad\qquad R \qquad\qquad R$$
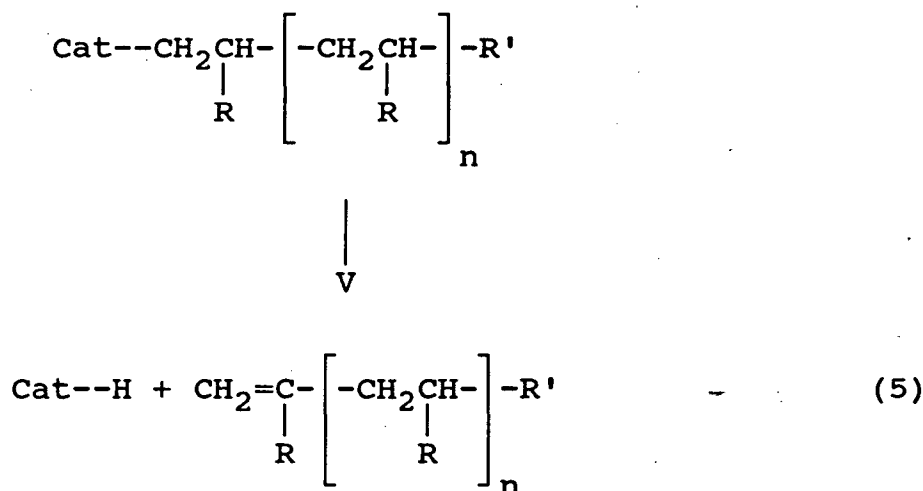
Experimental evidence indicates that initiation (**equation 1**) takes place at a transition metal-carbon bond with an alkyl group becoming attached to the monomer.

The propagation step (**equation 2**) consists of repeated insertion of the olefin into the transition metal-carbon bond. The stereoregularity of the resulting polymer is controlled by the propagation step.

The termination step in a Ziegler-Natta polymerization may be quite complex. Three possibilities are presented above (**equations 3-5**) and other termination processes are possible.

Any proposed mechanism should include these steps and also be able to account for chain transfer reactions and the stereoregulating ability of the catalyst. Of the various mechanisms that have been proposed, the two that are the most generally accepted are the so-called monometallic and bimetallic

mechanisms. The monometallic mechanism is favoured for heterogeneous polymerizations. Either the monometallic or the bimetallic mechanism will occur with soluble catalysts.

At the present time the majority of investigators, who support the concept of the monometallic polymerization mechanism of alpha-olefins and dienes employing Ziegler-Natta catalysts, hold to the models of Cossee or Cossee-Arlman or consider them to be the basis for their own theories (23).

According to Cossee (24, 25), the olefin and diene polymerization process is initiated by the transition metal and its ligands only. Besides, the alkylation reaction of a transition metal compound with the formation of respective organometallic compounds is suggested as a primary act. As a result, active sites having one vacancy in the octahedral configuration of the transition metal are formed on the edge and lateral faces of the crystals of the transition metal halide MeX_3.

Monomer coordination on the coordinate vacancy of the active site [] results in C=C bond rupture and monomer insertion into the Me-C bond. Migration of the growing chain brings the complex back to the initial state, thus making possible the addition of the subsequent monomeric unit. (See **Figure 3**.)
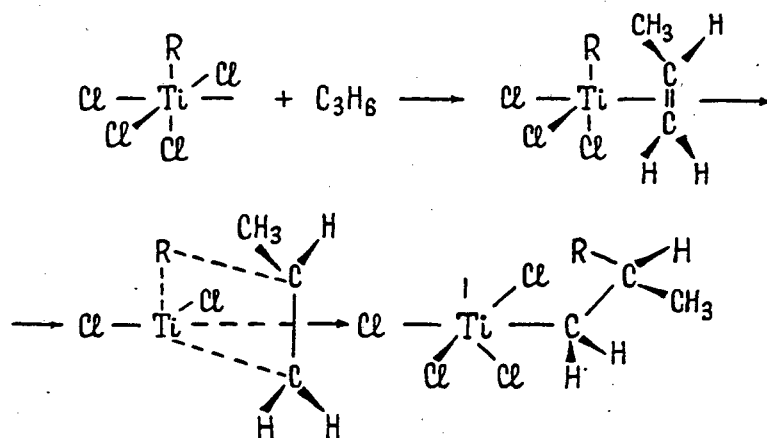
FIGURE 3. Cossee mechanism (23).

The role of the organoaluminium component in active site formation is said to be the alkylation of the catalyst surface only. The fact that alkyls of the most electropositive metals are fit for the formation of active Ziegler-Natta catalytic systems is accounted for by their higher alkylating capacity.

In the course of propagation, the chain migrates between two positions near the titanium ion, each time growing by one unit. Orientation of the growing chain, according to the above pattern, appears inessential for the stereospecific process. The chain can rotate freely round the Ti-C bond.

Arlman (26, 27) fully accepted Cossee's model and expanded it with due regard for the structure of the heterogeneous component of the catalyst. (See **Figure 4**.)
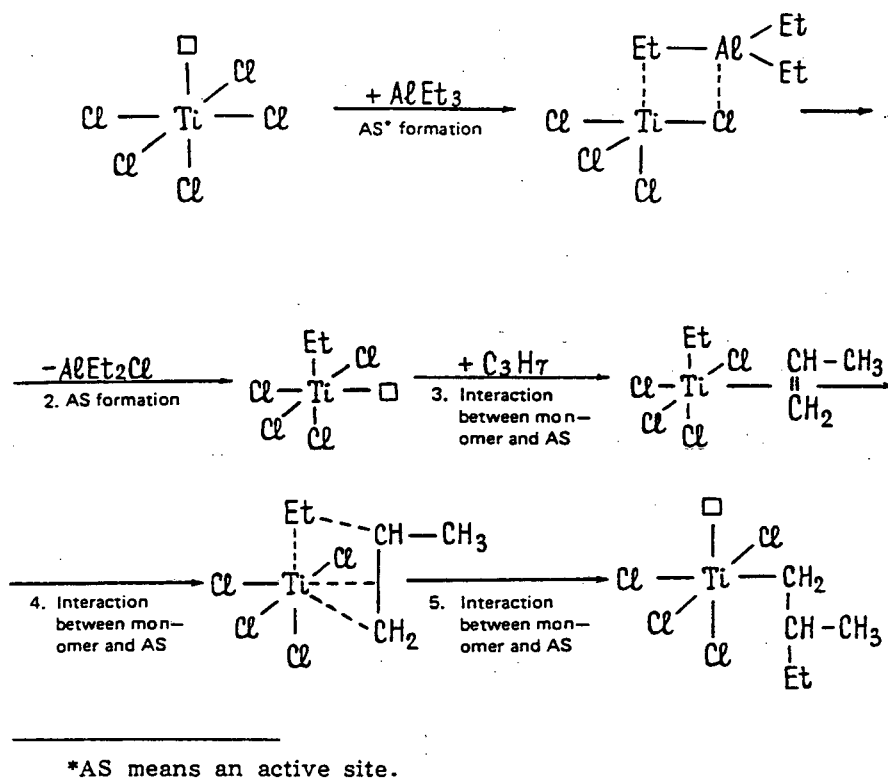
FIGURE 4. *Cossee-Arlman mechanism (23).*

2.2.2.3 STEREOREGULARITY

Stereoregularity arises because of order in the spatial structures of polymer chains. Such ordered spatial structures are determined by two phenomena. During the polymerization step the monomer units are joined together in a regular sequence determined by the catalyst used and by the polymerization conditions. Regularity of this type cannot be altered or changed during subsequent physical treatment of the polymer. (See **Figure 5** for representation of the different stereoregular forms of polymers.)

Polymers of higher alpha-olefins produced by polymerization with heterogeneous Ziegler-Natta catalysts have highly regular head-to-tail structures. The polymerization reactions proceed without isomerization of alkyl groups.

The crude polymers obtained in Ziegler-Natta polymerizations can be fractionated to separate crystalline fractions of high stereoregularity (isotactic, usually insoluble in boiling n-heptane), fractions of moderate stereoregularity, and amorphous irregular fractions.
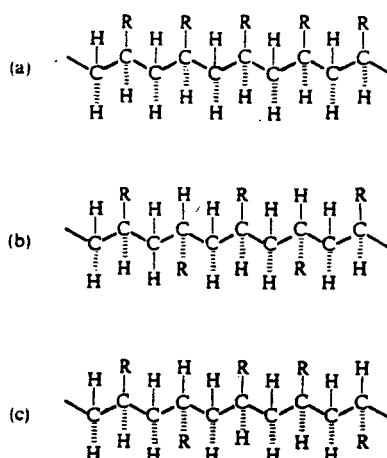
FIGURE 5. Planar representations of chains of poly(alpha-olefins): (a) isotactic; (b) syndiotactic; (c) atactic.

Yields of the highly crystalline fractions depend strongly on the catalytic system used. For example, yields of boiling *n*-heptane-insoluble fractions of poly(3-methylbutene-1) are 60-70% for the $TiCl_4$-$Al(C_2H_5)_3$ system but 85-95% for the $TiCl_3$-$Al(C_2H_5)_3$ system. Titanium-based supported Ziegler-Natta catalysts produce the best yield of highly crystalline materials **(29)**.

It has long been recognized that stereochemical regularity, in addition to chemical regularity, is a necessary requisite for polymer crystallizability **(31)**. Actually, even partially stereoregular polymers can give partial, but observable crystallization and, in the end, the percentage of crystalline polymer will be related to the degree of stereoregularity.

The degree of stereoregularity also affects the melting range and glass transition temperature of crystalline polymers. Stereoregularity has a pronounced effect on other properties in the solid state, particularly on mechanical properties. Solubility is also affected by stereoregularity and increases when the latter decreases.

The evaluation of stereoregularity type and degree is discussed in **Appendix B**.

2.3 POLY(3-METHYLBUTENE-1)

It is well known that poly(3-methylbutene-1) may be prepared in isotactic form with Ziegler-Natta catalysts, and the resulting polymer is highly crystalline with a high melting point (about 310 °C). These isotactic polymers have highly regular structures with head-to-tail incorporation of monomer units in the chain.

Poly(3-methylbutene-1) has been known for a long time as a high melting point, heat-resistant polyolefin, but as yet there are only a few examples of its use as an industrial material. One of the reasons for this is that in the past the 3-methylbutene-1 polymer mentioned in the literature was of low molecular mass, so that it did not have sufficient stretch and impact strength, which are necessary in industrial materials.

Olefins with gamma-substituted carbon atoms, such as 3–methylbutene–1, have high activation energies, thus the polymerization of these olefins with a coordination catalyst made from a combination of ordinary titanium trichloride and a organic alumininium compound, lacks the necessary amount of polymer activation needed for industrial production.

2.3.1 SYNTHESIS OF POLY(3–METHYLBUTENE–1)

3–Methylbutene–1 is usually polymerized in the presence of a catalyst composition comprising of a transition metal halide, such as titanium trihalide, and a trialkyl aluminium compound. 3–Methylbutene–1 is considered to be a difficult monomer to polymerize with Ziegler-Natta catalysts, because of its extremely low reactivity. The reason for this is that the rate of polymerization of monomers depends to a great degree on the steric hindrance about the vinyl group and the degree of crowding in the polymer chain due to the bulkiness of the substituents. Therefore 3–methylbutene–1 polymerizes slowly and in poor yield.

Poly(3–methylbutene–1), having high molecular mass and stereoregularity (38), is manufactured by the polymerization of 3–methylbutene–1, optionally with other olefins, such as ethylene, propylene, butene-1, pentene-1, 4-methylpentene-1, hexene-1, octene-1, decene-1, vinylcyclohexane, *etc.*, in the presence of solid $TiCl_3$ complex catalysts (Al/Ti atomic ratio < = 0,15) containing chelating agents and AlR_3 (R = C_{1-12} alkyl) as a cocatalyst. The alpha-olefin comonomers act as activators for the polymerization system. The proportion that these olefins occupy in the polymer is at most about 30 weight %, probably below 20 weight %. Increasing the other olefin comonomer amounts to more than the abovementioned levels is not desirable, as the polymer loses the special characteristics of high melting point, high strength, *etc.* of the 3–methylbutene–1 homopolymer. Also, the method of copolymerization is not just random copolymerization, but normally includes block copolymerization with propylene polymers.

2.3.1.1 POSSIBLE SIDE REACTIONS

Ketley *et al.* (39) reported that the polymerization of 3—methylbutene—1 by $TiCl_3$-$Al(C_2H_5)_3$ catalysts in dilute solution (low monomer concentration) at temperatures above 80 °C yields a polymer contaminated with highly crystalline polyethylene. The source of ethylene is ascribed to the presence of cocatalyst, triethyl aluminium.

Polyethylene formation occurs only above 60 °C, with the amount increasing with increased temperature, and it copolymerizes with 3–methylbutene–1 below 60 °C. This is supported by Ziegler's (40) findings that, in the polymerization of propylene by the same catalyst, ethylene is incorporated into the polymer, yielding a decrease in the apparent isotacticity. In this case, ethylene seems to copolymerize randomly with propylene. In the case of 3–methylbutene–1, side reactions can compete much more with the normal polymerization since this monomer is polymerized much more slowly by $TiCl_3$-$Al(C_2H_5)_3$ than is propylene or ethylene.

The formation of polyethylene and ethylene copolymers at low monomer concentration (high catalyst concentration), has detrimental effects on the properties of poly(3–methylbutene–1) (41). The effect on the melting point is especially remarkable (see **Figure 6**). The melting point of the polymer decreases with increasing catalyst concentration. In parallel to this, the density of the polymer

decreases and the solubility increases with increasing catalyst concentration. These effects indicate that the crystallinity of the polymer, and thus, the isotacticity of the polymer, decreases with increasing catalyst concentration.
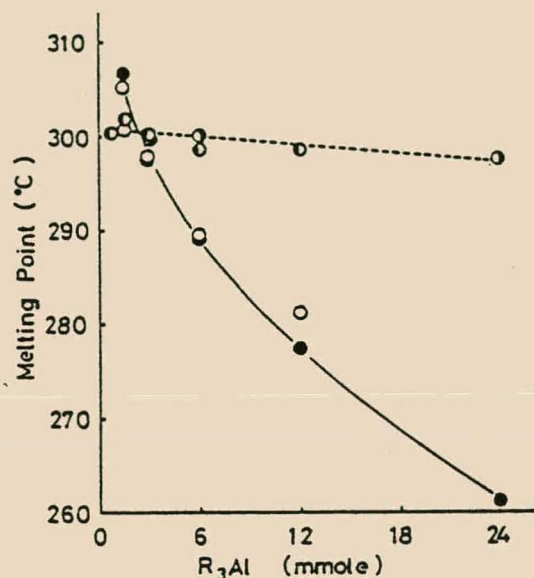
FIGURE 6. *Variation of melting point with the concentration of catalyst:* (◉) *TiCl$_3$(CH$_3$)$_3$Al, molar ratio 1,5;* (○) *TiCl$_3$(C$_2$H$_5$)$_3$Al, molar ratio 1,5;* (●) *TiCl$_3$(C$_2$H$_5$)$_3$Al, molar ratio 3,0;* (◉) *TiCl$_3$(i– CH$_4$H$_9$)$_3$Al, molar ratio 3,0 (41).*

Atarashi (41) studied the mechanism of polyethylene formation in the polymerization of 3–methylbutene–1. The high crystallinity of polyethylene indicates that ethylene, at least some part of it, is polymerized to form pure polyethylene segments without comonomer. The catalyst, therefore, has two kinds of active sites, one of which polymerizes only ethylene and another one which polymerizes both monomers. The activity of the former is more temperature dependent than that of the latter, which explains the observation that polyethylene formation increases with increasing temperature above 60 °C.

The mechanism of ethylene formation will be as follows:

(A) Through alkylation of TiCl$_3$:

$$TiCl_3 + Al(C_2H_5)_3 \longrightarrow Al(C_2H_5)_2Cl$$

$$C_2H_5TiCl_2 \longrightarrow TiCl_2 + C_2H_5$$

$$2C_2H_5 \longrightarrow C_2H_4 + C_2H_6$$
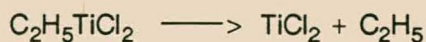
(B) Olefin exchange reaction in alkylaluminum compounds:

$$Al(C_2H_5)_3 \longrightarrow AlH(C_2H_5)_2 + C_2H_4$$

$$AlH(C_2H_5)_2 + H_2C=CH\text{-}CH(CH_3)_2 \longrightarrow (C_2H_5)_2AlC_5H_{11}$$

or

$$Al(C_2H_5)_3 + H_2C=CH\text{-}CH(CH_3)_2 \longrightarrow (C_2H_5)_2AlC_5H_{11} + C_2H_4$$
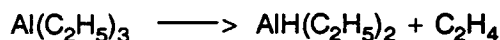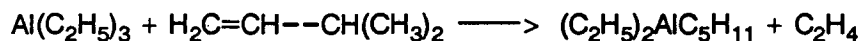
Atarashi reasoned that route A is not important and that route B should be the main route for ethylene formation.

2.3.2 PHYSICAL PROPERTIES

The physical properties of high polymeric materials in the solid state are functions of the internal mobility of the individual polymeric chains. The physical properties of isotactic poly(3-methylbutene-1) are given in **Table III**. The polymer, like all isotactic polymers, has the helix conformation in the crystalline state. Poly(3-methylbutene-1) exists in two polymorphic modifications, the type of which depends on the crystallization conditions **(39, 42)**.

TABLE III: Physical properties of poly(3-methylbutene-1).

PROPERTY	VALUE
melting point, °C	305
crystal type	monoclinic
density, g/cm³	
crystalline	0,93
average	0,90

Single branching on the alpha-carbon atom of 3-methylbutene-1 and vinylcyclohexane gives poly(3-methylbutene-1) and poly(vinylcyclohexane) the highest crystallinity of any of the other polymers of the higher alpha-olefins. The melting point of poly(3-methylbutene-1) is also very high, being in the range 250-360 °C, due to the presence of a branched alkyl substituent, an *iso*-propyl group.

Many authors have sought to locate and explain the glass transition of poly(3-methylbutene-1). Reding et al. **(43)** reported the glass transition temperature to be 50 °C by Instron testing, and Dunham et al. **(44)** found 53 °C by a softening point measurement which was claimed to correlate well with DTA values of the glass transition temperature. Similarly, NMR and dynamic mechanical property measurements by Woodward et al. **(45, 46)** indicated a "major transition" in the region 50-110 °C. Kirschenbaum et al. **(47, 48)** found a torsional damping peak at 60 °C, which they identified with the glass transition, and a higher temperature process extending from about 100 to 150 °C, which they

interpreted as the onset of disordering in the crystalline phase. It was noted also that the degree of crystallinity changes very little up to about 100 °C.

Quynn et al. (49) reported that isotactic 3 – methylbutene – 1 homopolymers and copolymers exhibit a major transition between 50 and 100 °C, which dilatometric, density, and NMR observations indicate is not a glass transition, but rather some kind of crystal-crystal transition occurring within the crystalline phase, the only phase present in significant amount.

2.3.3   MECHANICAL PROPERTIES

The mechanical properties of the higher alpha-olefin polymers depend strongly on the substituent. Poly(3 – methylbutene – 1), having a branched alkyl side chain, exhibits good mechanical properties compared with polypropylene (see **Table IV**).

TABLE IV: Properties of poly(3-methylbutene-1) and polypropylene.

PROPERTY	POLY(3-METHYL-BUTENE-1)	POLYPROPYLENE
Crystalline melting point, °C	305 ± 5	170
Tensile strength at break, Nm^{-2}	34,5	33,8
Elongation at break, %	3	12
Flexural modulus, Nm^{-2}	3 378,4	965,3-1 206,6
Flexural yield strength, Nm^{-2}	47,6	-
Izod impact at 25 °C, Jm^{-1}		
Notched	33,9	113,0
Unnotched	158,2	-
Heptane-insolubles, (% isotacticity)	96	-
Heat distortion temperature, °C	> 185	110
Density at 20 °C, g/cm^3	0,89	0,9

Because of its high crystallinity and melting point, poly(3 – methylbutene – 1) is very rigid (hard). This brittleness of the polymer is a consequence of the polymer being below its glass transition temperature at ambient temperatures.

2.3.4   CHEMICAL PROPERTIES

The chemical properties of poly(3 – methylbutene – 1) resemble those of polypropylene. The two tertiary carbon atoms per monomer unit in the polymer make it especially susceptible to oxidative degradation. Thermal degradation occurs at temperatures above 400 °C, whereas thermooxidative degradation of the polymer starts below 100 °C. The two adjacent tertiary C-H bonds per monomer unit in the polymer, have high reactivity in radical hydrogen abstraction processes. In the process of thermooxidative degradation, molecular mass decreases, hydroxyl and carbonyl groups form, and low

molecular mass compounds are produced. Initially, oxygen attacks tertiary C-H bonds, which, in turn, initiate radical chain reactions.

The polymer can be stabilized with the same products, such as substituted phenols and organic phosphites, as those used for stabilization of polypropylene and poly(4-methylpentene-1).

Poly(3 – methylbutene – 1) is insoluble in all common solvents, such as toluene, heptane, xylene, *etc.*

2.3.4.1   THERMAL AND THERMOOXIDATIVE DEGRADATION

The thermal and thermooxidative degradation of poly(3 – methylbutene – 1) takes place in a way typical of the poly(alpha-olefins) **(6)**.

Poly(3 – methylbutene – 1) displays sufficient stability during heating in the absence of oxygen up to 300 °C. Intensive decomposition of the polymer starts only from 400 °C. The products of thermal degradation of poly(3 – methylbutene – 1) are hydrocarbons of various compositions. A mass spectrum at 400 °C **(50) (Table V)** consists of the lines appropriate to the ions given in **Figure 7**. The line of m/e 126 ions, the highest mass number, can apparently be attributed to the molecule of diisopropylcyclopropane, which is the initial product of decomposition of poly(3 – methylbutene – 1) at 400 °C. The diagram of secondary decomposition of this molecule has mass numbers appropriate to all the lines in the mass spectrum **(Table V)**, and is in confirmation of this structure.   Thus poly(3 – methylbutene – 1) is a high-melting thermoplastic sufficiently stable at temperatures up to 300 °C.

Molecular oxygen considerably accelerates the decomposition of poly(3 – methylbutene – 1). Thermooxidative degradation of the polymer product is observed below 100 °C. The rate of the process increases with an increase of oxygen in the reaction volume, as well as with an increase in temperature. Hydroperoxides, which are the initial products of the oxidation of the polymer, are the branching products of the reaction.

Oxidation of amorphous samples of poly(3 – methylbutene – 1) takes place much more easily than that of crystalline ones, which in general is typical for crystalline polymers.

Gaseous products are formed during thermooxidative degradation of poly(3 – methylbutene – 1); among them are carbon monoxide and carbon dioxide. Formaldehyde, water and acetone are produced in large quantities during degradation. The products of the reaction of poly(3 – methylbutene – 1) with oxygen testify to the fact that oxidation of poly(3 – methylbutene – 1) proceeds by the same mechanism as poly(alpha-olefins) **(50)**, which is by the bimolecular decomposition of hydroperoxides. Water, alkyl and alkoxy radicals are characteristic products of this decomposition process. The formation of formaldehyde, acetone, isobutyric aldehyde and other volatile products during decomposition of alkoxyl radicals can be expected. In addition to volatile products, non-volatile alcohols, ketones and aldehydes form during decomposition of alkoxyl radicals.

TABLE V: Mass spectrum of poly(3−methylbutene−1) (50).

m/e	RELATIVE INTENSITY, %	m/e	RELATIVE INTENSITY, %
13	3	69	53
15	19	71	67
16	21	73	15
17	67	74	8
28	39	82	12
29	57	83	75
38	5	85	40
39	60	95	35
40	10	97	65
41	100	98	23
42	80	107	18
55	50	109	45
56	25	123	15
57	78	125	46
59	6	126	43

$$\left[(CH_3)_2CH-\overset{\overset{\displaystyle CH_2}{\diagup\diagdown}}{CH}-?-CH-CH(CH_3)_2 \right]^+ \longrightarrow$$
$$m/e\ 126$$

$$\longrightarrow (CH_3)_2-CH-\overset{\overset{\displaystyle CH_2}{\diagup\diagdown}}{CH}-?-CH-CH\overset{+}{=}CH \qquad [CH_4]^+$$
$$m/e\ 109 \qquad\qquad m/e\ 16$$

$$\longrightarrow (CH_3)_2-CH-\overset{\overset{\displaystyle CH_2}{\diagup\diagdown}}{CH}-?-CH-\overset{+}{CH_2} \qquad H_3C-\overset{+}{CH_2}$$
$$m/e\ 97 \qquad\qquad m/e\ 29$$

$$\longrightarrow (CH_3)_2-CH-\overset{\overset{\displaystyle CH_2}{\diagup\diagdown}}{CH}\underline{\quad}\overset{+}{C}=CH \qquad [H_3C-CH_3]^+$$
$$m/e\ 95 \qquad\qquad m/e\ 30$$

$$\longrightarrow (CH_3)_2-CH-\overset{+}{CH}-CH_2-CH_3 \qquad H_2C-CH\overset{+}{=}CH$$
$$m/e\ 85 \qquad\qquad m/e\ 41$$

$$\longrightarrow (CH_3)_2-CH-\overset{\overset{\displaystyle CH_2}{\diagup\diagdown}}{CH}\underline{\quad}\overset{}{\underset{+}{CH}} \qquad (CH_3)_2-\overset{+}{CH}$$
$$m/e\ 83 \qquad\qquad m/e\ 43$$

$$\longrightarrow (CH_3)_2-CH-\overset{+}{CH}-CH_3 \qquad (CH_3)_2-C\overset{+}{=}CH$$
$$m/e\ 71 \qquad\qquad m/e\ 55$$

$$\longrightarrow (CH_3)_2-CH-CH\overset{+}{=}CH \qquad (CH_3)_2-CH-\overset{+}{CH_2}$$
$$m/e\ 69 \qquad\qquad m/e\ 57$$
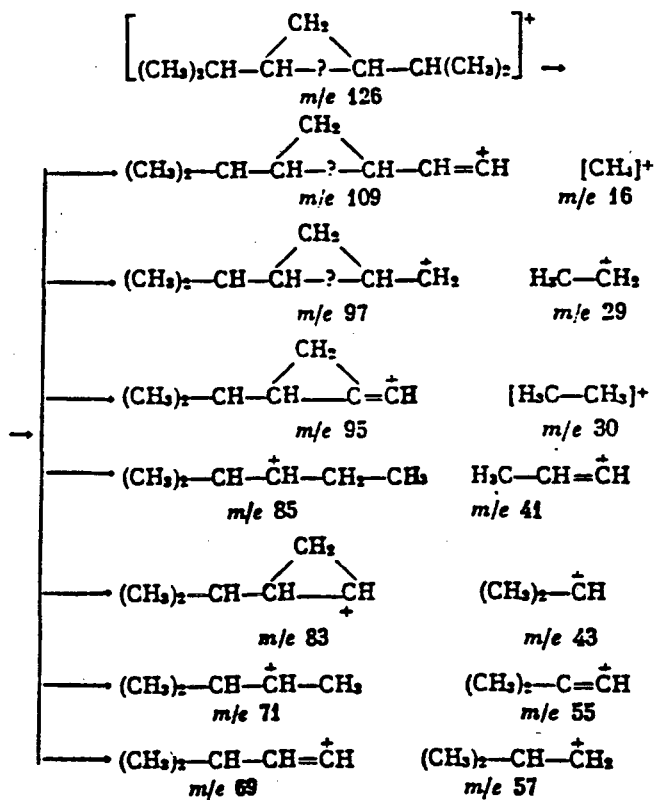
FIGURE 7. Thermal decomposition products of poly(3–methylbutene–1) (50).

2.3.5 USES

Although 3–methylbutene–1 polymers have good mechanical characteristics, their high melting points, poor oxidative stability and brittleness preclude industrial application.

Isotactic poly(3–methylbutene–1), although relatively easy to prepare at high molecular mass and to melt-spin, has never been commercialized successfully as a fibre, primarily because of its serious shortcomings of low strength at moderately elevated temperatures, poor abrasion resistance, poor resistance to oxidation, and the failure to attain a high modulus, among others (51).

Films and fibres of this polymer have desirable characteristics such as high melting point and good tensile strength. Poly(3–methylbutene–1) will find particular application in the moulding of relatively stiff articles by injection, compression, or extrusion molding. It is also especially suitable for use in such fields as extruded tubing, molded articles of all kinds, films, sheetings, coatings and laminates (49).

The following uses of poly(3–methylbutene–1) have been patented:

(a)   Transparent films of polypropylene containing 410 ppm poly(3–methylbutene–1) (1).

(b)   3–Methylbutene–1 polymer release films, useful for electronic devices, are prepared by melt extruding a 3–methylbutene–1 polymer into film (2).

(c)   Oil-permeable laminated film, or sheets for carton manufacture for use as food
        containers in microwave ovens **(3)**.

(d)   3–Methylbutene–1 polymer compositions for heat-resistant containers for foods
        (4).

2.4   COPOLYMERIZATION

Copolymerization is most usefully defined as polymerization in which two or more structurally distinct monomers are incorporated into the same polymer chain. No sequence information is implied **(structure 1)**.

$$xA + yB \longrightarrow \text{--(A)}_x\text{-(B)}_y\text{--} \tag{1}$$
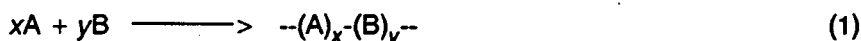
Copolymers are then defined as polymers that contain two or more distinct structural units. The monomers enter into the copolymer in a relatively random manner in overall amounts determined by their relative concentrations and reactivities.

According to Meyer **(52)**, copolymerization was first described in 1914 by Klatte **(53)**, who polymerized a mixture of vinyl esters. In the subsequent period of intensive applied research, the interest in copolymerization was spurred by the observation that copolymers frequently had more desirable physical properties than either polymers of single monomers or mixtures of such homopolymers. The investigation of the nature of the copolymerization reaction lagged. Nevertheless, during the 1930s evidence accumulated that striking differences existed in the tendencies of monomers to enter into copolymers.

Copolymerization is the most general and powerful method of effecting systematic changes in polymer properties, and is widely used in the production of commercial polymers and in fundamental investigations of structure-property relations. Copolymerization modifies the symmetry of the polymer chain and modulates both intramolecular and intermolecular forces, so that properties such as melting point, glass temperature, crystallinity, solubility, elasticity, permeability and chemical reactivity may be varied within wide limits.

Copolymerization allows the synthesis of an almost unlimited number of different products by variations in the nature and relative amounts of the two monomer units in the copolymer product.

Copolymerization is very important from a technological viewpoint. It greatly increases the ability of the polymer scientist to tailor-make a polymer product with specially desired properties. Polymerization of a single monomer is relatively limited as to the number of different products that are possible.

2.4.1   CLASSIFICATION OF COPOLYMERS

The properties of a copolymer depend not only on its composition but also on the arrangement or sequencing of the units in the molecule. Hence the need for a system for classification of copolymers.

Different types of copolymerization behavior depend on the values of the monomer reactivity ratios. A monomer reactivity ratio is defined as a measure of the tendency for a comonomer to show a

preference for insertion into a growing chain in which the last inserted unit was the same, rather than the other comonomer.

Copolymers are classified into the following classes:

(a)   Random copolymerization: $r_1 r_2 = 1$.

(b)   Alternating copolymerization: $r_1 = r_2 = 0$.

(c)   Block copolymerization: $r_1 > 1, r_2 > 1$.

A detailed discussion on the different classes of copolymers is given in **Appendix C**.

2.4.2   COPOLYMERIZATION EQUATION

Each monomer in a copolymerization reaction competes for the available active catalytic centres, and the composition, structure and molecular mass of the copolymer produced reflect this competition **(56)**. The mechanistic features of the copolymerization reaction are assumed to be essentially similar to those of the homopolymerization reaction, although certain modifications are requested to allow for the added complexity of the propagation step which can proceed in at least four ways (See **equations 6** below).

2.4.2.1   *ASSUMPTIONS AND DERIVATION*

Although the four reactions of chain growth in copolymerization were first recognized by Dostal in 1936, and the necessity of expressing copolymer compositions in terms of easily measurable parameters was realized by Wall in 1941, a publication of the combination of the two principles did not appear for three more years **(57)**.   In large measure, the slow development of a theory of copolymerization was due to inadequate data. Thus it is found that almost all of the available data are unsuitable for quantitative calculation, because they are obtained from experiments run to high conversion, because they do not cover a sufficient range of feeds, or because they lack essential information on feed composition, polymer composition, or conversion. Uncertainty is also introduced by poor or unstated isolation and analytical techniques.

2.4.2.1.1 The Terminal Model

The widespread interest in copolymerization in the early years is shown by the fact that in 1944, besides the generalized treatment of Simha and Branson **(58)**, three independent developments of what is now generally termed the "copolymerization equation" were published by Alfrey and Goldfinger **(59)**, Mayo and Lewis **(60)**, and Wall **(61)**. In every case, four assumptions were made:

(1)   That one was dealing with a chain reaction involving long chains so that consumption of monomer could be discussed solely in terms of chain propagation reactions.

(2)   That these chains had very short lives compared with the duration of the overall reaction, so that steady-state expressions might be set up for the concentrations of active centres.

(3)   That the rate constant for addition of each monomer was assumed to depend on the identity of the terminal unit on the growing chain; the terminal model (62) (thus four propagation rate constants are required).

(4)   That the propagation reactions, which were assumed to be irreversible, could be adequately described by **equations 6**.

Reaction		Rate
$M_1^* + M_1 \longrightarrow M_2^*$		$k_{11}[M_1^*][M_1]$
$M_1^* + M_2 \longrightarrow M_2^*$		$k_{12}[M_1^*][M_2]$
$M_2^* + M_2 \longrightarrow M_2^*$		$k_{22}[M_2^*][M_2]$
$M_2^* + M_1 \longrightarrow M_1^*$		$k_{21}[M_2^*][M_1]$

(6)
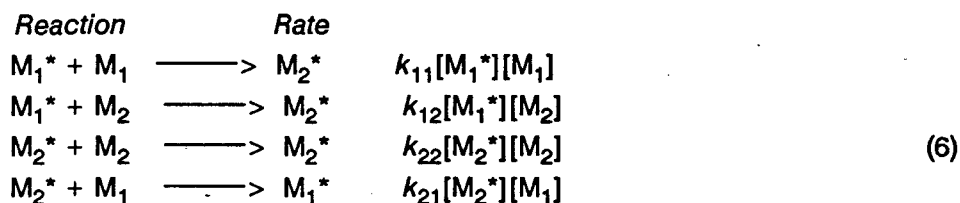
where M_i refers to a monomer molecule arbitrarily designated i (where i = 1,2), and M_i^* refers to a growing polymer chain to which monomer i has most recently become attached.

The parameter r_i is defined as the ratio of the specific reaction rate constants for M_i, k_{ii}/k_{ij} (where j = 1,2; i not equal to j). **Equations 6** assume that there are only two types of reacting monomers, only two types of active centres, and that the type of active centre depends solely upon which type of monomer reacted last. In other words, it is assumed that the specific reaction rate constants are unaffected by polymer chain length (or at least maintain the same ratio regardless of chain length), that the active centres do not change character in any way that would alter their relative reactivity, and that there are no penultimate, solvent, or like effects (63).

Under these conditions, the rate of disappearance of the two monomers in a copolymerization is given by the expressions

$$-\frac{d[[M_1]}{dt} = k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1] \qquad (7a)$$

$$-\frac{d[[M_2]}{dt} = k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2] \qquad (7b)$$

where $[M_1]$ and $[M_2]$ are monomer-feed concentrations, and $[M_1^*]$ and $[M_2^*]$ are the concentrations of growing chains with terminal residues derived from M_1 and M_2, respectively. The representation M^* designates an active centre without specifying its character. In **equations 7** the monomer consumed in chain initiation and termination is neglected.

The relation between $[M_1^*]$ and $[M_2^*]$ is given by the steady-state expression:

$$k_{21}[M_2^*][M_1] = k_{12}[M_1^*][M_2] \qquad (8)$$

Dividing **equation 7a** by **7b**, eliminating the concentrations of active centres by combining the result with **equation 7**, and introducing the parameters, $r_1 = k_{11}/k_{12}$, $r_2 = k_{22}/k_{21}$, leads by straightforward algebra to the final copolymerization equation (**equation 9**),the validity of which was first established

by Mayo and Lewis **(60)** for the system styrene-methyl methacrylate and which has been confirmed repeatedly by subsequent investigations.

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1] \, (r_1[M_1] + [M_2])}{[M_2] \, ([M_1] + r_2[M_2])} \tag{9}$$

where

$d[M_1]/d[M_2]$ = molar ratio of two monomer units in copolymer;

$[M_1]$ = instantaneous concentration of comonomer 1 in reaction feed;

$[M_2]$ = instantaneous concentration of comonomer 2 in reaction feed;

$r_1 = k_{11}/k_{12}$ = reactivity ratio of comonomer 1;

$r_2 = k_{22}/k_{21}$ = reactivity ratio of comonomer 2.

The reactivity ratios r_1 and r_2 are most frequently used to describe the ability of added comonomers to add to the copolymer chains.

Equation 9 has become the standard for the treatment of copolymerization, and has been used to correlate an enormous volume of copolymerization data. This equation is widely known as the Mayo-Lewis equation or the copolymer composition equation. Although its derivation involves the use of steady-state assumptions, several workers **(64)** have shown that the same expression can be obtained by a statistical method without resorting to the use of any steady-state assumptions.

The unique contribution by Wall **(61)** was the development of a graphical presentation of the dependence of copolymer composition on monomer-feed composition. This dependence is examined for several different combinations of reactivity ratios that describe real copolymerizations in **Appendix D**.

Despite the rather large volume change, 10-20%, which occurs during the polymerization of monomers to polymers, this effect appears to have been ignored by most authors **(65)**. However, it may be shown that the volume terms cancel out from the relative instantaneous rate expressions **(Appendix E)**.

2.4.2.1.2 The Penultimate Model

Merz, Alfrey, and Goldfinger suggested in 1946 that the relative rates of monomer addition at the ends of growing copolymer chains might depend not only on the identity of the terminal unit, but also on the identity of the preceding, or penultimate, one. This effect, often referred to as the penultimate effect, manifests itself in a particular copolymerization by giving inconsistent values of monomer reactivity ratios for different comonomer feed compositions. This has been observed in many radical copolymerizations where the monomers contain highly bulky or polar substituents **(63)**. These authors cited no experimental evidence in support of their suggestion, but it is certainly plausible.

2.4.2.2 *RANGE OF APPLICABILITY*

The copolymerization equation is equally applicable to radical, cationic, and anionic chain copolymerizations although the r_1 and r_2 for any particular comonomer pair can be drastically different depending on the mode of initiation **(64)**. These different values of r_1 and r_2 give rise to large differences in the copolymer composition depending on the mode of initiation. The ionic copolymerization is predictably much more selective than radical copolymerization. The high selectivity of ionic copolymerization limits its practical use.

For any specific type of initiation (*i.e.*, radical, cationic, or anionic), the monomer reactivity ratios and therefore, the copolymer composition equation, are independent of many reaction parameters. Since termination and initiation rate constants are not involved, the copolymer composition is independent of differences in the rates of initiation and termination, or of the absence or presence of inhibitors or chain transfer agents. Under a wide range of conditions, the copolymer composition is independent of the degree of polymerization. The only limitation on the generalization is that the copolymer must be a high polymer. Further, the particular initiation system used in copolymerization has no effect on copolymer composition as long as the type of initiation is the same.

2.4.2.2.1 Ziegler-Natta copolymerization

In the derivation of the copolymer composition equation **(equation 9)** certain assumptions were made which may render it inapplicable to Ziegler-Natta catalyst systems. The features of these systems which may give rise to problems of applicability and interpretation are the time dependent changes which occur in polymerization kinetics and also the nature of the active catalytic centre itself **(56)**.

1. **Changes in polymerization kinetics.**
   Time dependent changes in catalytic activity are well-known in Ziegler-Natta systems. Such changes, whether due to changes in active centre concentration, changes in the rate constant or constants, or to diffusion phenomena, will make it difficult to apply the copolymer composition equation unambiguously. Changes in any of these as comonomer concentration in the reaction feed is varied will also increase complications.

2. **The nature of the active centre.**

2.1 **Multiplicity of active centres.**
   The derivation of the copolymer composition equation assumes only one type of active centre to participate in chain propagation. This may be true in certain homogeneous Ziegler-Natta catalyst systems but in most heterogeneous systems multiple centres often exist, so that quantities derived from the copolymer composition equation merely represent average values for the different sites present. An underestimation of the true blockiness present in a copolymer may therefore result if a single centre model is assumed. A more rigorous mathematical treatment which accounts for multiple centres can be undertaken. If multiple centres are present, the reactivity ratios will be a function of the mode of catalyst addition, and the reactivity ratios determined by the normal copolymerization equation will not predict the sequence distribution of the copolymer.

2.2 Steric factors.

The influence of the last inserted unit upon subsequent insertions is crucial in copolymerizations as the last unit may dictate which comonomer will next be inserted and also the mode of that insertion. The derivation of the copolymer composition equation assumes the active centre to be totally regiospecific; **Scheme 1** may therefore require modification to account for regiospecific primary and secondary insertion, although in most heterogeneous systems primary insertion is believed to predominate and no modification is necessary. Comonomer structure and the stereochemistry of the active centre profoundly influence copolymer composition.

2.4.2.3 USES AND LIMITATIONS

The copolymerization equation or Mayo-Lewis equation gives the composition of the copolymer at any specific instant during the reaction (*i.e.* instantaneous copolymer composition). If the Mayo-Lewis equation is integrated, the so-called Mayo-Lowry equation is obtained, from which the composition drift with copolymerization is predicted. If, however, the conversion is kept below 5%, the Mayo-Lewis equation is applicable. This is possible as the composition of the comonomer feed is relatively unchanged from its initial value at such low degrees of conversion **(57)**.

