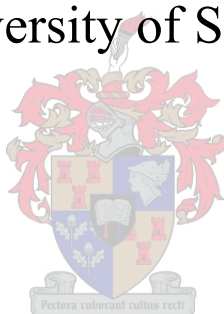


New monomer for hydrophobic acrylic copolymers and their novel properties

by

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Dissertation presented for the degree of
Doctor of Science (Polymer Science)
at the University of Stellenbosch



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December 2006

Declaration

I, the undersigned, hereby declare that the work contained in this dissertation is my own original work and that I have not previously, in its entirety or in part, submitted it at any university for a degree.

Signature:

Date:

Summary

The synthesis and characterization of a new tertiary alcohol (2-octyl-2-dodecanol) and “bushy-tailed”, hydrophobic acrylic monomer (2-octyl-dodecyl acrylate) from a 1-decene dimer (2-octyl-1-dodecene) precursor that was synthesized with metallocene technology is reported. Some preliminary applications of the newly synthesized 2-octyl-dodecyl acrylate were investigated. These applications included the use of 2-octyl-dodecyl acrylate as a reactive hydrophobe in mini-emulsion polymerizations, and as a reactive (internal) plasticizer.

In an attempt to selectively dimerize 1-decene, the effect of various factors on the oligomerization of 1-decene was investigated. These factors include the following:

- i. Different temperatures: 5, 35, 70 and 90°C
- ii. Different co-catalyst [methylaluminoxane (MAO)] concentrations
- iii. Different catalysts: bis(cyclopentadienyl)zirconium dichloride (Cp_2ZrCl_2) and bis(cyclopentadienyl)hafnium dichloride (Cp_2HfCl_2)
- iv. Different reaction times.

In all instances the final product obtained, under the abovementioned conditions, was a mixture of residual monomer, the dimer and trimer of 1-decene. These findings were corroborated with GC-MS and $^1\text{H-NMR}$ spectroscopy.

The isolation and further processing of the dimer of 1-decene (2-octyl-1-dodecene) was investigated. The efficiency, in terms of the final product-composition for the amount of catalyst used and reaction time, of Cp_2ZrCl_2 compared to bis(cyclopentadienyl)hafnium dichloride (Cp_2HfCl_2 ; hafnocene) as catalyst for the oligomerization of 1-decene is also reported on. The results obtained indicated that Cp_2ZrCl_2 is the more efficient catalyst for the oligomerization of 1-decene. The effect of different reaction times (1, 3, 6, 24 hours) on the final product-composition for the oligomerization of 1-decene was also investigated. Longer reaction times (24 hours) seemed to be excessive. A reaction time of 6 hours was optimal.

The purified 1-decene dimer (2-octyl-1-dodecene) was converted to the new tertiary alcohol (2-octyl-2-dodecanol) using the oxymercuration-demercuration procedure. The 2-octyl-dodecyl acrylate was synthesized by the esterification of the tertiary alcohol with acryloyl chloride in the presence of triethylamine. The new tertiary alcohol and acrylate were characterized by FT-IR and $^1\text{H-NMR}$ spectroscopy.

Stable polymer latex particles were successfully synthesized with the novel reactive hydrophobe 2-octyl-dodecyl acrylate in the mini-emulsion polymerization of butyl acrylate, methyl methacrylate and styrene. Phase-separation experiments showed that the presence of 2-octyl-dodecyl acrylate in the dispersed phase retards Ostwald ripening.

The novel acrylic monomer, 2-octyl-dodecyl acrylate, was copolymerized with styrene via conventional free radical polymerization. Both low and high molecular weight copolymers were prepared. Thermal analysis of the copolymers showed that 2-octyl-dodecyl acrylate does act as a reactive (internal) plasticizer. Blends of commercial virgin polystyrene and the synthesized low and high molecular weight copolymers were prepared. Partially miscible blends were obtained. Decreases in the glass transition temperatures of the blends compared to the virgin polystyrene were observed. The higher molecular mass styrene/2-octyl-dodecyl acrylate copolymers produced larger decreases in glass-transition temperatures.

Opsomming

Hierdie studie behels die sintese en karakterisering van 'n nuwe tersiêre alkohol, 2-oktiel-2-dodekanol, en unieke, vertakte, hidrofobiese akriliese monomeer (2-oktiel-dodekielakrielaat) vanaf 'n 1-dekeen-dimeer (2-oktiel-1-dodekeen) wat met behulp van metalloseen tegnologie gesintetiseer was. Twee aanvanklike toepassings van die nuwe hidrofobiese, vertakte akrielaat is ondersoek, naamlik, die gebruik van 2-oktiel-dodekielakrielaat as reaktiewe hidrofobiese kostabiliseerder in mini-emulsiepolimerisasies en as 'n reaktiewe interne plastiseerder.

Die effek van 'n verskeidenheid van faktore op die oligomerisasie van 1-dekeen is ondersoek. Hierdie faktore sluit die volgende in:

- i. Verskeie temperature: 5, 35, 70, 90 °C
- ii. Verskeie ko-katalisator (metielalumienoksaan) konsentrasies
- iii. Verskeie katalisators: bis(siklopentadiëniel)zirkoniumdichloried (Cp_2ZrCl_2) en bis(siklopentadiëniel)hafniumdichloried (Cp_2HfCl_2)
- iv. Verskeie reaksietye.

In alle gevalle is 'n finale produk bestaande uit oorblywende 1-dekeen, 1-dekeen-dimeer en 1-dekeen-trimeer verkry. GC-MS en $^1\text{H-NMR}$ spektroskopie het dit bevestig.