The copolymer composition equation **(equation 9)** permits evaluation of the monomer reactivity ratios for any monomer pair from two or more experiments; once the ratios have been evaluated, the composition of the copolymer formed at any conversion from any mixture of that monomer pair can be predicted **(60)**. Since the development of **equation 9** considers only the chain growth process, it will not apply to very low molecular mass polymers if one monomer predominates unduly among the terminal groups. The reactivity ratios, r_1 and r_2, determine the directions in which the polymer chain grows; although they are in general dependent on temperature; thus far there is no evidence that they are affected by the addition of small quantities of added materials or moderate quantities of solvents.

In the normal copolymer model in which only two variables must determined, it is customary to obtain information about the concentration of the two monomers in the feed and in the copolymer. With these facts determined for each experiment, the two variables r_1 and r_2 can be unambiguously computed.

The copolymer composition equation supplies a quantitative method for comparing the rates of reaction of any propagating species (which occurs in a growing polymer) with a series of monomers.

Although it should be obvious that the copolymerization equation can apply only to the simple cases in which all of the assumptions are justified, in a large number of publications attempts are made to fit the results of a complex polymerization system to the copolymerization equation. It should be obvious that the first requirement for the application of the copolymerization equation is that it should correspond to the real physical system which it models, or else it has no valid meaning.

However valid the simple copolymer equation may be in certain situations, the inappropriate use of the differential form of this equation in situations where the monomer feed ratio changes appreciably is an example of the use of an inappropriate model. This occurs most often in situations where the reactivity

ratios are quite different in magnitude. The monomer concentrations in these circumstances may change dramatically at conversions well below 10%.

2.4.3 SCIENCE OF DETERMINING COPOLYMERIZATION REACTIVITY RATIOS

The original developers of methods for measuring and calculating r_1r_2 values were interested only in obtaining reasonable estimates of relative reactivity. Their experimental methods and their calculation procedures were designed to guide the qualitative development of copolymerization theory.

With the gradual development of copolymerization theory, r_1r_2 values have gradually ceased to be regarded as only qualitative or semiquantitative estimates of relative reactivity and have begun to be treated in a strictly quantitative manner.

2.4.3.1   THE PROBLEM OF DETERMINING REACTIVITY RATIOS

When the reactivity ratio estimates obtained by one group of workers are not in agreement with those obtained by other workers, the causes for the difference must arise from one or more of the following (63):

(a)   The estimation methods used.

(b)   The use of an inappropriate mathematical equation to describe the relationship between copolymer composition (or final monomer composition) and initial monomer concentrations.

(c)   The experimental conditions used to generate the data.

(d)   Inadequate analytical procedures.

These factors will now be considered in detail.

2.4.3.2   CHOICE OF ESTIMATION PROCEDURE

A number of methods can be found in the polymer literature which illustrate how to calculate reactivity ratios from polymer composition and initial monomer concentrations.

A good estimation procedure should include the following properties (66):

(a)   The method should give unbiased estimates of the parameters.

(b)   The method should use all, or nearly all, the information in the data with regard to the variables to be estimated, thus providing precise estimates.

(c)   The variable values calculated by the method should not depend upon arbitrary factors, such as which monomer is subscribed 1 and the starting point of the calculation.

(d)   The method should supply a valid measure of the errors of the resulting estimates.

(e)   The method should be reasonably easy to use.

The procedure which meets at least the first four of the above criteria is the Method of Maximum Likelihood. The method of least squares, which is well-known, is a maximum likelihood method if the random errors associated with the observations are independently and normally distributed with

constant variances. With the advent of the digital computer, the criterion of ease of use of the estimation procedure is also satisfied.

There exist five methods for the computation of copolymerization reactivity ratios; for the sake of convenience these methods are denoted as (1) approximation; (2) curve fitting; (3) intersection; (4) linearization; and (5) non-linear least-squares. Although all of these methods are different, the first four methods share the common failing of relying on a subjective weighting of the data in the evaluation of the reactivity ratios. Further, the first four methods provide no means of establishing how well these reactivity ratios are determined, that is, they furnish no quantitative error limits for the computed values. However, all the above mentioned problems are solved by the use of the non-linear least-squares method; the criteria specified in b, c, and d above are met only by this method.

The various linear estimation procedures are discussed in detail in **Appendix F**.

2.4.3.3 THE NON-LINEAR LEAST-SQUARES METHOD

The non-linear least-squares (NLLS) method is a modification or extension of the curve-fitting method. It differs from the curve-fitting method in that the values of r_1 and r_2 satisfy the criterion that, for the selected values of these ratios, the sum of the squares of the differences between the observed and computed polymer compositions is minimized.

The NLLS method for solving r_1 and r_2, is superior to all other methods that have been discussed up to now in the following ways **(67)**:

(a)   A unique pair of values is obtained which is independent of the judgement of the experimenter.

(b)   This pair of values can be shown mathematically to be the best pair obtainable from the data at hand.

(c)   The errors are quantitatively defined in meaningful terms.

(d)   The data are evaluated to see how well they fit the copolymer equation.

In considering the copolymerization procedure, the weight of the experimental data should be taken into account. Actually, the compositions of the feed and copolymer are calculated from the amounts of monomers charged, the data from the elemental analysis of the copolymer, and the conversion. The weighting of the experimental data should depend on them.

The existing NLLS methods are most suitable when the following conditions are met **(69)**:

(1)   The errors in the dependent or response variable are random, statistically independent from observation to observation with constant variance; this method is equivalent to the maximum-likelihood method if the error distribution of the observations is normal.

(2)   The independent variable contains no measurement error.

(3)   The copolymerization model is consistent with the experimental data.

Briefly the NLLS method consists of the following: given initial estimates of r_1 and r_2, a set of computations is performed which, on repetition, rapidly leads to a pair of values of the reactivity ratios which yields the minimum value of the sum of the squares of the differences between the observed and computed copolymer composition.

According to Tidwell and Mortimer **(67)**, if reasonably good initial estimates are used, three iterations are sufficient to provide realistic least-squares estimates so that additional calculations are seldom required. The Fineman-Ross and Mayo-Lewis methods are normally used to obtain initial estimates for the NLLS method.

To obtain the optimum values of the monomer reactivity ratios for copolymerization systems with largely different reactivities between both monomers, use of the nonlinear least-squares procedure which takes into account the weights of experimental data has been proposed **(68)**. The weights of the data have been treated for the errors which arise from the amounts of monomers charged, the densities of monomers, the weights of copolymer formed, and the composition of the copolymer. The least-squares procedure with the consideration of the weights is applicable to the differentiated and integrated form of the copolymer equation. It is known that errors from the copolymer composition are more important than those from the other factors, and that the use of the integrated equation is recommended even when the copolymers are isolated at low conversions.

2.4.3.4 *IMPROVED METHODS FOR ESTIMATING MONOMER REACTIVITY RATIOS IN COPOLYMERIZATIONS*

Since 1944, when the simple copolymer equation was derived by Alfrey and Goldfinger **(59)** and Mayo and Lewis **(60)**, two developments in copolymerization kinetics, namely, computerized calculation and gas-liquid chromatography (GLC), have governed progress in this science. The use of electronic computers has rendered possible more complicated and extended calculations for the determination of monomer reactivity ratios, but the introduction of gas chromatographic analysis (GLC) of monomer feed composition during a copolymerization reaction was an important step forward, for it made the laborious and inaccurate copolymer analysis redundant.

Unfortunately, all the above procedures do not take the real-error structure of the observations into account. Van der Meer *et al.* **(69)** has described an algorithm that does account correctly for measurement errors in both variables. They also illustrated a computational method for copolymerization data obtained from quantitative gas chromatographic analysis (GLC) of the monomer feed throughout the reaction. It was found that the actual error structure of the variables corresponds to the assumed error structure. Reliability of the estimates is substantially increased, compared with the methods discussed above. The standard deviations of the monomer reactivity ratios appear to be in good agreement with reality.

Van der Meer's highly accurate method of computing monomer reactivity ratios is based on the integrated copolymer equation, and it considers experimental errors in both measured variables, whereas the other procedures considered measurement errors in only one of the variables.

It must be emphasized that the present method of accounting for the measurement errors can be applied to other existing procedures; for example, the curve-fitting procedure leads similarly to more accurate *r* values, especially in copolymerization systems with one high and one low reactive monomer, shown by the large distance (*b*), observation (2), **Figure 8**.
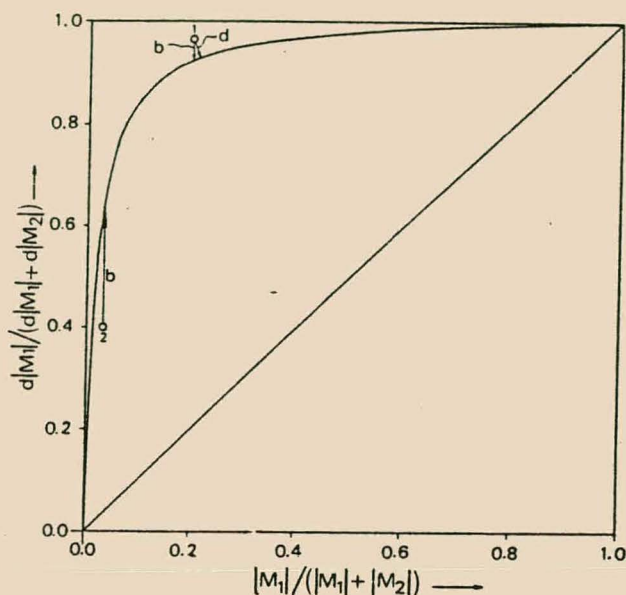
FIGURE 8. *Initial molar feed composition $[M_1]/([M_1] + [M_2])$ versus the instantaneous molar copolymer composition $d[M_1]/(d[M_1] + d[M_2])$ for an arbitrarily chosen monomer combination with $r_1 = 50$ and $r_2 = 0,02$ and two devised observations (69).*

Finally, considering the errors in both measured variables, it may be concluded that Van der Meer's novel algorithm will yield more accurate monomer reactivity ratios, which are of theoretical as well as practical importance. It will contribute to a more accurate comparison of copolymerization data and to a significant evaluation of more detailed model descriptions.

2.4.3.5   COPOLYMERIZATION WITH HIGHLY ACTIVE ZIEGLER-NATTA CATALYST

In homogeneous as well as in heterogeneous Ziegler-Natta processes the rate of polymerization is proportional to monomer concentration if the polymerization process is kinetically controlled.

This correlation between rate of polymerization and monomer concentration and other experimental observations can be best understood by assuming that this catalytic process occurs as described by the Rideal mechanism. It has been shown that the Rideal mechanism also includes the Cossee model, which has been proposed to explain the Ziegler-Natta polymerization process. According to this mechanism the most important step is the complexation of the active transition metal centre by the monomer molecule.

2.4.3.5.1 Determination of the r parameters

It is known that these copolymerization parameters differ by orders of magnitude, and it has often been reported that the reactivity ratio product, $r_1 r_2$, is close to 1. For small comonomer contents in the copolymer, the Mayo-Lewis equation can thus be written as

$$\left[\frac{n_2}{n_1} \right]_P = \frac{1}{r_1} \frac{[M_2]}{[M_1]} \tag{10}$$

For different temperatures the data are plotted according to **equation 10** in the range of proportionality from $(n_2/n_1)_P$ to $[M_2]/[M_1]$ (**Figure 9**). From the slope of these lines the parameters r_1 can be calculated.
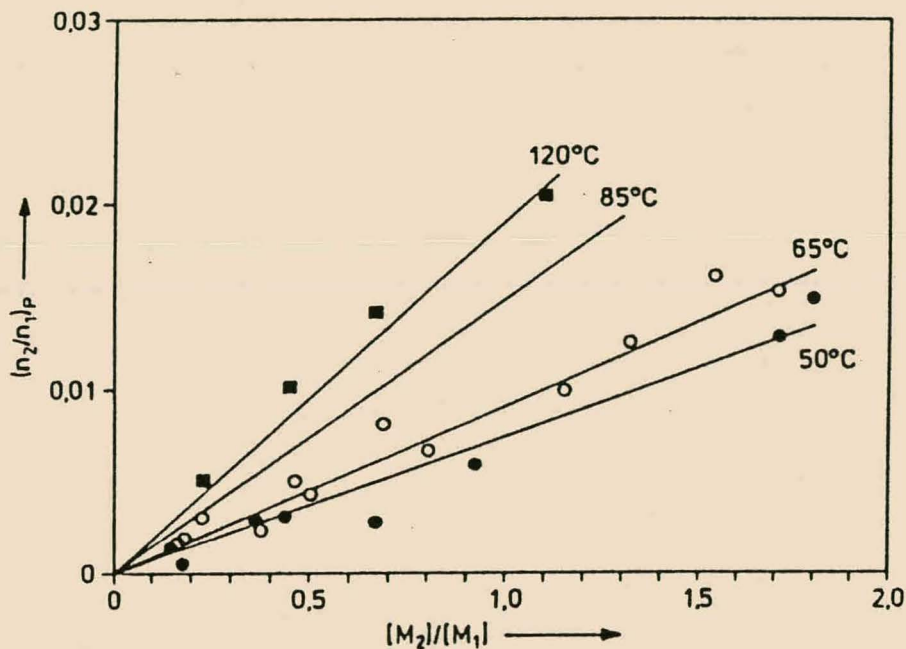
FIGURE 9. *Plot of copolymerization data according to equation 10; ethylene (1) and butene-1 (2); variable: temperature (71).*

Using the calculated r_1 values, the r_2 parameters can be evaluated by approximating the experimental data by means of calculated lines according to the Mayo-Lewis equation. The temperature dependence of the r parameters is not very strong. It can be described within experimental error by the following equations:

$$\log r_1 = -0.2 + 750/T \tag{11}$$

$$\log r_2 = -3.2 + 750/T \tag{12}$$

2.4.3.6   EXPERIMENTAL DETERMINATION OF MONOMER REACTIVITY RATIOS

This section is discussed in **Appendix G**.

2.4.3.7   THE PROBLEM OF DISCREPANCIES

Data from the literature is examined in **Appendix H** to establish why the $r_1 r_2$ values on practical systems appear to vary according to author.

2.4.4   COPOLYMER COMPOSITION

It was clear by the end of the 1930s that chain-growth copolymers from olefinic monomers differed in composition from that of the monomer-feed mixture. Because this compositional inequality would lead to changes in composition with conversion, it was suggested that the homogeneity of the product could be increased by addition of the more reactive monomer during the course of the polymerization.

The difference between the copolymer composition and the comonomer feed composition, shows that different monomers have differing tendencies to undergo copolymerization. The relative copolymerization tendencies of monomers bear little resemblance to their relative rates of homopolymerization. Some monomers are more reactive in copolymerization than indicated by their rates of homopolymerization; other monomers are less reactive. Thus, the composition of a copolymer cannot be determined from the knowledge of the homopolymerization rates of the two monomers.

On the basis that the copolymerization of any two monomers involves the reaction of the two kinds of monomer molecules with the two kinds of active centers derived from them, it has been found that the composition of a copolymer can be expressed as a function of the initial monomer concentrations, of the conversion, and of two constants which are characteristic of each monomer pair **(60)**.

A detailed study of the following is given in **Appendix I**:

1.   Characteristics of monomer reactivity ratios.

2.   Relation between feed and instantaneous copolymer composition.

3.   Prediction of comonomer sequence length.

4.   Prediction of instantaneous copolymer composition.

5.   Variation of copolymer composition with conversion.

6.   Microstructure of copolymers.

2.4.4.1   EXPERIMENTAL CONTROL OVER THE ARCHITECTURE OF COPOLYMER CHAINS IN ZIEGLER-NATTA SYSTEMS

Both physical and chemical reaction conditions can influence copolymerization kinetics, and these influences become manifest not only in their effect upon the rate of reaction but also in the structure and composition of the copolymer produced. The properties of Ziegler-Natta type copolymers depend to a large extent on several structural features of the copolymer chains **(56)**: (i) the relative content of comonomer units in a polymer chain, the distribution of comonomer units along each individual chain (intramolecular composition), and the variation in comonomer content and distribution between different chains (intermolecular composition); (ii) molecular mass and molecular mass

distribution; and (iii) the relative content of normal head-to-tail additions to head-to-head or tail-to-tail additions (*i.e.* degree of regiospecificityty).

The architecture of a copolymer can be controlled experimentally to a large degree by **(86)**: (i) reaction conditions; (ii) chemical composition of catalyst; (iii) physical state of catalyst; (iv) physical state of the copolymer being formed; and (v) structure of comonomers. Some of these are closely interdependent. Theses factors are discussed in **Appendix J**.

2.4.5   ZIEGLER-NATTA COPOLYMERIZATION

The discovery of the transition-metal catalysts for olefin polymerization made possible the synthesis of not only various stereoregular olefin polymers, but also that of olefin copolymers.

In stereospecific polymerization on heterogeneous catalysts, it is difficult or impossible to separate the role of the catalyst (geometry of the active site) from that of the stereoregular copolymer itself (structure of the last monomer unit in the chain) as a driving force in the production of stereoregularity **(89)**. Many of the same catalysts under slightly modified conditions produce high molecular mass atactic (unordered) copolymers.

Each monomer in a copolymerization reaction competes for the available active catalytic centres, and the composition, structure and molecular mass of the copolymer produced reflect this competition. The mechanistic features of the copolymerization reaction are assumed to be essentially similar to those of the homopolymerization reaction, although certain modifications are required to allow for the added complexity of the propagation step which can proceed in at least four ways **(56)**:

$$T_M\text{-}M_1\text{-}P \ + \ M_1 \ \xrightarrow{\ k_{11}\ } \ T_M\text{-}M_1\text{-}M_1\text{-}P$$

$$T_M\text{-}M_1\text{-}P \ + \ M_2 \ \xrightarrow{\ k_{12}\ } \ T_M\text{-}M_2\text{-}M_1\text{-}P$$

$$T_M\text{-}M_2\text{-}P \ + \ M_1 \ \xrightarrow{\ k_{21}\ } \ T_M\text{-}M_1\text{-}M_2\text{-}P$$

$$T_M\text{-}M_2\text{-}P \ + \ M_2 \ \xrightarrow{\ k_{22}\ } \ T_M\text{-}M_2\text{-}M_2\text{-}P$$
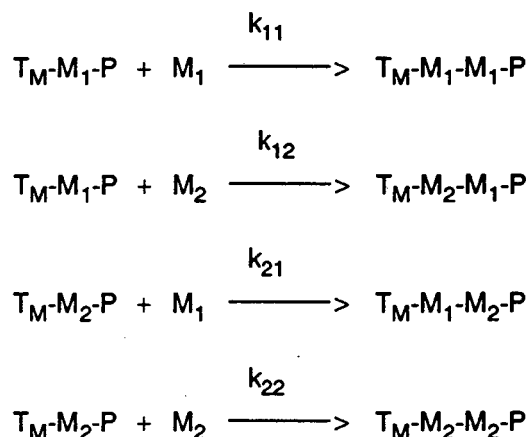
where T_M = transition metal and P = polymer chain.

SCHEME 1

The monomer sequences in the copolymers have the same stereoregular structure as the corresponding homopolymers **(90)**, so that, both homopolymerization and copolymerization of olefins take place on the same stereospecific sites.

The degree of randomness of the olefin copolymers varies significantly, depending on the combination of olefins and the on catalytic system chosen. The most striking feature of this is that some olefin

copolymers evidently have a strong tendency toward block formation. Such copolymers were obtained mainly with highly specific catalytic systems.

The distribution of chemical units in a stereoregular copolymer depends on the copolymer composition, the stereospecificity of the catalytic system in respect of a given monomer, and the reactivity ratio product $r_1 r_2$.

The examination of $r_1 r_2$ values for hundreds of different comonomers polymerized by different mechanisms reveals that values of $r_1 r_2 > 1$ can be regarded as being characteristic of complex catalysis (90). This tendency is especially pronounced when the comonomers have alkyl groups of different size (ethylene-4-methylpentene-1, propylene-butene-1, propylene-styrene, propylene-4-methylpentene-1, propylene-vinyl cyclohexane). On the other hand, when the alkyl groups are of similar bulkiness (4-methylpentene-1-vinyl cyclohexane, 4-methylpentene-1-3-methylbutene-1, vinyl cyclohexane-styrene), the copolymers obtained are mainly random or have a tendency to alternation. Special mechanisms have been proposed, which attribute this phenomenon to the peculiarities of the growth of the helix chain on the surface of the heterogeneous catalyst.

2.4.6 EXPERIMENTAL METHODS FOR THE STUDY OF COPOLYMER STRUCTURES

A detailed discussion of the experimental methods for the study of copolymer structures is given in **Appendix K**.

2.4.7 STRUCTURE OF HIGH-OLEFIN COPOLYMERS

This section contains experimental results relating the structures of different copolymers of high olefins.

2.4.7.1 ETHYLENE-3-METHYLBUTENE-1 COPOLYMERS

These copolymers have been obtained with a V-acetylacetonate-Al(isoC$_4$H$_9$)$_2$Cl catalytic system at 10-30 °C. The introduction of 3-methylbutene-1 units increases the solubility of the copolymerization products, and decreases their melting points, which is an indication of random copolymerization ($r_1 r_2 = 0,24$):

3-methylbutene-1 content, %	7,5-7,9	14,9	23,4
solubility in n-heptane, %	61-65	77,4	81,5
melting point, °C	127-129	110	90

2.4.7.2 BUTENE-1-3-METHYLBUTENE-1 COPOLYMERS

The copolymer compositions have been measured mainly by IR methods, for example, by using the 746 cm^{-1} band (ethyl group mode) and 1180 cm^{-1} band (isopropyl group mode, insensitive to monomer distibution) (90).

The copolymers are highly crystalline (50-60%) over the whole range of compositions and have relatively high melting points (117-310 °C). At least six crystalline phases are observable, varying in proportion to the copolymer composition; this fact is attributed to the high degree of isodimorphism

and cocrystallization. Nevertheless, some peculiarities of the behavior of copolymer crystallinity suggest a tendency to block formation.

2.4.7.3 3-METHYLBUTENE-1-HIGHER LINEAR OLEFIN COPOLYMERS

The structures of 3–methylbutene–1 copolymers with pentene-1 and decene-1 have been studied (98). The composition of these copolymers are determined by the IR method. The A_{1050}/A_{1150} ratio is used in the case of 3-methylbutene-1-pentene-1 copolymers, and the analytical curve is calibrated with the homopolymer mixtures.

Decene-1 units in the copolymer chains practically cannot be incorporated into the poly(3-methylbutene-1) lattice due to the steric hindrance of the pendant groups. These copolymers are nearly random ($r_1 r_2 = 1,73$ for the $TiCl_4 - Al(C_2H_5)_3$ system) and the crystallinity of the poly(3-methylbutene-1) type virtually vanishes after the introduction of about 40% of decene-1 into the copolymer chain.

On the other hand, poly(3-methylbutene-1) and poly(pentene-1) have practically the same crystallographic values, and the copolymers of these monomers are crystalline over the total range of compositions (the poly(pentene-1) crystallinity is 74%, poly(3-methylbutene-1) crystallinity is about 90%, and the minimum crystallinity of the copolymer with 25% C_{3mb1} is about 30%). The copolymer melting points change almost linearly from about 71 °C to about 289 °C in this range. The absence of IR data does not allow any conclusion about the monomer distribution in these copolymers.

The only IR data available for 3-methylbutene-1-heptene-1 copolymers show a gradual decline in the relative intensities of the 778 and 1218 cm^{-1} bands with increasing heptene-1 content, indicating real copolymer formation.

2.4.7.4 3-METHYLBUTENE-1-4-METHYLPENTENE-1 COPOLYMERS

These copolymers are highly crystalline (98) and have very high melting points:

4-methyl-pentene-1 content, %	100	93	87	80	75	52-50	25	0
melting point, °C	248-240	240	225	236	208	230-218	260	300

Nevertheless, the IR spectrum of such a copolymer (Figure 10) demonstrates the absence of helix bands in both monomers, indicating random unit distribution, in agreement with the $r_1 r_2$ value ≈ 1 (98). The high crystallinity of the copolymer is due to isomorphism (98).
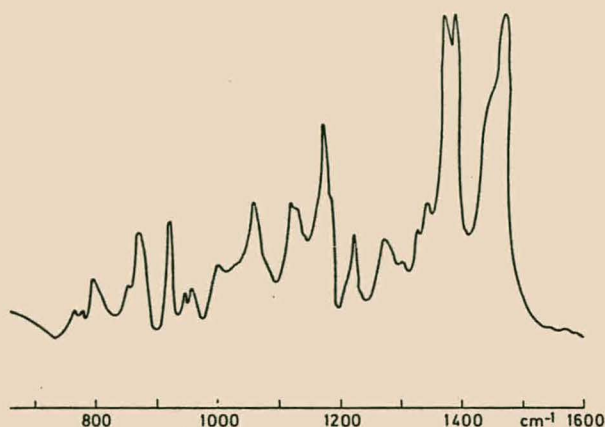
FIGURE 10. IR spectrum of a 3 – methylbutene – 1-4-metylpentene-1 copolymer obtained with the $TiCl_3$-$Al(C_2H_5)_2Cl$ system (90).

2.4.7.5   3-METHYLBUTENE-1-VINYL CYCLOHEXANE COPOLYMERS

The IR spectra demonstrate that real copolymerization of these monomers occurs when $TiCl_4$–$Al(isoC_4H_9)_3$ is used as the catalyst system. The 778 cm-1 band (the helix band of poly(3-methylbutene-1)) disappears from the copolymer spectra, beginning from about 50% vinyl cyclohexane content, and the relative intensity of the 1120 cm-1 band decreases significantly:

3-methylbutene-1 content, mol-%	100	90	84	55	40
$(A_{1120}/A_{1385})_{cop}/(A_{1120}/A_{1385})_{p3mb1}$	1,0	0,72	0,72	0,22	0,14

2.4.8   ACTIVITIES OF DIFFERENT HIGH OLEFINS IN COPOLYMERIZATION REACTIONS

2.4.8.1   REACTIVITY RATIOS FOR HIGH OLEFIN COPOLYMERIZATION

The reactivity ratios for different high olefin pairs are listed in **Table VI**.

TABLE VI: Reactivity ratios for high olefin copolymerization (90).

OLEFIN PAIR	CATALYTIC SYSTEM	r_1	r_2	r_1r_2	REF.
ethylene-butene-1	$TiCl_3$-containing catalytic system	60,0	0,025	1,5	(101)
	$TiCl_3$-CH_3TiCl_3	3,6	0,16	0,58	(102)
	VCl_3-$Al(C_6H_{13})_3$	29,96	0,043	1,16	(88)
	VCl_4-$Al(isoC_4H_9)_2Cl$	32,5	0,0186	0,60	(103)

ethylene-pentene-1	VCl_4-$Al(isoC_4H_9)_2Cl$	42,1	0,015	0,63	(103)
	V acetylacetonate-$Al(isoC_4H_9)_2Cl$	33,2	0,0145	0,48	(96)
ethylene-hexene-1	V acetylacetonate-$Al(isoC_4H_9)_2Cl$	46	0,0125	0,58	(104)
ethylene-3–methyl-butene–1	V acetylacetonate-$Al(isoC_4H_9)_2Cl$	243,0	0,001	0,24	(105)
ethylene-4-methyl-pentene-1	$TiCl_3$-$Al(C_2H_5)_2Cl$	195,1	0,028	4,8	
	V acetylacetonate-$Al(isoC_4H_9)_2Cl$	47	0,015	0,70	(96)
ethylene-styrene	$TiCl_3$-$Al(C_2H_5)_3$	81	0,012	0,97	(106)
propylene-butene-1	$TiCl_3$-$Al(C_2H_5)_2Cl$	4,5	0,2	0,90	(107)
propylene-4-methyl-pentene-1	$TiCl_3$-$Al(C_2H_5)_2Cl$,	6,5	0,3	1,95	(108)
propylene-vinyl cyclohexane	$TiCl_3$-$Al(C_2H_5)_2Cl$, (70 °C)	80	0,049	0,392	(109)
butene-1-3–methyl-butene–1	$TiCl_3$-$Al(isoC_4H_9)_3$, (60 °C)	8,5	0,013	0,11	(110)
	$TiCl_4$-$Al(C_2H_5)_3$, (45 °C)	6,22	0,33	2,05	(98)

3-methylbutene-1- pentene-1	$TiCl_3$-$Al(C_2H_5)_3$, (45 °C)	0,28	8,32	2,33	(98)
3-methylbutene-1- decene-1	$TiCl_4$-$Al(C_2H_5)_3$, (45 °C)	0,05	34,5	1,72	(98)
3-methylbutene-1- 4-methylpentene-1	$TiCl_4$-$Al(C_2H_5)_3$, (45 °C)	0,11	9,00	0,99	(98)
3-methylbutene-1- vinyl cyclohexane	$TiCl_4$-$Al(isoC_4H_9)_3$	1,02	0,98	1,00	(111)
4-methylpentene-1- hexene-1	$TiCl_3$-$Al(C_2H_5)_2Cl$	0,37	3,4	1,26	(100)
4-methylpentene-1- 3-methylpentene-1	$TiCl_3$-$Al(C_2H_5)_3$, (80 °C)	6,2	0,1	0,62	(112)
4-methylpentene-1- styrene	$TiCl_3$-$Al(C_2H_5)_3$, (45 °C)	3,67	0,89	3,27	(113)
4-methylpentene-1- vinyl cyclohexane	$TiCl_3$-$Al(isoC_4H_9)_3$	3,17	0,38	1,20	(114)

2.4.8.2   RELATIVE ACTIVITIES OF OLEFINS IN COPOLYMERIZATION REACTIONS

Table VII contains data that allow semiquantitative comparison of olefin activities in homopolymerization and copolymerization reactions **(90)**. The diagonal of **Table VII** contains the data on the absolute constants of chain propagation in homopolymerization. Comparison of these results, show that they were obtained with different samples of $TiCl_3$ and under different experimental conditions, and that this introduces some bias in the final results.

	Ethylene	Propylene	Butene-1	Other linear olefins	4-Methylpentene-1	Styrene	3-Methylburene-1	Vinylcyclohexane	
Ethylene	$K_p = 78$ l/m·s TiCl$_3$(Al)— —Al(C$_2$H$_5$)$_2$Cl, 60° C, (191)	15.7–0.11 (121) TiCl$_3$—Al(C$_6$H$_{13}$)$_3$	60.0–0.025 TiCl$_3$ (138)	33.2–0.0145ᵇ (pentene-1) (149)	195.1–0.025 TiCl$_3$—Al(C$_2$H$_5$)$_2$Cl	81–0.012 TiCl$_3$—Al(C$_2$H$_5$)$_3$ (194)	243.0–0.001ᵇ (149, 152)		Ethylene
Propylene		$K_p = 18$–6.2 l/m·s, 60° C, (191, 192) $K_p = 10$–6 l/m·s, 70° C, (23, 109) (TiCl$_3$, TiCl$_3$(Al)	4.67–0.51 (138) 4.5–0.2 (185) 1.62–0.5 (38) TiCl$_3$—AlC$_2$H$_5$)$_3$— —Al(C$_2$H$_5$)$_2$Cl		6.4–0.31 (66) TiCl$_3$(Al)— —Al(C$_2$H$_5$)$_2$Cl	20.5–0.3 (159) TiCl$_3$—Al(C$_2$H$_5$)$_3$		80–0.049 (106) TiCl$_3$(Al)— —Al(C$_2$H$_5$)$_2$Cl	Propylene
Butene-1			$K_p = 7.3$ l/m·s (191) TiCl$_3$(Al)— —Al(C$_2$H$_5$)$_2$Cl, 60° C				8.5–0.013 (188) TiCl$_3$—Al(isoC$_4$H$_9$)$_3$		Butene-1
Other linear olefins					5.4–0.62 (167) 3.4–0.37 (48) (hexene-1) TiCl$_3$—Al(C$_2$H$_5$)$_2$Cl	9.7–0.19 (170) (hexene-1) 5.7–0.61 (170) (heptene-1)	8.32–0.28 (39) (pentene-1) 34.5–0.05 (39) (decene-1) TiCl$_3$, TiCl$_4$		Other linear olefins
4-Methylpentene-1					$K_p = 2.5$ l/m·s (190) TiCl$_3$(Al)— —Al(C$_2$H$_5$)$_2$Cl, 70° C	3.92–0.98 (45) 3.67–0.89 (169) TiCl$_3$—Al(C$_2$H$_5$)$_3$— —Al(isoC$_4$H$_9$)$_3$	9.0–0.11 (39) TiCl$_4$—Al(C$_2$H$_5$)$_3$	3.17–0.38 (43) TiCl$_3$—Al(isoC$_4$H$_9$)$_3$	4-Methylpentene-1
Styrene						$K_p \sim 0.1$ l/m·s (189) TiCl$_3$—Al(C$_2$H$_5$)$_3$ 70° C		2.12–0.18 (44) TiCl$_3$—Al(isoC$_4$H$_9$)$_3$	Styrene
3-Methylbutene-1								1.02–0.98 (44) TiCl$_4$—Al(isoC$_4$H$_9$)$_3$	3-Methylbutene-1
Vinylcyclohexane								$K_p = 0.022$ l/m·s (109) TiCl$_3$(Al)— —Al(C$_2$H$_5$)$_2$Cl, 70° C	Vinylcyclohexane

TABLE VII (90).

40

Table VII demonstrates that there is good correlation between the propagation rate constants for different monomers and their relative activities in the copolymerization reactions represented by r_1 and r_2 values. The order of the olefin activities in the case of heterogeneous complex catalysts according to **Tables VI** and **VII** is:

ethylene > propylene > olefins with linear chains >

> 4-methylpentene-1 > styrene >

> 3-methylbutene-1 $\approx$ vinyl cyclohexane.

With olefins with branched alkyl groups, the order of activities is:

5-methylhexene-1 $\approx$ 4-methylpentene-1 > 4-methylhexene-1 >

> 3-methylpentene-1 $\approx$ 3-methylbutene-1.

A comparison of these scales with Taft's induction constants σ^* and Taft's steric constants E_s (90) for different alkyl groups leads to the conclusion that both electronic and steric factors influence the double bond activity in stereospecific catalysis; but that steric factors seem to be more important. An especially significant decrease in the olefin activity was found for olefins branched vicinally to the double bond (3-methylpentene-1, 3-methylbutene-1, vinyl cyclohexane, styrene). This is probably connected with the space limitations for monomer coordination in the stereospecific active sites.

The examination of $r_1 r_2$ values for hundreds of different comonomers polymerized by different mechanisms reveals that the vast majority of these $r_1 r_2$ values are close to or less than 1; very few examples of ionic processes were found with $r_1 r_2 > 1$ (90). For this reason the appearance of a significant number of cases with $r_1 r_2 > 1$ can be regarded as characteristic of complex catalysis. The mentioned tendency is especially pronounced when the comonomers have alkyl groups of different size (ethylene-4-methylpentene-1, propylene-butene-1, propylene-styrene, propylene-4-methylpentene-1, propylene-vinyl cyclohexane). On the other hand, when alkyl groups are of similar bulkiness (4-methylpentene-1-vinyl cyclohexane, 4-methylpentene-1-3–methylbutene–1, vinyl cyclohexane-styrene), the copolymers obtained are mainly random or have a tendency to alternation.

2.4.9 COPOLYMERIZATION OF 3–METHYLBUTENE–1 WITH DIFFERENT COMONOMERS

2.4.9.1 *3-METHYLBUTENE-1-BUTENE-1 COPOLYMERS*

Ketley (110) investigated the copolymerization of 3–methylbutene–1 and butene with Al–i–Bu$_3$–TiCl$_3$ to copolymers of high 3–methylbutene–1 content.

Al–i–Bu$_3$–TiCl$_3$ is the most active Ziegler-Natta catalyst for the polymerization of bulk 3-methylbutene-1, which has a low catalyst activity and polymerizes only to low conversions. In contrast, when small amounts (up to 5% by weight) of butene-1 are added to the monomer feed, high conversions are obtained and catalyst activity is greatly increased.

Ketley states that the heptane insoluble (>97%) fractions of the copolymers are crystalline with relatively long blocks of 3–methylbutene–1, whereas the heptane soluble fractions are predominantly

random copolymer of 3−methylbutene−1 and butene-1. Since incorporation of butene-1 in the soluble fractions is about twice that in the corresponding insoluble fractions, two different types of catalytic sites must be present, one of which favours random copolymerization and the other favours formation of block copolymers.

Although the rate of copolymerization is higher than that of 3−methylbutene−1 homopolymerization, it is not great enough to account for the much higher activities originally noted. The explanation of this apparent discrepancy is that the rate of homopolymerization falls almost to zero after about one hour, whereas the copolymerizations continue to high conversions. 3-Methylbutene-1 homopolymer is extremely crystalline and highly insoluble. As polymerization proceeds it evidently forms a layer on the catalyst surface which is impervious to monomer and consequently the reaction ceases. A similar phenomenon has been observed in the Ziegler-Natta polymerization of styrene in aliphatic hydrocarbon media (115). The copolymer being largely either noncrystalline or weakly crystalline, is more swollen by its own monomer, and therefore does not inhibit polymerization. It is interesting that even after all the butene-1 has been consumed, further polymerization of 3-methylbutene-1 proceeds at a higher rate than that of the normal homopolymerization of this monomer. Apparently, the initially formed random copolymer increases the solubility of the poly(3-methylbutene-1) block to which it is joined.

Ketley (110) found the reactivity ratios of the two comonomers to be: $r_1 = 0,013$ (M_1 = 3−methylbutene−1) and $r_2 = 8,5$ (M_2 = butene−1); the product $r_1 r_2 = 0,11$ indicates considerable deviation from random copolymerization. This is due partly to the steric hindrance between the bulky 3−methylbutene−1 chain end and the incoming monomer.

Jones (99) investigated the copolymerization of 3−methylbutene−1 and butene-1 with $TiCl_3/AlEt_2Cl$. He designed the polymerization methods used to give as random copolymers as possible, but true random copolymerization was not achieved, and is likely to be inherently difficult with comonomers with widely different rates of polymerization. Jones found that the copolymers were well crystalline over the whole composition range, about 60% near the homopolymer ends of the range and about 50% in the centre of the range.

A high degree of isodimorphism and cocrystallization is evident in these copolymers from the high crystallinity present over the whole composition range. This is different from either of the homopolymer phases, which must form in order to accommodate chains containing both types of monomer units. Nevertheless, the presence of poly(3−methylbutene−1) crystallinity in copolymers of low (20%) 3−methylbutene−1 content, and the multiplicity of crystal phases and phase changes developed on slow cooling, show clearly that, particularly in the middle composition ranges, the copolymers are not completely homogeneous and random as designed, but must contain chains which vary probably both in overall composition and in degrees of blocking.

The melting of the copolymers is gradual, and particularly with the poly(3−methylbutene−1) phase, takes place over a wide temperature range indicating a range of compositions within one phase.

The drop in melting point of the poly(3−methylbutene−1) phase shows that butene-1 units are being included in the lattice, but, being of smaller size, they are readily accommodated with little change in lattice dimensions.

In a system such as this in which the crystal forms of the homopolymers are not isomorphous and in which, because of, the similarity in size of the two monomer units, cocrystallization might be expected as discussed generally by Natta, with mixtures of homopolymer chains, blocked chains, and random copolymer chains of varying composition, and in which probably all types in fact coexist to some degree at all copolymer compositions, the phase development will be particularly influenced by the crystallization conditions and is likely to be very complicated.

2.4.9.2   3-METHYLBUTENE-1-4-METHYLPENTENE-1 COPOLYMERS

In a normal polymer only a small amount of comonomer is required to greatly disrupt or completely destroy crystallinity. The properties of a normal crystalline polymer also change drastically with increasing amounts of comonomer. Specifically, the melting point and the stiffness modulus above the glass transition temperature are severely lowered by the addition of comonomer.

Reding and Walter (94) found that the copolymer system of 3-methylbutene-1-4-methylpentene-1 does not behave in the manner characteristic of the typical copolymers discussed above. This is shown very clearly by the stiffness modulus vs. temperature curve of a 50-50 3-methylbutene-1-4-methylpentene-1 copolymer (Figure 11). If this copolymer were predominantly or entirely amorphous as would be expected, its stiffness would fall off precipitiously at 50 °C, the glass transition temperature. This is indicated by the dashed curve. The very unusual behavior of this copolymer system is perhaps more strikingly demonstrated by the melting points as a function of composition (Table VIII). It is seen that the melting point decreases to a minimum of about 208 °C at a 4-methylpentene-1 concentration of 75%, but over the entire composition range the melting points of copolymers remain quite high. Such behavior would not be expected from the Flory copolymer melting point equation.
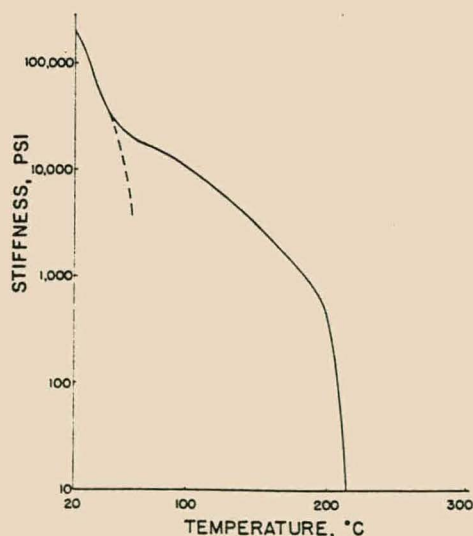
FIGURE 11. Stiffness modulus vs. temperature curve for a 50/50 3−methylbutene−1-4-methylpentene-1 copolymer (94).

TABLE VIII.   Crystalline melting points of 3–methylbutene – 1-4-methylpentene-1 copolymers (94).

% 3–methylbutene–1	% 4-methylpentene-1	Melting point, °C
100	0	300
75	25	256
50	50	218
25	75	208
13	87	225
0	100	240

The above properties indicate that 3-methylbutene-1-4-methylpentene-1 copolymers remain highly crystalline over the entire range of composition in distinct contradiction to normal copolymer behaviour.

A few other examples of cocrystallization of copolymers, such as ethylene-carbon monoxide and ethylene-vinyl alcohol systems, are known.   However, with these the crystal system of one of the components (ethylene) is maintained as the composition of the copolymer is changed.   The 3-methylbutene-1-4-methylpentene-1 copolymer is the first example of a vinyl cocrystalline copolymer which changes crystal structure continuously with composition.