Die isolasie en verdere verwerking van die dimeer van 1-dekeen (2-oktiel-2-dodekeen) is ondersoek. Die effektiwiteit, in terme van finale produksamestelling, vir die hoeveelheid katalis gebruik, asook reaksietyd, is ondersoek vir beide Cp_2ZrCl_2 en Cp_2HfCl_2 as oligomerisasiekataliste vir 1-dekeen. Die resultate toon aan dat die Zr-katalis meer effektief is as die Hf-monoloog. Daar is ook gevind dat 'n reaksietyd van 6 uur optimaal is.

Die nuwe tersiêre alkohol (2-oktiel-2-dodekanol) is gesintetiseer vanaf die gesuiwerde 1-dekeen-dimeer (2-oktiel-1-dodekeen) deur middel van die oksiemerkurasie-demerkurasie proses. Die esterifikasie van 2-oktiel-2-dodekanol met akrolielchloried

in die teenwoordigheid van trietielamien het die nuwe monomeer, 2-oktiel-dodekielakrielaat, gelewer. Die alkohol en akrielaat is deur middel van FT-IR en ^1H -NMR spektroskopie gekarakteriseer.

Die gebruik van 2-oktiel-dodekielakrielaat as reaktiewe hidrofoob (kostabiliseerder) in die mini-emulsie polimerisasie van butielakrielaat, metielmetakrielaat en stireen het stabiele lateks partikels gelewer. Faseskeidingseksperimente het getoon dat die teenwoordigheid van 2-oktiel-dodekielakrielaat in die disperse fase Ostwald-rypwording vertraag.

Lae- en hoë-molekulêre-massa stireen/2-oktiel-dodekielakrielaatkopolimere is gesintetiseer deur middel van konvensionele vrye-radikaalpolimerisasie. Termiese analise van die kopolimere het getoon dat 2-oktiel-dodekielakrielaat as 'n reaktiewe (intêrne) plastiseerder optree. Mengsels van stireen met lae en hoë molekulêre massa kopolimere is berei. Gedeeltelik-mengbare mengsels is verkry. In alle gevalle is 'n verlaging in die glas-oorgangstemperatuur waargeneem. Die hoë molekulêre massa stireen/2-oktiel-dodekielakrielaat kopolimere het groter verlaging in die glas-oorgangstemperatuur tot gevolg gehad.

Acknowledgments

I herewith wish to acknowledge and offer my appreciation to the following individuals:

Prof. Ron Sanderson for the opportunity and all his support;

Dr. Albert van Reenen for all his input;

Dr. Margie Hurndall for painstakingly and willingly editing this dissertation;

My mom, Lettie de Vries, for always believing in me;

My brothers and sisters for all their support and encouragement over the years;

My friends, you know who you are, for just being who you are.

My Lord and Saviour, Jesus Christ; apart from You I can do absolutely nothing. You bring meaning and purpose to my life.

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List of Abbreviations

AIBN:	Azobisisobutyronitrile
BA:	Butyl acrylate
CDCl ₃ :	Deuterated chloroform
CHDF:	Capillary hydrodynamic fractionation
Cp ₂ ZrCl ₂ :	Bis(cyclopentadienyl)zirconium dichloride
Cp ₂ HfCl ₂ :	Bis(cyclopentadienyl)hafnium dichloride
DDI:	Distilled and deionized
DMA:	Dynamic mechanical analysis
HD:	Hexadecane
IR:	Infrared
MMA:	Methyl methacrylate
NMR:	Nuclear magnetic resonance
PDI:	Polydispersity index
SDS:	Sodium dodecyl sulphate
THF:	Tetrahydrofuran
TMS:	Trimethyl siloxane
TEM:	Transmission electron microscopy
\bar{M}_w :	Weight average molecular weight
\bar{M}_n :	Number average molecular weight
\bar{M}_p :	Peak average molecular weight
T _g :	Glass transition temperature
DDM	Dodecyl methacrylate
CA	Cetyl alcohol
LMA	Lauryl methacrylate
SMA	Stearyl methacrylate
CMC	Critical micelle concentration
HIPS	High impact polystyrene
SBS	Styrene-butadiene-styrene
HEMA	Hydroxyethyl methacrylate

CHAPTER 1

Introduction and Objectives

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ABSTRACT

A brief introduction to acrylic polymers and some of their applications, along with some basic polymer chemistry concepts, are presented here. The objectives of the study and the layout of this dissertation are also presented.

1.1 Introduction

All materials have their origin in nature. Polymers are no exception; they originate from such basic chemical elements as carbon, oxygen, hydrogen, nitrogen, chlorine, or sulphur. These materials are extracted from nature's storehouse of air, water, gas, oil, coal, and even living organisms, such as plants.

From the basic sources come the feedstocks we call 'monomers' (from the **words** 'mono', which means one, and 'mer', which means unit - in this case, the specific chemical unit). Monomers undergo chemical reactions known as polymerization, which causes the small molecules to link together into longer molecules. Chemically, the polymerization reaction converts the original monomer into a 'polymer' (many 'mers'). Thus, a polymer may be defined as a high-molecular-weight compound that contains comparatively simple recurring units.

A monomer can contribute to the synthesis of a variety of different polymers, each with its own distinctive characteristics. A number of factors play a role in the ultimate properties of a particular polymer. These include the following:

- ❑ The way in which the monomers link together into a polymer, resulting in linear, branched, star or crosslinked polymers;
- ❑ The length of the molecular chain, in other words, the molecular weight of a polymer;
- ❑ The molecular weight distribution (assortment of molecular chain lengths);
- ❑ The type of monomer;
- ❑ Polymerizing two or more different monomers together, in a process known as copolymerization; copolymers can have a number of arrangements of the monomers along the chain: random, alternating, block or graft;



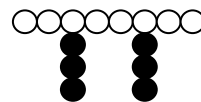
Random



Alternating



Block



Graft

- Incorporating various chemicals or additives during or after polymerization.