Since the placement of the two different monomer units along the copolymer chain must be a reasonably random event, it is evident that the isopropyl side chain of 3-methylbutene-1 is essentially interchangeable with the isobutyl side chain of the 4-methylpentene-1 in the crystal lattice. It is most likely that the ability to cocrystallize in this manner depends upon the structural similarity between the pendent side chains and also on the fact that the crystal structures of the two homopolymers are very similar.

CHAPTER 3

EXPERIMENTAL

3.1   POLY(3–METHYLBUTENE–1)

3.1.1   POLYMERIZATION

3.1.1.1   REAGENTS

SOLVENT

The *n*-heptane solvent used in the polymerization reactions had the analysis below (**Table I**). Because of the high purity of the heptane, it was treated only with activated 4Å molecular sieves. The solvent was left in contact with the molecular sieves for one day before it was used.

TABLE I: Specification sheet for n-heptane.

Heptane		94,0 - 97,7	% (v/v)
Aromatic compounds	max.	2,3 - 6,0	% (v/v)
Sulphur	max.	2	ppm (m/m)
Water	max.	2	ppm (m/m)
Bromine number		0,1/100	gr/gr
Boiling range		90 - 100	°C (atmospheric)

MONOMER

3–Methylbutene–1 was obtained from Aldrich (1990-1991 Cat no. 25,7931) and was used without further purification. The gas chromatographic-mass spectrometry (GC-EI-MS) analysis, with a Carlo Erba QMD 1000 mass spectrometer under GC conditions, indicated that the purity of the monomer was 96%. The major impurity was 2-methylbutene-1, but trace amounts of 2-butene, 1-pentene and hexane were also present. The vapour pressure of 3–methylbutene–1 at various temperatures is given in **Figure 1**.
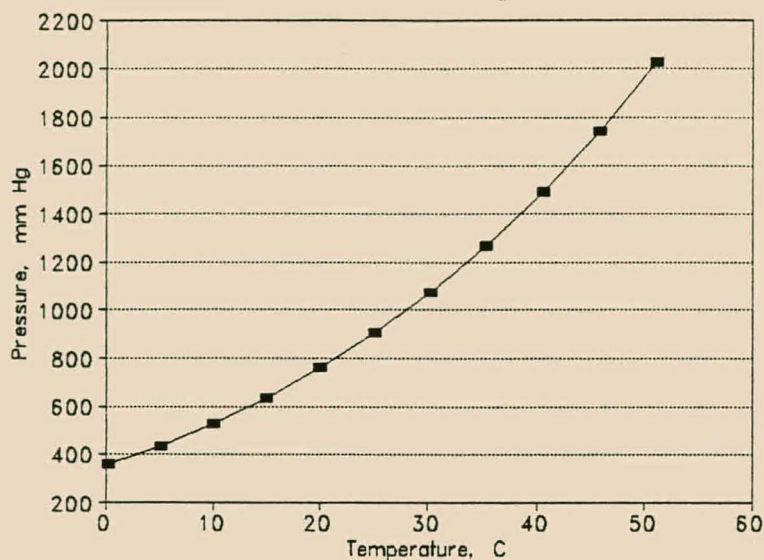
FIGURE 1. The vapour pressure of 3−methylbutene−1 as a function of temperature.

TITANIUM CATALYST

A commercial catalyst (δ-TiCl$_3$ (AlCl$_3$)$_{1/3}$(n-propylbenzoate)$_{1/3}$) was used.   It was stored in a stoppered round-bottomed flask in a desiccator to isolate it from moisture and oxygen.

ALUMINIUM COCATALYST

The cocatalyst, diethylaluminium chloride, was supplied by Ethyl Corporation, Baton Rouge, LA in the concentrated form (**Table II**).

TABLE II: Specification sheet for diethylaluminium chloride

Aluminium, wt%	22,3
Cl:Al mole ratio	1,02
Chloride, wt%	29,9
Hydrolysis gas composition, mole%	
Hydrogen	0,00
Ethane	99,8
n-Butane	0,2
Isobutane	0,0

OTHER

The purities of the isopropyl alcohol and hydrochloric acid used to terminate the reaction and the isopropyl alcohol used to wash the polymer powder were not critical, and solvent grade was used.

3.1.1.2   LABORATORY SAFETY

Almost without exception, polymerization reactions are dangerous in some respect.   In the polymerization with Ziegler-Natta catalysts, safety precautions beyond those normally observed in any chemical laboratory are required.

Titanium halides are rapidly decomposed by moisture and oxygen to titanium oxides and hydrogen halides. Care was exercised in handling to avoid contact with air; hence, it was handled only in a nitrogen atmosphere.

Aluminium alkyls self-ignite in air and react violently with water so that all operations had to be carried out with complete exclusion of air and moisture. These substances can cause severe burns and scarring when allowed to come into contact with skin. When alkylaluminium halides burn, they give off fumes which contain aluminium oxyhalides and hydrogen halides which are particularly dangerous and cause inflammation of the respiratory tract. The fumes resulting from the decomposition of aluminium alkyls in air are just as hazardous as smoke from a fire, even if no ignition occurs.

3 – Methylbutene – 1 is a gas at ambient temperature and pressure. It is highly combustible and can form explosive mixtures with air, so that special care was taken to avoid open flames, as well as sparks from switches or any other electrical equipment. The primary health hazards are associated with inhalation and prolonged skin contact which can cause irritation.

3.1.1.3   PREPARATION OF NITROGEN DRY-BOX

The charging of the reagents for the polymerization reactions had to be done in a nitrogen dry-box, because of the sensitivity of the Ziegler-Natta catalyst to air and moisture system as was mentioned above.

EQUIPMENT

The nitrogen dry-box is shown in **Figure 2**. A nitrogen cylinder was connected to the dry-box; the nitrogen was passed through an activated 4Å molecular sieve column and a silica gel column before entering the dry-box. Liquid nitrogen was placed inside the dry-box with dewar flasks. A drying tube was fitted to the dry-box to enable the air and moisture to be removed. A vacuum pump and a drying tube were connected to the loading compartment of the dry-box.

A humidity meter was used to determine roughly the water content in the preparation of the dry-box. Surgical gloves were worn during work inside the dry-box to prevent the evaporation of any skin moisture into the dry-box.
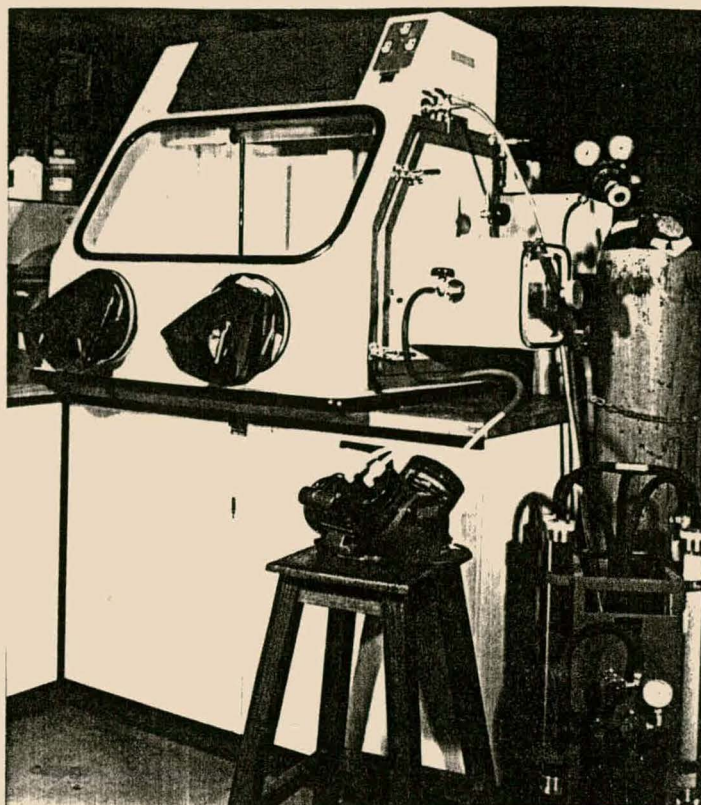
FIGURE 2. Nitrogen filled dry-box.

METHOD

The floor of the dry-box was covered with newspaper for protection against spills of the reagents used. Before the door of the dry-box was sealed with silicon sealant, it was ensured that all the large equipment used for the polymerizations, such as the balance and the laboratory stand, were inside the dry-box. The window and every possible source of leakage were sealed with silicon sealant.

Two empty dewar flasks were placed inside the nitrogen dry-box and the inside door of the loading compartment was closed. A third dewar flask was filled with liquid nitrogen, placed inside the loading compartment, and the outside door of the loading compartment was closed tightly. The vacuum pump was switched on for about 15 s, but not longer as the cabinet could not tolerate a very high negative pressure. The nitrogen cylinder was connected to the loading compartment, and nitrogen was blown through the loading compartment for about 30 s. These last two operations were repeated three times.

The inside door of the nitrogen dry-box was opened, and the dewar flasks inside the dry-box were filled with liquid nitrogen. Care had to be taken to add the liquid nitrogen very slowly to the dewar flasks, as a large positive pressure was created inside the dry-box when the very cold liquid nitrogen ($-196\,°C$) was poured into the dewar flask at room temperature. The inside door of the loading compartment could be left open as a precaution during the transfer of the liquid nitrogen, because if the positive pressure became too high inside the dry-box, the outside door of the loading compartment could be opened quickly to relieve the pressure inside the dry-box.

The empty dewar flask was placed inside the loading compartment and the inside door was closed tightly. The outside door of the loading compartment was opened and the dewar flask was taken out.

The abovementioned method of filling the dewar flasks was repeated until the dewar flasks inside the dry-box were full. The nitrogen cylinder was again connected to the dry-box and the nitrogen was bubbled through the liquid nitrogen. The bubbling rate had to be monitored so that the positive pressure inside the dry-box did not become excessive.

The dewar flasks were refilled from time to time when necessary. The nitrogen cylinder had to be closed every time an operation had to be done inside the dry-box, otherwise the high positive pressure inside the dry-box would have made it impossible to work inside it.

It was found that the inside door of the loading compartment was not airtight. This problem was solved by bubbling nitrogen through the liquid nitrogen when the outside door of the loading compartment was open.

During the night the dewar flasks were partly covered with polystyrene foam to prevent the fast evaporation of the liquid nitrogen, so that the dewar flasks would not run dry overnight. Nitrogen was not bubbled through the liquid nitrogen during the night.

The abovementioned procedure was continued for five days before the air and moisture content were low enough for the Ziegler-Natta catalyst system to be handled freely inside the dry-box. This conclusion was made on the basis of the humidity level measured inside the dry-box and the time taken for silica gel placed inside the dry-box to become discoloured.

3.1.1.4   POLYMERIZATION

The procedure followed was a combination of those described in the literature for the polymerization of 3-methylbutene-1 (41, 3, 79, 80). The amounts of the reagents used, especially the Al/Ti ratio, were selectively chosen from the values given in the literature (41, 3, 79, 80).

EQUIPMENT

The charging of the reagents was done inside the nitrogen dry-box. The polymerization reactor (Figure 3) was a 500-mL pressure bottle with a special seal mechanism. The rubber seal had to be covered with Teflon tape to prevent any damage caused by the Ziegler-Natta catalyst system. The reactor was wrapped in metal gauze to guard against any possible explosion. The pressure bottle was shaken on a stirrer bath (Figure 3) filled with ethylene glycol.
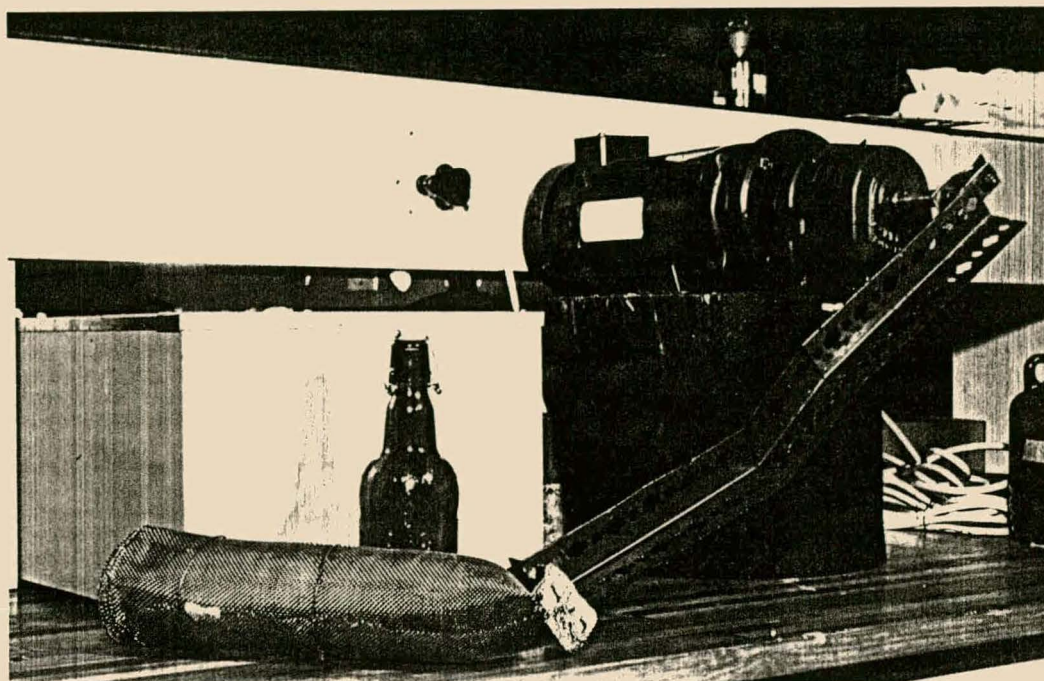
FIGURE 3. Pressure bottle and shaker bath.

METHOD

The glassware was kept overnight in an oven at 100 °C to remove any residual water that could poison the Ziegler-Natta catalyst system. The monomer, which is a gas at room temperature, was placed overnight in a refrigerator to cool it to 5 °C to make it available in liquid form.

The glassware was cooled in the nitrogen dry-box for 1 h before use. During this time, nitrogen was bubbled through the liquid nitrogen to remove any air or moisture that might possibly have leaked into the dry-box when the glassware was placed inside it.

The reagents were charged inside the nitrogen dry-box to prevent deactivation of the Ziegler-Natta catalyst system by water and oxygen. The catalyst, titanium trichloride, was too coarse for immediate use in the polymerization reaction and was ground with a mortar and pestle to get it into a finer form. The precise amount of titanium trichloride needed for the reaction was weighed on a balance inside the dry-box.

The 500-mL pressure reactor was charged with the ground titanium trichloride through a funnel. 60 mL of n-heptane was added to the reactor to cover the titanium trichloride and to prevent any deactivation of the catalyst.

The cocatalyst mixture, diethylaluminium chloride, had to be prepared before its addition to the pressure reactor. 0,07 g of Irganox 1076 was added to about 9 g of n-heptane. 2,35 mL of diethylaluminium chloride was drawn with a syringe from a cylinder, and immediately added to the n-

heptane mixture. The syringe was rinsed with *n*-heptane as a safety precaution. The cocatalyst mixture was added to the catalyst in the pressure reactor.

The reactor was closed and the catalyst and cocatalyst solution left to age for 10 min, while the monomer was fetched from the refrigerator. The monomer container was clamped upside down on the laboratory stand and 30 mL was collected in a measuring cylinder. The monomer and 30 mL of *n*-heptane were added to the catalyst system in the reactor. The pressure reactor was sealed and removed from the nitrogen dry-box by the usual method of removing any article from the dry-box as described in the section on the preparation of the dry-box.

The reactor was shaken in a ethylene glycol bath at a temperature of 80 °C at 100 rpm for 5 h.

The used glassware, especially that used for titanium trichloride and diethylaluminium chloride, was removed carefully from the dry-box and placed in a vapour cabinet (a gas mask was worn for this operation). The glassware used for diethylaluminiumchloride was placed inside a diluted hydrochloric acid solution to ease the cleaning of the glassware.

The polymerization reaction was stopped after 5 h by the slow addition of the polymerization reaction mixture to 600 mL of an isopropyl alcohol-hydrochloric acid mixture (2:1) in a 2 000 mL round-bottomed flask, while stirring. The alcohol deactivated the active catalyst sites and the hydrochloric acid reacted with the aluminium complexes. The remainder of the mixture in the reaction vessel was washed out with 300 mL of the isopropyl alcohol-hydrochloric acid mixture. The polymerization mixture was left to stand overnight to allow complete precipitation of the polymer.

The polymer slurry was filtered through a sintered glass filter of porosity 4. The remainder of the polymer slurry in the flask was washed out with isopropyl alcohol. The resulting fine white powder was dissolved in 170 mL *n*-heptane, containing hydroquinone as stabilizer, at 70 °C. The polymer was then precipitated by pouring the solution into 250 mL of isopropyl alcohol with stirring. The polymer was washed with isopropyl alcohol to remove the catalyst residue. The polymer powder was again filtered through a sintered glass filter of porosity 4. Finally, the product was dried for 24 h in a vacuum oven at 60 °C. The resulting polymer was weighed and the percentage conversion was calculated.

3.1.2   CHARACTERIZATION

3.1.2.1   *DIFFERENTIAL SCANNING CALORIMETRY (DSC)*

The DSC is a very useful instrument in the study of polymers. Each polymer has its own characteristic melting-point range, and therefore the melting point of a polymer can be used in the identification of a specific polymer.

EQUIPMENT

Differential scanning calorimetry (DSC) was carried out on a Du Pont 910 DSC with a Du Pont 9900 Computer/Thermal analyzer to determine the melting points, T_m, of the polymers.

METHOD

The 5-7 mg samples of the polymers were heated in open aluminium pans in a nitrogen atmosphere at a rate of 20 °C/min from ambient temperature to 330 °C and annealed at 330 °C for 10 min, which was found to be sufficient to destroy the thermal history and allow the polymer chains to rearrange. The samples were cooled to 25 °C at a rate of 10 °C/min. They were then rescanned in a nitrogen atmosphere at a rate of 10 °C/min from room temperature up to 330 °C. The scans were done in duplicate.

3.1.2.2   STEREOREGULARITY

3.1.2.2.1 Infrared Spectroscopy (IR)

Infrared spectroscopy is a valuable tool in the identification of polymers, as well as in the evaluation of stereoregularity of tactic polymers. The IR methods of stereoregularity evaluation are more reliable than the solvent-extraction method.

EQUIPMENT

The IR spectra of the polymer were recorded on a Nicolet 20 SXB instrument.

METHOD

The IR spectra of the polymer were recorded in the form of a KBr disk on the spectrometer.

3.1.2.2.2 Soxhlet extraction

Soxhlet extraction with a solvent for the atactic polymer is not a very accurate method for the determination of the degree of isotacticity, but it is convenient and fast. The extraction method has the advantage that it separates the atactic from the isotactic polymer.

EQUIPMENT

The equipment is shown in **Figure 4**. The equipment consisted of round-bottomed 500 mL flask connected to a vapour-jacketed soxhlet extractor, containing a sintered glass extraction thimble. The vapour-jacketed soxhlet extractor was connected to a condensor, which had a nitrogen inlet tube inside it. The nitrogen inlet tube was in turn connected to a rotameter which was connected to a nitrogen cylinder.
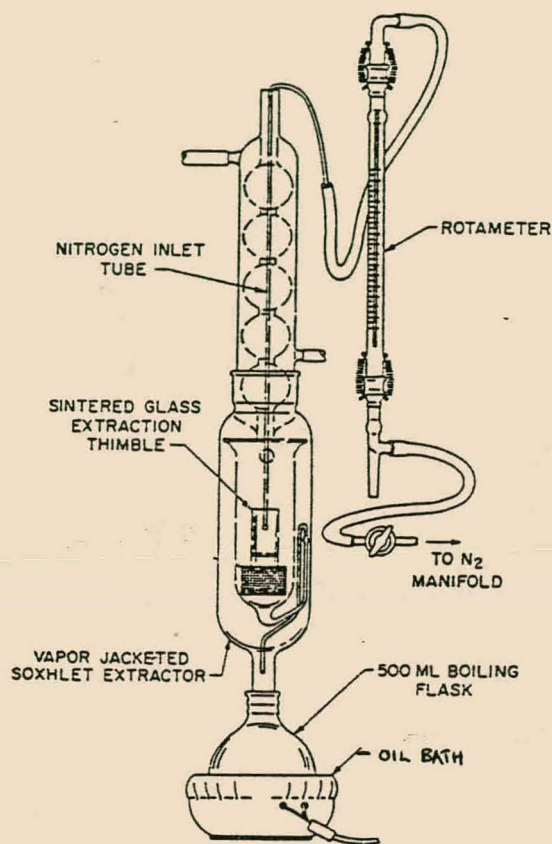
FIGURE 4. Extraction apparatus.

METHOD

About 2 g of polymer was weighed into a sintered glass extraction thimble of porosity 4. A 500-mL round-bottomed flask was charged with 300 mL of *n*-heptane, chemically pure grade, and a Teflon stirrer bar was added.

The oil bath was thermostatically controlled at a temperature of 110 °C. The polymer was extracted for 6 h with a controlled nitrogen flow of 100 mL/min. The polymer was dried in a thermostatically controlled oil bath at 60 °C with a nitrogen flow of 100 mL/min for 24 h. The polymer, insoluble in *n*-heptane, isotactic poly(3 – methylbutene – 1), was weighed, and the degree of isotacticity determined.

The soxhlet extraction of the polymer (Al/Ti = 1,5) was done in duplicate to determine the reproducibility of the extraction method. A soxhlet extraction of the polymer (Al/Ti = 2,0) was also done.

3.1.2.2.3 Broad-band Nuclear Magnetic Resonance (NMR)

NMR is useful in structure determination and polymer identification. Isotactic poly(3 – methylbutene – 1) is insoluble in most common solvents, so that it is insoluble in solvents suitable for NMR examination. The polymer can, however, be solubilized by conversion to a heavy oil by vacuum pyrolysis **(7)**. This is reasonably satisfactory from an NMR standpoint, since the number of double-bond hydrogens introduced into the spectra is not more than 6% of the total number of hydrogens.

EQUIPMENT

The NMR spectra of the polymer were recorded on a Bruker minispec PC120 at a temperature of 40 °C.

METHOD

Broad-band NMR was used in the tacticity measurement of poly(3-methylbutene-1) (Al/Ti = 1,5). The raw polymer powder was used as the sample.

3.1.2.3   INFRARED SPECTROSCOPY (IR)

EQUIPMENT

The IR spectra was recorded on a Perkin Elmer 17170 Infrared Fourier Transform spectrometer (FTIR) with a Barnes analytical/Spectra-tech Diffuse Reflectance (DRIFT) accessory.

METHOD

No preparation of the samples was needed, as the fine powder could be used directly in the IR spectrometer, because of the DRIFT accessory. The powder samples were levelled and smoothed in the sample cups before the spectra were recorded.

3.1.2.4   NUCLEAR MAGNETIC SPECTROSCOPY

As was mentioned earlier, isotactic poly(3 – methylbutene – 1) has a high solvent resistance. It is not easily dissolved even in highly chlorinated solvents at high temperatures **(Section 3.1.2.4.1)**. Atactic poly(3 – methylbutene – 1), on the other hand, dissolves fairly easily in most chlorinated solvents and it is therefore much easier to obtain NMR spectra of this polymer than of the isotactic fraction.

EQUIPMENT

A solid-state ^{13}C NMR spectrum of isotactic poly(3-methylbutene-1) was recorded on a Bruker 200 MHz NMR at 25 °C.

METHOD

No preparation of the sample was needed.

3.1.2.4.1 Solubility of poly(3 – methylbutene – 1) in NMR solvent

The solubility of poly(3 – methylbutene – 1) in the NMR solvent, hexachloro-1,3-butadiene was examined with a light-intensity thermal analyzer (LITA).

EQUIPMENT

Figure 5 shows the instrumental arrangement of the LITA **(81)**. Essentially it consists of a hot-stage microscope with polarizers.
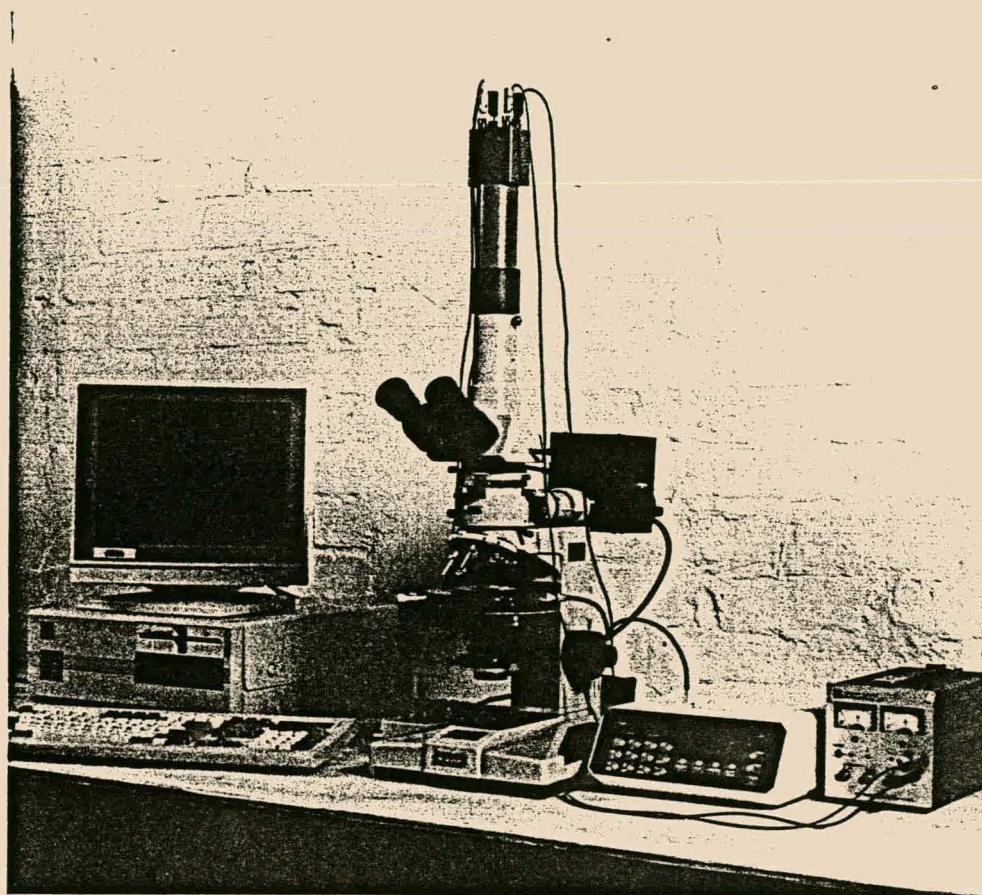
FIGURE 5. Instrumental arrangement of the LITA (54).

METHOD

A 10% (m/v) solution of poly(3 – methylbutene – 1) and hexachloro-1,3-butadiene was prepared, and placed on a glass pan. The glass pan was placed inside the hot stage of the light-intensity microscope and heated at a rate of 10 °C/min. The change of the intensity of the light beams passing through the solution with increasing temperature was recorded with LITA.

This method was repeated four times to test the reproducibility of the method.

3.1.2.5   THERMAL AND THERMOOXIDATIVE DEGRADATION

Thermal and thermooxidative stability of poly(3 – methylbutene – 1) can be determined by the DSC. The oxidation induction time (OIT) is a measure of the oxidative stability of the polymer and is defined as the time from the beginning of oxygen exposure up to the start of autoxidation.   The thermal decomposition temperature is determined in an inert atmosphere and is taken as the temperature of the decomposition exotherm.

EQUIPMENT

The determination of the thermal and thermooxidative stability of the polymer was carried out on a Du Pont 910 DSC with a Du Pont 9900 Computer/Thermal analyzer.

METHOD

5-7 mg samples of the homopolymer were given a thermal history before the actual determination was done. They were heated in open aluminium pans in a nitrogen atmosphere at a rate of 20 °C/min from ambient temperature to 330 °C and annealed at 330 °C for 5 min.

The thermal stability of the polymer was determined by heating the polymer in a nitrogen atmosphere at a rate of 10 °C/min up to 550 °C. This was done in duplicate.

The oxidation induction time (OIT) of the polymer was determined under different conditions. The polymer was heated at a rate of 10 °C/min to 300 °C in a nitrogen atmosphere and then held isothermal at 300 °C until a temperature equilibrium was reached. The atmosphere of the sample was rapidly changed from inert to oxidizing. The time to the onset of the exothermic oxidation of the polymer was a measure of the oxidative stability of the polymer. This method was repeated with switching from an inert atmosphere to an oxidizing atmosphere at 200 °C.

The oxidation induction temperature was determined by heating the polymer in air at a rate of 10 °C/min up to 320 °C. This was done in duplicate.

3.1.2.6   STABILIZATION

As was mentioned earlier, poly(3 – methylbutene – 1) can be stabilized with similar stabilizers as those used for stabilization of polypropylene. The polymer was very susceptible to decomposition by oxygen, and therefore it was not easy to blend the stabilizer into small quantities of polymer. However, a possible method for the thorough blending of poly(3 – methylbutene – 1) and stabilizers was, however, found.

EQUIPMENT

Test tubes wrapped in metal gauze were used to do the experiments. The polymer was examined with a Hitachi S-405A scanning electron microscope (SEM).

METHOD

9 mg polymer and 1 mg stabilizer, 9,10-dehydro-andraseen, were mixed in a test tube with 703,7 mg of an antistatic agent, Dehydat 51 special, obtained from Henkel. The test tube was wrapped in metal

gauze and heated over a flame, with nitrogen bubbling through the solution, until the polymer was dissolved. The solution was cooled to room temperature and a gel formed. The dehydat was leached out of the gel with methylene chloride. A white spongy polymer granule was formed. This was examined with a scanning electron microscope (SEM). The amount of stabilizer blended into the polymer granule was determined by calculating the weight gain of the polymer.

3.2 POLY(VINYLTRIMETHYLSILANE)

3.2.1 POLYMERIZATION

The polymerization of vinylsilanes in the presence of heterogeneous Ziegler-Natta catalysts based on AlR_3 and $TiCl_4$, violet $TiCl_3$, or VCl_3 give isotactic polymers (116), which are highly crystalline and insoluble in most organic solvents. It has a very high melting point of about 340 °C (117). The very low yield obtained with vinyltrimethylsilane is probably due to steric factors. High yields of poly(vinyltrimethylsilane) (**Figure 6**) were obtained in the presence of LiR as a catalyst (118) in anionic "living" polymerization. These polymers have a relatively low molecular mass and are either amorphous or paracrystalline.

$$-(-CH_2-CH-)-$$
$$|$$
$$CH_3——Si——CH_3$$
$$|$$
$$CH_3$$
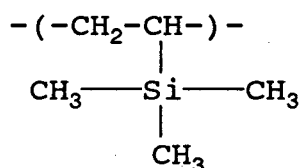
FIGURE 6. Poly(vinyltrimethylsilane).

3.2.1.1 REAGENTS

The reagents used were the same as in **Section 3.1.1.1**.

MONOMER

Vinyltrimethylsilane was obtained from Monomer-Polymer Laborotories (Cat no. 8585) and was purified before use. The gas chromatographic-mass spectrometry (GC-EI-MS) analysis with the Carlo Erba QMD 1000 mass spectrometer under GC conditions, indicated that the purity of the comonomer was 95,89%. The main impurity was ethyltrimethylsilane, 3,13%.

3.2.1.2 PURIFICATION OF MONOMER

The monomer was purified to remove the phenolic antioxidants, as they might have deactivated the Ziegler-Natta catalyst.

EQUIPMENT

The equipment consisted of a round-bottomed 250-mL flask, placed in a heating mantle, and connected to a condensor which in turn was connected through a vacuum adapter to a conical 250 mL flask. The condensor was also connected to a thermometer and water flowed through the condensor.

METHOD

200 g of vinyltrimethylsilane was washed with 100 mL of caustic soda solution with pH 9. This was repeated at least three times or until the pH of the comonomer solution was 9. The comonomer was then washed twice with 100 mL distilled water to remove the caustic soda.

The vinyltrimethylsilane was distilled in apparatus described above; the fraction distilled at 54 to 57 °C was taken as the pure comonomer.

3.2.1.3   LABORATORY SAFETY

See **Section 3.1.1.2**.

3.2.1.4   PREPARATION OF NITROGEN DRY-BOX

See **Section 3.1.1.3**.

3.2.1.5   POLYMERIZATION

The vinyltrimethylsilane homopolymer was synthesized to determine the effect of the incorporation of the silane comonomer on the IR spectrum of the 3 – methylbutene – 1 homopolymer.

Two vinyltrimethylsilane polymers were polymerized according to the procedure used for the polymerization of 3 – methylbutene – 1 **(Section 3.1.1.3)**.

3.2.2   CHARACTERIZATION

3.2.2.1   DIFFERENTIAL SCANNING CALORIMETRY (DSC)

EQUIPMENT

DSC scans of the polymer were recorded on a Du Pont 910 DSC with a Du Pont 9900 Computer/Thermal analyzer to determine the melting point of poly(vinyltrimethylsilane).

METHOD

2-3 mg samples of the polymer were heated in open aluminium pans in a nitrogen atmosphere at a rate of 20 °C/min from ambient temperature to 360 °C and then cooled to ambient temperature. The samples were rescanned in a nitrogen atmosphere at a rate of 10 °C/min to 550 °C.

3.2.2.2   INFRARED SPECTROSCOPY (IR)

EQUIPMENT

IR spectra of the polymers were recorded on a Perkin Elmer 17170 Infrared Fourier Transform spectrometer (FTIR) with a Barnes analytical/Spectra-tech Diffuse Reflectance (DRIFT) accessory.

METHOD

The DRIFT accessory allowed the use of powder samples in a sample cup. The powder samples were levelled and smoothed before the spectra were recorded.

3.3   3-METHYLBUTENE-1-VINYLTRIMETHYLSILANE COPOLYMERS

The processability of poly(3–methylbutene–1) can be improved by lowering the melting point by copolymerization with an alpha-olefin.   The lowering of the melting point of the polymer will be accompanied by a decrease of the degree of crystallinity of the polymer, and therefore the polymer will also be less brittle.

The choice of a comonomer is limited by two factors:

(a)   The comonomer must be compatible with Ziegler-Natta catalysts.   It is of great importance that it does not poison, that is, deactivate, the catalyst or cause any side reactions.

(b)   The comonomer must break up the crystallinity of poly(3–methylbutene–1) to yield a less brittle polymer. The comonomer will be able to meet this requirement only if it has a structure completely different from that of 3–methylbutene–1, and if it has more or less the same reactivity as 3–methylbutene–1.   If the two comonomers have the same reactivity, a random copolymer will be synthesized to yield a less brittle polymer.

A few comonomers meet the above requirements, such as vinylnaphthalene-1, but for economic reasons it could not be used in this study.   A silicon-containing alpha-olefin, vinyltrimethylsilane, was used instead, as the incorporation of the comonomer into the copolymer could be followed by the determination of the number of silicon atoms in the copolymer formed.

Vinyltrimethylsilane has a very low activity (119) because of the silicon atom attached directly to the double bond; and should therefore be prone to form a random copolymer with 3–methylbutene–1, which also has a very low activity.

3.3.1   COPOLYMERIZATION

3.3.1.1   REAGENTS

SOLVENT

n-Heptane was used as the solvent in the copolymerization reactions.   See **Section 3.1.1.1** for the specifications of the solvent.

3-METHYLBUTENE-1

3-Methylbutene-1 was used as obtained from Aldrich without further purification.   See **Section 3.1.1.1** for the purity of this comonomer.

VINYLTRIMETHYLSILANE

Vinyltrimethylsilane was obtained from Monomer-Polymer Laboratories(cat no. 8585) and was purified before use.   See **Section 3.2.1.2.**

ZIEGLER-NATTA CATALYST SYSTEM

Titanium trichloride and diethylaluminium chloride formed the catalyst system. See **Section 3.1.1.1** for details.

OTHER

The purities of the isopropyl alcohol and hydrochloric acid used to terminate the reaction, and the isopropyl alcohol used to wash the copolymer powder, were not critical, and solvent-grade material was used.

3.3.1.2   LABORATORY SAFETY

See **Section 3.1.1.2**.

Vinyltrimethylsilane is a flammable liquid and care was taken to keep it away from open flames. The primary health hazard is associated with prolonged skin contact which can cause irritation.

3.3.1.3   PREPARATION OF NITROGEN FILLED DRY-BOX

See **Section 3.1.1.3**.

3.3.1.4   COPOLYMERIZATION

The 3-methylbutene-1-vinyltrimethylsilane copolymers were synthesized according to the same procedure used for the homopolymerization of 3-methylbutene-1.

EQUIPMENT

The reagents were charged inside the nitrogen dry-box. The copolymerizations were carried out in a 500-mL pressure bottle with a special seal mechanism (**Figure 3**). The rubber seal of the bottle was covered with Teflon tape to protect it against damage by the Ziegler-Natta catalyst system. The pressure bottle was wrapped in metal gauze as a safety precaution. The pressure bottle was shaken on a stirrer bath (**Figure 3**) filled with ethylene glycol.

METHOD

The glassware was kept overnight in an oven at 100 °C to remove any residual water that could deactivate the titanium trichloride or the diethylaluminium chloride. The monomer, which is a gas at room temperature, was placed overnight in a refrigerator to cool it to 5 °C to make it available in liquid form.

The glassware was cooled in the nitrogen dry-box for 1 h before the copolymerization reaction was done. During this hour, nitrogen was bubbled through the liquid nitrogen to remove any air or moisture that may possibly have leaked into the dry-box while the glassware was being placed inside it.

The reagents were charged inside the nitrogen dry-box to prevent deactivation of the Ziegler-Natta catalyst system by water and oxygen. The catalyst, titanium trichloride, was too coarse for direct use

in the polymerization reaction, was ground into a finer form with a mortar and pestle. The 3,70 g of titanium trichloride was weighed on a balance inside the dry-box (Al/Ti = 1,5).

The 500 mL pressure reactor was charged with the ground titanium trichloride through a funnel. 60 mL of n-heptane was added to the reactor to cover the titanium trichloride and to prevent any deactivation of the catalyst.

The cocatalyst mixture, diethyl aluminiumchloride, was prepared before its addition to the pressure reactor. 0,07 g of Irganox 1076 was added to about 9 g of n-heptane. 2,35 mL of diethyl aluminiumchloride was drawn with a syringe from a cylinder, and quickly added to the n-heptane mixture. The syringe was immediately rinsed with n-heptane as a safety precaution. The cocatalyst mixture was added to the catalyst in the pressure reactor.

The reactor was closed and the catalyst and cocatalyst solution left to age for 10 min, while the 3 – methylbutene – 1 was fetched from the refrigerator. The 3 – methylbutene – 1 cylinder was clamped upside down on the laboratory stand and the 3 – methylbutene – 1 was collected in a measuring cylinder. The 3 – methylbutene – 1 was added to the catalyst solution in the pressure reactor.

The vinyltrimethylsilane was weighed on the balance inside the dry-box and added to the pressure reactor together with 30 mL of n-heptane. The reaction vessel was sealed and removed from the nitrogen dry-box by the typical method used to remove any article from a dry-box as described in the section on the preparation of the nitrogen dry-box.

The reactor was shaken in a ethylene glycol bath at a temperature of 80 °C at 100 rpm. The copolymerization reactions were terminated at various times.

The used glassware, especially that used for titanium trichloride and diethylaluminium chloride, was removed carefully from the dry-box and placed in a vapour cabinet (a gas mask was worn for this operation. The glassware used for diethylaluminium chloride was placed inside a dilute hydrochloric acid solution to ease the cleaning of the glassware.

The copolymerization reactions were terminated by the slow addition of the copolymerization mixture to 600 mL of an isopropyl alcohol-hydrochloric acid mixture (2:1) in a 2 000-mL round-bottomed flask, while stirring. The alcohol deactivated the active catalyst sites and the hydrochloric acid reacted with the aluminium complexes. The remainder of the mixture in the reaction vessel was washed out with 300 mL of the isopropyl alcohol-hydrochloric acid mixture. The copolymerization mixture was left to stand overnight to allow complete precipitation of the polymer.

The copolymer slurry was filtered through a sintered glass filter of porosity 4. The remainder of the polymer slurry in the flask was washed out with isopropyl alcohol. The resulting fine white powder was dissolved in 170 mL n-heptane, containing hydroquinone as stabilizer, at 70 °C. The copolymer was then precipitated by pouring the solution into 250 mL of isopropyl alcohol with stirring. The copolymer was washed with isopropyl alcohol to remove the catalyst residue. The copolymer powder was again filtered through a sintered glass filter of porosity 4. Finally, the product was dried in a vacuum oven at 60 °C for 24 h. The resulting copolymer was weighed and the percentage conversion was calculated.

3.3.2   CHARACTERIZATION

3.3.2.1   DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The DSC was very useful for the approximate determination of the extent of incorporation of vinyltrimethylsilane into the copolymer, and its effects on the copolymer properties and structure. The silane comonomer disrupted the crystalline structure of poly(3–methylbutene–1), and lowered the degree of crystallinity and the melting point of poly(3–methylbutene–1). The lowering of the melting point of poly(3–methylbutene–1) would, therefore, indicate the amount of vinyltrimethylsilane incorporated into the copolymer.

EQUIPMENT

The melting points of the copolymers were determined by DSC scans recorded on a Du Pont 910 DSC with a Du Pont 9900 Computer/Thermal analyzer.

METHOD

5-7 mg samples of the various copolymers were heated in open aluminium pans in a nitrogen atmosphere at a rate of 20 °C/min from room temperature to 330 °C after which they were left to cool to room temperature. The copolymer samples were rescanned in a nitrogen atmosphere at a rate of 10 °C/min from ambient temperature to 330 °C.

3.3.2.2   INFRARED SPECTROSCOPY (IR)

The IR spectra of the copolymers were used in combination with their melting points, determined with the DSC, to study the extent of incorporation of the vinyltrimethylsilane comonomer into the copolymer. The IR spectra of the two homopolymers were compared with those of the copolymers.

EQUIPMENT

IR spectra of the various copolymers were recorded on a Perkin Elmer 17170 Infrared Fourier Transform spectrometer (FTIR) with a Barnes analytical/Spectra-tech Diffuse Reflectance (DRIFT) accessory.