The need for new and improved materials for existing and new applications is an ongoing pursuit in the field of polymer science. The discovery of man's ability to synthetically produce materials, with significant and distinctive qualities, was the birth of a new era - the polymer age. This discovery opened up the way for products that have become commonplace in our everyday lives. Due to the infinite number of combinations and permutations of molecules at our disposal, a world of infinite possibilities has become ours for the taking.

Acrylic-based polymers have been of continuing interest for many years, since the incorporation of functional acrylates or methacrylates into polymers provides adaptable routes for the preparation of reactive polymers. Homopolymers and copolymers of acrylic or methacrylic materials were found to be very versatile in different applications¹. Chern and Chen reported on the use of long-chain alkyl methacrylates, like dodecyl and octadecyl methacrylate, as reactive hydrophobes in the mini-emulsion polymerization of styrene². Amphiphilic copolymers of these hydrophobic monomers have been successfully used to act as both stabilizer (surfactant) and costabilizer (hydrophobe) in the mini-emulsion polymerization of styrene³.

Acrylic polymers have also been widely used in the medical industry, due to the fact that they are resistant to many biological and chemical agents. For medical devices, special impact-modified grades, formulated to resist breaking and cracking, are employed more often than standard grades. The leading uses of acrylic polymers in the medical industry today are for cuvettes and tubing connectors, but they are also used to produce test kits, syringes, blood filters, drainage wands, flow meters, blood-pump housings, fluid silos, surgical-blade dispensers, incubators and surgical trays⁴.

'Bushy-tailed' hydrophobic acrylic monomers (like the one synthesized in this study) have, by nature, very interesting properties. 'Bushy-tailed' refers to a branched, as oppose to a linear, hydrophobic component in the acrylic monomer structure. Their structural and

chemical nature affords them the ability to be used in a variety of applications. Of special interest here is the fact that they can be used as reactive hydrophobes in the mini-emulsion polymerization of various monomers. They can also be used as internal plasticizers, as they alter the structural properties, and hence the thermal and mechanical properties, of any rigid and brittle polymer.

The work presented in this dissertation is my small, but hopefully significant, contribution to the global database of new compounds and polymeric materials with (hopefully) unquestionable usefulness.

1.2 Motivation

This study was motivated by the need for new monomers, more specifically, the need for uniquely branched ('bushy-tailed') hydrophobic monomers and their applications. These applications take advantage of the hydrophobicity and 'branchiness' of these types of monomers.

In this study, the newly synthesized hydrophobic monomer was used as a reactive hydrophobe, forming a copolymer with a specific monomer, in the mini-emulsion polymerization process. Such an application is motivated by the need to eliminate low-molecular-weight unreactive hydrophobes, like hexadecane, from the final polymer product.

An internal (reactive) plasticizer that chemically bonds with a polymer, acting as a comonomer, is useful in eliminating the problems associated with unreactive plasticizers, such as migration to the surface of the polymer or even the evaporation of the plasticizer. Exploiting the reactive 'bushy-tailed' monomer in this regard for the plasticization of polystyrene and using the synthesized copolymers in the modification of commercial virgin polystyrene by means of blending was investigated. The blending of the commercial virgin polystyrene with the internally plasticized polystyrene was expected to

minimize immiscibility, as most polymer blends are immiscible and require some sort of compatibilizer.

1.3 Objectives

In an effort to synthesize new monomers, with a view to using them to prepare new polymeric materials, which find applications such as coatings, surfactants, co-surfactants, drug binders, sound absorbers and reinforcement materials, I report here on the synthesis of the highly hydrophobic ('bushy-tailed') 2-octyl-dodecyl acrylate (2-ODA).

Will this novel acrylate be an adequate reactive hydrophobe substitute for the conventional unreactive hydrophobes like hexadecane and cetyl alcohol in the mini-emulsion polymerization of various monomers? This question will be answered in Chapter 5.

When one mentions the need for new polymeric materials and the requirement for new material properties, the copolymerization method of preparing such materials is one of the obvious choices that spring to mind. Thus, the copolymerization of 2-ODA with styrene was investigated, and how its incorporation affected the thermal and mechanical properties of the polystyrene.

This study endeavoured to realise the following objectives:

- The selective dimerization of 1-decene, with the use of a metallocene-based catalytic system;
- The synthesis and characterization of a new acrylic monomer, 2-octyl dodecyl acrylate;
- The use of 2-octyl-dodecyl acrylate as a reactive hydrophobe, equivalent to hexadecane, in the stabilization of conventional mini-emulsion polymerizations of various monomers;

- The synthesis of low- and high-molecular-weight styrene/2-octyl-dodecyl acrylate copolymers via conventional free radical copolymerization;
- The blending of the abovementioned copolymers with commercial virgin polystyrene;
- Determining the thermo-mechanical properties of the aforementioned copolymers and blends.

1.4 Outline of Dissertation

This dissertation is structured in the following manner:

- **Chapter 1**

A general introduction to this study and the aims are the highlights of this chapter.

- **Chapter 2**

A brief historical overview on the oligomerization of α -olefins, common and novel acrylic and methacrylic monomers and polymers, and some theoretical background to the concepts and procedures used in this study are outlined in this chapter.

- **Chapter 3**

This chapter details the effects of various factors, such as temperature, co-catalyst concentration, type of catalyst and reaction time, on the oligomerization of 1-decene.

- **Chapter 4**

The synthesis and characterization of a new tertiary alcohol, 2-octyl-2-dodecanol, and a novel acrylic monomer, 2-octyl dodecyl acrylate, are described in this chapter.

- **Chapter 5**

This chapter discusses the possible use of the novel reactive acrylic monomer as a suitable alternative to hexadecane as hydrophobe (costabilizer) in the mini-emulsion polymerization of various common monomers.