METHOD

No preparation of samples was needed, as the fine powder could be used directly in the IR spectrometer, because of the DRIFT accessory. The powder samples were levelled and smoothed in the sample cups before the spectra were recorded.

3.3.2.3   SOXHLET EXTRACTION

The degree of isotacticity of one of the copolymers was determined by soxhlet extraction with a solvent for the atactic polymer.

EQUIPMENT

See **Section 3.1.2.2.2**.

METHOD

About 1 g of the 53,57 mole% vinyltrimethylsilane copolymer was weighed into a sintered glass extraction thimble of porosity 4. A 500-mL round-bottomed flask was charged with 300 mL of *n*-heptane, chemically pure grade, and a Teflon stirrer bar was added.

The oil bath was at a temperature of 110 °C. The copolymer was extracted for 6 h; in a controlled nitrogen flow of 100 mL/min. The copolymer was dried in a vacuum oven at 60 °C for 24 h. The copolymer insoluble in *n*-heptane, isotactic 3 – methylbutene – 1-vinyltrimethylsilane copolymer, was weighed and the degree of isotacticity determined.

3.3.2.4   *^{13}C NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY (^{13}C NMR)*

Poly(vinyltrimethylsilane) and poly(3 – methylbutene – 1) both had a very high solvent resistance. The 3 – methylbutene – 1-vinyltrimethylsilane copolymer was also insoluble in common solvents, and therefore it was possible to obtain only solid-state ^{13}C NMR spectra of the copolymers. The high cost of these analyses allowed the recording of the spectrum of only one copolymer.

EQUIPMENT

The solid-state ^{13}C NMR spectrum was recorded on a Bruker 200 MHz NMR at 25 °C.

METHOD

The solid-state ^{13}C NMR spectrum of the copolymer that was found on reacting 3-methylbutene-1 (97,08 mole%) with vinyltrimethylsilane (2,91 mole%) for 5 h was recorded.

3.3.3   DETERMINATION OF THE SILICON CONTENT OF THE COPOLYMERS

The silicon content of each of the copolymers was used as a measure of the precise amount of vinyltrimethylsilane comonomer incorporated into the various copolymers, and could be used to explain the degree of lowering of the melting points of each copolymer.

3.3.3.1   *ELEMENTAL ANALYSIS METHOD*

Determination of silicon in insoluble polymers necessitates the decomposition of the polymers into soluble forms by acid digestion or fusion with various fluxes (120). The procedure for bringing the silicon of the sample into solution is that of fusion of the copolymer in sodium carbonate. The fusion of silicates with anhydrous sodium carbonate brings them into forms that are completely soluble in hydrochloric acid. A large excess of the sodium carbonate flux, such as a sodium carbonate/sample ratio of 4:1, must be used to ensure the complete dissolution of the the fused sample in acid.

EQUIPMENT

A platinum crucible with a lid was used for the analysis. The amount of silicon in the copolymers was determined on an atomic absorption spectrometer (AA), model AA 1275 Varian.

METHOD

A copolymer sample (0,1 g) was placed in a tared, ignited, platinum crucible of 20 mL capacity. The crucible was placed at a slight angle on a triangle of Nichrome wire on a ring stand. The cover was placed so that about one fifth of the crucible top was open. The sample was ignited with a low flame to prevent any sudden or violent ignition of the copolymer. After the copolymer had been consumed, the cover was adjusted for a wider crucible top opening, and the flame was gradually increased until it imparted a cherry redness to the crucible bottom (about 900 °C ignition temperature). The crucible was covered, cooled in a desiccator and weighed.

Anhydrous sodium carbonate (0,5 g) was added to the crucible. The sodium carbonate was thoroughly mixed by means of a spatula with the ignited sample. Any particles of sodium carbonate and the sample adhering to the spatula were brushed into the crucible. Sodium carbonate (0,1 g) was placed on top of the mixture.

The covered crucible was placed at a slight angle on a triangle, and heated over a Meker burner. Care was taken not to let the reducing portion of the flame come in contact with the crucible, and not to let the flame envelop the crucible. The crucible was heated with a low flame for the first 10 min. The cover was cautiously lifted to let in air after the initial danger of spattering had passed. The heat was gradually increased by using almost the full flame of the burner.

The Meker burner flame intensity was increased until the bottom of the crucible was a cherry red, about 900 °C. This temperature was maintained for 15-20 min. The cover was lifted periodically to provide an oxidizing environment. During the later stages of fusion, the cover was adjusted so that the crucible top was about one-fourth open. The heat was increased until the crucible bottom was a bright cherry red, about 1 000 °C, and heating was continued for 5-10 min. Patches of fused material sticking to the sides of the crucible was heated to cause all the material to run together into one mass. The cover was removed, and the crucible was heated for a few minutes more to finish the fusion. The flame was removed, the crucible grasped with tongs, and rotated in such a way that the fusion solidified along the sides.

Approximately 5 mL of 6N hydrochloric acid was added to the crucible, heated cautiously on a sand bath to disintegrate the remaining cake, and the crucible contents were transferred to a 25-mL measuring flask. A policeman and a few drops of 6N hydrochloric acid was used to transfer all materials adhering to the cover into the measuring flask.

The amount of silica in the measuring flasks, that is, the amount of silica in the copolymer sample, was recorded on atomic absorption spectrometer (AA) with 20, 50 and 100 ppm silicon standards.

3.3.3.2   *PROTON-INDUCED GAMMA EMISSION (PIGE): ANALYTE AND NON-ANALYTE SPIKING METHODS*

The amount of silicon present in the copolymers was determined by two PIGE techniques, an analyte spiking method and a non-analyte spiking method. In the non-analyte spiking method a concept of relative deceleration values has been introduced to correct for matrix effects (121). The results of the analyte spiking method are often dependent on the concentration of the spike used, but this tendency could be corrected for by back-extrapolating to zero-added spike (122).

The copolymer samples were spiked with Li_2SiO_3 containing both an analyte and non-analyte element, allowing the simultaneous application of the analyte as well as the non-analyte spiking method. Li_2SiO_3 acted as a spike and comparator.

The accuracy of these methods was tested by analyzing two standard reference materials, British Chemical Standard BCS 308 and Standard Chrome Ore XXXI, and a simulated silicon-containing polymer sample prepared by mixing known amounts of polyethylene wax with silicon powder.

EQUIPMENT

The copolymer tablets were irradiated with 5-MeV proton beams from the Van de Graaff accelerator of the National Accelerator Centre at Faure, with typical currents ranging from 2-15 nA.

METHOD

Spiked samples of the reference standards were prepared by mixing known masses of about 0,1-0,8 g of Li_2SiO_3 with 1,0 g of the sample, giving an elemental concentration for lithium of about 1-7% and an additional silicon concentration of 2-13%. The spiked copolymer samples were prepared by mixing known masses of about 0,02-0,2 g Li_2SiO_3 with about 0,2 g of the copolymers, giving an elemental concentration for lithium of about 1,5-8% and an added silicon concentration of 4-17%. The simulated polymer sample was prepared by mixing polyethylene wax with silicon powder to provide a silicon concentration of about 5%.

Targets were irradiated with 5-MeV proton beams from the Van de Graaff accelerator.

The silicon in the copolymers was determined by measuring the 1 273 keV 29Si (1,0) and the 1 779 keV 28Si (1,0) gamma rays induced by 5 MeV protons, and using Li_2SiO_3 as the spike and comparator.

CHAPTER 4

POLY(3−METHYLBUTENE−1)

4.1 POLYMERIZATION

3−Methylbutene−1 was polymerized with two different cocatalyst/catalyst ratios, as shown in **Table I** below, to determine the effect of the cocatalyst/catalyst ratio on the yield and melting point of the polymer.

TABLE I: Poly(3−methylbutene − 1) prepared by varying the cocatalyst/catalyst ratio.

HOMOPOLYMER	Al/Ti	Al (mmole)	Ti (mmole)	YIELD (g)	PERCENTAGE CONVERSION
1	1,5	18,6	12,4	16,97	84,55
2	2,0	24,8	12,4	17,63	87,84

DISCUSSION

The experiment with the cocatalyst/catalyst ratio of 2,0 produced a higher polymer yield due to the higher concentration of reactive sites. It was necessary to determine the melting point of the two polymers to determine whether the Al/Ti ratio of 2,0 did not affect the properties of the polymer adversely.

4.2 CHARACTERIZATION

4.2.1 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The DSC scans of the homopolymers are shown below (**Figures 1** and **2**).
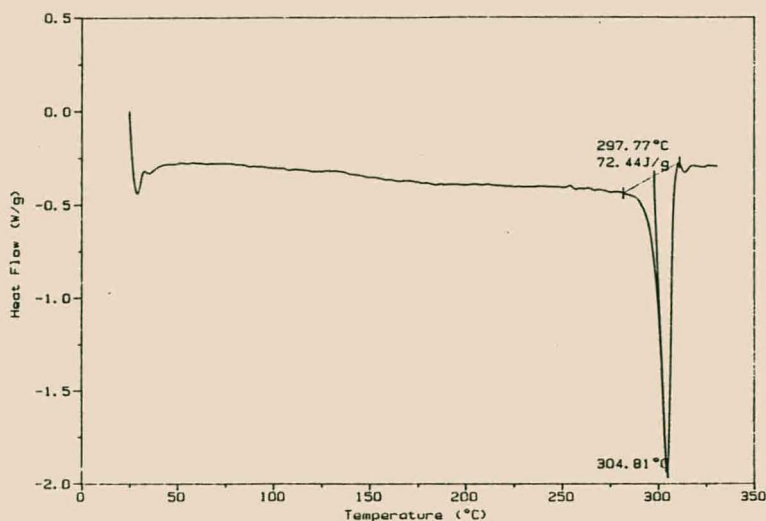
FIGURE 1. *DSC scan of poly(3−methylbutene−1) (Al/Ti = 1,5) showing the melting endotherm. The scan was carried out at a rate of 10 °C/min.*
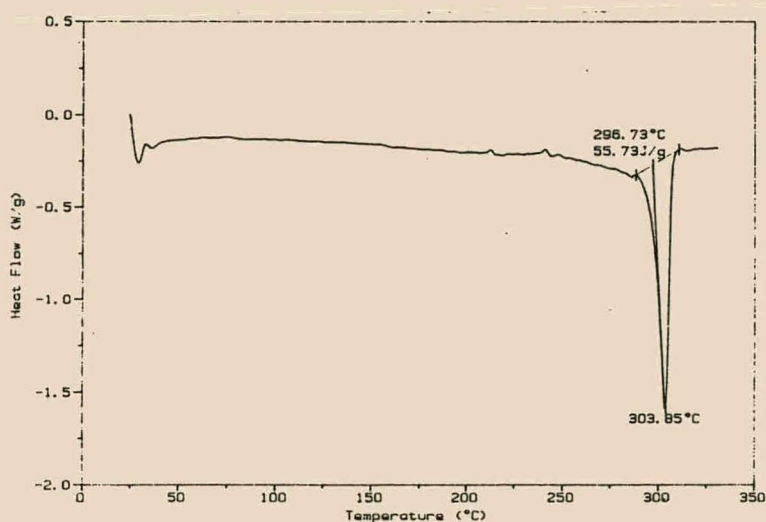
FIGURE 2. *DSC scan of poly(3−methylbutene−1) (Al/Ti = 2,0) showing the melting endotherm. The scan was carried out at a rate of 10 °C/min.*

DISCUSSION

Both polymers showed sharp peaks in the melting area. It was clearly indicated that the two polymers, polymerized with different Al/Ti ratios, showed a small difference in melting points. The melting point of the polymer with Al/Ti ratio of 1,5 was 304,81 °C, and the melting point of the polymer with Al/Ti ratio of 2,0 was 303,85 °C. Thus, although an Al/Ti ratio of 2,0 gave a polymer with a higher yield, the polymer had a melting point slightly lower than that of the polymer yielded with an Al/Ti ratio of 1,5.

4.2.2 STEREOREGULARITY

4.2.2.1 INFRARED SPECTROSCOPY (IR)

The IR spectra of isotactic poly(3 – methylbutene – 1) **(Figure 3)** and atactic poly(3 – methylbutene – 1) **(Figure 4)** is shown below.
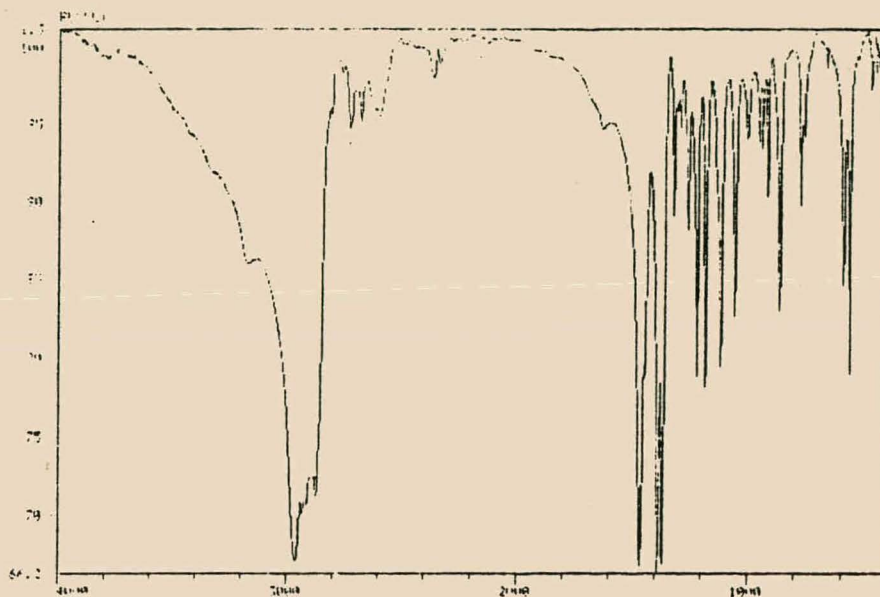
FIGURE 3. IR spectrum of poly(3 – methylbutene – 1) - crystalline polymer (isotactic).
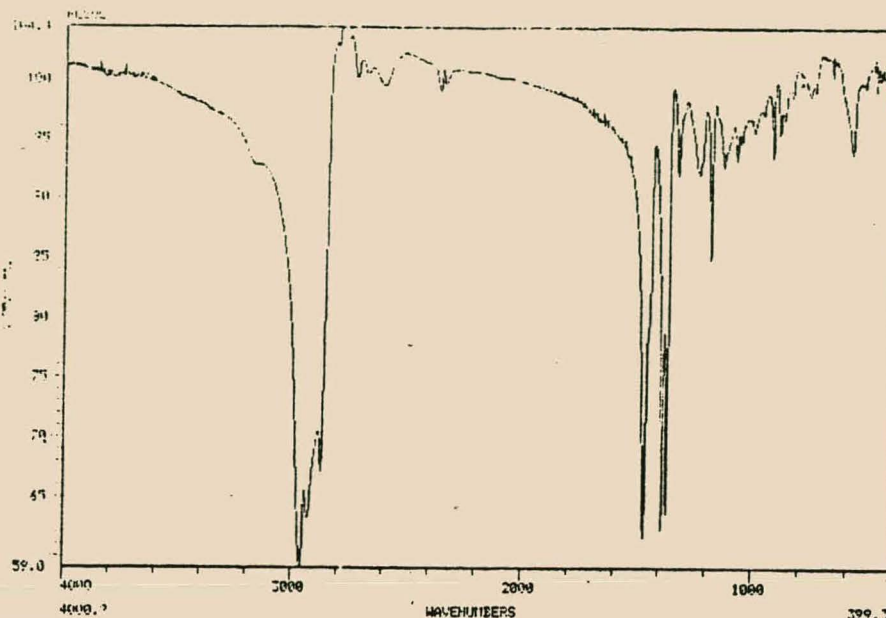
FIGURE 4. *IR spectrum of poly(3−methylbutene−1) - atactic polymer with the courtesy of D. Joubert.*

DISCUSSION

The band frequencies of the polymer IR spectra are enumerated in **Table II**.

It emerges from **Figures 3** and **4** and **Table II** that during the amorphization of the polymer the IR spectrum underwent significant changes. Some bands disappeared almost completely and the intensities of others were considerably reduced (1218, 1057 and 592 cm-1), the 1057 cm-1 band moved noticeably to a long-wave area. The bands which disappeared during the amorphization of the polymer could be used for quantitative evaluation of stereoregularity of a crystalline polymer. In poly(3−methylbutene−1) the two bands, 778 and 1218 cm-1, were used for this purpose. The 778 cm-1 band disappeared completely and the intensity of the 1218 cm-1 band dropped sharply during the amorphization of poly(3−methylbutene−1). The 1180 cm-1 band, which intensity changed slightly during the amorphization of the polymer, was conveniently used as an inner standard of film thickness.

The degree of isotacticity of poly(3−methylbutene−1) was calculated according to the formula: $I = (D_{778}/D_{1180})/x$, where $x = 0,47$, the conventional value of the ratio D_{778}/D_{1180} for a 100% isotactic polymer (**Table IV**).

TABLE II: IR spectra of isotactic poly(3-methylbutene-1).

BAND FREQUENCY, cm⁻¹ CRYSTALLINE POLYMER	BAND FREQUENCY, cm⁻¹ MELTED POLYMER	ALTERATION OF BANDS DURING POLYMER MELTING
2958 (v.s)		remains
2931 (v.s)		remains
2913 (v.s)		remains
2890 (v.s)		remains
2874 (v.s)		remains
2858 (s.sh)		remains
1465 (v.s)	1465 (v.s)	remains
1388 (v.s)	1385 (v.s)	remains
1369 (v.s)	1367 (v.s)	remains
1328 (m)	1322 (m)	remains
1307 (v.w)		
1295 (w)	-	disappears
1258 (m)	1258 (w)	decreases
1218 (s)	1218 (s)	decreases
1180 (s)	1178 (s)	remains
1135 (sh)		
1117 (s)	1120 (m)	decreases
1057 (m)	1048 (m)	decreases
1003 (w)	1000 (w)	remains
957 (m)	960 (w.sh)	decreases
940 (m)	-	disappears
918 (m)	918 (m)	remains
865 (s)	862 (m)	decreases
778 (m)	-	disappears
770 (sh)	-	disappears
763 (m)	767 (m)	remains
592 (m)	593 (w)	decreases
565 (m)	568 (m)	remains

vs = very strong; s = strong; m = medium; w = weak; sh = shoulder.

4.2.2.2 SOXHLET ECTRACTION

The results of the soxhlet extractions are shown in **Table III**.

TABLE III: Determination of the degree of isotacticity of the 3 – methylbutene – 1 polymers with the soxhlet extraction method.

Al/Ti	DEGREE OF ISOTACTICITY (%)
1,5	. 98,53
1,5	98,70
2,0	97,75

DISCUSSION

The results indicated that poly(3 – methylbutene – 1) had a very high degree of isotacticity and that the soxhlet extraction method had a high reproducibility. It is also shown that, not only did the polymer with Al/Ti ratio of 2,0 have a slightly lower melting point than the polymer with Al/Ti 1,5, but it also had a slightly lower degree of isotacticity.

4.2.2.3   BROAD-BAND NUCLEAR MAGNETIC RESONANCE (NMR)

The result of this method is given in **Table IV**.

TABLE IV: The degree of isotacticity of poly(3 – methylbutene – 1) (Al/Ti = 1.5) determined with three different techniques.

METHOD	DEGREE OF ISOTACTICITY (%)
Soxhlet extraction (n-heptane)	98,61
Infrared spectroscopy	96,8
NMR spectroscopy	96,8

CONCLUSION

The degrees of isotacticity of poly(3 – methylbutene – 1) (Al/Ti = 1,5) determined by the three above-mentioned methods correlated very well. The high degree of isotacticity of poly(3 – methylbutene – 1) indicated that this polymer had a very high degree of crystallinity.

4.2.3   INFRARED SPECTROSCOPY (IR)

The IR spectrum poly(3 – methylbutene – 1) is given in **Figure 5** below.
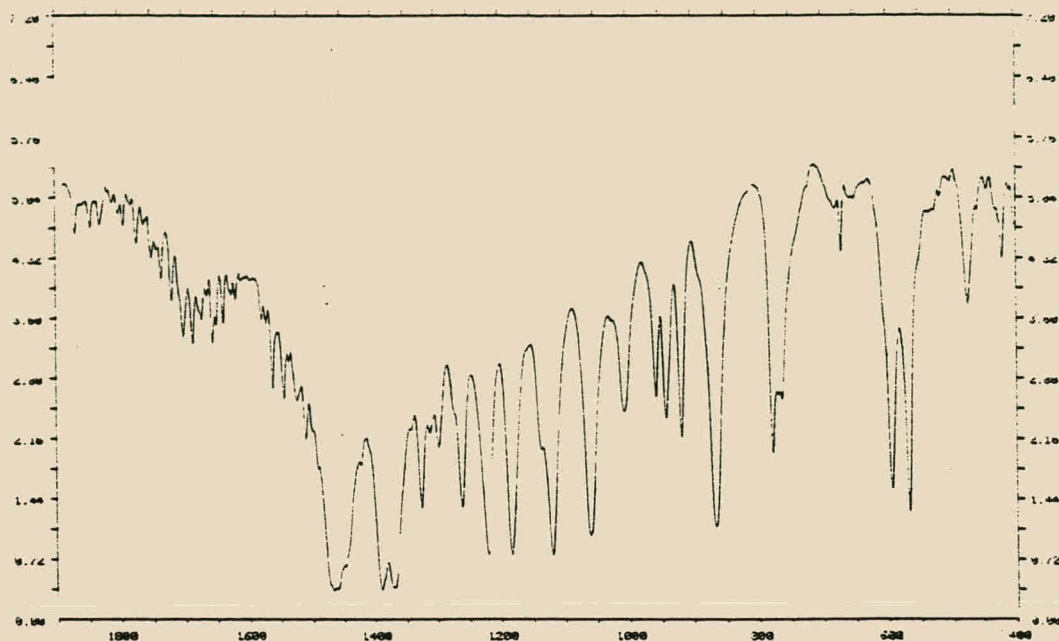
FIGURE 5. IR spectrum of isotactic poly(3 – methylbutene – 1)

DISCUSSION

The polymer showed the characteristic carbon-hydrogen oscillations of the CH_2- and CH_3-groups in the region 3000-2700 cm-1 **(7)**. This region, as well as the region 2700-1500, could not be used to indentify structure.

The doublet at 1388-1370 cm-1 can be attributed to the symmetrical deformation oscillations of CH_3-groups in the isopropyl grouping. The tertiary CH bending vibration should be close to 1340 cm-1, but the intensity of this band was too low to be identified, for the reason that the CH vibration was obscured by the presence of intense CH_3 deformation vibrations.

The 1180 cm-1 band, as in branched hydrocarbons, could be attributed to oscillations of the isopropyl group and the 918 cm-1 band to pendulum oscillations of methyl groups (in the polypropylene spectrum the analogous band was located in the area 920 cm-1). This spectrum had no absorption at 721 cm-1 characteristic of long-chain methylene groups **(39)**. On the analogy of the results obtained for polypropylene, it could be assumed that the majority of the bands, located in the area lower than 1300 cm-1, had a complex nature and were related to mutual oscillations of the skeleton and deformation oscillations of C-H-bond in various groupings.

4.2.4   NUCLEAR MAGNETIC SPECTROSCOPY

The solid-state 13C NMR spectrum of isotactic poly(3-methylbutene-1) is given in **Figure 6**.
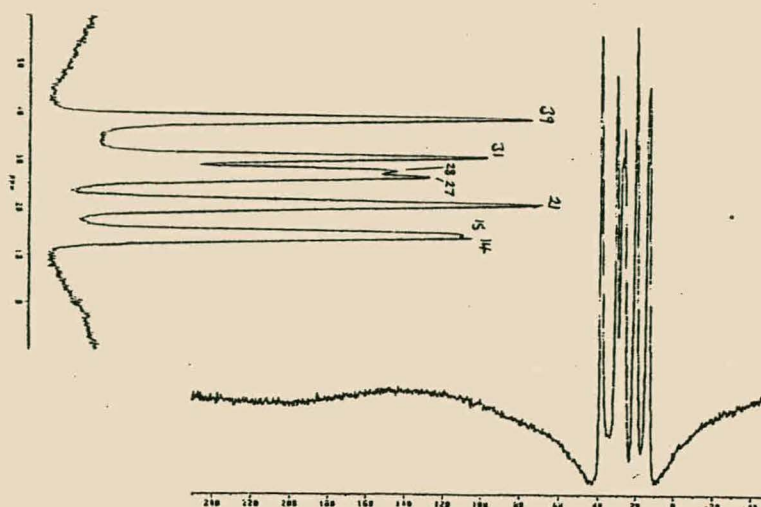
FIGURE 6. Solid-state ^{13}C NMR spectrum of isotactic poly(3-methylbutene-1).

DISCUSSION

The solid-state ^{13}C NMR spectrum of isotactic poly(3-methylbutene-1) showed five peaks. The peak at 31 ppm was assigned to the backbone CH groups in the isotropic region, and the peak at 39 ppm was assigned to the backbone CH groups in the crystalline region. The backbone CH groups were affected much more by their environment than the backbone CH_2 groups were. The peaks at 27 and 28 ppm were assigned to the backbone CH_2 groups. The complete peak assignment of the solid-state ^{13}C NMR spectrum of isotactic poly(3-methylbutene-1) was as follows (48):

CH_3	14 ppm
CH_2	27, 28 ppm
CH (backbone)	31, 39 ppm
CH (sidegroup)	21 ppm

where δ was accurate to ± 2ppm.

4.2.4.1   SOLUBILITY OF POLY(3-METHYLBUTENE-1) IN NMR SOLVENT

The LITA scans of the poly(3-methylbutene-1)-hexachloro-1,3-butadiene solutions is given in **Figure 7**.

DISCUSSION

The five LITA scans all showed that the polymer started to dissolve at 110 °C. The polymer precipatated when the solution was cooled. It was difficult to dissolve a sufficient amount of poly(3-methylbutene-1) in hexachloro-1,3-butadiene for use in NMR. The polymer had a very low solubility in hexachloro-1,3-butadiene.
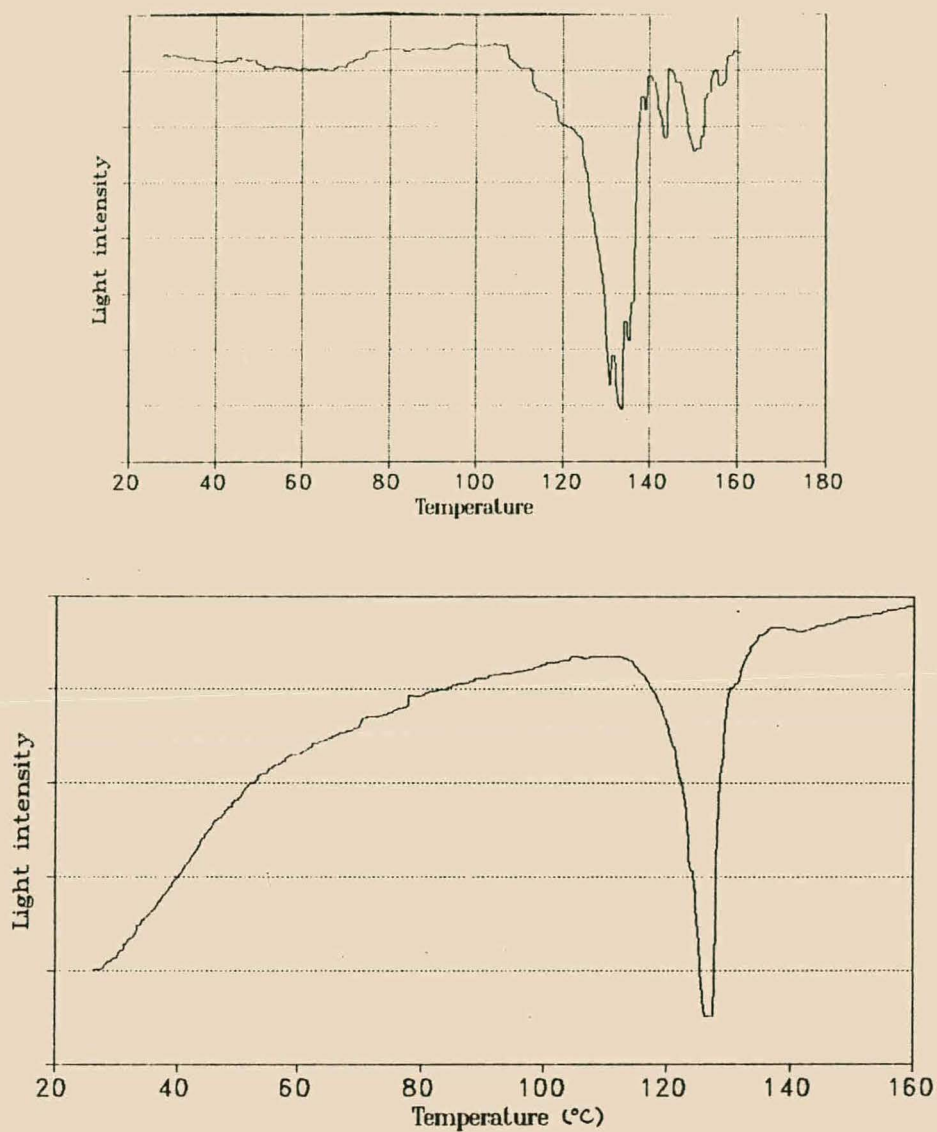
FIGURE 7. *LITA scans of a 10% poly(3−methylbutene−1) hexachloro-1,3-butadiene solution.*

4.2.5   THERMAL AND THERMOOXIDATIVE DEGRADATION

The thermal stability of the polymer was given by the thermal degradation temperature of the polymer **(Figure 8)**.
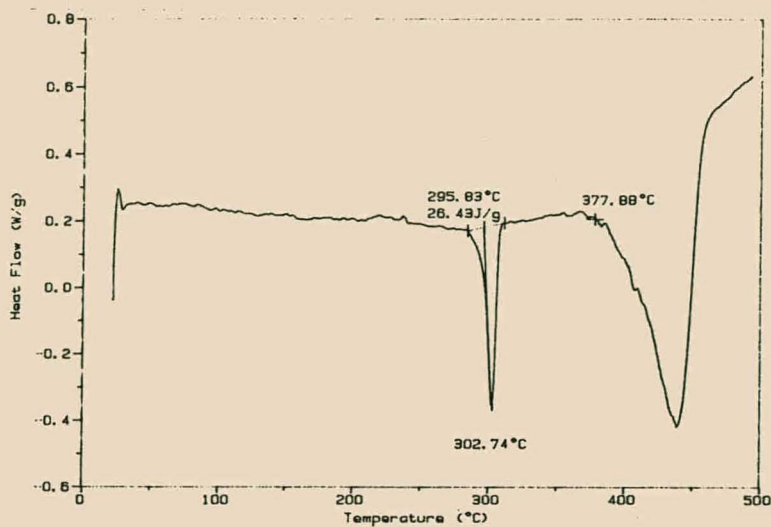
FIGURE 8. DSC scan of poly(3−methylbutene−1) showing the thermal degradation temperature.

The thermooxidative stability of the polymer was given by its oxidation induction time (OIT) **(Figure 9)** and its oxidation induction temperature **(Figure 10)**
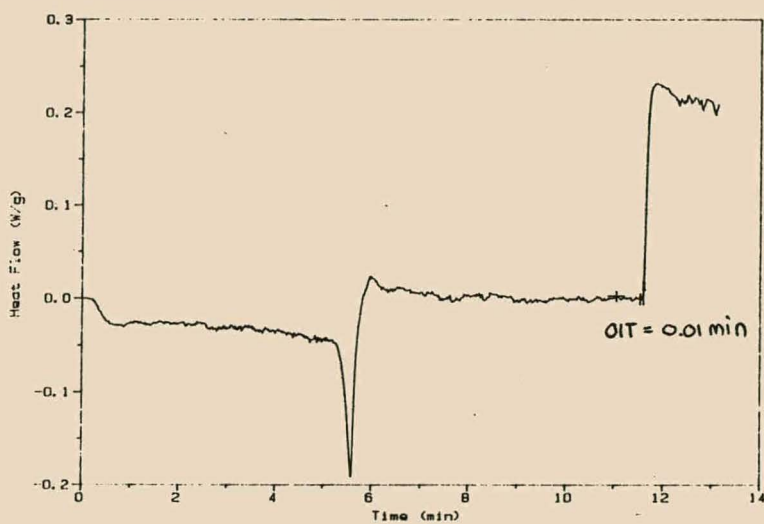
FIGURE 9. DSC scan of poly(3−methylbutene−1) showing the oxidation induction time (OIT).
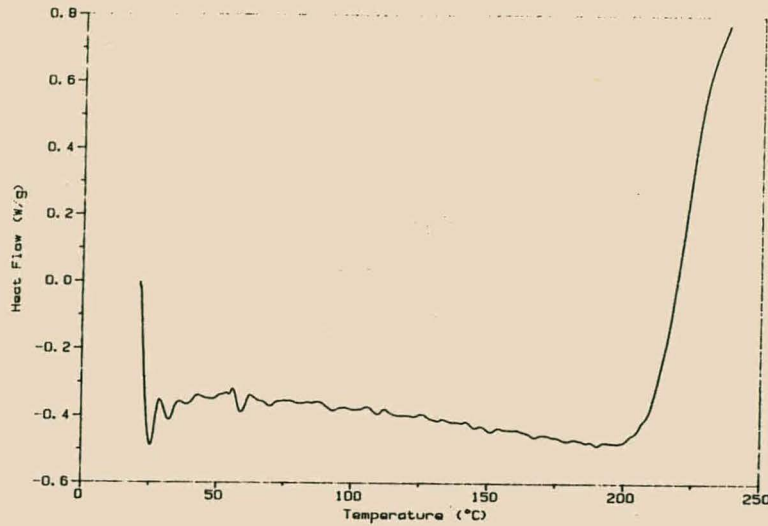
FIGURE 10. DSC scan of poly(3−methylbutene−1) showing the oxidation induction temperature.

DISCUSSION

Figure 8 shows that the polymer was thermally stable at up to 377,88 °C in the presence of a nitrogen atmosphere, whereas **Figure 10** shows that the polymer was thermally stable only up to about 200 °C in the presence of air. **Figure 9** led to the conclusion that the polymer degrades instantly on exposure to air at high temperatures. Thus, poly(3−methylbutene−1) was very susceptible to thermal and thermooxidative degradation, and had to be well stabilized before use.

4.2.6   STABILIZATION

Figure 11 shows the outside surface of the spongy polymer granule obtained, **Figure 12** shows the cross-section of the spongy polymer granule.
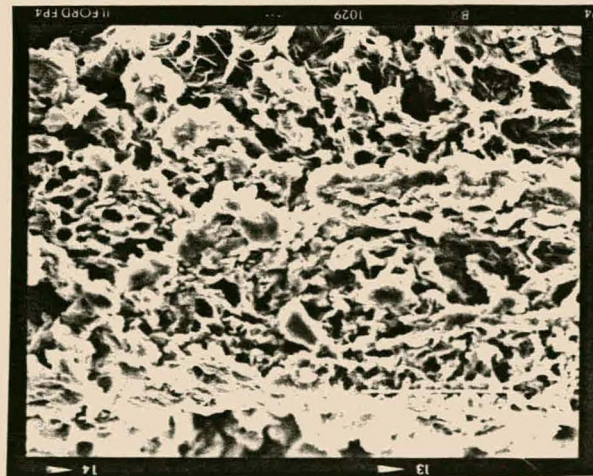
FIGURE 11. SEM photo of the outside surface of the poly(3−methylbutene−1) granule.
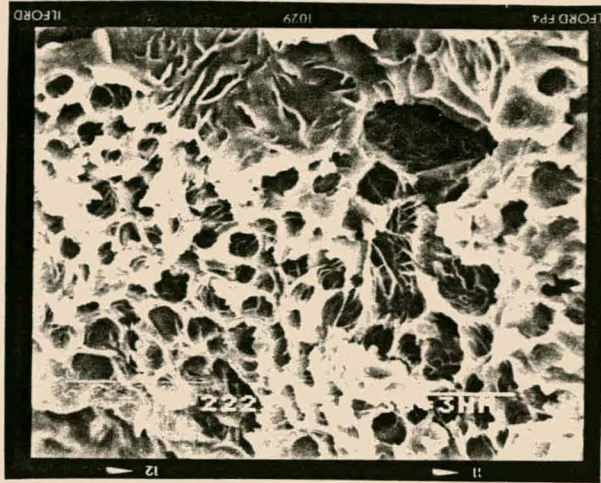
FIGURE 12. *SEM photo of the cross-section of the poly(3−methylbutene−1) granule.*

DISCUSSION

This method not only stabilized the poly(3−methylbutene−1), but it also proved to be a way of dissolving poly(3−methylbutene−1).

CHAPTER 5

POLY(VINYLTRIMETHYLSILANE)

5.1 POLYMERIZATION

The results of the two polymerizations of vinyltrimethylsilane is given in **Table I**.

TABLE I: Homopolymerization of vinyltrimethylsilane.

MONOMER-(ml)	Al/Ti	Al (mmole)	Ti (mmole)	POLYMERIZA-TION TIME (h)	YIELD (g)	% CON-VERSION
40,0	1,5	18,6	12,4	70	0,0240	0,093
27,26	1,5	18,6	12,4	70	0,0087	0,049

DISCUSSION

The very low yields of the vinyltrimethylsilane polymers after such a long reaction time, illustrated the low reactivity of vinyltrimethylsilane, which was due to the silicon atom attached directly to the double bond (steric factors). The low yields of the polymers rendered the characterization of the polymers more difficult.

5.2 CHARACTERIZATION

5.2.1 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The DSC scan of the polymer is given in **Figure 1** below.
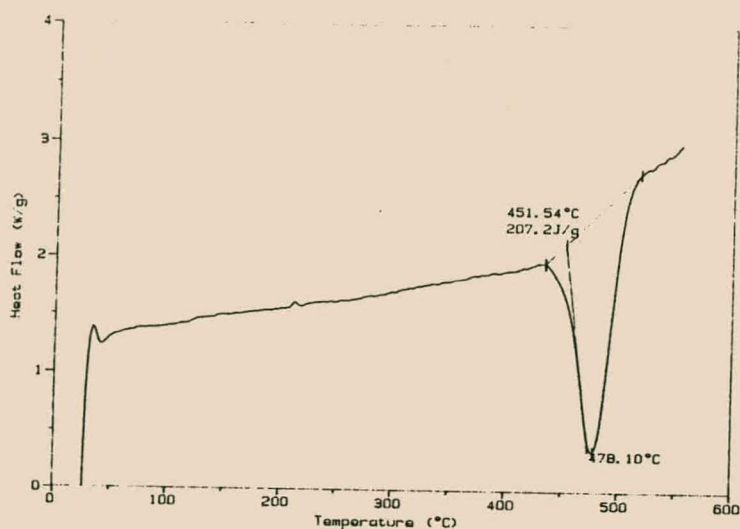
FIGURE 1. DSC scan of poly(vinyltrimethylsilane.

DISCUSSION

Poly(vinyltrimethylsilane) had a much higher melting point, 478,10, than poly(3−methylbutene−1), 304,81. It was also noted that poly(vinyltrimethylsilane) had a broad melting peak, whereas poly(3−methylbutene−1) had a very sharp melting peak.

5.2.2   INFRARED SPECTROSCOPY (IR)

The IR spectrum of the polymer is given in **Figure 2** below.
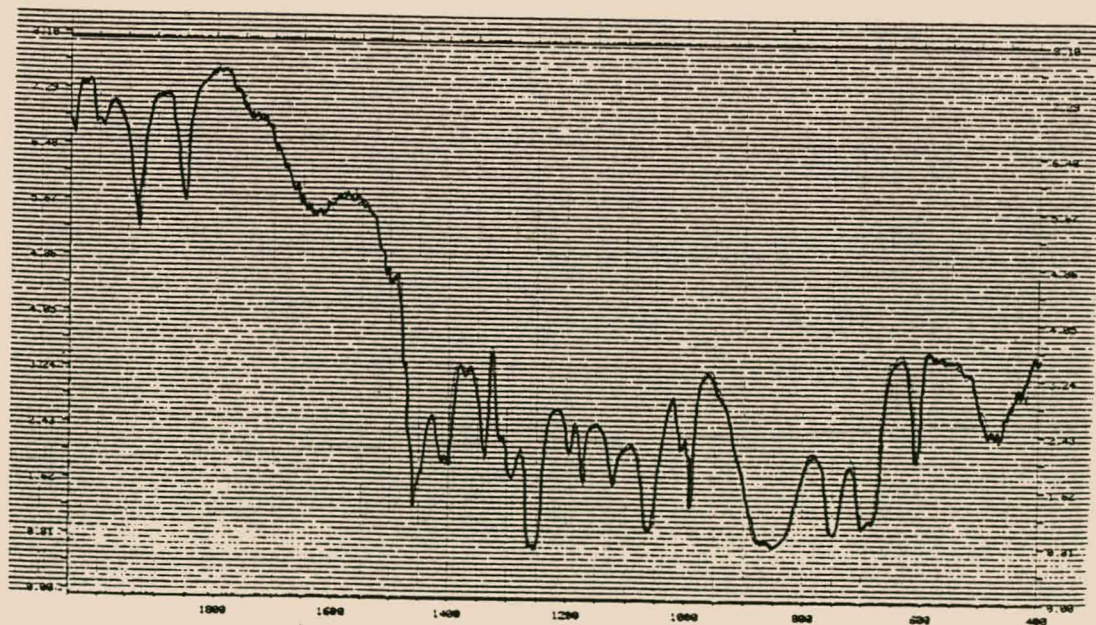
FIGURE 2. IR spectrum of poly(vinyltrimethylsilane).

DISCUSSION

The doublet at 1460-1400 cm^{-1} was attributed to the antisymmetric deformation oscillations, and the broad peak at 1250 cm^{-1} was attributed to the symmetric deformation oscillations of the CH_3-groups in the $Si(CH_3)_3$ grouping (123). The CH and CH_2 symmetric bending vibrations appeared as a sharp peak at 1340 cm^{-1}, whereas the antisymmetric bending vibrations of the CH_2 groups appeared at 1290 cm^{-1}. The very strong sharp band at 1255 cm^{-1} with a shoulder on its high frequency side, was attributed to the CH_3 symmetric deformation.

The C-C skeletal stretching modes resulted in a strong band at about 1060 cm^{-1}. The CH bending vibrations appeared as a sharp peak with a shoulder at 990 cm^{-1}. The very broad band at 880-820 was attributed to the rocking oscillations of the CH_3-groups in the $Si(CH_3)_3$ grouping. The SiC_3 stretching modes of the $Si(CH_3)_3$-groups appeared at 750 and 690 cm^{-1}.

CHAPTER 6

3 – METHYLBUTENE – 1-VINYLTRIMETHYLSILANE COPOLYMERS

6.1   POLYMERIZATION

The details of the various copolymers synthesized are given in **Table I**.

TABLE I: Copolymerization of 3-methylbutene-1 and vinyltrimethylsilane.

COMONOMER FEED COMPOSITION		COPOLYMERI-ZATION TIME (h)	YIELD (g)	PERCENTAGE CONVERSION
3-METHYL-BUTENE-1 (mole%)	VINYLTRIMETHYL-SILANE (mole%)			
97,08	2,91	5	7,71	36,84
97,08	2,91	10	9,19	43,91
90,91	9,09	5	1,74	7,59
86,96	13,04	5	2,02	8,29
83,34	16,65	5	4,16	16,12
46,43	53,57	50,5	3,58	13,97
25,68	74,32	5	0,1185	0,46
6,62	93,38	120	0,0687	0,26

DISCUSSION

The percentage conversion of the copolymers over a period of 5 h compared with that of the homopolymers over a period of 5 h (**Table I Chapter 4**), indicated that the reactivity of vinyltrimethylsilane was much lower than that of 3 – methylbutene – 1. The low reactivity of vinyltrimethylsilane in Ziegler-Natta polymerizations was already suspected from the homopolymerization of vinyltrimethylsilane (**Table I Chapter 5**). The large difference in reactivity of these two comonomers led to the conclusion that the formation of random copolymers was impossible. This statement will be supported by the characterization of the copolymers discussed in the following sections.

6.2   CHARACTERIZATION

6.2.1   DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The DSC scans of the 3–methylbutene–1-vinyltrimethylsilane copolymers are given below (**Figures 1-8**).

FIGURE 1. *DSC scan of the copolymer that was formed on reacting 3-methylbutene-1 (97,08 mole%) and vinyltrimethylsilane (2,91 mole%) for 5 h at 80 °C.*

FIGURE 2. *DSC scan of the copolymer that was formed on reacting 3-methylbutene-1 (97,08 mole%) and vinyltrimethylsilane (2,91 mole%) for 10 h at 80 °C.*

FIGURE 3. *DSC scan of the copolymer that was formed on reacting 3-methylbutene-1 (90,91 mole%) and vinyltrimethylsilane (9,09 mole%) for 5 h at 80 °C.*

FIGURE 4. *DSC scan of the copolymer that was formed on reacting 3-methylbutene-1 (86,96 mole%) and vinyltrimethylsilane (13,04 mole%) for 5 h at 80 °C.*

FIGURE 5. *DSC scan of the copolymer that was formed on reacting 3-methylbutene-1 (83,34 mole%) and vinyltrimethylsilane (16,65 mole%) for 5 h at 80 °C.*

FIGURE 6. *DSC scan of the copolymer that was formed on reacting 3-methylbutene-1 (46,43 mole%) and vinyltrimethylsilane (53,57 mole%) for 50,5 h at 80 °C.*

FIGURE 7. *DSC scan of the copolymer that was formed on reacting 3-methylbutene-1 (25,68 mole%) and vinyltrimethylsilane (74,32 mole%) for 5 h at 80 °C.*

FIGURE 8. *DSC scan of the copolymer that was formed on reacting 3-methylbutene-1 (6,62 mole%) and vinyltrimethylsilane (93,38 mole%) for 120 h at 80 °C.*

DISCUSSION

The 2,91 mole% vinyltrimethylsilane copolymer (5 h) had a lower melting point, 303,93 °C, than that of the 2,91 mole% vinyltrimethylsilane copolymer (10 h), 304,30 °C, which could be attributed to the homopolymerization of 3–methylbutene–1. A very small amount of the vinyltrimethylsilane was present during the reaction, and because of its low reactivity, homopolymerization of 3–methylbutene–1 would be favoured.

The melting points of the copolymers decreased with increase in the amount of vinyltrimethylsilane in the reaction feed up to the 16,65 mole% vinyltrimethylsilane copolymer. The melting point of the 53,57 mole% vinyltrimethylsilane copolymer showed an increase in melting point, but the melting point of the 74,32 mole% vinyltrimethylsilane copolymer showed a decrease in melting point again. These trends

are illustrated in **Figure 9**, where the value at the peak of the melting endotherm was taken as the melting point, and in **Figure 10**, where the value at the onset of melting of the copolymer was taken as the melting point.   The mole% vinyltrimethylsilane given in **Figures 9** and **10**, is the mole% vinyltrimethylsilane in the comonomer feed.
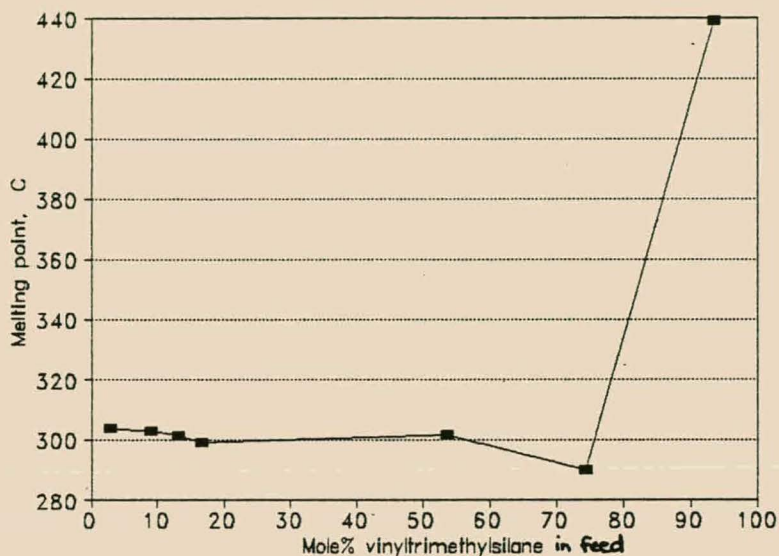
FIGURE 9. *Illustration of the trends in the melting points of the copolymers (melting point was taken as the value at the peak of the melting endotherm).*
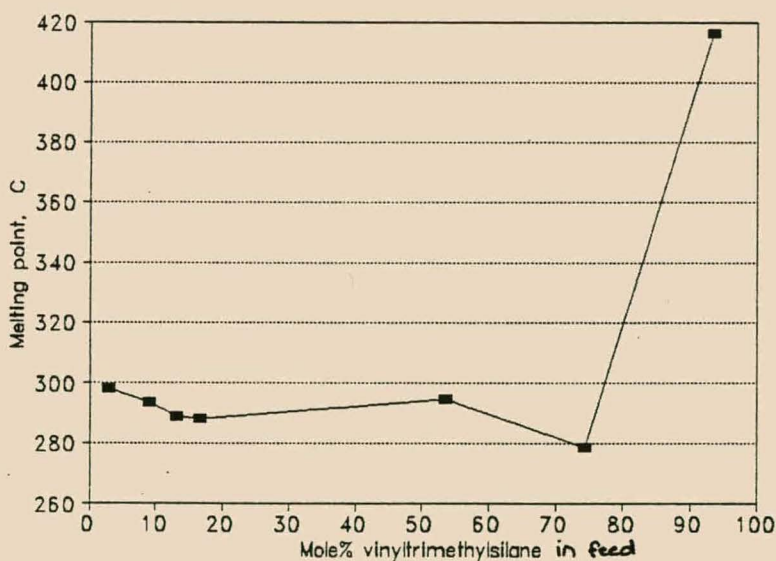
FIGURE 10. *Illustration of the trends in the melting points of the copolymers (melting point was taken as the value at the onset of melting of the copolymer).*

It was suggested that the silane comonomers lowered the degree of isotacticity of the copolymers; the degree of crystallinity was therefore lowered, which resulted in lower melting points.   The melting points of the copolymers did not decrease as much as was expected; this was because of the low reactivity of vinyltrimethylsilane, because of which only a small amount was incorporated.

The 93,38 mole% vinyltrimethylsilane copolymer (feed ratio) had a very high melting point; this was higher than that of poly(3 – methylbutene – 1), which led to the conclusion that in this case

3 – methylbutene – 1 acted as the comonomer and decreased the melting point of poly(vinyltrimethylsilane).

The DSC scans indicated that the fraction of copolymer melting lower than the melting point (taken as the value of the peak of the melting endotherm), increased with increasing amount of vinyltrimethylsilane added to the reaction feed. This suggested a broadening of the molecular mass distribution of the copolymers.

6.2.2   INFRARED SPECTROSCOPY (IR)

The IR spectra of the 3 – methylbutene – 1-vinyltrimethylsilane copolymers are given below (**Figures 11-19**).
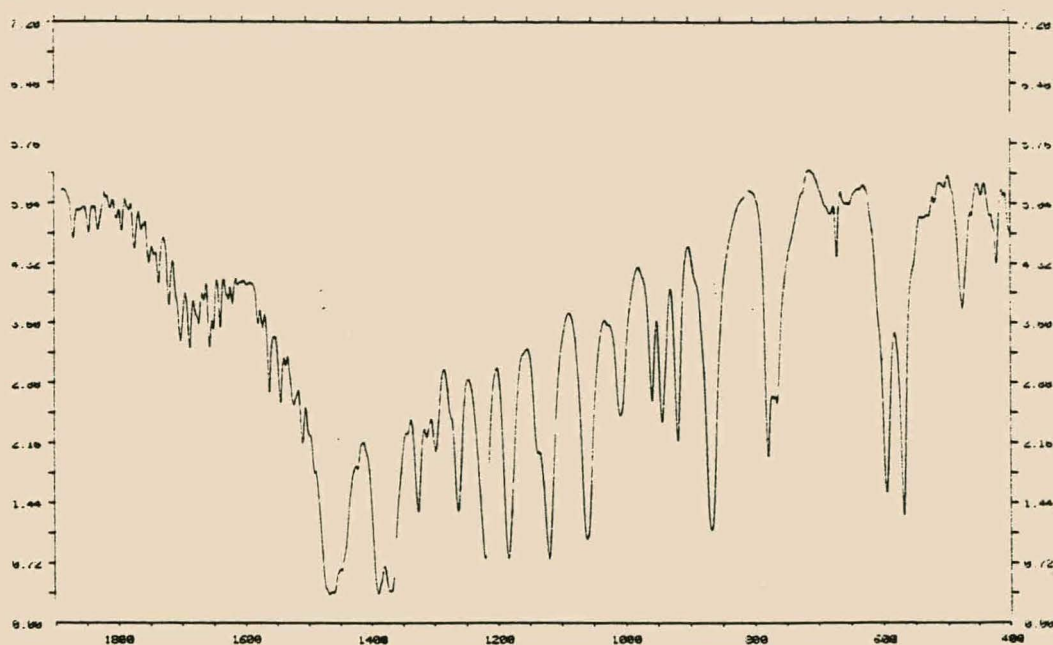
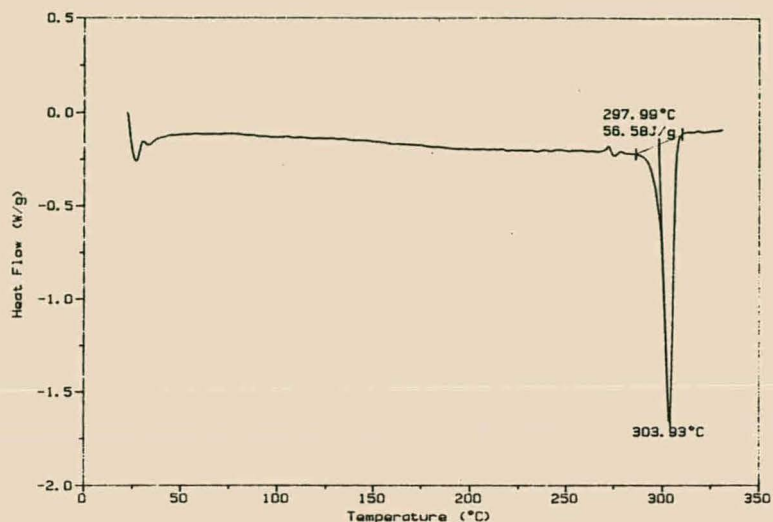*FIGURE 11. IR spectrum of poly(3 – methylbutene – 1).*
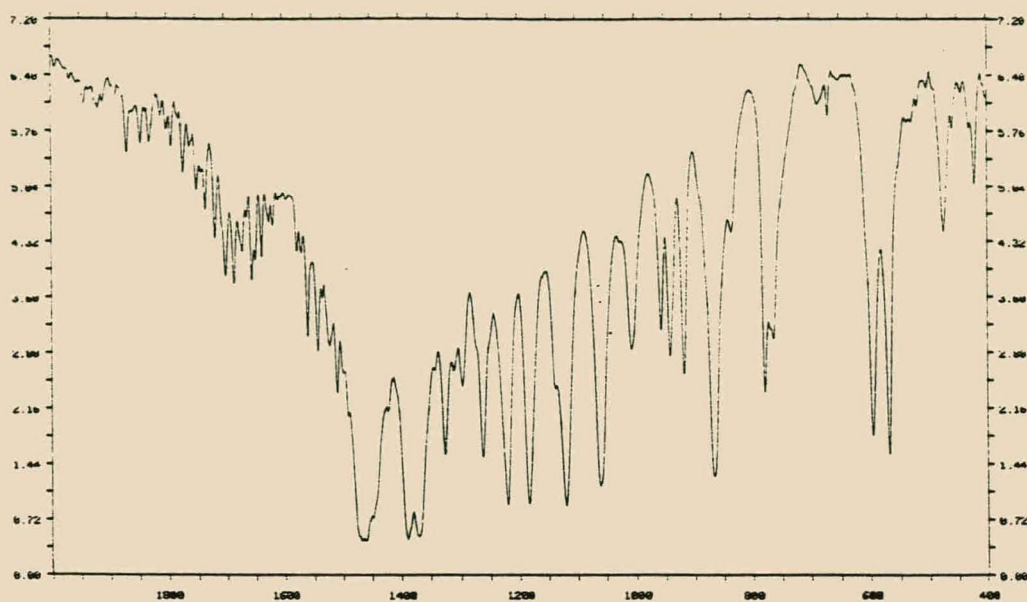
FIGURE 12. *IR spectrum of the copolymer that was formed on reacting 3-methylbutene-1 (97,08 mole%) and vinyltrimethylsilane (2,91 mole%) for 5 h at 80 °C.*
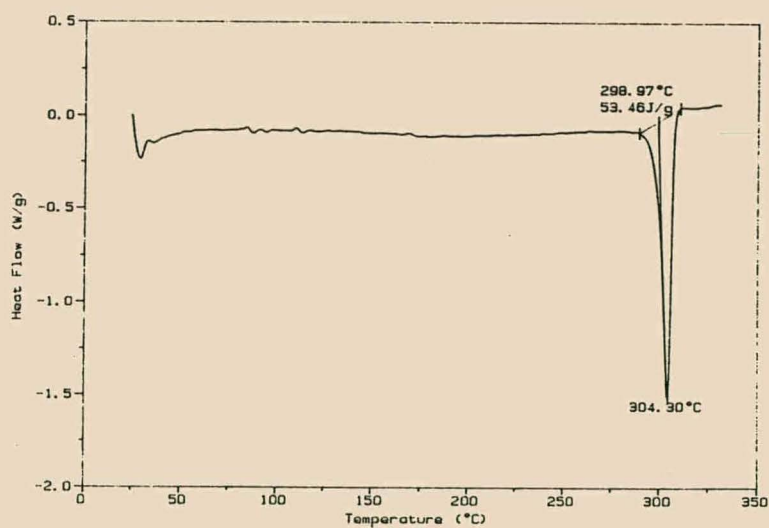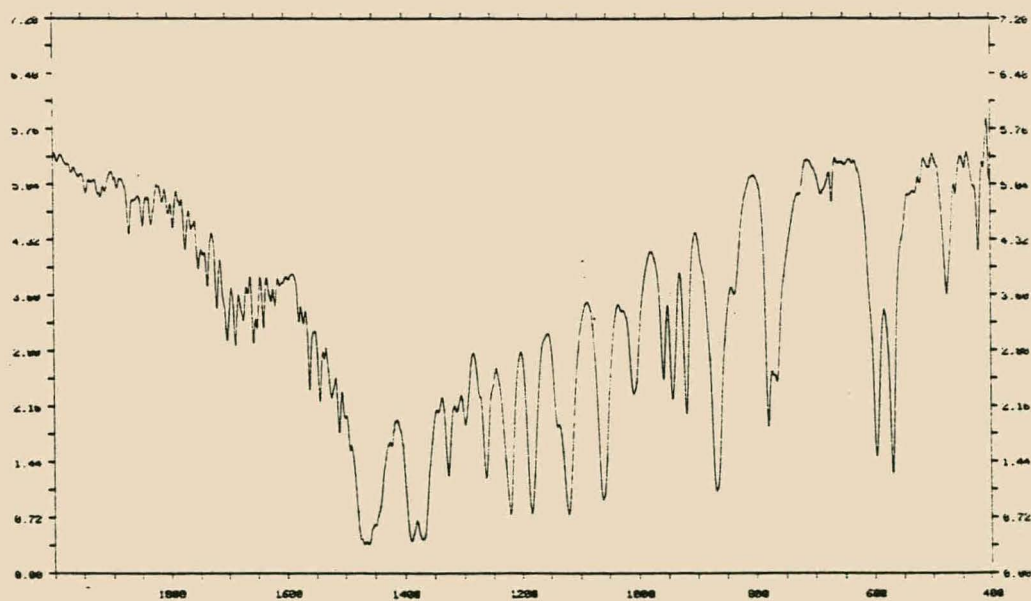

FIGURE 13. *IR spectrum of the copolymer that was formed on reacting 3-methylbutene-1 (97,08 mole%) and vinyltrimethylsilane (2,91 mole%) for 10 h at 80 °C.*
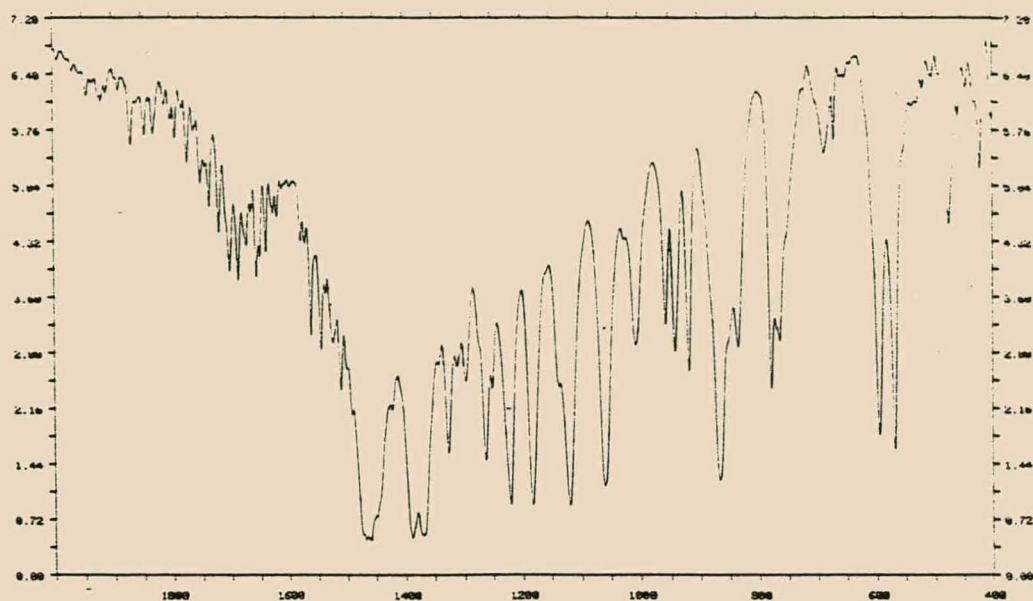
FIGURE 14. *IR spectrum of the copolymer that was formed on reacting 3-methylbutene-1 (90,91 mole%) and vinyltrimethylsilane (9,09 mole%) for 5 h at 80 °C.*
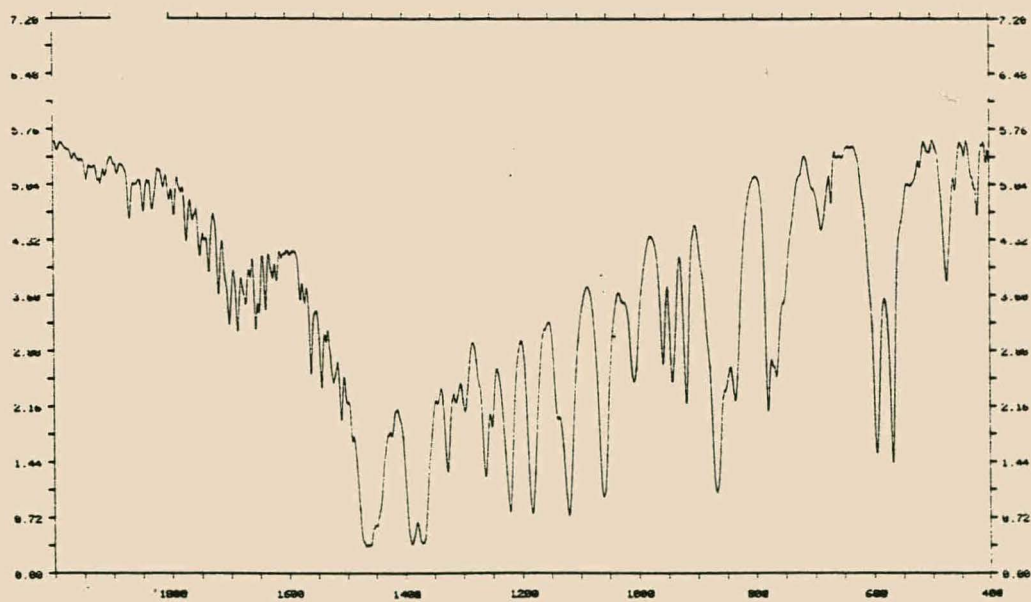
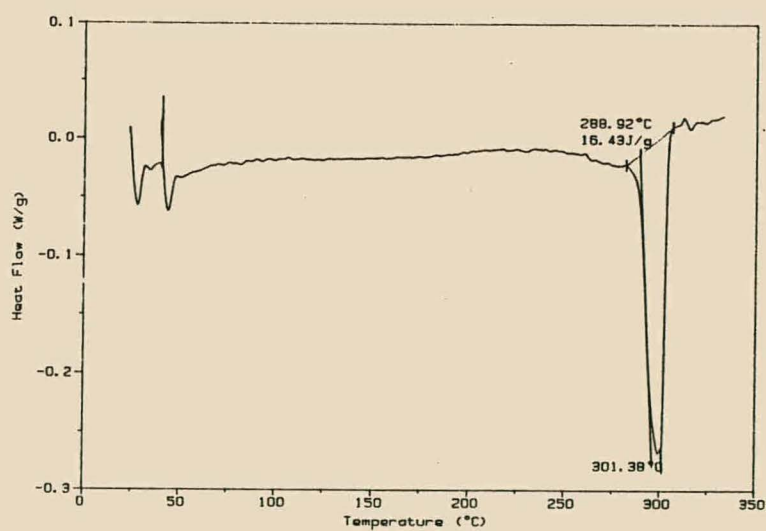FIGURE 15. *IR spectrum of the copolymer that was formed on reacting 3-methylbutene-1 (86,96 mole%) and vinyltrimethylsilane (13,04 mole%) for 5 h at 80 °C.*
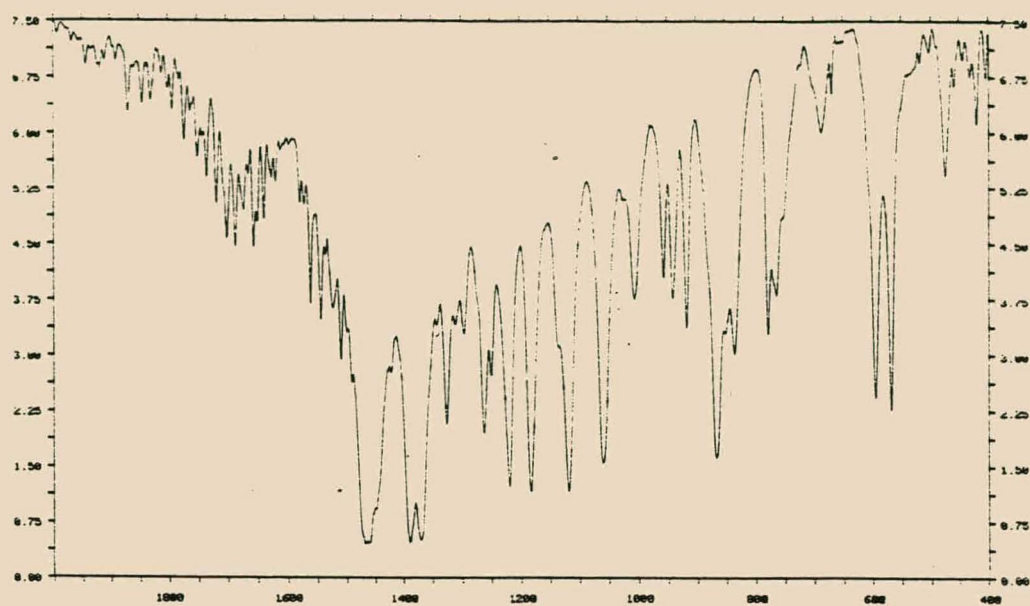
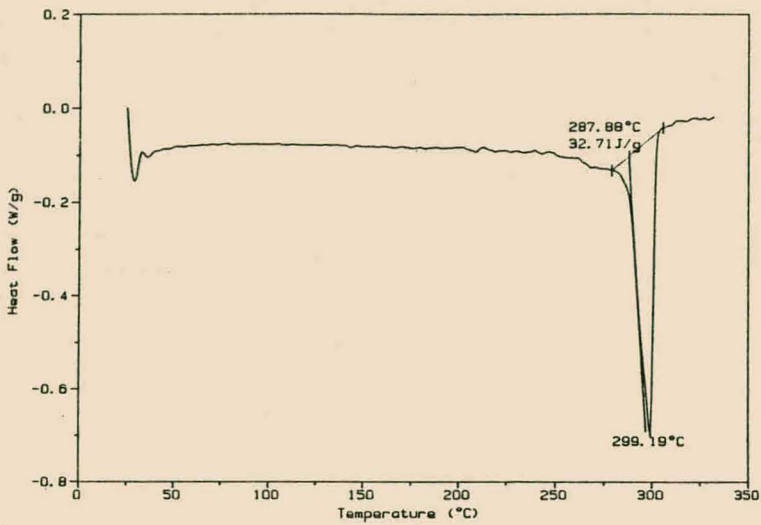FIGURE 16. *IR spectrum of the copolymer that was formed on reacting 3-methylbutene-1 (83,34 mole%) and vinyltrimethylsilane (16,65 mole%) for 5 h at 80 °C.*
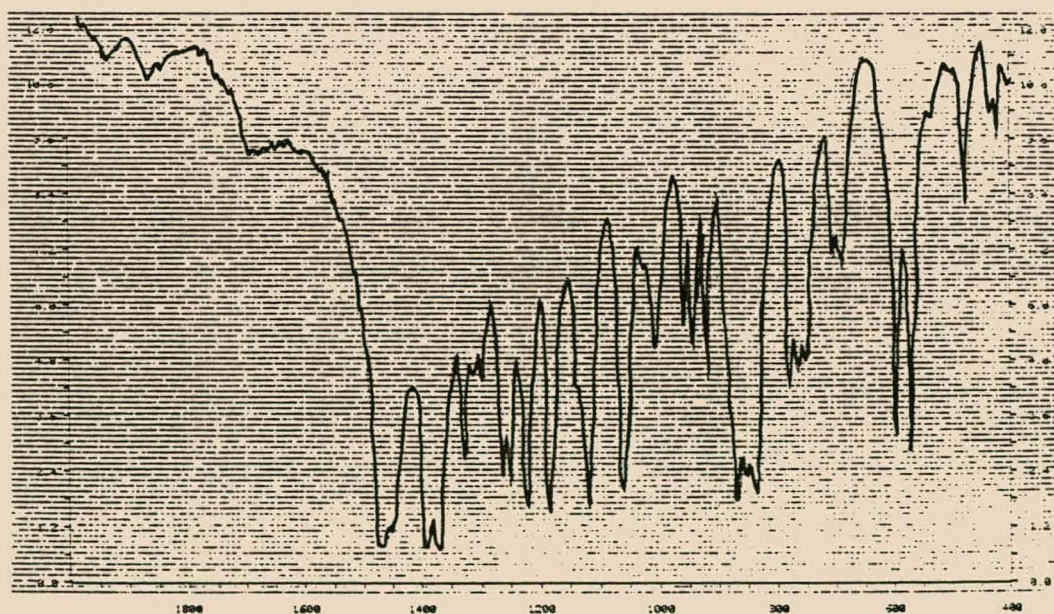
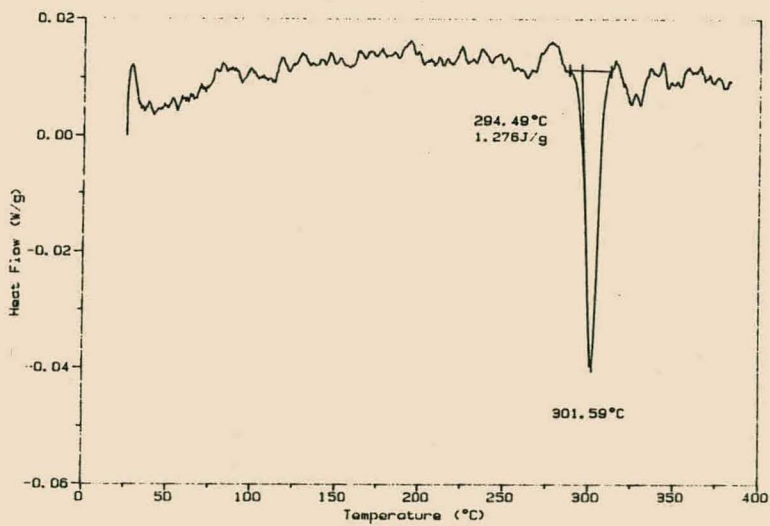FIGURE 17: *IR spectrum of the copolymer that was formed on reacting 3-methylbutene-1 (46,43 mole%) and vinyltrimethylsilane (53,57 mole%) for 50,5 h at 80 °C.*
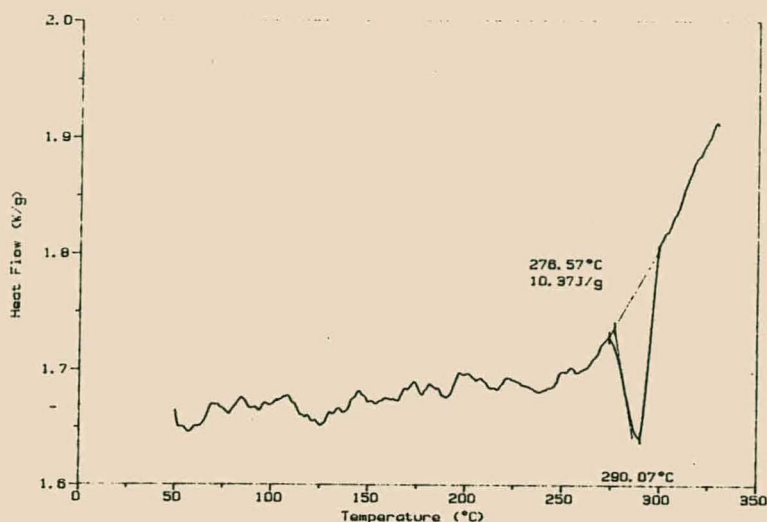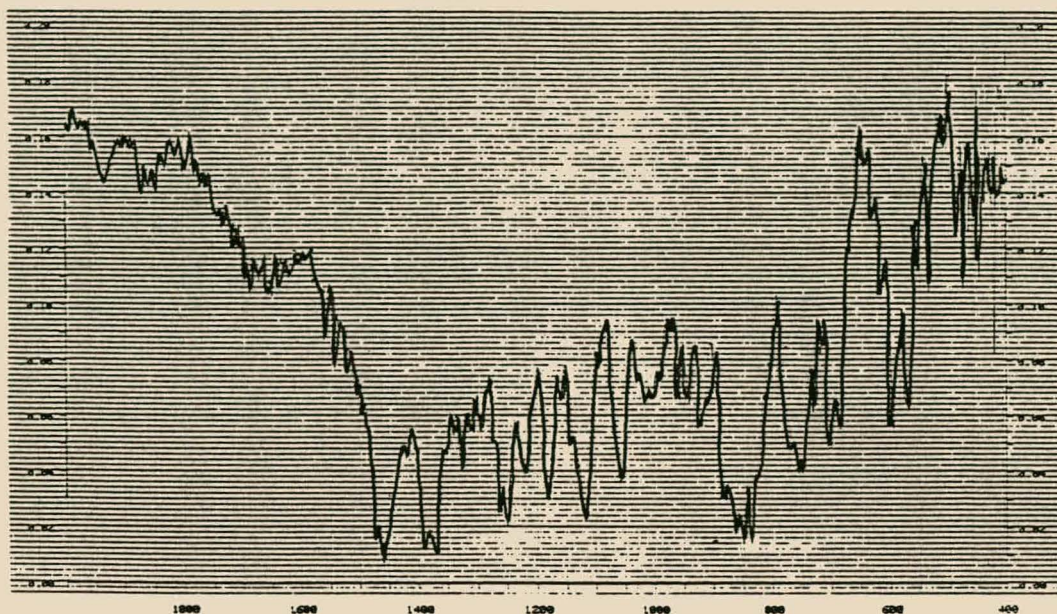
FIGURE 18. IR spectrum of the copolymer that was formed on reacting 3-methylbutene-1 (25,68 mole%) and vinyltrimethylsilane (74,32 mole%) for 5 h at 80 °C.
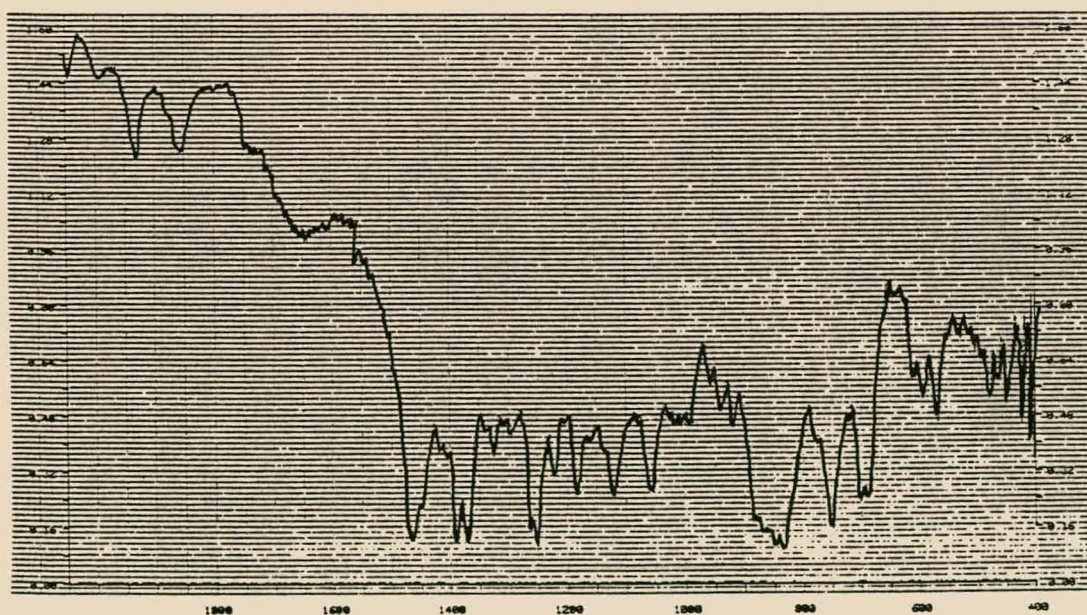
FIGURE 19. IR spectrum of the copolymer that was formed on reacting 3-methylbutene-1 (6,62 mole%) and vinyltrimethylsilane (93,38 mole%) for 120 h at 80 °C.

DISCUSSION

With progress from a 3–methylbutene–1 homopolymer to a 3–methylbutene–1-vinyltrimethylsilane copolymer, there were a few changes in the IR spectra of these polymers because of the increasing amounts of vinyltrimethylsilane incorporated in the copolymer. The sharp band at 1270 cm-1 in the

poly(3 – methylbutene – 1) IR spectrum formed a shoulder on its low-frequency side; this was attributed to the oscillations of the CH_3-groups in the $Si(CH_3)_3$ grouping. The sharp peak at 870 cm-1 broadened and formed two shoulders on its low-frequency side with increase in the amount vinyltrimethylsilane incorporated into the copolymer, because of the rocking oscillations of the the CH_3-groups in the $Si(CH_3)_3$ grouping. The intensity of the shoulder on the low-frequency side of the band in the region 780-750 cm-1 increased, and the band at 690 cm-1 broadened and formed a shoulder on its low-frequency side, because of the Si-C stretching modes of the $Si(CH_3)_3$-groups.

6.2.3   SOXHLET EXTRACTION

The degree of isotacticity of the 53,57 mole% vinyltrimethylsilane copolymer was determined by the solvent-soxhlet extraction method.

The amount of copolymer insoluble in *n*-heptane was 90,80%, that is, the degree of isotacticity of the 53,57 mole% vinyltrimethylsilane copolymer (feed ratio) was 90,80%. This result indicated that the vinyltrimethylsilane comonomer lowered the isotacticity of poly(3 – methylbutene – 1) by about 8%, which resulted in a copolymer with a lower melting point **(Figure 6)**. The lowering of the melting point was probably due to steric factors introduced by the incorporation of the bulky vinyltrimethylsilane units into the copolymer chain. The lower degree of isotacticity of the copolymer also indicated a lower degree of crystallinity.

6.2.4   13C NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY (13C NMR)

The solid-state 13C NMR spectrum of the 2,91 mole% vinyltrimethylsilane copolymer (5 h) (feed ratio) is given below **(Figure 20)**.
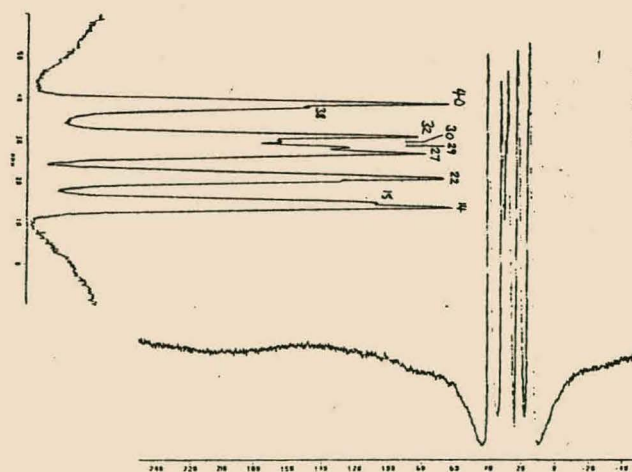
FIGURE 20. *Solid-state 13C NMR spectrum of the copolymer that was formed on reacting 3-methylbutene-1 (97,08 mole%) and vinyltrimethylsilane (2,91 mole%) for 5 h at 80 °C.*
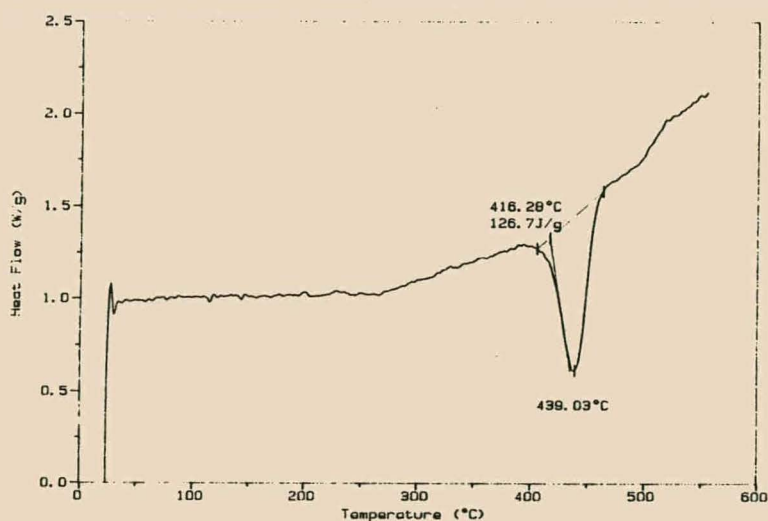
DISCUSSION

The ^{13}C NMR spectrum of the 2,91 mole % vinyltrimethylsilane copolymer (feed ratio) was nearly identical to that of poly(3-methylbutene-1) (**Figure 6 Chapter 4**), for the reason that the vinyltrimethylsilane content of this copolymer was too low to be seen as separate peaks in the spectrum. The ^{13}C NMR spectrum of this copolymer did, however, show that the vinyltrimethylsilane comonomer lowered the degree of isotacticity of the copolymer as all the peaks formed shoulders. It was calculated from the intensities of the peaks and their shoulders in the spectrum that the isotacticity of the copolymer was lowered by $19,42 \pm 10\%$ compared with that of isotactic poly(3-methylbutene-1).

The complete peak assignment of the solid-state ^{13}C NMR spectrum of the 2,91 mole % vinyltrimethylsilane copolymer was as follows

CH_3	14 ppm
CH_2	27, 29 ppm
CH (backbone)	32, 40 ppm
CH (sidegroup)	22ppm

where δ is accurate to ± 2ppm.