□ **Chapter 6**

The conventional free-radical copolymerization of the novel acrylic monomer (2-octyl-dodecyl acrylate) with styrene, and the blending of the newly synthesized copolymers with commercial virgin polystyrene, with their resultant thermo-mechanical property modifications, are the subjects of this chapter.

□ **Chapter 7**

General conclusions, and recommendations for further research, are presented here.

1.5 References

1. Z.T. Hamaudi, N. Nugay, T. Nugay, **Turkish Journal of Chemistry**, 28, 387 (2004)
2. C.S. Chern, T.J. Chen, **Colloid Polymer Science**, 275, 546 (1997)
3. G. Baskar, K. Landfester, M. Antonietti, **Macromolecules**, 33, 9228 (2000)
4. W.A. Whitaker, **Medical Plastics and Biomaterials Magazine**, January (1996)

CHAPTER 2

Historical and Theoretical Background

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ABSTRACT

The historical development of some of the most common monomers and their polymers are highlighted. Background information on α -olefin oligomerization is provided. The various concepts used in this study, as they pertain to α -olefin oligomerization and mini-emulsion polymerization, are also given attention.

Keywords: acrylic monomers, α -olefin oligomerization, mini-emulsion polymerization, polymer blends

2.1 A Brief History of Polymeric Materials

2.1.1 General

A study of this nature warrants the need to have a brief look into the history of polymeric materials. Where did it all begin and how did we progress to where we are today?

Well, natural polymers have been with us since the beginning of time, but the centenary of purely synthetic polymers will only be celebrated in 2009. Natural polymers began to be chemically modified during the 1800's to produce many materials. The most famous amongst these materials were vulcanized rubber (Goodyear and Hancock), gun cotton (Schoenbein), and celluloid (Hyatt). It was not until 1909 that synthetic polymers became a reality. It all started with Leo Baekeland who produced the first synthetic plastic, a thermosetting plastic resin called Bakelite, from the condensation reaction between phenol and formaldehyde. This was soon followed by the development of the first semi-synthetic fibre, Rayon, in 1911. By the end of the 1930's many purely synthetic polymers were in commercial production. One of these was poly(vinyl chloride) (1933), which was used as cable insulation during the Second World War. Wallace Carothers discovered the first purely synthetic fibre (nylon) in 1935. One of the very first products produced from nylon were stockings, which went on sale in 1939 as a novelty. The end of World War II ushered in a polymer industry that has never looked back since.

2.1.2 Acrylics, methacrylics and vinylics

The industrial revolution of polymeric materials allowed these materials to be used in a wide range of applications due to the unique physical, chemical and mechanical properties that they possess. Some of these applications include coatings, adhesives, furniture, clothing, packaging and cosmetics. Various homo- and copolymers of acrylics, methacrylics and vinylics are used in all of these applications. The difference between acrylics, methacrylics and vinylics, as used in the context of this dissertation, is as illustrated in Figure 2.1.

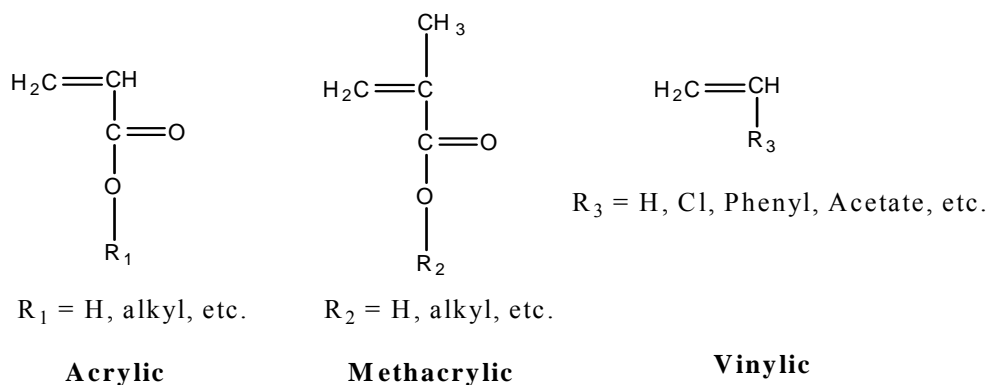


Figure 2.1 Illustration of the chemical difference between acrylics, methacrylics and vinylics.

The basis for modern acrylic polymers was the work of the German scientist Otto Rohm in 1901. Rohm produced solid transparent polymers of acrylic acid in laboratory experiments and observed some of their characteristics. A handy discovery was made when it was observed that colourless, liquid acrylic monomers, such as methyl and ethyl acrylate, could be polymerized into transparent solids. Rohm & Haas produced poly(methyl acrylate), marketed as Acryloid and Plexigum moulding powder by 1927. By 1931 they introduced Plexiglas, poly(methyl methacrylate) sheeting. From around 1929, ICI Ltd. (UK) started conducting major research into the properties of acrylic plastics. From about 1936, Klein and Pearce, Farben, Du Pont and others started investigating the potential use of aqueous dispersions of acrylic polymers in for example surface coatings. The first water-borne acrylic was developed and launched in 1955. Today water-based paints utilizing acrylic dispersion binders already have good application properties and, in comparison to traditional solvent-borne paints, low volatile organic compound (VOC) content and low odour. In 1990 Lee suggested an attractive alternative strategy for zero-VOC future paint binders¹; the idea was to create structured or multiphase acrylic particles by a stepwise, semi-batch emulsion polymerization process. A two-phase system of butyl acrylate as the soft phase and methyl methacrylate as the hard phase was successfully used to formulate solvent-free paints with good physical properties, such as blocking resistance, gloss, surface hardness and elasticity.