6.2.6   DETERMINATION OF THE SILICON CONTENT OF THE COPOLYMERS

6.2.6.1   ELEMENTAL ANALYSIS METHOD

TABLE II: Determination of the silane content of the copolymers by the elemental analysis method.

mole% vtms in feed	ppm Si in: * 25 ml, # 50 ml	%Si in sample	mole% vtms in copolymer
13,04	24 *	0,2	0,50
53,57	16 #	0,27	0,68
74,32	20 *	0,5	1,26

vtms = vinyltrimethylsilane

DISCUSSION

This method was not very accurate, but it was useful for the determination of the silicon content of the copolymers with low yields, as the other determination methods used larger quantities of the copolymers. The method did, however, illustrate the low amounts of vinyltrimethylsilane comonomer incorporated into the copolymers, in spite of the high mole% vinyltrimethylsilane present in the reaction feed. The low incorporation could be explained by the low reactivity of vinyltrimethylsilane in Ziegler-Natta polymerizations, as was mentioned before.

6.2.6.2   *PROTON-INDUCED GAMMA EMISSION (PIGE): ANALYTE AND NON-ANALYTE SPIKING*
            METHODS

TABLE III: Analytical results of the non-analyte spiking method.

| SAMPLE | Silicon concentration (mass%) | | |
	^{29}Si(1 273 (KeV)	^{28}Si(1 779 KeV)	Known
BCS 308	1,666±0,048 (2,88%)	1,988±0,057 (2,87%)	1,987
Cr XXXI	4,267±0,126 (2,95%)	4,192±0,123 (2,93%)	4,174
PE wax (Si)	5,932±0,287 (4,84%)	5,735±0,277 (4,83%)	5,247
Copolymer preparation (mole% vtms in feed)			
53,57	0,7044±0,0154 (2,19%)	0,6699±0,0146 (2,18%)	
16,65	0,4655±0,0263 (5,65%)	0,4682±0,0264 (5,64%)	
13,04	0,1493±0,0128 (8,57%)	0,1747±0,0149 (8,53%)	
9,09	0,2546±0,0415 (16,30%)	0,2654±0,0432 (16,28%)	
2,91	0,0513±0,0077 (15,01%)	0,0592±0,0088 (14,86%)	

TABLE IV: Corrected analytical results for the reference standards and the copolymer samples using the analyte spiking method and back-extrapolation.

SAMPLE	Silicon concentration (mass%)		Known
	^{29}Si(1 273 KeV)	^{28}Si(1 779 KeV)	
BCS 308	1,38±0,20 (14,55%)	2,21±0,08 (3,6%)	1,99
Cr XXXI	4,32±0,39 (9,0%)	4,81±0,10 (2,1%)	4,17
PE wax (Si)	4,55±0,28 (6,2%)	5,18±0,38 (7,3%)	5,25
Copolymer preparation (mole% vtms in feed)			
53,57	0,753±0,024 (3,2%)	0,711±0,012 (1,7%)	
16,65	0,384±0,042 (10,9%)	0,390±0,023 (5,9%)	
13,04	0,131±0,009 (6,9%)	0,142±0,008 (5,6%)	
9,09	0,221±0,018 (8,1%)	0,217±0,030 (13,8%)	
2,91	0,036±0,007 (19,4%)	0,045±0,007 (15,6%)	

DISCUSSION

The Proton-Induced Gamma Emission (PIGE) techniques had a high degree of accuracy, so that the results obtained by these techniques could be used with confidence.

It was now possible to calculate the amount of vinyltrimethylsilane comonomer incorporated into the copolymer from the amount of silicon present in the various copolymer samples.   The mass percentage of Si present in the 1,0 g samples given by the 1 779 Si peak was used in the calculations as it was the most accurate.

Calculation method illustrated for 53,57 mole% vinyltrimethylsilane copolymer.

From the non-analyte method it is known that the copolymer sample contains 0,6699 mass% silicon.

Mr(Si) = 28,0855 mole/g

Mr(vinyltrimethylsilane) = 100,2353 mole/g

Mr(3 – methylbutene – 1) = 70,134 mole/g

Thus,

1 g (say) sample contains 0,6699 mass% Si.

Mass of Si in 1 g: $0,6699/100 \times 1$ g $=$ $6,699 \times 10^{-3}$ g

Moles Si in sample: $6,699 \times 10^{-3}$ g$/28,0855$ mole/g $=$ $2,385 \times 10^{-4}$ mole

Thus, have $2,385 \times 10^{-4}$ moles vinyltrimethylsilane (vtms) units in sample.

Mass of vtms in sample: $2,385 \times 10^{-4}$ mole $\times 100,2353$ mole/g $=$ $2,391 \times 10^{-2}$ g

The mass of 3 – methylbutene – 1 (3mb1) in the sample is 1 g minus the mass of vinyltrimethylsilane in the sample.

Mass of 3mb1 in sample: 1 g $-$ $2,391 \times 10^{-2}$ g $=$ $9,761 \times 10^{-1}$ g

Moles 3mb1 in sample: $9,761 \times 10^{-1}$ g$/70,134$ mole/g $=$ $1,392 \times 10^{-2}$ mole

Total moles of both comonomers in sample: $2,385 \times 10^{-4} + 1,392 \times 10^{-2}$ $=$ $1,416 \times 10^{-2}$ mole

Thus,

Mole% vinyltrimethylsilane units in sample: $2,385 \times 10^{-4}/1,416 \times 10^{-2} \times 100$ $=$ 1,69 mole%

The results of the calculations of the amounts of silicon present in all the copolymers are given in **Table V**.

TABLE V: The amount of vinyltrimethylsilane comonomer present in the various copolymers.

VINYLTRIMETHYLSILANE PRESENT IN THE MONOMER FEED (mole%)	mole% VINYLTRIMETHYLSILANE PRESENT IN THE COPOLYMERS	
	ANALYTE	NON-ANALYTE
53,57	1,79	1,69
16,65	0,98	1,15
13,04	0,36	0,44
9,09	0,54	0,60
2,91	0,11	0,15

The results indicated that only small amounts of the vinyltrimethylsilane were actually incorporated into the copolymer. This explained why the melting points of the copolymers were lowered by only a few degrees, as the crystal structure of poly(3 – methylbutene – 1) was disrupted to only a small degree by the small quantity of vinyltrimethylsilane incorporated into the 3 – methylbutene – 1-vinyltrimethylsilane

copolymers; this small amount could be explained by the low reactivity of the compound compared with that of 3 – methylbutene – 1, as was previously mentioned.

6.2.7 DETERMINATION OF MONOMER REACTIVITY RATIOS OF COPOLYMERS

The monomer reactivity ratios of copolymers are very important parameters used in the prediction of copolymer composition and sequence distribution for any comonomer feed. They also assist in the understanding of some aspects of the kinetics of the copolymerization, for example, the rate of copolymerization, molecular mass, and molecular mass distribution.

All procedures for the evaluation of r_1 and r_2 involve the experimental determination of the copolymer composition formed from several different comonomer feed compositions.   (See **Section 2.4.3 Chapter 2**)

6.2.7.1   ASSESSING THE ADEQUACY OF THE COPOLYMERIZATION MODEL

The use of any of the procedures for the determination of the reactivity ratios of the copolymers would have been pointless had the mathematical expression employed to describe the physical system been wrong. It was, therefore, important to establish beyond reasonable doubt that the copolymerization model did adequately represent the behaviour of the 3 – methylbutene – 1-vinyltrimethylsilane copolymerization system.

Plots of the percentage conversion versus the residual of 3 – methylbutene – 1 comonomer were prepared from the two sets of data in **Table V** to establish a model fit (**Figures 21** and **22**).
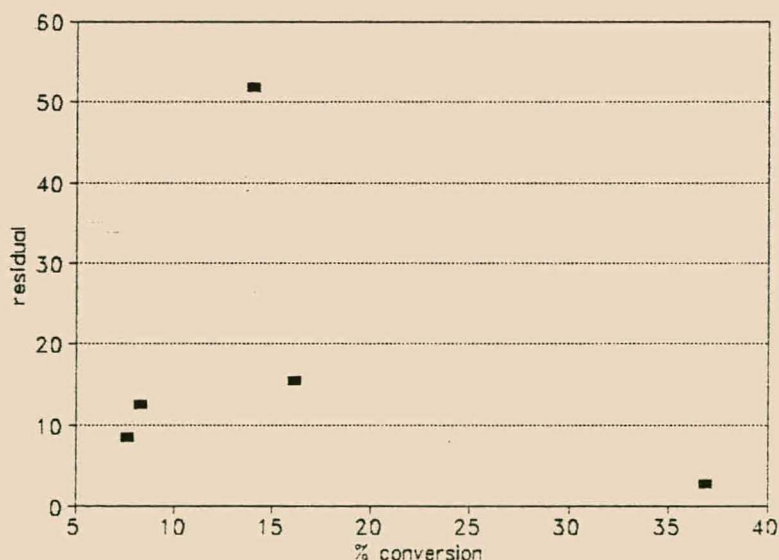
FIGURE 21: *Graph for the establishment of the fit of the copolymerization model as mathematical model on the data of the 3 – methylbutene – 1-vinyltrimethylsilane copolymerization system (Non-analyte spiking PIGE technique).*
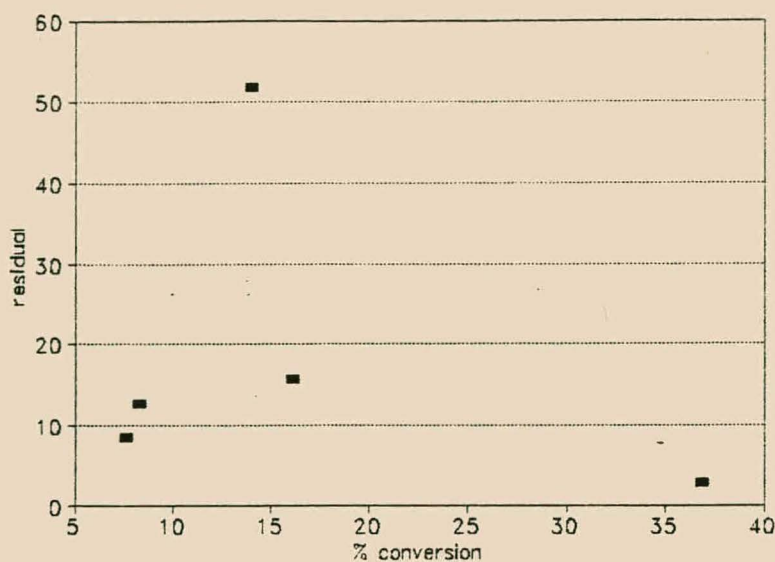
FIGURE 22: Graph for the establishment of the fit of the copolymerization model as mathematical model on the data of the 3−methylbutene − 1-vinyltrimethylsilane copolymerization system (Analyte spiking PIGE technique).

The relatively random distribution of the plotted points indicated that the copolymerization model could be employed to determine the monomer reactivity ratios of the 3−methylbutene−1-vinyltrimethylsilane copolymerization system. It was expected that the copolymerization model would not perfectly describe this copolymerization system (**Section 2.4.2.2.1 Chapter 2**), because certain assumptions had been made in the derivation of the copolymer composition equation which may have rendered it inapplicable to the Ziegler-Natta systems. The features of these systems which may give rise to problems of applicability and interpretation are the time-dependent changes which occur in polymerization kinetics and also the nature of the active catalytic centre itself.

6.2.7.2   FINEMAN-ROSS LINEARIZATION METHOD

The Fineman-Ross procedure was used for the initial estimation of the monomer reactivity ratios. This procedure is not very accurate, but it is very useful as a first approximation of the reactivity ratios of the copolymerization system.

The procedure is based on the equation (**Appendix F**):

$$\frac{F}{f}(f-1) = r_1 \frac{F^2}{f} - r_2$$

where $f = (m_1/m_2)$ and $F = (M_1/M_2)$; M_1 and M_2 refer to the monomer composition and m_1 and m_2 to the copolymer composition.

A plot of $(F/f)(f-1)$ as ordinate and (F^2/f) as abscissa is a straight line whose slope is r_1 and whose intercept is minus r_2. Plots for the data of the non-analyte and analyte PIGE techniques are given in **Figures 23** and **24**, and the resulting monomer reactivity ratios are given in **Table VI**, where r_1 refers to 3−methylbutene−1 and r_2 refers to vinyltrimethylsilane.
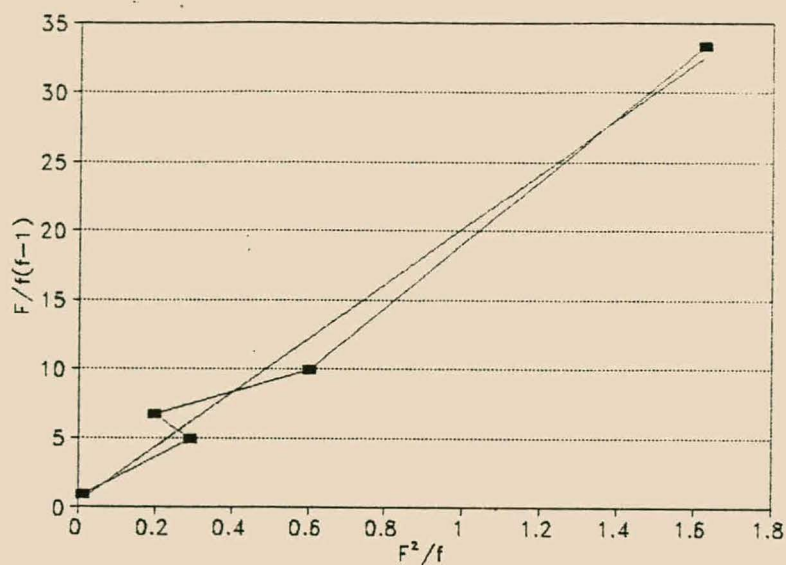
FIGURE 23. *Fineman-Ross plot using the Non-analyte PIGE technique.*
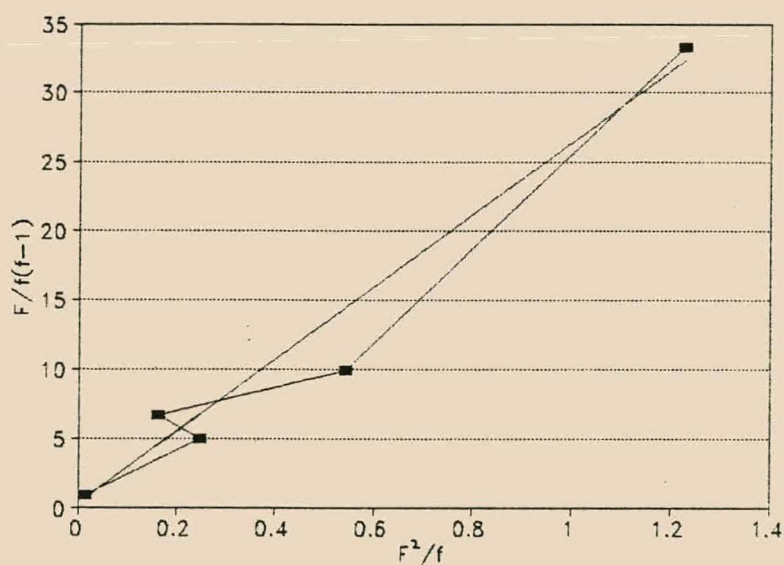
FIGURE 24. *Fineman-Ross plot using the Analyte PIGE technique.*

TABLE VI: *The monomer reactivity ratios of the $3-methylbutene-1-vinyltrimethylsilane$ copolymers.*

PIGE TECHNIQUE	r_1	r_2
NON-ANALYTE	19,85	-0,31
ANALYTE	26,11	0,30

The non-analyte PIGE technique illustrated one of the drawbacks of the Fineman-Ross method, that is, the possibility of a negative value for a monomer reactivity ratio when the best straight line was drawn through the data points. Since neither monomer reactivity ratio can be negative, r_2 was taken as zero.

6.2.7.3   TIDWELL-MORTIMER NON-LINEAR LEAST-SQUARES METHOD

The Tidwell-Mortimer method was used to refine the monomer reactivity ratios to give more precise values. Briefly, the method consists of the following: given initial estimates of r_1 and r_2 (calculated with the Fineman-Ross method in the previous section), a set of computations is performed which, on repetition, rapidly leads to a pair of values of the reactivity ratios, which yields the minimum value of the sum of the squares of the differences between the observed and computed polymer composition.

A computer program in which the non-linear least-squares method, adjusted according to the Tidwell-Mortimer method for copolymerization data, was written. The working of the program was in accordance with the description of the Tidwell-Mortimer calculation method.

The monomer reactivity ratios obtained with both the analyte and non-analyte PIGE techniques were used as initial estimates for the Tidwell-Mortimer method. The results are given in **Table VII**.

TABLE VII: The results of the Tidwell-Mortimer method.

PIGE TECNIQUE	INITIAL ESTIMATES		AMOUNT OF ITERATIONS	r_1	r_2
	r_1	r_2			
NON-ANALYTE	19,85	0	6	17,90	0
ANALYTE	26,11	0,3	6	21,33	0

The reactivity ratio product $r_1 r_2 = 0$ which meant that random copolymerization did not occur as was intended, because $r_1 r_2 = 1$ for random copolymerization. When $r_1 >> r_2$, as in this case, both types of propagating species preferentially added monomer M_1. There was a tendency toward consecutive homopolymerization of the two monomers.

CHAPTER 7

CONCLUSIONS

In the study of the synthesis of 3 – methylbutene – 1 homopolymers and copolymers the following conclusions were made:

7.1 HOMOPOLYMERIZATION

1) The theoretical study of the two methods of homopolymerization of 3 – methylbutene – 1, that is, Ziegler-Natta and isomerization polymerization, indicated that polymers with better properties were synthesized with Ziegler-Natta catalysts.

2) Two isotactic 3 – methylbutene – 1 homopolymers with different Al/Ti ratios were successfully synthesized with a Ziegler-Natta catalyst system, titanium trichloride and diethylaluminium chloride. The catalyst system with Al/Ti = 1,5 was found to be more favourable.

3) Isotactic poly(3 – methylbutene – 1) had the following properties
   (a)   melting point 305 °C;
   (b)   degree of isotacticity 98%;
   (c)   insoluble in all common solvents;
   (d)   thermal decomposition of the polymer starts at 378 °C;
   (e)   thermal oxidative degradation of the polymer starts at 200 °C; and
   (f)   9,10-dehydro-andraseen is a possible stabilizer for the polymer, and could be incorporated into the polymer with the help of an antistatic agent, Dehydat 51 special. Dehydat 51 special also proved to be a solvent for poly(3 – methylbutene – 1).

4) Isotactic poly(vinyltrimethylsilane) was synthesized under the same conditions as poly(3 – methylbutene – 1), and it had a very high melting point, 478 °C.

7.2 COPOLYMERIZATION

1) Eight 3 – methylbutene – 1-vinyltrimethylsilane copolymers were synthesized with the Ziegler-Natta catalyst system of titanium trichloride and diethylaluminium chloride.

2) The melting point of poly(3 – methylbutene – 1) was lowered through copolymerization with vinyltrimethylsilane, but not as much as was expected.

3) ^{13}C NMR and soxhlet extraction indicated that the copolymerization of vinyltrimethylsilane with 3 – methylbutene – 1 lowered the degree of isotacticity of poly(3 – methylbutene – 1).

4) The measuring of the amount of Si present in the various copolymers with elemental analysis techniques indicated that a small percentage of vinyltrimethylsilane was actually incorporated into the copolymers, although large amounts of it were added to the comonomer feed.

5) The monomer reactivity ratios of the copolymers were determined with the Fineman-Ross linearization method and refined with the Tidwell-Mortimer non-linear least-squares method. The reactivity ratio of 3−methylbutene−1 was 19,5, and the reactivity ratio of vinyltrimethylsilane was 0. The low reactivity of vinyltrimethylsilane compared with that of 3−methylbutene−1 explained the low incorporation of vinyltrimethylsilane into the copolymers. The resulting copolymers were not random copolymers, as for random copolymerization $r_1 r_2 = 1$ and for the 3−methylbutene−1-vinyltrimethylsilane copolymer system $r_1 > 1$ and $r_2 = 0$, implying that the monomer vinyltrimethylsilane does not homopolymerize in the mixture. The polymer structure:
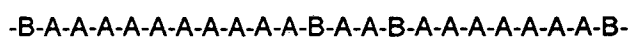
-B-A-A-A-A-A-A-A-A-A-A-B-A-A-B-A-A-A-A-A-A-A-B-

where A = 3-methylbutene-1 and B = vinyltrimethylsilane.

7.3   RESEARCH PROPOSALS

1) The investigation of the copolymerization of 3−methylbutene−1 with a more reactive alpha-olefin, such as hexene-1, to obtain a copolymer with a much lower melting point as well as a more random copolymer.

2) The investigation of the stabilization of copolymers of 3−methylbutene−1 with the properties mentioned above to obtain an environmentally degradable copolymer.

3) The investigation of the foamability of 3−methylbutene−1 copolymers with the object of replacing styrene.

APPENDIX A

CHARACTERIZATION OF CATIONIC POLY(3–METHYLBUTENE–1)

1   PHYSICAL CHARACTERIZATION

The poly(3-methylbutene-1) obtained by cationic polymerization is a colourless, amorphous, somewhat rubbery material. It is soluble in aliphatic and aromatic hydrocarbons, carbon disulfide, carbon tetrachloride and ethers, but is insoluble in alcohol and acetone **(14)**. Its second-order transition point is in the range -25 to -15 °C **(7)**.

Cationically polymerized poly(3-methylbutene-1) melts at about 55 °C, whereas the Ziegler-Natta polymerized polymer has a melting point of about 300 °C. The difference between the properties of these two polymers is shown in **Table I**.

TABLE I: Differences between the properties of poly(3-methylbutene-1) (PMB) with a 1,2- and a 1,3 structure.

PROPERTIES	PMB (1,2 STRUCTURE)	PMB (1,3 STRUCTURE)
PHYSICAL FORM	white powder	white powder
MELTING POINT	300 °C	55 °C
GLASS TRANSITION POINT	50 °C	-12 °C
	brittle	tough
CRYSTALLINITY	highly crystalline	amorphous
TACTICITY	highly isotactic (ca. 96%)	no tacticity
SOLUBILITY	insoluble in all common solvents	insoluble only in alcohols and acetone

2   NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY

The NMR spectra of cationic poly(3-methylbutene-1) show only two sharp peaks, one at higher field representing *gem*-dimethyl hydrogens, and another at lower field due to the presence of methylene hydrogens (See **Figure 1**).
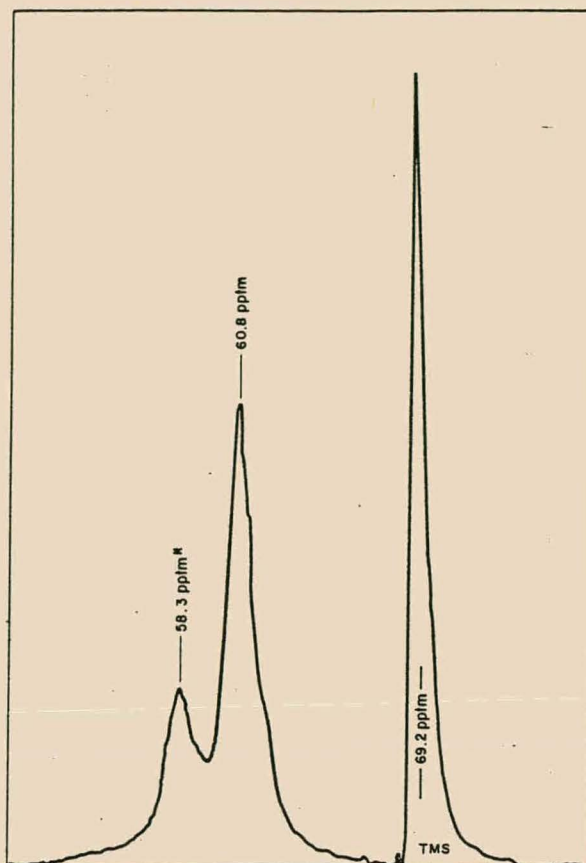
FIGURE 1. *Cationic poly(3-methylbutene-1): 60 Mcycle NMR spectrum; pptm* denotes parts per 10 million measured from benzene (15).*

A detailed quantitative analysis of these spectra has indicated that the NMR spectra were not sufficiently resolved to be used to determine whether cationic poly(3-methylbutene-1) represents exclusively a 1,3 structure, or mixtures of 1,3 and 1,2 structures. The study of these mixtures was impeded by the fact that the tertiary hydrogens were not clearly resolved. At best only the ratio of CH_3/CH_2 + CH protons could be considered, which made it impossible to distinguish between mixtures of the unusual 1,3 and the conventional 1,2 structures by NMR spectroscopy.

3 INFRARED SPECTROSCOPY

Infrared spectra of cationic poly(3-methylbutene-1) were used to distinguish this polymer from isotactic poly(3-methylbutene-1) (See **Figures 2 and 3**). Both polymers gave the characteristic carbon-hydrogen stretching vibration in the region 3000 to 2700 cm^{-1}; but without high resolution, this region did not reveal features useful for distinguishing between structures. Neither was the region 2700 to 1500 cm^{-1} revealing, since it was relatively transparent in saturated hydrocarbons.
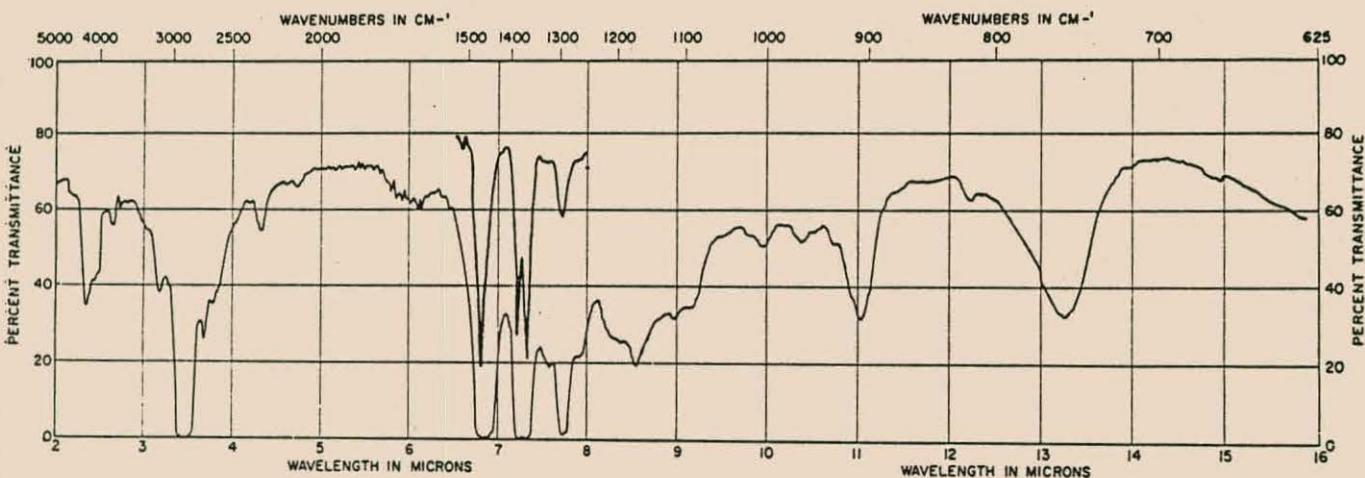
FIGURE 2. Infrared spectrum of cationic poly(3-methylbutene-1) (15).
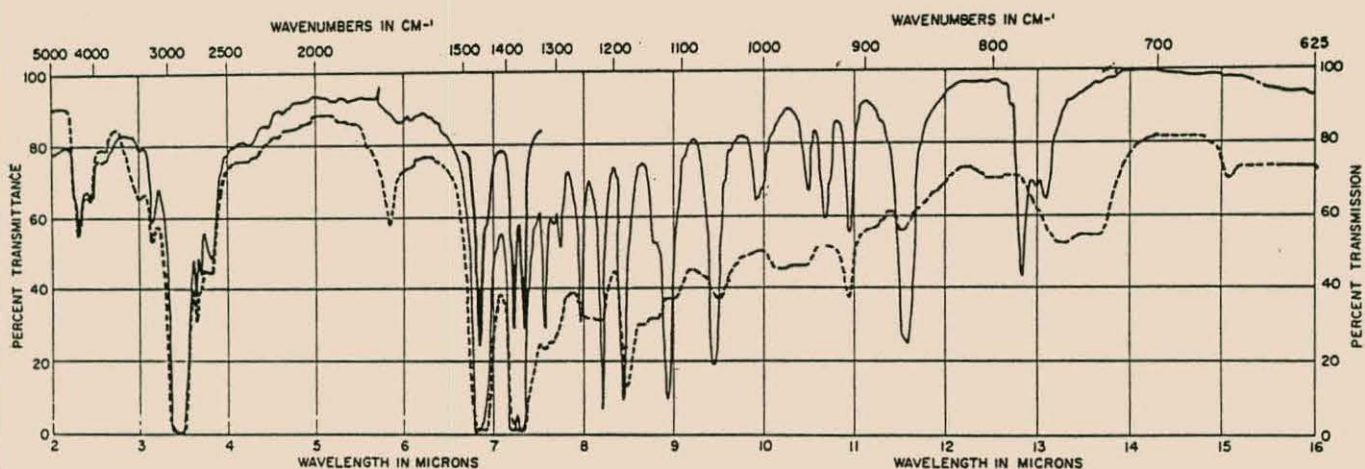
FIGURE 3. Infrared spectrum of isotactic poly(3-methylbutene-1) (15).

For each polymer, the CH_2 and CH_3 hydrogen bending vibrations were found at their assigned frequencies at about 1470 and 1455 cm^{-1}, respectively. The asymmetrical CH_3 bending vibration appeared as a shoulder on the CH_2 bending band. No distinguishing features were expected in this region.

The region of significant qualitative differences begins with the symmetrical CH_3 hydrogen deformation frequencies. The characteristic splitting of the symmetrical CH_3 deformation band, which occurs whenever two or more methyl groups are attached to the same carbon atom, was easily recognised. The spectrum of isotactic poly(3-methylbutene-1) showed approximately equal intensities at 1388 and 1370 cm^{-1}, indicating the presence of isopropyl groups. In contrast, the intensity of the first band (1379 cm^{-1}) in cationic poly(3-methylbutene-1) was found to be less than the second (1359 cm^{-1}), possibly a feature of the *gem*-dimethyl structure.

The prominent band at 1297 cm^{-1} in the cationic polymer is an important distinguishing feature which is not matched in intensity by any similar band in the isotactic product. This frequency is assigned to the - CH_2CH_2- group which can occur only in the proposed 1,1'-dimethylpropane type structure.

The band at 906 cm^{-1} in the cationic polymer is characteristic of the *gem*-dimethyl structure, while bands at 915 cm^{-1} in the isotactic modification result from two adjacent tertiary carbon atoms. The methylene rocking frequency of the cationic polymer occurs as a strong band at 754 cm^{-1} which is characteristic of the -CH_2CH_2- group.

Although it was not possible to completely assign all the IR bands of the two polymeric samples, this qualitative treatment was adequate to distinguish the structure of cationically obtained poly(3-methylbutene-1) from that of the isotactic modification.

APPENDIX B

EVALUATION OF STEREOREGULARITY TYPE AND DEGREE

From the same polymerization process polymers of different type and degree of stereoregularity are obtained.

For at least partially crystalline polymers, X-ray examination allows the unequivocal determination of stereoregularity type (32). However, X-ray data are not very useful from a quantitative point of view as the crystallinity is limited in general to a portion of the polymeric sample.

High-resolution NMR of the polymer appears at present to be the most powerful technique for determining the configuration of polymer chains. Relationships between magnetic shielding of nuclei and molecular symmetry can be used for this purpose. For example, in vinyl polymers, which are the polymers most investigated by NMR, the two protons of the methylene groups have the same chemical shift in syndiotactic chains, whereas differentiated bands are observed in isotactic sequences (33). The symmetry properties of a methylene group included in tactic sequences have different lengths (diads, triads, tetrads, and pentads) and their relationships with magnetic shieldings have been discussed in detail (33). This detailed analysis combined with the improved resolution power of the NMR spectrometers, has allowed determination of stereoregularity type and degree of a large number of vinyl polymers. The ^{13}C NMR method is widely used for structure characterization and conformations in the solid state (28, 34, 35).

IR spectra have also been used in many cases for determining stereoregularity. The type of stereoregularity can be identified by symmetry considerations and by comparison of the polymer spectra with those of suitable low molecular mass model compounds (36).

With crystalline polymers, a relative stereoregularity index can be obtained from solvent extraction data (37). This method has been used extensively for polypropylene, but reliable results can be obtained only by carrying out solvent extractions under similar conditions and on polymer samples having similar average molecular mass as well as molecular mass distribution. The fractionation by solvent extraction is in any case a very useful technique for obtaining, from the crude heterogeneous polymer, fractions which are more uniform with respect to molecular mass and stereoregularity. By this method it has been possible to demonstrate that during a polymerization process, especially by heterogeneous catalysis, macromolecules of various stereoregularity types can be formed.

APPENDIX C

CLASSIFICATION OF COPOLYMERS

1   RANDOM COPOLYMERIZATION $r_1 r_2 = 1$

$$x M_1^* + y M_2^* \longrightarrow --M_1 M_1 M_2 M_1 M_2 M_1 M_2 M_2 M_1 M_2-- \tag{1}$$

Random copolymerization occurs when the two types of propagating species M_1^* and M_2^* show the same preference for adding one or the other of the two monomers, $r_1 = 1/r_2$, or simply $r_1 r_2 = 1$. Under these conditions the relative rates of incorporation of the two monomers into the copolymer are independent of the identity of the unit at the end of the propagating species. Here monomer units will be arranged at random along the polymer chains in relative amounts determined by the feed and the relative reactivities of the two monomers **(structure 1)**. Most ionic copolymerizations are characterized by the ideal type of behaviour.

In ideal (true random) copolymerization, $r_1 = r_2 = 1$, the two monomers show equal reactivities toward both propagating species. The copolymer composition is the same as the comonomer feed with a random placement of the two monomers along the copolymer chain. For the case where the two monomer reactivity ratios are different, that is, $r_1 > 1$ and $r_2 < 1$ or $r_1 < 1$ and $r_2 > 1$, one of the monomers will be more reactive than the other toward both propagating species. The copolymer will contain a larger portion of the more reactive monomer in random placement.

Figure 1 shows the variation in the copolymer composition as a function of the comonomer feed composition for different values of r_1 **(55)**. The copolymer is richer in M_1 when $r_1 > 1$ and is poorer in M_1 when $r_1 < 1$. A very important practical consequence of random copolymerizations is that the production of copolymers containing appreciable amounts of both monomers becomes progressively more difficult as the difference in reactivities of the two monomers increases. This is one of the reasons why ionic copolymerization is of little practical significance. When, for example, $r_1 = 10$ and $r_2 = 0{,}1$, copolymers containing appreciable amounts of M_2 cannot be obtained. It is only when r_1 and r_2 do not differ markedly (for example, $r_1 = 0{,}5$-2) that there will exist a large range of comonomer feed compositions which yield copolymers containing appreciable amounts of both monomers.
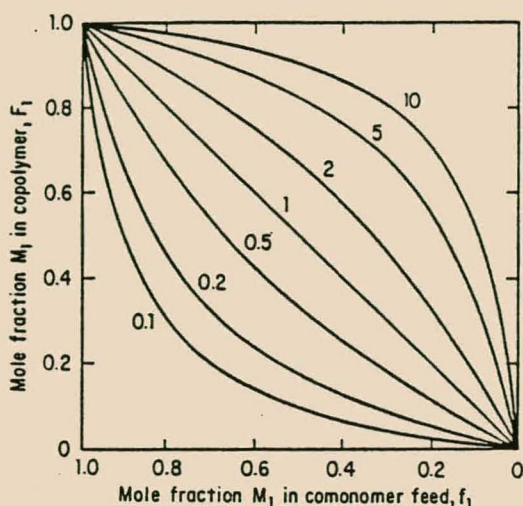
FIGURE 1. *Dependence of the instantaneous copolymer composition F_1 on the comonomer feed composition f_1 for the indicated values r_1 where $r_1 r_2 = 1$ (55).*

2 ALTERNATING COPOLYMERIZATION $r_1 = r_2 = 0$

$$xM_1{}^* + yM_2{}^* \longrightarrow --M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2-- \tag{2}$$
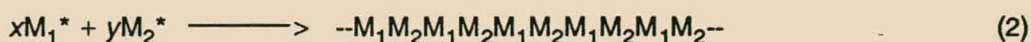
When $r_1 = r_2 = 0$ (and $r_1 r_2 = 0$), the two monomers enter into the copolymer in equimolar amounts in a non-random, alternating arrangement along the copolymer chain. This type of copolymerization is referred to as alternating copolymerization. Each of the two types of propagating species preferentially adds the other monomer, that is $M_1{}^*$ adds only M_2 and $M_2{}^*$ adds only M_1 (**structure 2**).

The behaviour of most comonomer systems lies between the two extremes of ideal and alternating copolymerization. It is of great practical significance that with increasing alternation tendency a larger range of feed compositions will yield copolymers containing sizeable amounts of both monomers. However, when $r_1 r_2$ is very small or zero, the alternation tendency is too great and the range of copolymer compositions which can be obtained is again limited. In the extreme case where both r_1 and r_2 are zero, only the 1:1 alternating copolymer can be produced.

A special situation arises when one of the monomer reactivity ratios is much larger than the other. For the case of $r_1 >> r_2$ (that is, $r_1 >> 1$ and $r_2 << 1$), both types of propagating species preferentially add monomer M_1. There is a tendency toward consecutive homopolymerization of the two monomers. Monomer M_1 tends to homopolymerize until it is consumed; monomer M_2 will subsequently homopolymerize. An extreme example of this type of behavior is the radical polymerization of styrene-vinyl acetate with monomer reactivity ratios of 55 and 0,01.

3 BLOCK COPOLYMERIZATION $r_1 > 1, r_2 > 1$

$$xM_1{}^* + yM_2{}^* \longrightarrow --M_1M_1M_1M_1M_2M_1M_2M_2M_2M_1-- \tag{3}$$
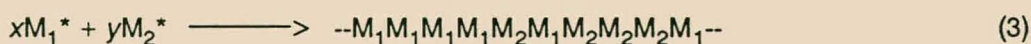
If both r_1 and r_2 are greater than unity (and therefore, also $r_1 r_2 > 1$), there is a tendency to form a block copolymer with blocks of both monomers present in the chain (**structure 3**). This type of behaviour has been encountered in only a few copolymerizations initiated by coordination catalysts.

Finally, the possibility that each type of radical may react preferentially with the corresponding monomer should be mentioned: both r_1 and r_2 would then be greater than 1, and there would be a tendency toward independent and concurrent polymerization. No such independent polymerization is known.

Each class of copolymers presents special challenges in synthesis and distinct opportunities for the control of polymer properties.

APPENDIX D

DEPENDENCE OF COPOLYMER COMPOSITION ON MONOMER-FEED COMPOSITION

1. $r_1 = r_2 = 1$ $(k_{11} = k_{12};\, k_{21} = k_{22})$

In this case, neither active centre shows any selectivity in adding monomer, and the monomers enter the copolymer in amounts determined only by their relative concentrations in the monomer feed; copolymer composition is always identical to feed composition (true random copolymerization). This is a special case of the earlier Wall treatment; **equation 9 (Section 2.4.2.1.1** in **Chapter 2)** simplifies to

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \qquad (1)$$

2. $r_1 r_2 = 1$ $(r_1 = 1/r_2;\, k_{11}/k_{12} = k_{21}/k_{22})$

In this case, both active centres show the same preference for addition of one of the two monomers, with the result that the copolymer is always richer in the more reactive monomer than is the feed mixture. This is equivalent to the more general, early Wall treatment; **equation 9 (Section 2.4.2.1.1** in **Chapter 2)** simplifies to

$$\frac{d[M_1]}{d[M_2]} = r_1 \frac{[M_1]}{[M_2]} \qquad (2)$$

Copolymerizations that behave in this way are often called ideal copolymerizations and may be considered to be special cases of the more general class for which $r_1 > 1$, $r_2 < 1$.

3. $r_1 = r_2 = 0$ $(k_{11} = k_{22} = 0)$

In this case, each active centre adds exclusively the monomer other than that which contributes the terminal residue on the growing chain. This demands the formation of an alternating copolymer of 1:1 composition regardless of feed composition. **Equation 9 (Section 2.4.2.1.1** in **Chapter 2)** simplifies to

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{[M_2]}{[M_1]} \qquad (3)$$

4. $r_1 < 1; r_2 < 1$ $\left(k_{12} > k_{11}, k_{21} > k_{22}\right)$

This case is intermediate between the first and third cases; each chain end prefers cross-propagation to homopropagation, but the preference is not absolute. There is thus a tendency toward alternation, which grows stronger as the $r_1 r_2$ product approaches zero. An important characteristic of such copolymerizations is the existence of a point in the Wall diagram at which monomer and polymer compositions are equal. This so-called azeotropic composition emphasizes the analogy to constant-boiling mixtures in distillation. The azeotropic composition is readily calculated from **equation 9** (**Section 2.4.2.1.1** in **Chapter 2**), since it is defined as the point at which

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \qquad (4)$$

Thus,

$$\frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} = 1 \qquad (5)$$

so

$$\frac{[M_1]}{[M_2]} = \frac{1 - r_2}{1 - r_1} \qquad (6)$$

5. $r_1 > 1; r_2 > 1$ $(k_{11} > k_{12}, k_{22} > k_{21})$

Each active centre prefers homopropagation to cross-propagation. The result is a mixture of homopolymers or a copolymer with long sequences of each monomer uninterrupted by the other (a "blocky" copolymer).