The research carried out by ICI Ltd. (UK) into the properties of acrylic polymers, in 1932, resulted in a commercial process for poly(methyl methacrylate) for cast sheet. It went into production in 1934, marketed as Perspex. For over 30 years poly(methyl methacrylate) has been used in orthopaedic surgery to fix prosthetic components². McCaskie and coworkers reported on the use of polymethyl methacrylate as a bone graft template and as a femoral window plug in total hip replacement².

Polystyrene, poly(vinyl acetate) (PVA) and poly(vinyl chloride) (PVC) are some of the most common and widely used vinyl polymers. In 1933 Gibson and Fawcett discovered the most popular polymer in use today, namely low-density polyethylene. Today's most widely used plastic evolved from the need for a superior insulating material that could be used for such applications as radar cabling during World War II. Today it is used in many applications, such as food packaging, films, grocery bags, etc.

Styrene as a monomer was first obtained by distilling the gum resin of a tree, liquid amber orientalis. M. Berthelot first prepared a synthetic styrene in 1869. (Interestingly, it was Berthelot who coined the term 'synthesis'). By 1900, Kronstein had developed polymers of styrene. I. G. Farben Industries, whose main interest was rubber synthesis, commenced experiments on styrene after 1924, with full-scale production commencing in 1929. I. G. Farben's work on Buna-S rubber, for which styrene was the comonomer, with butadiene, led to further research on the thermoplastic properties of the polymer. Staudinger's investigation of styrene polymers and copolymers in the 1920s and 1930s was the main vehicle for testing his revolutionary theories and experiments^{3,4}. Staudinger was the first to use the term 'macromolecules' in his May 1922 paper on rubber. Staudinger's work helped to explain the chemical nature of plastic materials and laid the foundation for future commercial exploitation of polymers. It took many years of work for him to convince his fellow researchers of the correctness of his theories. His outstanding work was rewarded with the Nobel Prize in 1953. Polystyrene was a commodity resin by 1949. Later, styrene copolymers, styrene acrylonitrile (SAN) and acrylonitrile butadiene styrene (ABS), contributed to the development of extremely tough engineering plastics.

Klatte discovered vinyl acetate in 1912, and patented its preparation from acetylene gas. Vinyl acetate readily polymerized to give dense solid materials, but had greater potential as a copolymer due to its ability to combine with other monomers, as described by Klatte in 1917. Production of vinyl acetate polymers on a commercial scale commenced after 1937; it was mainly adhesives, laminate glues and paints that were produced. Experimental production in the U.S.A. began in the same year at Monsanto, where the main interest was the use of vinyl acetate polymers for safety glass in the lucrative automobile industry.

Following Regnault's initial discovery of vinyl chloride in 1838, little work was done on the chemical analysis of the monomer until 1872, when Baumann succeeded in obtaining polymerized substances. Between 1912 and 1916 Ostromislensky did outstanding analytical work on PVC, demonstrating the potential of PVC and detailing polymerization techniques. Between 1927 and 1933 the B.F. Goodrich Company (also remembered for putting the 'bubble' into bubblegum) first developed and commercialized plasticized PVC. The first Goodrich PVC moulding compound was called Koroseal. PVC appeared in numerous forms, from toothbrushes to book bindings. It was first injection moulded around 1937. PVC products were widely available after 1938. Unplasticized PVC (UPVC) progressively became a major commodity resin after 1958, following its successful introduction in Europe as pipe for town water services, replacing cast iron systems.

2.1.3 Speciality polymers

Polymer supports based on glycidyl methacrylate (GMA), mainly used as excellent thermosetting adhesives, have gained popularity because of their superior performance. Recently, poly(4-propanoylphenyl methacrylate-co-GMA) was investigated by Godwin and coworkers as an adhesive for leather⁵. The authors reported on the peel strength of the copolymer obtained. The copolymer showed good adhesive characteristics. Poly(4-benzyloxycarbonylphenyl methacrylate-co-GMA) was also studied for leather adhesive applications⁶. It was shown that the peel strength of the adhesive increases with

increasing GMA composition. Glycidyl methacrylate-based coatings are also used in the automobile industry as a clear topcoat. Clear topcoats are used to protect an automobile's finish from environmental factors such as dirt, acid rain and ultraviolet rays. Glycidyl methacrylate-based coatings offer formulators and end users the highest levels of clarity, durability, weatherability, smoothness and chemical resistance.

Copolymers such as methyl methacrylate (MMA)/vinyl pyrrolidone (VP) and hydroxyethyl methacrylate (HEMA)/vinyl pyrrolidone largely find their application in the field of contact lenses. The first soft contact lens made from polyHEMA was patented in 1961. The first recorded work on HEMA/VP polymers appeared in the US in 1966. Lenses made from HEMA/VP polymers went into production in 1968, marketed as Permalens. The first recorded work on MMA/VP polymers in the US and UK appeared between 1969 and 1972. The first commercial MMA/VP lenses (known as Sauflon) appeared around 1970.

Since 1965, different special and new polymers with increasingly complex chemical structures were introduced. The properties of these polymers include very high thermal and chemical stability and high strength and stiffness. The following are examples of these polymeric materials and their trade names: poly (phenylene sulphide) (Ryton), polyaryletherketone (PEEK), polyimides (Kapton), aromatic polyesters (Ekonol and Vectra), aromatic polyamides (Nomex and Kevlar) and fluorine-containing polymers (Teflon and Viton).

2.1.4 Recent additions to the family of acrylic and methacrylic monomers

A number of new acrylic and methacrylic monomers have been synthesized in recent years. These novel monomers are listed in Table 2.1.

Table 2.1

Synthesis of novel acrylic and methacrylic monomers

Compounds synthesized	References
Substituted phenyl acrylates	7
5-indanyl acrylate	8
4-acetamidophenyl acrylate	9
4-benzyloxycarbonylphenyl methacrylate	6
4-propanoylphenyl methacrylate	10
4-benzoylphenyl methacrylate	11
2-methylbenzyl methacrylate	12
4-methylbenzyl methacrylate	12
3, 5-dimethylphenyl acrylate	13
3, 5-dimethylphenyl methacrylate	14
2-(N-phthalimido)-2-methylpropyl acrylate	15
4-(4'-chlorocinnamoyl) phenyl methacrylate	16
2-(3-methyl-3-phenylcyclobutyl)-2-hydroxyethyl methacrylate (PCHEMA)	17
2-(3-methyl-3-mesitylcyclobutyl)-2-hydroxyethyl methacrylate (MCHEMA)	17
3-cyclohexyloxy-2-hydroxypropyl acrylate	18

2.1.5 Copolymerization of alkyl acrylate monomers with styrene

Most of the work published on the free radical copolymerization of styrene with alkyl (meth)acrylates are concerned with the styrene-methyl methacrylate system¹⁹⁻²⁴. The free radical copolymerization of styrene with n-butyl methacrylate²⁵ and n-butyl acrylate^{23,26} has also been reported on. Very few publications describe the copolymerization of styrene with long side chain alkyl (meth)acrylates as comonomers. Dodecyl methacrylate (DDMA) (lauryl methacrylate) and octadecyl methacrylate (stearyl methacrylate) are the most commonly used long side chain alkyl methacrylates as comonomers in free radical copolymerizations with styrene^{25,27-28}. A few researchers reported on the reactivity ratios for the dodecyl methacrylate-styrene system via free radical copolymerization²⁷⁻²⁸. In addition, Vidović and coworkers reported on the copolymerization kinetics and other characteristic properties, such as the molecular weight, viscosities at different temperatures and the thermal behaviour of the dodecyl methacrylate-styrene and octadecyl methacrylate-styrene copolymer systems²⁸.

2.2 Olefin Oligomerization

2.2.1 General

The basic building blocks of the petrochemical industry are ethylene, propylene and butene. These olefins are very useful for the following reasons: they are relatively inexpensive, readily available, reactive and easily convertible to a range of products. The last couple of decades have witnessed an increasing importance of higher linear α -olefins (C_6 - C_{20}). The aforementioned α -olefins have become a major source of biodegradable detergents, lubricants, new kinds of polymers and many other industrially useful chemicals²⁹.

A number of processes are available for the production of α -olefins. The most common processes used to obtain α -olefins are thermal and catalytic cracking of paraffins (alkanes) and oligomerization of ethylene. Others include dehydrogenation of alkanes, dimerization and metathesis of olefins, dehydration of alcohols and electrolysis of C_3 - C_{30} straight-chain carboxylic acids²⁹. The thermal and catalytic cracking of alkanes is mainly used for the production of C_2 - C_5 α -olefins, whereas the oligomerization of ethylene has been industrially used to manufacture large amounts of linear α -olefins in the C_4 - C_{30} range, due to the abundance of ethylene and the high product quality.

Lower and higher α -olefins can be subjected to a variety of reactions, such as hydrocarboxylation, hydroformylation, epoxidation and alkylation, which can lead to compounds with possible applications as adhesives, blend compatibilizers, fragrances, lubricants, additives for fuels or in the paper and leather industry³⁰⁻³². In addition, α -olefins oligomers or derivatives thereof may be used as (macro) monomeric building blocks for novel graft copolymers containing oligo-olefin side chains³³⁻³⁵.

In the following sections the following will be discussed: the general mechanism of α -olefin oligomerization (2.2.2), the oligomerization of various higher α -olefins (C_5 and

upwards) (2.2.3) and, more specifically, a review of the oligomerization of 1-decene as reported in literature (2.2.4). Mention will also be made of the very few cases where α -olefins have been successfully selectively oligomerized (2.2.5).

2.2.2 Oligomerization of higher α -olefins

The higher α -olefins (longer chains) undergo a more difficult oligomerization reaction than ethylene or propylene for example³⁶⁻³⁷. Higher α -olefins can also form more isomers than ethylene and propylene. Thus, the selectivity of the oligomerization reaction for higher α -olefins is lower than in the case of ethylene and propylene for instance.

Several types of catalytic systems have been used in the oligomerization of higher α -olefins. The most common catalytic systems used include the titanium-, zirconium- and nickel-based systems, the Lewis and Bronsted acids (AlCl_3 and BF_3) and heterogeneous inorganic systems²⁹. The use of these various types of catalytic systems is highlighted here; a few selected literature examples of where they have been successfully used to oligomerize higher α -olefins are reported.

Isa and coworkers oligomerized 1-octene with the $\text{TiCl}_4/\text{AlCl}_3/\text{LiH}$ system³⁸. Octene trimers were the main product of the octene oligomerization in the presence of the $\text{TiCl}_4/\text{propylene oxide}/\text{Et}_2\text{Al}_2\text{Cl}_3$ system³⁹. Schoenthal and Slaugh oligomerized 1-hexene with the zirconium-based system $\text{Cp}_2\text{ZrCl}_2/(\text{CH}_3)_3\text{Al}/\text{H}_2\text{O}$ ⁴⁰. Wahner and co-workers and Mange reported on the oligomerization of 1-pentene using MAO-activated zirconium systems⁴¹⁻⁴². Various nickel-based systems have been shown to be active in the oligomerization of 1-hexene⁴³. $\text{AlCl}_3/\text{tertiary alcohols}$ and $\text{AlCl}_3/\text{quaternary alcohols}$ have been reported as 1-dodecene oligomerization catalysts⁴⁴. $\text{AlCl}_3/\text{poly}(\text{alcohol esters})$ were successfully used in the oligomerizations of higher α -olefins⁴⁵. A change from AlCl_3 to BF_3 gives active oligomerization catalysts for $\text{C}_6\text{-C}_{12}$ α -olefins⁴⁶. Shubkin and coworkers demonstrated the use of $\text{BF}_3/\text{alkanoic acids}$ for the oligomerization of 1-hexene and 1-tetradecene to highly branched di-, tri-, tetra- and pentamers⁴⁷. A number of heterogeneous inorganic catalytic systems have been used for the oligomerization of