APPENDIX E

THE EFFECT OF VOLUME CHANGE DURING COPOLYMERIZATION

The rate of disappearance of M_1 per unit time and per unit volume is:

$$-\frac{1}{V}\frac{d[M_1]}{dt} = k_{11}\frac{[m_1]}{V}\left[\frac{[M_1]}{V}\right] + k_{21}\frac{[m_2]}{V}\left[\frac{[M_2]}{V}\right] \tag{1}$$

or, on multiplying through by V

$$-\frac{d[M_1]}{dt} = k_{11}[m_1][M_1] + k_{21}[m_2][M_2] \tag{2}$$

Similarly, for M_2

$$-\frac{dM_2}{dt} = k_{12}[m_1][M_2] + k_{22}[m_2][M_2] \tag{3}$$

The steady-state assumption then leads to

$$[m_2] = \frac{k_{12}}{k_{21}}\frac{[M_2]}{[M_1]}[m_1] \tag{4}$$

The ratio of the rate of disappearance of M_1 and M_2 is then,

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\frac{(r_1[M_1] + [M_2])}{([M_1] + r_2[M_2])} \tag{5}$$

Thus, in this formulation of the problem, the volume cancels out. The instantaneous compositions and changes in composition during conversion depend only on the reactivity ratios and on the relative number of moles of both species present. This is in contrast to the molar quantities occasionally given in the literature. Experimentally, moles rather than the molar quantities which would require volume corrections with conversion, are used in the literature.

APPENDIX F

LINEAR REACTIVITY RATIO ESTIMATION PROCEDURES

As most of the procedures use least-squares methods, the following four assumptions are made:

    (a)   the mathematical model adequately describes the data;

    (b)   the random errors in the dependent variable, generally the copolymer composition, are statistically independent from experiment to experiment and have constant variance;

    (c)   the random errors in the dependent variable are normally distributed;

    (d)   the independent variable is assumed to be errorless.

In the discussion to follow, the following notation (where $u = 1,2$) is adopted:

M_u = the mole fraction of monomer u in the reaction system,

m_u = the mole fraction of monomer u in the polymer composed entirely of the two monomers,

r_u = the monomer reactivity ratio.

1   THE APPROXIMATION METHOD

The approximation method depends on the fact that at low concentrations of M_2, the composition of the copolymer is almost entirely dependent on r_1 **(67)**. In these circumstances,

$$r_1 \approx \frac{M_2}{m_2} \tag{1}$$

Whereas a single experiment will provide an approximate value for r_1, the limitations of this method are numerous. Extremely sensitive analytical procedures are required to determine the quantity m_2 of the copolymer. If $r_u < 0,1$, or $r_u > 10$, the computed value of r_u will be seriously biased. The method is also based on the assumption that the system under study obeys the usual copolymerization mechanism, and provides no means of independently evaluating the validity of this assumption. The method is valuable, however, since it provides the experimenter with a quick method for obtaining approximate values of r_1 and r_2.

2   THE CURVE-FITTING METHOD

This method is based on the copolymer composition equation (**equation 9** from **Section 2.4.2.1.1** in **Chapter 2**). It is based on the assumption that if the experimental conditions are such that the monomer concentrations do not change appreciably, and that if the polymer is of adequate molecular mass, then **equation 9 (Section 2.4.2.1.1** in **Chapter 2)** can be adequately represented by **equation 2**.

$$\frac{dM_1}{dM_2} = \frac{M_1 (r_1 M_1 + M_2)}{M_2 (M_1 + r_2 M_2)} \qquad (9)$$

$$\frac{m_1}{m_2} = \frac{r_1 M_1^2 + M_1 M_2}{r_2 M_2^2 + M_1 M_2} \qquad (2)$$

The curve-fitting method consists of the graphical comparison of the observed monomer-copolymer composition curve with the curve represented by **equation 2** - calculated for selected values of r_1 and r_2 by trial and error.

One advantage of this method is that the weights of the experimental points must be taken into account in obtaining r_1 and r_2 values. A second advantage is that it provides the observer with a visual check on the validity of the assumption that the model describes the observed physical phenomena, since the data used are generally collected over the whole range of monomer compositions. A third advantage is that it provides a qualitative measure of the experimental error even in the absence of repeated runs if one is willing to assume adequacy of the model. Finally, in some instances it provides a qualitative measure of how well the reactivity ratios are estimated **(68)**. Unfortunately, the method may require extensive calculations, and, as noted above, provides only a qualitative measure of the precision of the estimates of the values of r_1 and r_2.

However, this method has two disadvantages. The first is that the initial composition of the feed monomers is used instead of the instantaneous composition. If the reactivities of two monomers are identical, the more reactive monomer enters into the copolymer more easily than the less reactive monomer, and the residual monomer mixture progressively changes its composition, that is, there is a relative decrease in the concentration of the more reactive monomer.

Since the composition of the copolymer isolated also changes with conversion, the copolymer should be isolated at a conversion as low as possible to be able to use approximately the initial composition of the feed monomers. Such a limiting conversion depends on the composition and the reactivities of the feed monomers, and it seems not to be determined definitely for different copolymerization systems when **equation 9** is employed. Of course, the error originating from this might be expected to increase with the increase on the difference between the reactivities of the two monomers.

The second disadvantage is that the observer is required subjectively to weight the data, a task not consistently done even by the same observer. However, Tidwell and Mortimer **(67)** improved and facilitated this problem by using a nonlinear least-squares computer program.

3 THE INTERSECTION METHOD

Equation 2 can be rearranged to yield

$$r_1 = r_2 \left[\frac{m_1 M_2{}^2}{m_2 M_1{}^2} \right] + \frac{M_2}{M_1} \left[\frac{m_1}{m_2} - 1 \right] \tag{3}$$

Treating $m_1 M_2{}^2/m_2 M_1{}^2$ and $(M_2/M_1)[(m_1/m_2) - 1]$ as the slope and intercept, one can plot for each experiment a different straight line **(67)**, where r_1 represents the ordinate and r_2 represents the abscissa. The intersection of the straight lines determines r_1 and r_2. This method, originated by Mayo and Lewis **(60)**, has the same limitations as the curve fitting method.

In the intersection procedure, transformation of the original differential copolymer equation **(equation 9** from **Section 2.4.2.1.1** in **Chapter 2)** leads to transformation(s) of the original error structure of the measured variables **(69)**. The transformed error no longer has an expected value of zero, so that essential information will have been lost and only approximate r values will be found. Proposed improvements, based on a more objective calculation of the centre of gravity of the intersection points in the intersection procedure, therefore will never lead to reliable values, of r.

4 THE INTEGRATION (MAYO-LEWIS) METHOD

The Mayo-Lewis method applies the integrated form of the copolymer composition equation to monomer systems with low conversions, which is necessary for accuracy **(68)**.

$$r_2 = \frac{\log \left[\dfrac{[M_2]_0}{[M_2]} \right] - \dfrac{1}{p} \log \left[\dfrac{1 - p[M_1]/[M_2]}{1 - p[M_1]_0/[M_2]_0} \right]}{\log \left[\dfrac{[M_1]_0}{[M_1]} \right] + \log \left[\dfrac{1 - p[M_1]/[M_2]}{1 - p[M_1]_0/[M_2]_0} \right]} \tag{4}$$

where

$$p = \frac{1 - r_1}{1 - r_2}$$

$[M_1]_0$, $[M_2]_0$ = initial concentrations of respective monomers

$[M_1]$, $[M_2]$ = concentrations of respective monomers at time which copolymerization was stopped

The integrated form can solve the disadvantages inherent in the use of the initial composition of the feed. However, calculation is more complicated than with the other methods, and the rather wider arbitrariness in the r_1 and r_2 determination might be why it has not been used often.

5   THE LINEARIZATION (FINEMAN-ROSS) METHOD

The Fineman and Ross rearranged **equation 3**, as discussed by Tidwell and Mortimer **(67)**, to yield

$$\frac{M_1(m_2 - m_1)}{M_2 m_1} = - \left[\frac{m_2 M_1{}^2}{m_1 M_2{}^2} \right] r_1 + r_2 \tag{5}$$

Consequently if one graphs $M_1(m_2 - m_1)/M_2 m_1$ versus $-m_2 M_1{}^2/m_1 M_2{}^2$, the slope of the straight line will be r_1 and the intercept is r_2. Briefly, this method has the same advantages and disadvantages as the intersection and curve fitting methods. However, this method also has the disadvantage of a possibility of yielding a negative value of r_1 which has no meaning **(68)**.

The Fineman-Ross equation **(equation 5)** is an example of a linearized form of the copolymer composition equation **(equation 9** from **Section 2.4.2.1.1** in **Chapter 2)** [nonlinear in r_1 and r_2]. Such a transformation has an unfortunate consequence which has often been noted; the equation is no longer symmetrical with respect to the definition of which monomer is 1 and which is 2, and therefore the use of the equation can lead to two possible sets of values for r_1 and r_2 **(60)**. Linearization of **equation 9** (**Section 2.4.2.1.1** in **Chapter 2**) also transforms the error structure in the observed copolymer compositions (m_1 or m_2) with the result that the new errors no longer have mean zero and constant variance. The new error variance in the linearized equation is a function of the original independent variables. A subsequent least-squares analysis of data using the new linear form of the copolymer composition equation is not suitable as the transformed errors do not meet the requirements of the least-squares procedure. Therefore, strictly speaking, the only correct way to analyze copolymer composition data to determine r_1 and r_2 is to do a nonlinear least-squares (NLLS) analysis of it using **equation 9** (**Section 2.4.2.1.1** in **Chapter 2**) or some variant of it.

5   DISCUSSION OF THE LINEAR METHODS

The literature contains many instances in which linear least-squares procedures have been applied (inappropriately) to fit the Fineman-Ross linearized form of the copolymer equation and, in at least one case, to fit the Mayo-Lewis form. These procedures are inappropriate because fitting the data to a linearized form of the copolymer equation results in improper weights being applied to the "observations". The effect of giving certain experimental points an abnormal and inappropriate weight in determining the $r_1 r_2$ values is perhaps most clearly understood in terms of a Fineman-Ross plot. The experiments made at the lowest comonomer concentration lie furthest from the ordinate and, thus, have the greatest influence on the slope of a line calculated by the usual linear least-squares procedure. Although it may not be so immediately obvious, the Mayo-Lewis procedure, as well as the Joshi-Kapur method **(70)** of assigning weights to Mayo-Lewis intersection points based on the tangent of the angle of intersection, also improperly weights the data.

A further difficulty with these linearized equations is that no valid expression for the precision with which the estimates are known can be obtained from the "data" since the "independent" and "dependent" variables in the linear form contain the observed response, that is, the polymer composition. These linear forms certainly violate assumption 3 associated with the method of least squares, as explained above, and very likely assumption 4 also. Thus, no valid statement can be made with regard to how precisely or imprecisely these estimates are determined. This difficulty is at least partly responsible for the controversy over whose data to believe because, without a valid means for comparing data of different authors, no firm conclusions can be drawn.

These transformed copolymer equations have another akward feature, namely, that of occasionally yielding an r value which is less than zero. Thus, the pre-eminance of the nonlinear least-squares procedure is seen to reside in the fact that it gives the best pair of $r_1 r_2$ values obtainable from the data available and also gives a valid estimate of the precision with which these values are known.

Optimum values of r_1 and r_2 are calculated from appropriate copolymerization data by the NLLS procedure of Tidwell and Mortimer (67). In addition, the precision and reliabilities of the r_1 and r_2 values are estimated. However, the cause of the errors is discussed only briefly in the literature, and the copolymer composition is described by the composition of the feed and the values of r_1 and r_2 (68).

APPENDIX G

EXPERIMENTAL DETERMINATION OF MONOMER REACTIVITY RATIOS

1 EXPERIMENTAL PRACTICES AND PROCEDURES

A review by Tidwell and Mortimer **(63)** of experimental practices and procedures leads to the conclusion that the principal cause of difficulty in interpreting reactivity ratio data arises from poor experimental practices and procedures. Some of these practices are obvious, whereas others are more obscure. The major contributors to the problem are outlined below.

1.1 THE EFFECT OF EXPERIMENTAL CONDITIONS ON THE PRECISION OF THE ESTIMATED REACTIVITY RATIOS

It was observed by Alfrey *et al.* **(73)** that the best experimental conditions for determining reactivity ratios depend on the actual values of these ratios. Although this assumes some prior knowledge of the ratios before any experimental work can be done at the recommended monomer concentrations, the iterative nature of all experimental procedures, when correctly followed, will lead the experimenter to the proper conditions. Failure to employ experimental conditions appropriate to the circumstances leads to computed reactivity ratios which will be less precise than they would have been, had the correct conditions been employed.

1.2 CONSEQUENCES OF THE USE OF SOME LABOUR-SAVING PRACTICES

It is important to recognize that the by-passing of some experimental procedures can compromise some of the assumptions implicit in the procedures used to analyze the data. For example, one common practice is the preparation of stock solutions of monomers which are subsequently used in several experimental runs. This practice reduces the labour requirements, but it and many other commonly used labour-reducing procedures may, and often do, compromise the requirement that the errors (stochastic) between the experimental runs should be independent. When this requirement is not met, statements regarding the precision of the resulting parameter estimates are incorrect unless the nonindependence of the stochastic errors is considered in the estimation procedure. The basic requirement of independence of these stochastic errors inherent in the results consists of conducting the second and all subsequent experimental runs from the starting point employed in the first run.

1.3 BIAS

The data in the estimation of the reactivity ratios can be biased, that is, consistently inaccurate in one direction, as the consequence of biased polymer analysis procedures, or because of the use of initial monomer compositions in the computational procedure that are consistently different from the initial monomer composition actually used in the copolymerization. Although the importance of the use of

accurate (unbiased) data is acknowledged by all experimenters, it is informative to inquire about the consequences of using biased data to estimate reactivity ratios, since the literature indicates that polymer analysis procedures employed in some circumstances yield biased results.

The effect of using biased data to estimate the reactivity ratios can be studied by mathematical techniques. However, the more direct approach of the synthesis of data, either by adding a fixed amount or percentage to the computed polymer composition or by consistently altering the initial monomer composition, followed by fitting of the synthetic data shows that bias in either the initial monomer composition or the polymer analysis has dire consequences for the reactivity ratios.

1.4   EXPERIMENTAL METHODS

In practice the experimental determination of monomer reactivity ratios has always been done by the determination of the relation between feed and copolymer compositions for a given monomer pair for two or more feeds, but the application of studies of monomer distribution along the polymer chain has been suggested by Merz *et al* (74). The usual experimental procedure has been to fill suitable reaction vessels with known quantities of monomers, solvent and catalyst, heat them in a thermostat until they are partially polymerized, then to isolate the polymer by some sort of precipitation and drying technique, and finally to determine its composition (57).

In the isolation of the polymer, the main problem is that of quantitative separation of the polymer from unreacted monomer and from solvent. This is usually accomplished by multiple precipitations from a solvent by means of a nonsolvent for the polymer (but a solvent for the monomer), followed by drying under vacuum.

The techniques used for copolymer analysis include elemental analysis, radio-isotopic tagging, and ultraviolet, infrared, and nuclear magnetic spectroscopy. The older, more established procedures involve copolymerizations carried out to low degrees of conversion (approximately < 5%) (64).

1.5   ANALYSIS OF DATA

The experimental data can be analyzed in several ways. One method involves plotting the instantaneous copolymer composition versus the comonomer feed composition, and then determining which theoretical curve would best fit the data by trial and error selections of r_1 and r_2. This is a tedious procedure and it is usually easier to solve **equation 9 (Section 2.4.2.1.1 in Chapter 2)** simultaneously for the different sets of data. The accuracy of the r_1 and r_2 values will depend on the use of data for feed compositions for which the copolymer compositions are most sensitive to variations in the r values.

A second procedure involves the following rearranged form of **equation 9 (Section 2.4.2.1.1 in Chapter 2) (57)**:

$$r_2 = \frac{[M_1]}{[M_2]}\left[\frac{d[M_2]}{d[M_1]}\left[1 + \frac{r_1[M_1]}{[M_2]}\right] - 1\right] \qquad (1)$$

Data for the feed and copolymer compositions for each experiment with a given feed are substituted into **equation 1**, and r_2 is plotted as a function of various assumed values of r_1. Each experiment yields a straight line and the point of intersection of the lines gives the best values of r_1 and r_2 for that system, while the area encompassing the intersections of a number of experiments covering a range of feeds serves as a check of the validity of the copolymerization equation (see **Figure 1**).
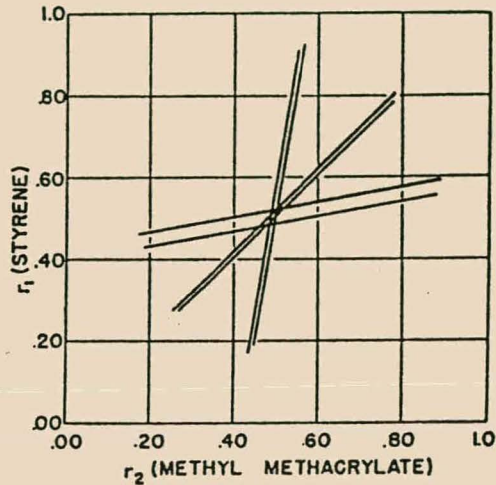
FIGURE 1. *Graphical solution of copolymerization equation for styrene-methyl methacrylate (six experiments) (55).*

The method of determining monomer reactivity ratios from a feed-copolymer composition plot is limited to low-yield experiments, although it can be extended somewhat by using average rather than initial feed compositions. However, even this technique may introduce serious errors when the extent of reaction exceeds 10-20 per cent. The r_1 vs. r_2 plot method, however, can be used on data obtained at any extent of reaction at which the residual monomers still contain significant amounts of both reactants, by employing **equation 2**.

$$r_2 = \frac{\log\left[\dfrac{[M_2]_0}{[M_2]}\right] - \dfrac{1}{p}\log\left[\dfrac{1 - p[M_1]/[M_2]}{1 - p[M_1]_0/[M_2]_0}\right]}{\log\left[\dfrac{[M_1]_0}{[M_1]}\right] + \log\left[\dfrac{1 - p[M_1]/[M_2]}{1 - p[M_1]_0/[M_2]_0}\right]} \qquad (2)$$

For each experiment, **equation 2** is solved for selected values of p (see below), yielding r_2-values, each of which is related to a corresponding r_1-value through the selected value of p. A plot of r_2 vs. r_1 then yields a curve for each experiment.

It has been found that **equation 2** describes a single-valued function which for positive values of r_1 and r_2, closely approximates a straight line of slope $(1/[M_1] - 1/[M_1]_0)/(1/[M_2] - 1/[M_2]_0)$. For negative

values of r_1, however, it may curve sharply and become discontinuous between the points $r_1 = -[M_2]_0/[M_1]_0$, $r_2 = -[M_1]_0/[M_2]_0$, and $r_1 = -[M_2]/[M_1]$, $r_2 = -[M_1]/[M_2]$. The generally linear nature of the function in the region of physically significant intersections greatly simplifies calculation, since three points are usually adequate for drawing the curve and checking calculations on a line corresponding to a given experiment. The labour required to carry out a calculation depends largely upon the computer's success in choosing suitable values of p for calculating r_1. Here an estimate of the expected values of r_1 and r_2 for the monomer pair, and the realization that the locus of all points with a given value of p lie on a line of slope p passing through $r_1 = r_2 = 1$, may save much time. (See **Figure 2**).
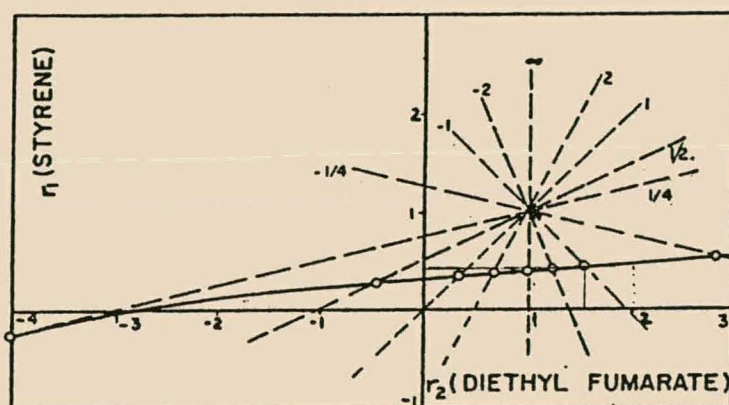
FIGURE 2. *Example of r_1-r_2 plot using integrated form of the copolymerization equation. Dashed lines are loci of points with indicated values of p (55).*

An alternative method of determining monomer reactivity ratios from high-conversion experiments, amounting essentially to determining copolymer compositions at several conversions for each feed and extrapolating back to zero conversion, has been employed by Wall *et al* **(75)**. However, it requires considerably more experimental data than the method described here.

1.6 EXPERIMENTAL ERRORS

The magnitude and effect of experimental errors in determining monomer reactivity ratios is of importance in judging the validity of tests of the copolymerization equation and of interpretations of the effect of structure on reactivity in copolymerization reactions based upon monomer reactivity ratios. With proper techniques of polymer isolation, the major experimental errors arise from errors in polymer analysis. The problem is thus one of estimating this error and of determining its effect upon the accuracy of the determination of the monomer reactivity ratios. This determination is particularly simple when the monomer reactivity ratios are determined from pairs (or pairs of groups) of experiments at high and low $[M_1]/[M_2]$ ratios (4:1 and 1:4 being convenient). Here the error in r_1 is determined almost entirely by the error in analysis in the high $[M_1]$ experiment, and the error in r_2 by the other, since for high M_1, the plot of data for **equations 2** or **10** (**Section 2.4.3.5.1** of **Chapter 2**) will be almost horizontal. If the probable error in analysis is known, new values of $[M_1]$ and $[M_2]$ (or

d[M$_1$]/d[M$_2$] if **equation 10** (**Section 2.4.3.5.1** of **Chapter 2**) is used) representing the possible range may be calculated and pairs of new solutions of the equation plotted for each experiment. The size of the parallelogram formed by intersection of these lines now gives the probable error. An example of such a treatment for four monomer pairs is shown in **Figure 3**. For most pairs, the spread between duplicate experiments is smaller than the analytical uncertainty, which is a good indication that other sources of error have been eliminated. In some cases, it is possible to make a good estimate of analytical error, or errors from other sources may be suspected.
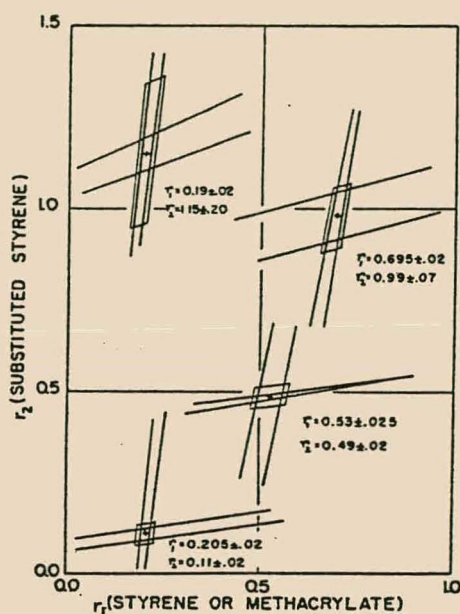
FIGURE 3. *Determination of experimental errors from analytical uncertainty. Upper right, styrene-p-bromostyrene; upper left, styrene-p-nitrostyrene; lower left, methyl methacrylate-p-dimethylaminostyrene; lower right, methyl methacrylate-m-methylstyrene (55).*

Further, a test of the validity of the copolymerization equation requires experiments with more than two feeds, and here the procedure based on analytical error is difficult to apply. Accordingly, some system for estimating uncertainty for such cases must be set up, based upon the size of the region in which the lines intersect. A typical example of data gathered at a variety of feeds is the results of six experiments on the copolymerization of ethyl methacrylate-vinylidene chloride at 68 °C, reported by Agron *et al.* (**76**); in **Figure 4** these are represented on an r_1-r_2 plot. Although the lines corresponding to the separated experiments do not meet at a point, all are touched by a circle of radius 0,07 with a centre at $r_1 = 2,01$, $r_2 = 0,28$. Since this is the smallest circle touching all the lines, one procedure is to take its centre as the "best" value and ±0,07 as the experimental error. However, if a single experiment (the line of the lowest slope) is neglected, a new best point ($r_1 = 2,13 \pm 0,03$, $r_2 = 0,33 \pm 0,03$) is obtained lying outside the original circle.
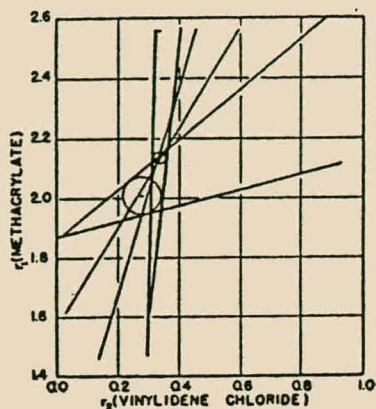
FIGURE 4. Ethyl methacrylate-vinylidene: Graphical solution of the copolymerization equation (55).

A more conservative treatment is to take the spread in intersections as the experimental uncertainty. The treatment, neglecting intersections of nearly parallel lines, would indicate $r_1 = 2,04 \pm 0,12$, $r_2 = 0,28 \pm 0,08$. Alfrey *et al.* (59) have chosen $r_1 = 202$, $r_2 = 0,35$ for this pair by means of a feed-copolymer composition plot, and curves corresponding to the two choices are illustrated in **Figure 5**. The difficulty in choosing the "best fit" from such a diagram is plainly evident, as is the fact that copolymer compositions are not usually very sensitive to small changes in *r*. This in turn emphasizes the necessity for good data for any accurate determination of monomer reactivity ratios.
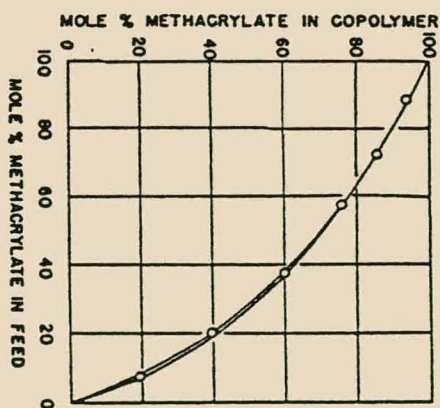
FIGURE 5. Ethyl methacrylate-vinylidene chloride: feed-copolymer composition diagram (55).

2   MEASURES OF PRECISION

In the early literature on reactivity ratios, little or no attention was paid to the precision with which the parameters were determined; however, in the more recent literature it has become common practice to give limits within which the true values are believed to exist.

At least part of the reason for the need for reasonable error estimates for the reactivity ratios is to assist in the resolution of the differences between copolymerization results on a particular system reported on by different authors.

Recent efforts provide a method whereby the uncertainty associated with a pair of reactivity ratios can be properly evaluated. The estimates of the reactivity ratios must be simultaneously determined, and, hence, they will not generally be statistically independent. This being so, the specification of joint confidence limits, within which the correct values are believed to exist, properly conveys the information in the data.

The joint confidence limits made available by the nonlinear least-squares procedure are correctly called "approximate limits", and two different levels of approximation can be used to compute these limits. A quadratic approximation can be employed. This procedure yields reasonably good approximate limits when the random variation in the responses is reasonably small and the data are generated in such a way as to minimize the statistical correlation between the estimated ratios.

These limits are approximate because the nonlinear estimation procedure does not estimate the experimental error independently of the parameters, a property that is enjoyed by linear least squares. As a consequence, the resulting contours are correct; however, the probability limits specified are approximate.

3   ASSESSING THE ADEQUACY OF THE MATHEMATICAL MODEL USED

Although it is of considerable importance to use estimation methods which can cope effectively with the stochastic (random error) properties of observations, it must be clearly understood by the user of these procedures that any computational effort is pointless if the mathematical expression employed to describe the physical system is wrong. The problem of the model used is one of (1) selecting a model from a number of candidates, and (2) establishing beyond reasonable doubt that it does adequately represent the behaviour of the system to which it is to be applied.

One procedure that can be used to determine whether a model fits a body of data is a test of significance for lack of fit (63). Such a test is appropriate only when the data are fitted by a nonlinear least-squares procedure (67).

The reasoning behind this test is as follows. If an inappropriate model is used, the experimental error variance obtained from the fitting procedure, in addition to containing a measure of the actual experimental error, will contain a quantity called the "squared bias". (If the correct model is employed, the squared bias would be expected to be zero.) The test of significance it is to be hoped, will disclose any large squared bias that would result from the use of the wrong model. It should be carefully noted that this procedure cannot prove that the model employed is correct but, only that a particular model is probably incorrect.

In the absence of replicated runs, no formal procedure can be used to determine if the model does in fact adequately describe the system. In these circumstances, a procedure that may be employed is the preparation of graphs where the ordinate is the difference between the observed and computed

response, and the abscissa may be the initial monomer concentrations or other relevant information. If the model fits the data, then the plotted points should be distributed randomly along a line parallel to the abscissa passing through an ordinal value of zero. If a definite trend or pattern is evident among the points, then there might be reason to doubt the adequacy of the model.

APPENDIX H

THE PROBLEM OF DISCREPANCIES

1   DISCREPANCIES   INTRODUCED   BY   CHOICE   OF CALCULATION PROCEDURE

The selection of a calculation procedure for converting data to reactivity ratios is of considerable importance, since the procedure determines not only the numerical values of r_1 and r_2, but also usually influences how precise these values are thought to be.

With the linearized form of the copolymer composition equation (*e.g.* the Fineman-Ross method), the calculated values of r_1 and r_2 clearly depend on which monomer is selected as M_1. Furthermore, the procedure produces negative values for the reactivity ratios, which is physical impossible.

Another problem associated with a linearized form of the copolymer composition equation is that it fails to provide a realistic estimate of the uncertainty associated with the reactivity ratios **(63)**. (See results in **Table I** and **II**). The two forms of the Fineman-Ross approach give grossly different estimates of the standard deviations of r_1 and r_2 even when the same data are used. The estimates of the precision commonly obtained from linear least-squares, when applied to the Fineman-Ross procedure, are not consistent in any way with those obtained from the nonlinear least-squares procedure. The difficulties with the Fineman-Ross estimate that arise from the selection of which monomer is M_1 can be shown to be due to the manner in which the resulting "observations" are weighted by the estimation procedure. The manner in which the data are weighted in the linear least-squares procedures determines the precision with which the estimates are computed, and this also explains the grossly different estimates of precision for the parameters.

TABLE I: Comparison of calculation methods using data from Table III of reference (67).

METHOD	r_1	r_2
Fineman-Ross(r_1 = slope)	0,179 ± 0,008	-2,0 ± 9
Fineman-Ross(r_2 = slope)	-0,09 ± 0,2	0,461 ± 0.002
Nonlinear least-squares	0,182 ± 0,011	0,488 ± 0,027

TABLE II: *Comparison of calculation methods using vinyl chloride-methyl acrylate data of Chapin et al. (77).*

METHOD	r_1	r_2
Fineman-Ross(r_1 = slope)	0,08 ± 0,02	9,3 ± 0,9
Fineman-Ross(r_2 = slope)	0,05 ± 0,08	8,9 ± 0,3
Nonlinear least-squares	0,09 ± 0,05	10,1 ± 3,0

It is again emphasized here that the simple plus-minus limits are not adequate delimiters of precision when parameters are jointly estimated. It is the joint confidence interval, such as shown in **Figure 1**, which clearly conveys the degree of uncertainty associated with the point estimates of the reactivity ratios.
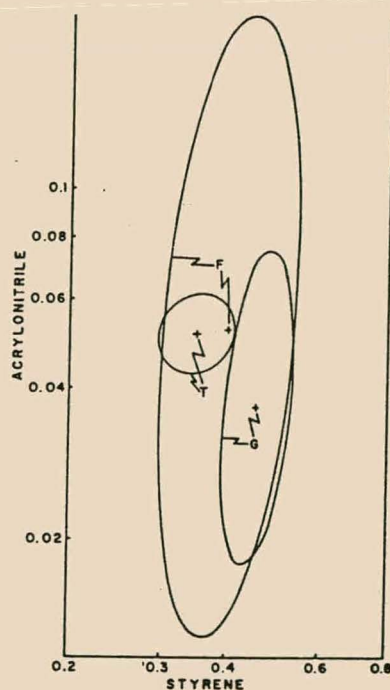
FIGURE 1. *Approximate joint r_1r_2 confidence intervals for the system acrylonitrile-styrene. (+) - Least-squares best estimate of r_1 and r_2 from each set of data; (F) - data of Fordyce and Chapin (78); (G) - data of Goldfinger and Steidlitz (79); and (T) - data of Thompson and Raines (80). The axis labelled "styrene" would be r_1 if styrene is defined as M_1, and r_2 if styrene is defined as M_2.*

2   DISCREPANCIES INTRODUCED BY CHOICE OF MODEL

In **Section 2.4.3.6.3** in **Chapter 2**, considerable discussion was presented on the adequacy of the model used to describe the system for generating copolymer data. Numerous examples can be found in the literature where the model does not meet the requirements. A second problem associated with

the model is the decision as to whether or not it is necessary to follow the more tedious route of integrating the model, or whether it is sufficient merely to use the more convenient differential form.

Apart from the physical considerations which should enter the formulation of the model, the evaluation of the adequacy of the model requires a careful examination of the residuals, the differences between the observed and computed results. The following two examples will illustrate the value of such model analysis.

The data used to prepare **Figure 2** are from the work reported by Russo and Munari **(81)** and show such a nonrandom pattern that there is little reason to believe that the simple copolymer model is adequate, and, indeed, they assert that it is not. The data used to prepare **Figures 3** and **4** are those of Meyer **(65)**, and the model fitted is the differential form of the copolymer model, a model which it could be asserted a *priori* would not be adequate but was, nevertheless, used for illustrative purposes. The graphs reveal that the model does not fit, as illustrated by the definite trends in the residuals for both of the monomer concentrations employed. These data, when fitted to the integral form of the simple copolymer model, fail to demonstrate any trends with feed composition, indicating that the drift shown in **Figures 3** and **4** is due to use of the incorrect differential model. These figures illustrate that this method of analysis is a sensitive one for assessing model adequacy.
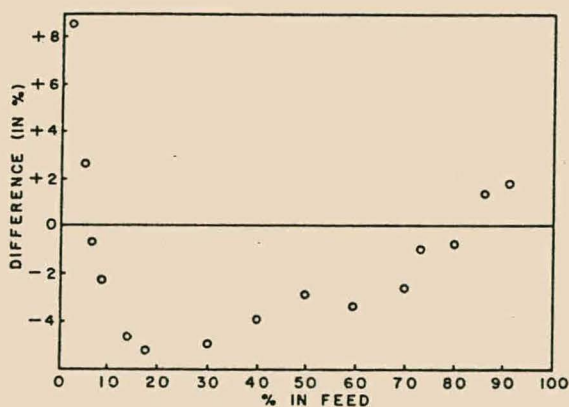
FIGURE 2. *Difference plot derived from the ethylene-carbon monoxide data of Russo and Munari (81), plotted as per cent CO.*
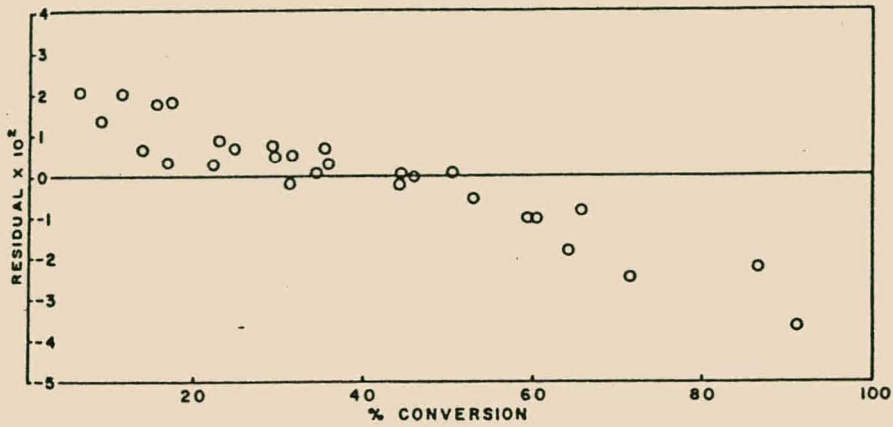
FIGURE 3. *Difference plot derived from the styrene-methyl methacrylate data of Meyer (65) using the differential form of the copolymer equation for data where $m_2 = 0,2$.*
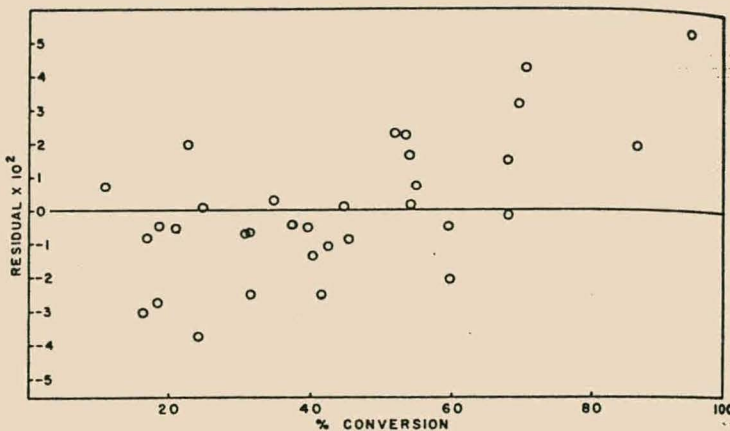
FIGURE 4. *Difference plot derived from the styrene-methyl methacrylate data of Meyer (65) using the differential form of the copolymer equation for data where $m_2 = 0,8$.*

Clearly, the differential form of the copolymer equation is not the correct one to use. The consequence of its use is a shift in the location of the joint confidence contour in $r_1 r_2$ space, and the extent and direction of shift corresponds to the difference between the starting and ending monomer feed compositions.

The data of Meyer (65) also appears to show that the errors in the polymer composition are roughly proportional to the concentration of M_2 in the copolymer. This evidence stems from the fact that the random variation in the data at high M_2 concentration in the copolymer is appreciably greater than that at the low concentrations of M_2. This violates assumption 2 in the least-squares computation procedure as explained previously, and results in placing statements with regard to the precision of $r_1 r_2$ estimates in jeopardy. The use of procedures described by Box and Cox (82) could be employed to permit valid statements to be made regarding the precision of the estimates.

3   DISCREPANCIES   INTRODUCED   BY   EXPERIMENTAL PRACTICES

It can be shown through mathematical analysis procedures that the use of imprecise polymer assay methods or the incorrect selection of experimental conditions to generate the data, merely result in less precise values of reactivity ratios. The use of inaccurate (biased) analytical procedures, however, can be shown to have dire consequences in the estimation of reactivity ratios.

4   RESOLVING DISCREPANCIES

From the discussion in above it should be clear that the principal causes of the inconsistencies in the literature on reactivity ratios are the use of either biased polymer assay procedures or of a model which fails to describe the copolymerization system used to create the polymer.

The detection of the failure of the system to be described by the assumed model can be done in two ways. First, replicate experimental runs should be made with exercise of sufficient care to ensure that they are *bona fide* replicates. These data can then be employed in the manner described in an earlier section on assessing the adequacy of the model (67). As a further check, the residuals, the differences between the observed and computed polymer composition, should be plotted against the initial monomer concentration, the calculated polymer composition, and the experimental run order as an additional method of evaluating the agreement or lack of agreement between experimental results and the copolymerization model. Evidence of model inadequacies should not be disregarded, since the use of a model that fails to describe the system indicates that either the experimental practices are inappropriate or that the assumptions made about the copolymerization scheme are not correct.

Almost none of the copolymerization data in the literature have been generated under conditions which simultaneously satisfy all of these criteria.

APPENDIX I

COPOLYMER COMPOSITION

1   CHARACTERISTICS OF MONOMER REACTIVITY RATIOS

The copolymerization equation (**equation 9** from **Section 2.4.2.1.1** in **Chapter 2**) relates the composition of the copolymer being formed at any instant, $d[M_1]/d[M_2]$, from a polymerizing mixture of two monomers at concentrations $[M_1]$ and $[M_2]$ by means of two variables, r_1 and r_2. These variables are evaluated simultaneously from the indicated experimental quantities of at least two feeds, using some form of **equation 9 (Section 2.4.2.1.1** in **Chapter 2)**. Relations at other feeds can then be calculated without additional data.

Actually, since the customary method of determining monomer reactivity ratios is to demonstrate that single values of r_1 and r_2 exist which predict the compositions of the copolymers obtained from a wide range of monomer ratios (and accordingly a wide range of media), the fact that **equation 9 (Section 2.4.2.1.1** in **Chapter 2)** applies at all actual sytems provides a general demonstration of this insensitivity.

The general conclusion that a single pair of monomer reactivity ratios suffices to describe the copolymerization of a given monomer pair under all conditions at a particular temperature is perhaps not surprising.

2   RELATION BETWEEN FEED AND INSTANTANEOUS COPOLYMER COMPOSITION

Except for monomer pairs of very similar reactivities, only a small range of feed compositions will yield copolymers containing appreciable amounts of both components. As alternation in copolymerization increases, more and more feeds will yield copolymers containing a large amount of each component. Indeed, it is the tendency to alternate in copolymerization, a property of monomer pairs, that makes practical the preparation of many known copolymers (57).

The picture of the copolymerization reaction from which **equation 9 (Section 2.4.2.1.1** in **Chapter 2)** is derived also permits analysis of the detailed structure of polymer chains. As mentioned earlier, the distribution of monomer units along a chain will cover the range from complete randomness in the "ideal" copolymer to strict alternation in the alternating copolymer. As shown by Alfrey and Goldfinger (59), for long chains the probability, P_{11}, of an M_1 radical adding M_1 (and similarly the other possibilities) is given by:

$$P_{11} = r_1[M_1]/(r_1[M_1] + [M_2])$$
$$P_{12} = [M_2]/(r_1[M_1] + [M_2])$$
$$P_{22} = r_2[M_2]/([M_1] + r_2[M_2])$$
$$P_{21} = [M_1]/([M_1] + r_2[M_2])$$

(1)

From **equations 1**, the probability of any sequence of M_1 units containing exactly m M_1 units (or the fraction of all M_1 sequences containing that number) is given by

$$N_1(m) = P_{11}^{(m-1)}P_{12}$$

(2a)

and, for M_2 sequences

$$N_2(m) = P_{22}^{(m-1)}P_{21}$$

(2b)

From **equations 2a** and **2b** the average sequence lengths become:

$$m_1 = \sum_1^\infty m P_{11}^{(m-1)} P_{12} \Big/ \sum_1^\infty P_{11}^{(m-1)} P_{12} = 1/P_{12}$$

(3)

$$m_2 = \sum_1^\infty m P_{22}^{(m-1)} P_{21} \Big/ \sum_1^\infty P_{22}^{(m-1)} P_{21} = 1/P_{21}$$

In general, m_1 will vary from unity for regular alternation up to the reciprocal of the fraction of M_2 in the copolymer, for the "ideal" case.