higher α -olefins. Anderson and coworkers used the HZSM-5 zeolite system for the oligomerization of 1-hexene⁴⁸. Johnson successfully used the TaCl₅/SiO₂ system for the oligomerization of 1-hexene⁴⁹. Tabak showed that 1-pentene and 1-octene could be successfully oligomerized with the HZSM-12 zeolite system⁵⁰. Bianchi and coworkers oligomerized 1-pentene in the presence of cluster ruthenium complexes⁵¹. Da Rosa and coworkers described the oligomerization of 1-hexene and 1-octene catalyzed by nickel(II)/alkylaluminum systems⁵². Janiak and coworkers used a series of alkyl-substituted cyclopentadienyl- and phospholyl-zirconium/MAO catalysts for the oligomerization of 1-hexene³². Stenzel and coworkers demonstrated the successful oligomerization of 1-pentene, 1-hexene and 1-octene in the ionic liquid 1-butyl-3-methylimidazolium tetrachloroaluminate, in the presence of ethylaluminiumdichloride⁵³.

2.2.3 Selective oligomerization of α -olefins

The Dimersol process is a well-known industrial process for the selective dimerization of ethylene, propylene and butene⁵⁴⁻⁵⁵. The branched dimers of propylene and 1-butene find application as plasticizer precursors or fuel additives. The selective trimerization of ethylene to 1-hexene with chromium-based catalyst systems has been reported⁵⁶. Christoffers and Bergman showed that a variety of α -olefins, ranging from ethylene to 1-heptene, could be dimerized successfully, without the presence of significant portions of the higher oligomers, using a very low ratio of Cp₂ZrCl₂ to MAO (approximately 1:1)⁵⁷. Small and Schmidt reported the catalytic dimerization of 1-butene by a variety of metal catalysts⁵⁸. The reaction products mainly consisted of linear and/or branched dimers. Wasserscheid and coworkers recently reported on the selective trimerization of 1-decene and 1-dodecene using a chromium catalyst of the general type (R₃TAC)CrCl₃ (R = alkyl, aryl) with MAO as cocatalyst⁵⁹. Ranwell and Tshamano highly selectively trimerized 1-decene in the ionic liquid [1-butyl-3-methylimidazolium][Et_{3n}Al_nCl]⁶⁰. They combined chromium(III) 2-ethylhexanoate, 2,5-dimethylpyrrole and triethylaluminium to form an active catalyst.

2.2.4 Oligomerization of 1-decene

A variety of conditions (different catalytic systems, temperatures, pressures) have been employed for the oligomerization of 1-decene. Table 2.2 gives a summary of the literature examples where 1-decene was successfully oligomerized.

Table 2.2

Oligomerization of 1-decene

Catalyst system	Reaction conditions	References
AlCl ₃ /Alkyl aromatic hydrocarbons containing O and N ligands	100 °C, 5 hours	37
BF ₃ /H ₂ O, alkanolic acids	30 °C, 24 hours	39
AlCl ₃ /alkylaluminum halide	70-80 °C	49
BF ₃ /SiO ₂ /H ₂ O	29-36 °C, 12 hours	50
HZSM-12 zeolite	200-400 psig, 120-210 °C	42
BF ₃ /C ₂ H ₅ OH or C ₄ H ₉ OH	10 psig, 20-25 °C, 4-6 hours	51
BF ₃ /O ₂ /SiO ₂	10-15 °C	52
BF ₃ /n-BuOH	50 psig, 50 °C	53
BF ₃ /n-BuOH, C ₂ H ₅ COOH	23-49 °C, 1-2.5 hours	54
ZrCl ₄ (HfCl ₃)/AlCl ₃	99 °C, 1 hour	55
BF ₃ /n-BuOH, CH ₃ COC ₂ H ₅ or HO(CH ₂)OH	20 psig, 50 °C	38
R ₃ Al ₂ X ₃ or R _n AlX _{3-n} X ₂ , R = hydrocarbyl; X = Br, I; n = 1, 3	42 °C, 15 minutes	56
TiCl ₄ /(C ₂ H ₅) _{3-n} AlCl _n /3RCl, n = 0, 1, 1.5	42 °C, 15 minutes	57
BF ₃ /alcohols C ₅₋₈	-10 °C and 40 °C	58
AlCl ₃	103 °C, 1 hour	59
[C ₅ H ₅ B-R] ₂ ZrCl ₂ /MAO (R = alkyl, alkoxy)	25 °C, 2 hours	61

2.2.5 Principle of α -olefin oligomerization

The oligomerization reaction consists of three steps, namely activation of the catalyst, propagation (chain growth) and chain-termination (β -hydrogen elimination: transfer to