The spread in compositions of chains again increases in going from alternating to ideal copolymers and, even in the latter case, is very small.

3   PREDICTION OF COMONOMER SEQUENCE LENGTH

As long sequence lengths of one monomer in a copolymer affect crystallizability, and, therefore, polymer properties, it is desirable to have a measurement of such lengths. The sequence length distribution can be statistically predicted from reactivity ratios.

A copolymer of a chain of fixed length and composition can exist in a great number of isomeric structures that differ from one another in comonomer sequence. The routine use of ^{13}C NMR spectrometry and the availability of NMR spectral editing techniques, has made the characterization of copolymer sequence a realistic objective **(62)**. Each of the known copolymerization models makes definite predictions concerning comonomer sequence lengths, and the comparison of predicted and measured sequence distributions provides a powerful test of the copolymerization mechanism. In those instances where the sequence distribution is not experimentally accessible, calculation provides the only means for baring inferences concerning the relation of chain microstructure and macroscopic polymer properties.

A convenient method of describing the sequence structure of a copolymer is to state the fraction of sequences of each monomer (M_1 and M_2) that are of a particular length. As an example, consider the short copolymer chain below:

$$M_1M_2M_1M_1M_2M_1M_2M_2M_1M_1$$

The chain contains four sequences of M_1 units uninterrupted by M_2. Of these, two are of length 1 and two are of length 2. Thus the number fractions of sequences of M_1 of lengths 1 (N_1^1) and 2 (N_2^1) are each $1/2$ $(2/4)$. For M_2, the corresponding fractions are $N_1^2 = 2/3$ and $N_2^2 = 1/3$. A complete description of the comonomer sequence distribution for any chain is provided by specification of N_x^1 and N_x^2 for all values of x.

3.1 THE TERMINAL MODEL

The number fraction of sequences of M_1 of length x (N_x^1) is identical to the probability that any particular sequence of M_1 units is x units long. Such a sequence arises in the terminal model when a growing chain carrying a terminal M_1 unit adds $(x - 1)$ M_1's followed by an M_2. Thus,

$$N_x^1 = P_{11}^{(x-1)}P_{12} \qquad (4)$$

where P_{11} is the probability that a growing chain carrying a terminal M_1 adds M_1:

$$P_{11} = \frac{k_{11}[M_1^*][M_1]}{k_{11}[M_1^*][M_1] + k_{12}[M_1^*][M_2]} = \frac{r_1}{r_1 + [M_2]/[M_1]} \qquad (5)$$

and $P_{12}(= 1 - P_{11})$ is the probability that the same growing chain adds M_2. Similarly for M_2 sequences,

$$N_x^2 = P_{22}^{(x-1)}P_{21} \qquad (6)$$

Equations 4 and **6** allow calculation of the comonomer sequence distribution from a knowledge of the terminal model, reactivity ratios and the monomer-feed composition.

3.2 ALTERNATIVE APPROACH

An alternative approach to sequence length estimation is the run number. Here the distribution of interunit linkages (homoaddition vs cross-addition linkages) can be applied to the calculation of uninterrupted monomer sequences, or runs, per 100 monomer units. This quantity is the run number R'.

The run number for olefin polymers can be calculated from the feed composition and reactivity ratios:

$$R' = 200/[2 + (r_1m_1/m_2) + (r_2m_2/m_1)] \qquad (7)$$

4 PREDICTION OF INSTANTANEOUS COPOLYMER COMPOSITION

The relative rates of incorporation of comonomers M_1 and M_2 are not, in general, equal to their relative concentrations in the initial reaction mixture. Thus the copolymer formed at any instant differs in

composition from the feed mixture, and the feed composition changes continuously from the beginning of the reaction to the end **(62)**. A central problem of copolymerization theory has been the prediction of copolymer composition given a fixed, or instantaneous, feed composition.

The nature of the products of copolymerization, like those of any chemical reaction, may be dictated by the kinetics or by the thermodynamics of the reaction. With few exceptions, chain-growth copolymerization products are kinetically determined, so that instantaneous copolymer composition can be predicted by a set of differential equations that describe the rates of monomer consumption. Developing these equations requires an appropriate kinetic model of the copolymerization process. Most published models have been developed to treat copolymerizations by radical intermediates, but they are potentially applicable to any chain-growth copolymerization.

5 VARIATION OF COPOLYMER COMPOSITION WITH CONVERSION

The copolymerization equation **(equation 9** from **Section 2.4.2.1.1** in **Chapter 2)** gives the instantaneous copolymer composition, that is, the composition of the copolymer formed from a particular feed composition at very low degrees of conversion (approximately < 5%) such that the composition of the comonomer feed is relatively unchanged from its initial value. But, in general, the copolymer formed at any instant differs in composition from the feed mixture, so the feed composition itself drifts, that is, changes continuously, from the beginning of the reaction to the end. Exceptions are terminal-model copolymerizations in which $r_1 = r_2 = 1$, or in which azeotropic behavior is observed **(62)**.

The knowledge of the overall composition of the copolymer that has formed at a given conversion is of more practical importance than knowing the instantaneous composition at that conversion. Thus it may be found that a copolymer taken to 85% conversion has the properties desired for a specific application, while the same copolymer taken to 75% or 95% conversion has less satisfactory properties.

The comonomer feed changes in composition as one of the monomers preferentially enters the copolymer. Thus, there is a drift in the comonomer composition toward the less reactive monomer as the degree of conversion increases. This results in a similar variation of copolymer composition with conversion. Further, since it is essential in practice to carry polymerizations to high conversions, the manner in which copolymer compositions vary as reaction proceeds is of great importance.

Operationally, compositional drift can be eliminated by feeding the reactor continuously at a rate that matches the copolymerization rate, with a monomer mixture identical in composition to the copolymer that is being formed. It is useful,however, to examine the consequences of compositional drift with conversion.

The relation between copolymer composition and conversion was first obtained by Mayo and Lewis **(60)** by integration of **equation 9 (Section 2.4.2.1.1 in Chapter 2)** to yield

$$\log \frac{[M_2]}{[M_2]_0} = \frac{r_2}{1 - r_2} \log \frac{[M_2]_0[M_1]}{[M_1]_0[M_2]}$$
$$- \frac{1 - r_1 r_2}{(1 - r_1)(1 - r_2)} \log \frac{(r_1 - 1)[M_1]/[M_2] - r_2 + 1}{(r_1 - 1)[M_1]_0/[M_2]_0 - r_2 + 1}$$

(8)

Mayo *et al.* **(57)** stated, the most convenient method for determining copolymer compositions and distributions is the method of graphical or numerical integration developed by Skeist **(83)**. According to the Skeist method **equation 6** may be expressed in the form

$$\frac{d[M_1]}{d([M_1] + [M_2])} = F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}$$

(9)

where f_1 and f_2 are mole fractions of monomers in the feed.

Consider a system initially containing a total of M moles of the two monomers and in which the copolymer formed is richer in monomer M_1 than the feed is (that is, $F_1 > f_1$). When dM moles of monomers have been copolymerized, the polymer will contain $F_1 dM$ moles of M_1 and the feed will contain $(M - dM)(f_1 - df_1)$ moles of M_1 Consequently the material balance of M_1 gives

$$f_1 M - (M - dM)(f_1 - df_1) = F_1 dM$$

(10)

whence

$$\frac{dM}{M} = \frac{df_1}{F_1 - f_1}$$

(11)

or

$$\int_{M_0}^{M} \frac{dM}{M} = \ln \frac{M}{M_0} = \int_{(f_1)_0}^{f_1} \frac{df_1}{F_1 - f_1}$$

(12)

where M_0 and $(f_1)_0$ are the initial values of M and f_1 **(64)**.

If the quantities F_1 and $1/(F_1 - f_1)$ are now computed from **equation 6** at suitable intervals for $0 < f_1 > 1$, the fraction of total monomers which must react to change the composition of residual monomers from any value to any other value may quickly be obtained by determining $\ln(M/M_0)$ by graphical or numerical integration of **equation 15 (Appendix E)** between the desired values of f_1, and the corresponding value of F_1 (the composition of the polymer being formed at that point in the reaction). The average composition of the total polymer formed at that point follows by graphical integration of a plot of F_1 *vs.* M_1 or as the difference between the composition and amount of residual monomers and those originally present. In this manner one can obtain the variations in the feed and copolymer compositions with the degree of conversion (defined as $1 - M/M_0$).

The variation of these compositions with extent of reaction for various feeds can conveniently be represented by block diagrams (**Figure 1** and **2**).
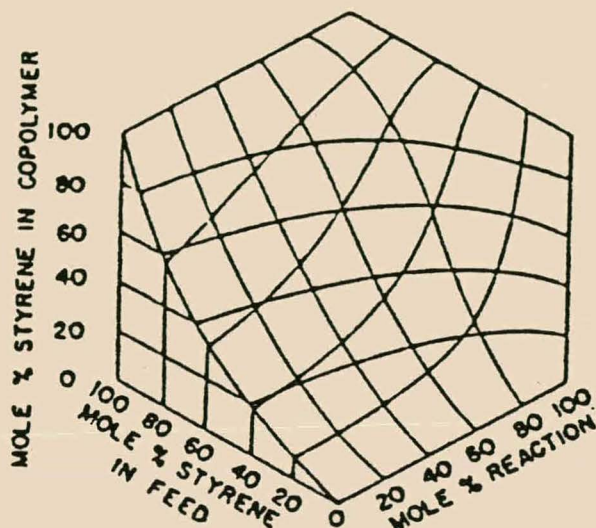
FIGURE 1. *Styrene-2-vinylthiophene: Variation in instantaneous composition of copolymer being formed with initial feed and per cent reaction (55).*
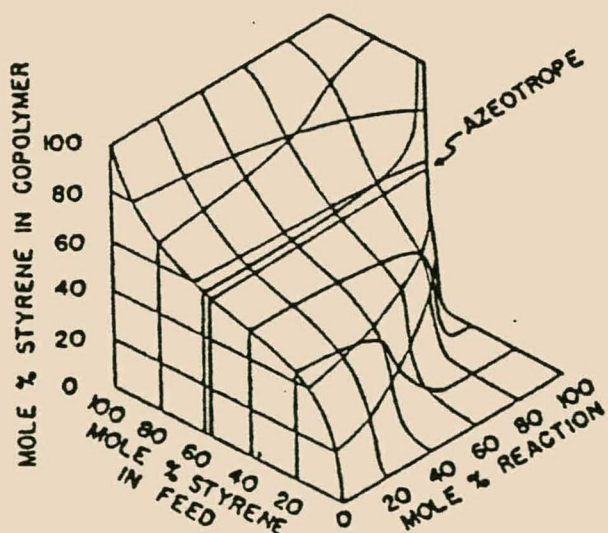
FIGURE 2. *Styrene-diethylfumarate: Variation in instantaneous composition of copolymer being formed with initial feed and per cent reaction (55).*

Meyer *et al.* **(84)** integrated **equation 12** to the useful closed form

$$1 - \frac{M}{M_0} = 1 - \left[\frac{f_1}{(f_1)_0}\right]^{\alpha} \left[\frac{f_2}{(f_2)_0}\right]^{\beta} \left[\frac{(f_1)_0 - \delta}{f_1 - \delta}\right]^{gamma} \quad (13)$$

where M is the total number of moles of monomer, f_1 and f_2 are the mole fractions of monomers 1 and 2 in the feed, $\delta = (1 - r_2)/(2 - r_1 - r_2)$, and the superscript 0 denotes initial values of the various quantities. The exponents are defined as $\alpha = r/(1 - r_2)$, $\beta = r_1/(1 - r_1)$, gamma $= (1 - r_1 r_2)/[(1 - r_1)(1 - r_2)]$; r_1 and r_2 are the usual terminal-model reactivity ratios. Knowledge of the values of r_1 and r_2 then allows calculation of the conversion, as a function of the change in the monomer-feed composition. The validity of this equation has been verified for radical copolymerizations of styrene and methyl methacrylate carried to conversions greater than 85%. **(Figure 3)**
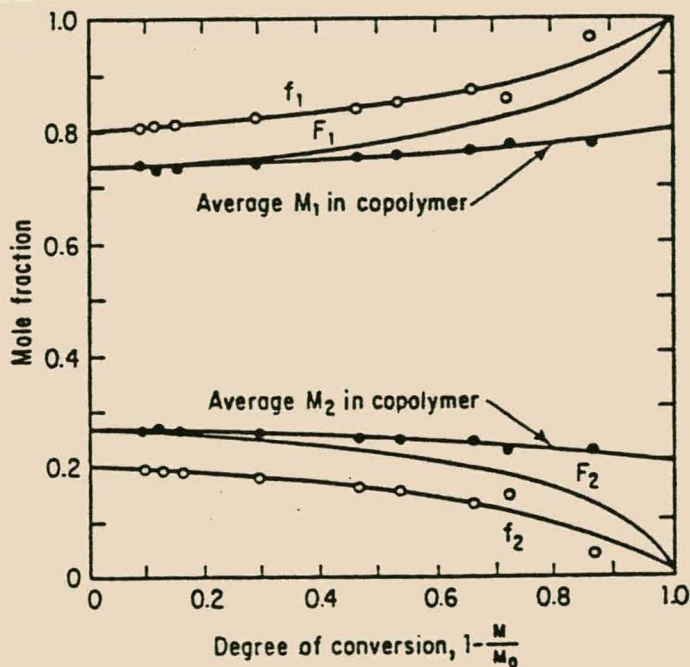
FIGURE 3. *Variations in feed and copolymer compositions with conversion for styrene(M_1)-methylmethacrylate(M_2) with $(f_1)_0 = 0,80$, $(f_2)_0 = 0,20$, and $r_1 = 0,53$, $r_2 = 0,56$ (64).*

Although the instantaneous polymer composition diagrams indicate how polymer compositions vary with conversion, a more accurate picture is obtained by considering polymer composition distributions. Only for the ideal case has the distribution function been obtained in explicit form, but, since the amount of polymer formed of composition lying between F_1 and $(F_1 + dF_1)$ is given by dM/dF_1 at that value, the distribution arising from polymerization of any feed may be obtained by graphical differentiation of a conversion-instantaneous polymer plot. The results, rather than being represented as curves, may be better visualized as bar-charts. See **Figures 4** and **5**.
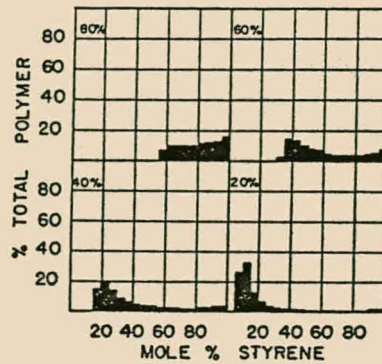
FIGURE 4. *Styrene-2-vinylthiophene: Distribution of copolymer compositions in completely polymerized sample for indicated percentage styrene in total polymer (and initial feed) (55).*
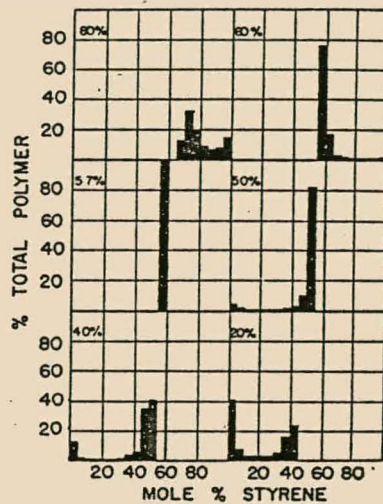
FIGURE 5. *Styrene-diethyl fumarate: Distribution of copolymer compositions in completely polymerized sample for indicated percentage styrene in total polymer (and initial feed) (55).*

The distribution diagrams show clearly that for some feeds in these systems, not only are a wide variety of polymer compositions produced, but appreciable quantities of two distinct compositions appear, with little material of intermediate composition. For an ideal copolymer, it can be shown that this U-shaped distribution arises whenever $r < 0,5$ or $r > 2$.; empirically, the same rule appears to hold true for the general case.

Technically, it is frequently desirable to prepare homogeneous copolymers rather than those having a wide distribution of compositions. If this composition does not correspond to an azeotrope, two methods are available: either the polymerization may be interrupted at a point somewhat short of complete conversion, or the polymerization may be started with a feed yielding the proper polymer, and its composition maintained by continuous or portionwise addition of the more reactive monomer.

6   MICROSTRUCTURE OF COPOLYMERS

The copolymerization equation describes the copolymer composition on a macroscopic scale, that is, the overall composition of a copolymer sample produced from a comonomer feed. This leaves unanswered two questions concerning the microscopic composition of the copolymer. The first concerns the exact arrangement of the two monomers along the polymer chain. Any particular overall polymer composition would be consistent with many different microscopic compositions **(64)**. For example, a copolymer with a composition of $f_1 = 0.6$, $f_2 = 0.4$ could have the regular copolymer structure

$$--M_1M_1M_1M_2M_2M_1M_1M_1M_2M_2M_1M_1M_1M_2M_2M_1M_1M_1M_2M_2--$$

or the random copolymer structure

$$--M_1M_2M_1M_2M_2M_1M_1M_1M_1M_2M_2M_1M_1M_2M_1M_1M_2M_1M_1M_2--$$

or the block copolymer structure

$$--M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_1M_2M_2M_2M_2M_2M_2M_2M_2--$$
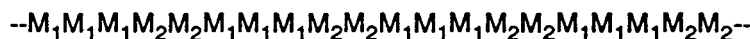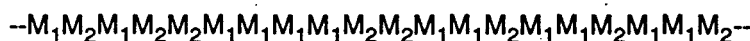
Statistical analysis of the copolymerization equation predicts that copolymerizations will usually proceed to yield the random copolymer structure. A tendency toward alternation occurs for comonomer pairs whose r_1r_2 products approach zero. The block copolymer structure is obtained only under special conditions. (There is an appreciable probability of producing long blocks of one monomer in a copolymer with feeds containing large proportions of a reactive monomer.)

Although these theoretical conclusions are generally accepted, verification of the random nature of copolymerization is experimentally difficult. This generally involves the experimental determination of the relative amounts of the three possible types of inter-monomer linkages in the copolymer, that is, M_1-M_1, M_2-M_2, M_1-M_2, and comparison with the relative amounts calculated on the basis of statistically random distribution. Chemical methods have been successful in some comonomer systems. More recently, high-resolution NMR has been used to verify the random distribution of monomer units in copolymerization. Thus, NMR has been used to determine the relative amounts of M_1-M_1, M_2-M_2, M_1-M_2 linkages in poly(ethylene-vinyl chloride) by analysis of the different types of methylene protons indicative of each linkage. In all instances, the experimental data verify the random distribution of monomers in copolymerization.

Another uncertainty concerning copolymer composition is the distribution of composition from one copolymer molecule to another in a sample produced at any given degree of conversion. Stockmayer **(85)** has indicated that the distribution of copolymer composition due to statistical fluctuations generally follows a very sharp Gaussian curve. Although the distribution is wider for low molecular mass copolymers, and for ideal copolymerizations compared with alternating copolymerizations, it is essentially zero in all practical cases.

APPENDIX J

EXPERIMENTAL CONTROL OVER THE ARCHITECTURE OF COPOLYMER CHAINS IN ZIEGLER-NATTA SYSTEMS

1   REACTION CONDITIONS

The strictest adherence to reaction conditions is required if copolymers of a desired monomer composition are to be synthesized. Whichever polymerization process is chosen - solution, gas phase or slurry - a drift in comonomer feed composition may result in a copolymer of non-uniform composition. In batch copolymerizations, especially those conducted to low yield, a constant comonomer ratio may be approximated but this may prove more difficult to achieve in continuous processes, as diffusion effects may aggravate the problem. In a process in which the reacting olefins are continuously passed through the solvent and unreacted olefins are vented, the rate of flow of olefins must be higher than the rate of reaction. In slurry processes the monomers dissolved in the diluent must be equilibrated with the gas phase of known composition to keep the monomer concentration constant throughout the copolymerization. To ensure saturation of the reacting olefins at all times, it is necessary to maintain high stirring rates, low solution viscosities, and low reaction rates; otherwise, the kinetics will become dominated by mass transfer barriers.

Cozewith and Ver Strate (87) found that the very high initial rates in an ethylene-propylene copolymerization resulted from a single batch addition of catalyst, and that this caused deviations from saturation. To counteract this, they added the catalyst components continuously to a well-stirred reactor containing solvent saturated with olefin mixture.

Temperature can exert an influence by its effect upon monomer solubility and also upon the overall reaction rate, and the rate of chain transfer reactions. Additionally, if temperature influences monomer coordination it may affect copolymer composition. A slight decrease in reactivity ratios with increasing temperature has been reported during ethylene-butene-1 copolymerization, although no dependence upon temperature was found at temperatures of up to 75 °C for ethylene and propylene copolymerization in the VCl_4–$Al(C_6H_{13})_3$ system. Finally, the order of addition of reaction components may be important.

2   CHEMICAL COMPOSITION OF THE CATALYST

The structure of the transition metal component and sometimes the nature of the metal alkyl component can influence copolymer composition. It has been shown that the relative reactivities of comonomers can be influenced by the electronegativity and the oxidation state of the transition metal centre. Reactivity also decreases with decreasing oxidation state in both titanium- and vanadium-based systems. In the series $VOCl_3$, VCl_4, and VCl_3, as well as $TiCl_4$ and $TiCl_3$, the relative reactivity of ethylene decreased as the valence of V and Ti decreased.

In general, the trends observed in overall polymerization rate with variation in catalyst-cocatalyst ratio are as observed in homopolymerization but copolymerization systems may be more sensitive to over-reduction by cocatalyst.

Large compositional spreads are attributed to the presence of multiple catalyst centres. Cozewith and Ver Strate (68) illustrated that this leads to an enrichment in longer sequences of ethylene over that present in a homogeneous polymer of the same ethylene-propylene composition. Thus, the heterogeneous polymers appear too crystalline (relative to those prepared with true homogeneous catalysts) for their composition and reactivity ratios. When only one type of centre is present in the homogeneous catalyst, the compositional spread is absent.

If multiple centres are present, reactivity ratios are a function of the mode of catalyst addition, and reactivity ratios determined by the normal copolymerization equation do not correctly predict the sequence distribution of the copolymer. Differences in methods of preparation and use may produce catalysts with different contents of multiple centers.

Natta (88) arrived at two conclusions about the sequence distribution for copolymers:
 (1)   As the content of the olefin in the copolymer increases, the probability of longer sequences of that olefin increases.
 (2)   The largest dispersion of sequence lengths is found for copolymers that contain equimolar amounts of the two olefins.

3   PHYSICAL STATE OF THE CATALYST

As already mentioned, variability in site structure can play an important role in determining the composition of the copolymer.

The presence of multiple centres, particularly in heterogeneous catalysts, is believed to be responsible for the production of a molecular mass distribution ($M_w/M_n = 10$) in Ziegler-Natta systems. Although diffusion phenomena may be important, such a multiplicity of active centres is also capable of producing a distribution in the extent of comonomer incorporation, that is copolymer composition, as the variation in ligand environment at different centres influences the ease of comonomer coordination at a centre. It should be noted that copolymerization is a particularly effective method of demonstrating the presence of a distribution of active centres of different steric behaviour in Ziegler-Natta catalysts.

The heterogeneous catalyst such as $AlEt_3$-$TiCl_3$ contains mostly isotactic-regulating centres, but a small number of syndiotactic-regulating and non-regulating centres are also present.

The compositional distribution may additionally be superimposed upon the molecular mass distribution to add to the structural complexity of the copolymer. Control of the molecular mass by transfer agents, variation in operating procedure and transfer reactions, which may also involve the comonomer, will all further increase compositional heterogeneity.

In comparison with copolymers prepared by means of heterogeneous catalysts, those obtained from homogeneous systems generally posses a narrow molecular mass distribution ($M_w/M_n = 2$) which

shows little compositional variation. Such catalysts generally possess a single type of active site and produce random or alternating copolymers.

4 STRUCTURE OF COMONOMERS

In Ziegler-Natta copolymerization reactions, reactivity ratio values for each comonomer that differ in magnitude by an order of three are often obtained. In contrast, those values obtained in radical copolymerization vary in magnitude by a few factors, which clearly implies a close interaction between the active centre and the monomer in Ziegler-Natta systems. This fact is well established from homopolymerization studies, and following the trend in homopolymerization, higher alpha-alkenes become less and less readily copolymerized as they increase in size. Despite the sometimes poor correlation between copolymer structure and reactivity ratio values, such values can be used with more confidence to compare relative comonomer reactivity in a copolymerization system.

Copolymers can be formed from combinations of monomers of different structure. In general, the more active the monomer is for homopolymerization with the catalyst being used, the more active is its reactivity in copolymerization, that is, ethylene > propylene > butene-1 > 3-methylbutene-1. A suitable catalyst must be selected for certain combinations.

The comonomer can influence copolymer structure by acting as a chain transfer agent during copolymerization, although as the bulkiness increases, its efficiency in this respect decreases. Comonomer presence can therefore broaden the molecular mass distribution. The presence of the comonomer can decrease the average molecular mass of the polymer, as well as the average degree of polymerization.

The disruption of long isotactic sequences of alpha-olefin units by other monomer units sometimes, but not always, lowers the ability of the resulting copolymer to crystallize. This is true when ethylene and propylene are copolymerized. Both monomers produce crystalline homopolymers, but the copolymer is elastomeric. This is not true when the two olefins have similar structures. For example, for 3-methylbutene-1 and 4-methylpentene-1, the copolymer can be crystalline since either monomer can fit into the crystal lattice structure of the other homopolymer.

APPENDIX K

EXPERIMENTAL METHODS FOR THE STUDY OF COPOLYMER STRUCTURES

1   SYNTHESIS OF COPOLYMERS IN STATIONARY CONDITIONS

The ordinary equation for the copolymer composition **(equation 1)** is, in fact, differential and corresponds to the instantaneous copolymer composition.

$$f = F(r_1 F + 1)/(r_2 + F) \tag{1}$$

where

$$f = (M_1/M_2)_{cop}$$
$$F = (M_1/M_2)_{feed}$$

r_1, r_2 are the reactivity ratios of monomers M_1 and M_2, respectively.

The equation becomes integral only when F is constant during a given run. The simplest way to maintain stationary conditions in normal batch copolymerization experiments is to have low yields of copolymers **(90)**. If the yields are lower than 10% we can assume as a first approximation that F was kept practically constant.

There are two kinds of modified batch experiments that allow F us to kept constant. The first arises where one of the monomers is liquid and the other is a gas, and when polymerization takes place in pure liquid comonomer under constant pressure of the gaseous comonomer. The second is to pass the mixture of both monomers (gases or liquids) into the reactor at a rate equal to the rate of copolymerization. Such experiments have setting periods, which can be avoided by the preparation of two monomer mixtures - one to fill the reactor (with the monomer ratio F) and the second for permanent feeding (with the monomer ratio f, that is, with a ratio corresponding to the composition of the forming copolymer). The other method of copolymer synthesis in stationary conditions is continuous copolymerization.

2   CALCULATIONS OF r_1 AND r_2

The values of the reactivity ratio products $r_1 r_2$ are the variables of main significance for the statistical description of the copolymer structure, which is why they are so carefully evaluated. Detailed reviews of the methods used are given in **Appendix F** and reference **(89)**.

3   INFRARED METHODS

Infrared (IR) spectroscopy is one of the most important methods for the determination of both copolymer composition and sequence distribution. The requirements of IR bands used for these purposes are practically opposite and are therefore discussed separately.

3.1   CHOICE OF ANALYTICAL BANDS FOR THE DETERMINATION OF COPOLYMER COMPOSITION

The main a *priori* requirements of an analytical band for determining composition are that there should be proportionality between the absorbance and the content of the given monomer in a copolymer and insensitivity to the distribution of the units. These requirements are very desirable but are hardly attainable. It is well known that practically all vibrations of a given molecular group are influenced by the neighbouring groups. Thus, in practice one is obliged to follow less rigid but more realistic requirements. They are:

1)   The preferred bands are those of modes highly localized on small groups (side groups are best of all), such as stretching or bending modes of CH_3, $CH(CH_3)_2$, C_6H_5, *etc.*

2)   The absorption coefficients of the analytical bands for a given unit in a copolymer should not depend on the stereoregularity of the corresponding homopolymer, that is, they must be the same for isotactic and atactic fractions. The reason for this is that usually bands sensitive to the stereoregularity of a polymer are usually also sensitive to the monomer distribution in copolymers.

There are also some requirements of analytical bands from the point of view of their practical utility (proper absorption coefficients; absence of strong overlap with other bands).

3.2   SEQUENCE-SENSITIVE INFRARED BANDS

The problem of the choice of bands sensitive to the distribution of monomer units in copolymers is closely connected with the problem of the regularity bands in the IR spectra of stereoregular polymers, and to the problem of the vibrational spectroscopy of nonregular polymers in general.

3.2.1   THEORETICAL APPROACH

In the vibrational spectra of ideally regular polymers only those modes absorb in which the phase differences between the equivalent motions of neighbouring units in the chain are either zero or equal to $2\pi k/l$, where k is the number of turns and l is the number of units in the identity period.

There are three general types of disorder of the ideal polymer chain:
1)   Conformational disorder in a melt or in solutions.
2)   Configurational disorder, that is, the nonideal stereoregularity of the polymer chain, which depends on the catalyst specifity only.
3)   Chemical disorder due to copolymerization or isomerization of a homopolymer chain.

The spectral changes due to all these types of disorder are roughly the same. In every case the shortening of sterically regular blocks and the appearance of defects between them induce certain changes in the IR spectra:

1) New bands arise due to defect vibrations (local modes); the positions of these bands are determined by the nature of the defect. In copolymer spectra the new bands are, generally speaking, those of the second comonomer.

2) The strictness of selection rules is weakened and some forbidden bands can appear, but with low intensities.

3) According to the theory the length of the regular block and the frequency of the bands (as well as their intensity) are interdependent:

$$v_n{}^2 = \sum_{k=0}^{M} A_k \cos k\pi/(n+1), \tag{2}$$

where

v_n = frequency of block with length n

A_k = constant

M = 1 or 2.

The dependence of v_n on the vibrational variables of defects is rather small. For this reason, the appearance of a set of short blocks in nonregular polymers sometimes brings about the asymmetric widening of some bands and induces significant changes in their intensities. The variation of the absorption coefficients K_n with n is found to be empirical, rather than theoretical.

3.2.2   EMPIRICAL APPROACH

The empirical classification of the bands sensitive to chain regularity has been discussed. There are three kinds of IR bands suitable for the study of unit distribution (see also **Figure 1 (90)**):

1) Crystallinity bands sensitive to the three-dimensional order in a polymer. These bands are relatively rare in the polyolefin spectra.

2) Helix bands that disappear from the polymer melts and solutions due to the shortening of the helix sequences in the amorphous state. These bands are specific for a particular type of stereoregularity, and are sensitive to the monodimensional order in a polymer.

3) Regularity bands having relatively low sensitivity to the aggregate state of a homopolymer but sensitive to the type of polymer stereoregularity. In the spectra of nonregular polymers and copolymers these bands become asymmetrical, and their relative intensities decrease (**Figure 1**). According to the theoretical approach stated above, these bands are typical examples of bands sensitive to regular block length.
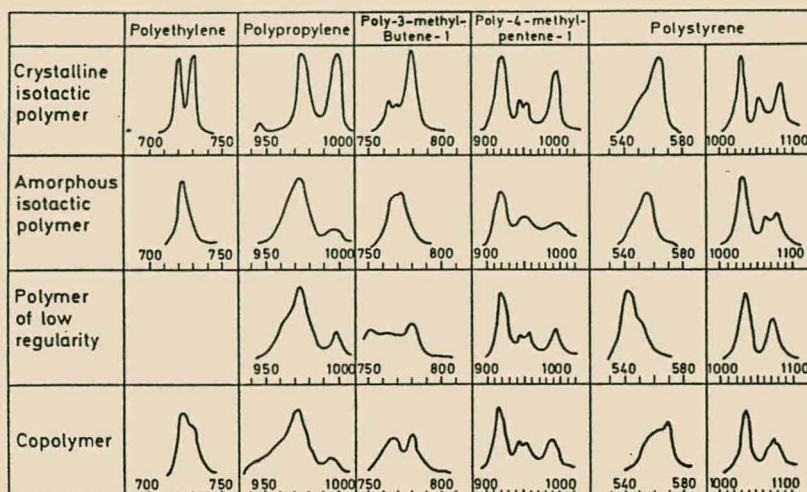
	Polyethylene	Polypropylene	Poly-3-methyl-Butene-1	Poly-4-methyl-pentene-1	Polystyrene	
Crystalline isotactic polymer	700 750	950 1000	750 800	900 1000	540 580	1000 1100
Amorphous isotactic polymer	700 750	950 1000	750 800	900 1000	540 580	1000 1100
Polymer of low regularity		950 1000	750 800	900 1000	540 580	1000 1100
Copolymer	700 750	950 1000	750 800	900 1000	540 580	1000 1100

FIGURE 1. IR bands for different olefins sensitive to unit distribution in copolymers (90).

3.2.3   QUANTITATIVE METHODS FOR EVALUATING UNIT DISTRIBUTION

The most used quantitative method for estimating unit distribution in olefin copolymer spectra is that of extinction coefficients with threshold sensitivity. This method was qualitatively formulated and then developed by many authors, according to whom, one can expect a smooth dependence of K_n on n in the case of regularity bands: K_n increases with increasing n and gradually becomes constant (as does v_n) for large n. The main assumption of the approximation used is that this smooth dependence is replaced by threshold dependence: for small n $K_n = 0$ and, beginning from any particular n, K_n becomes constant and independent of n.

The threshold method is widely used because the statistical dependencies for fractions of units in the sum of sterically regular blocks, beginning from any given n value, can be used for the comparison of experimental and statistical data.

Another important method of treating the spectral data is by analysis of the band shapes, which allows one to separate the complex asymmetrical band consisting of the overlapping bands that originate from blocks of different lengths on the initial bands.

3.2.4   ELIMINATION OF CONFORMATIONAL DEFECTS

As mentioned above, all three kinds of polymer disorder (chemical, configurational and conformational) produce approximately the same changes in the IR spectra. Hence, if one wants to estimate only the chemical and configurational disorder in a copolymer, the conformational defects must be eliminated from the samples under investigation as completely as possible. There are two general ways of doing this:

1.   To study the IR spectra of polymer solutions at low temperatures.

2.   To study the IR spectra of carefully crystallized products.

Both methods yield the helical conformation for practically all isotactic segments. The use of the first method is severely limited for high-olefin copolymers due to their low solubility, but the second method is very convenient and has been widely applied. The simplest crystallization technique is the annealing of copolymers at suitable temperatures.

3.2.5   SEQUENCE-SENSITIVE BANDS IN THE COPOLYMER INFRARED SPECTRA

All papers dealing with the IR spectra of high olefin copolymers include a study of the relatively small number of sequence-sensitive bands. They are briefly examined below.

Bands of Propylene Units.   Most of the sequence-sensitive bands in the spectra of propylene copolymers are situated in the 1000-800 cm-1 region **(Figure 1)**.

Bands of 3-Methylbutene-1 Units.   Data on the IR spectra of poly(3-methylbutene-1) are very scarce. A comparison of the spectra of a crystalline isotactic sample, the polymer melt, and an atactic material reveals the presence of some stereoregularity bands. Two of these bands are specific only for the crystallized sample and may be regarded as helix bands: 778 cm-1 **(Figure 1)** and 940 cm-1. Another band sensitive to the unit distribution is the 1218 cm-1 band, the relative intensity of which is much lower in the spectra of amorphous samples than those of crystalline ones.

Bands of 4-Methylpentene-1 Units.   The study of the spectra of isotactic 4-methylpentene-1 reveals stereoregularity bands at 1129, 997, 943, and 848 cm-1. Two bands (997 and 848 cm-1) are used for the study of unit distribution. According to the classification given above **(Section 3.2.2)**, they can be regarded as helix bands. The value of the threshold variable n for the 997 cm-1 band as estimated from the IR spectra of 4-methylpentene-1 copolymers is 4-5.

4   NUCLEAR MAGNETIC RESONANCE

Although nuclear magnetic resonance (NMR) spectroscopy is a powerful method for studying the structure of different vinyl copolymers, its usefulness for the olefin copolymers is rather limited. The main reason for this is undoubtedly the strong overlap between the resonances of the main-chain protons and those of the pendant groups. Unfortunately, this situation is unlikely to be improved by increasing the spectrometer frequency. One of the possible solutions to this problem is copolymerization with fully or partially deuterated monomers. The only exceptions to this difficult situation are ethylene-propylene copolymers and some styrene copolymers, and here important information about the copolymer structures has been obtained, including data relevant to the mechanism of stereospecific polymerization.

The development of ^{13}C NMR spectrometry has not contributed significantly to the determination of high olefin structure either, due to difficulties in separating the carbon atom resonances of main chains and pendant groups.

5 MELTING POINT MEASUREMENTS

The theory of the melting point depression of crystalline polymers with defects was developed by Flory (91) and has been applied to copolymers (92, 93). According to the theory, the relationship between the equilibrium melting point of a copolymer T_m and that of the corresponding homopolymer T_m^0 is:

$$1/T_m - 1/T_m^0 = -(R/\delta H_u)\ln p,$$

where δH_u is the heat of fusion per crystallized unit, and p is the probability that a given stereo unit, selected at random, will be followed by the same unit.

Kissin (90) found that for the given kind of units the melting point depression depends on the copolymer composition, on the stereospecifity of the catalyst, and on the product of the reactivity ratio $(r_1 r_2)$.

If there is a tendency to block formation $(r_1 r_2 > 1)$, the melting points of copolymers will be higher, and if there is a tendency to alternating addition $(r_1 r_1 < 1)$, they will be lower than for random copolymers.

Experimental tests of the theory have shown that in some cases the correlation between theory and experiment is good, but that sometimes deviations from dependence occur, and these can be both positive and negative; the latter may be attributed to the non-equilibrium conditions of the crystallization of long blocks and to the difference between the δH values for copolymers and homopolymers. At any rate, the data on melting point depression make it easy to distinguish between random and block copolymers of the same composition.

In practice, there are two other kinds of limitations in the application of this method to copolymers:

1) When the second comonomer incorporates the crystallites of the first comonomer, melting point behavior changes significantly and can sometimes lead to an increase of the melting point with the growth of the content of the second monomer.

2) The procedure for measuring the equilibrium melting point is very complicated and is sometimes replaced by more rapid procedures, such as DTA analysis, which reduce the validity of comparisons between experimental and theoretical data.

6 CRYSTALLINITY MEASUREMENTS

Quantitative estimation of copolymer crystallinity by the X-ray method, dilatometry, *etc.*, is a useful tool for characterizing unit distribution in copolymers.

If no copolymerization takes place and if the materials are mixtures of homopolymers, the degree of crystallinity would be expected to be approximately the sum of the crystallinities of the homopolymers crystallizing separately, and the crystallinity versus composition curve would be approximately linear between the crystallinities of the homopolymers.

In a normal polymer only a small amount of comonomer is required to greatly disrupt or completely destroy crystallinity. For example, completely linear polyethylene is about 80 to 90% crystalline (94).

The incorporation of 2 mole per cent vinyl acetate decreases this to about 60% and much more than 10 mole per cent vinyl acetate destroys crystallinity entirely.

The effect of copolymerized alpha-olefin units in reducing the degree of crystallinity will depend upon the degree of randomness in their distribution, and may be due to the inclusion of the one comonomer unit within the crystal lattice of the other comonomer unit, and hence introduction of imperfections, particularly if the unit is too large to be easily accommodated. Alternatively, it may be due to a reduction in crystal size because the fold length and fold regularity are limited when comonomer units have to be incorporated into the amorphous regions between lamellae, or to both of these factors.

The properties of a normal crystalline polymer change drastically with increasing amounts of comonomer. Specifically, the melting point and the stiffness modulus above the glass transition temperature are severely lowered by the addition of comonomer.

The ratio 1:2 of the comonomers (*i.e.* about 305 "foreign" units) is given as the limit of the region of the completely amorphous copolymer (90). From this point of view, if both olefins produce crystalline homopolymers, we can expect a U-shaped curve in the plot of "total crystallinity versus copolymer composition".

This simple sitiuation is frequently altered by (1) isomorphism phenomena and (2) by the inhomogeneity of copolymer composition. Cocrystallization may occur in random copolymers due to isomorphism of monomer units. Isotactic copolymers which are highly crystalline over a wide range of composition have been described by Reding and Walter (94) for 4-methylpentene-1 with 3-methylbutene-1.

Natta (95) has discussed isomorphism and solid solution formation in mixtures of isotactic polymers with macromolecular chains of similar chemical nature and structure. In the same paper he discussed 'isomorphism phenomena among monomeric units' and 'isodimorphism'. The former occurs when copolymerizing monomer units are able to replace each other isomorphously in the unit cell of the homopolymers, which must have an anologous crystal structure, the same identity period and only very slightly different lattice constants. Copolymers of 4-methylpentene-1 and 3-methylbutene-1 form such a system. Here the physical properties, for example lattice dimensions, melting point and crystallinity, vary in a strictly continuous way as a function of composition.

Natta describes as 'isodimorphic' those systems which are crystalline over the whole composition range, even though the homopolymers have different crystal structures. The majority of isotactic polyolefins have similar helices (3_1-4) and pendant groups of similar volume, which significantly favours the isodimorphism of their copolymers. Disregard of this phenomenon can lead to a serious overestimation of the block content of olefin copolymers, so that a careful evaluation of possible isomorphism is necessary in every case.

The main practical method for measuring crystallinity is based on X-ray diffractometer scans of copolymers and is similar to that used for polypropylene. It consists of the division of the area under the peaks by linear baselines into amorphous (A) and crystalline (C) areas, the degree of crystallinity being $C/(C+A)$.

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