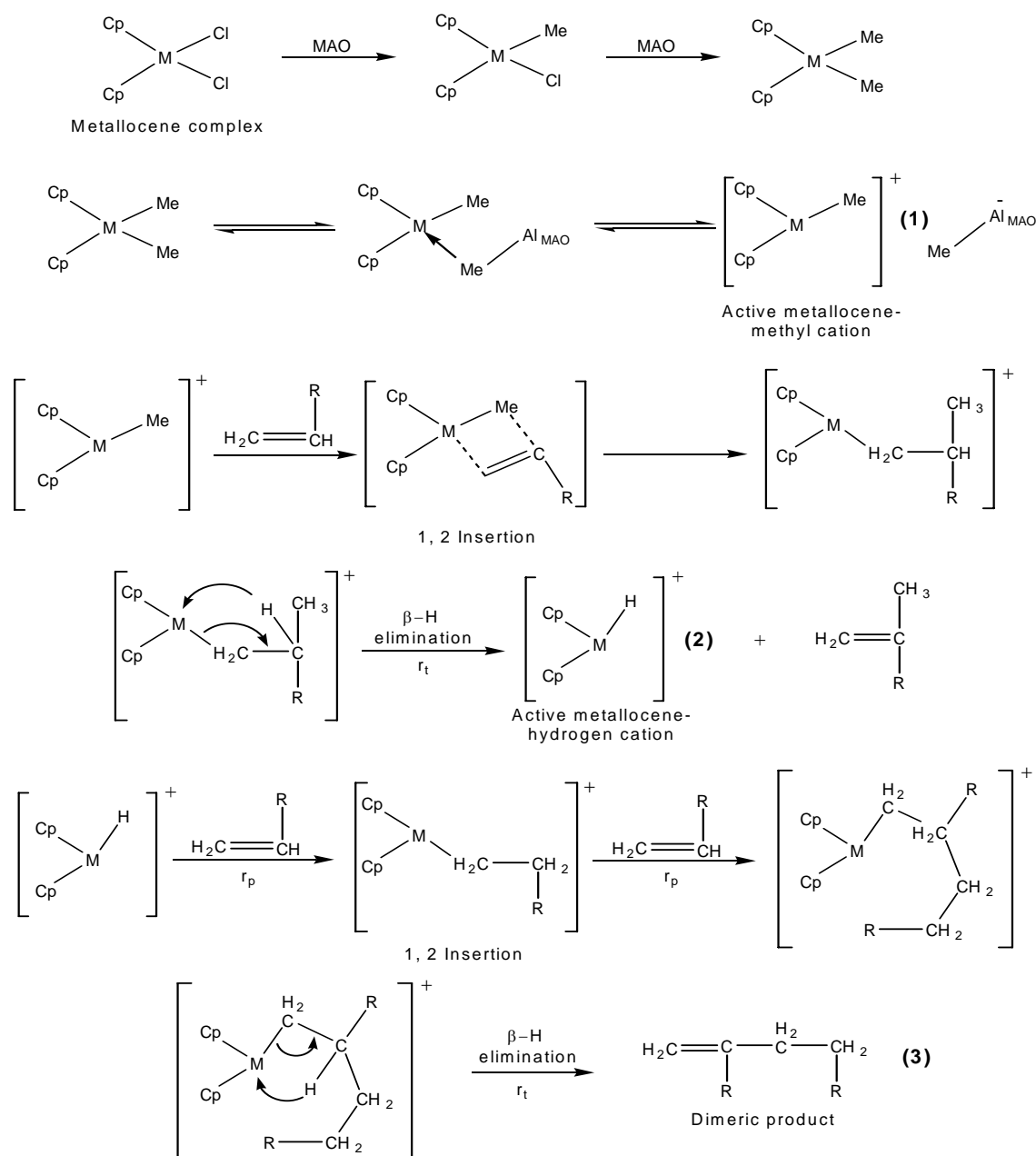
metal or monomer). The relative rates of propagation (r_p) and chain-termination (r_t) determine the molecular weight of the obtained product. If $r_p \gg r_t$, many propagation steps occur before chain-termination takes place, resulting in the formation of a high molecular weight polymer. When $r_t \gg r_p$, dimers are obtained. In the case where $r_p \approx r_t$, oligomers are produced.

This study focuses on the use of metallocene catalyst systems for the oligomerization of α -olefins. A metallocene catalyst system consists of a metallocene complex (a group 4 transition metal compound) and a cocatalyst, mainly methylaluminoxane (MAO). Other cocatalysts in use include borates or boranes.

A number of parameters can be changed in a metallocene catalyst system. These include the ligand, the substituents on the ligand, the bridging between ligands, the metal and the cocatalyst.

The cocatalyst (MAO) is the key to the activity of the metallocene. MAO is typically used in large excess to ensure the activation of the catalyst and the destruction of catalyst poisons, such as water or oxygen for example. MAO acts as both an alkylating agent and a Lewis acid, to form the catalytically active metallocene-methyl cation. The first function of the MAO is the monomethylation of the halogenated metallocene complex, which takes place within seconds (Scheme 2.1). An excess of MAO leads to dialkylated species. The methylation has been studied by UV/VIS and NMR spectroscopy⁶²⁻⁶⁸. These studies have suggested the formation of a monomethylated species for a metallocene/MAO complex at low [Al]/[Zr] ratios of 10-20. After the methylation, the MAO complex seizes a methyl anion from the metallocene, forming the catalytically active metallocene-methyl cation (**1**, Scheme 2.1). The formation of the metallocene-methyl cation has been detected by X-ray photoelectron spectroscopy as well as by ¹³C and ⁹¹Zr NMR spectroscopic techniques⁶⁹⁻⁷¹. The presence of cationic metallocene species has also been verified by the use of weakly coordinating anions, such as (C₆H₅)₄B⁻ and (C₆F₅)₄B⁻, as counterions for alkylated metallocene cations⁷².

The active metallocene-methyl cation reacts with one or more α -olefin monomer units (by way of 1,2-insertion) before undergoing β -hydrogen elimination to form the active metallocene-hydrogen cation (**2**, Scheme 2.1). The addition of two or three monomer units to the active metallocene-hydrogen cation, for example, results in a dimeric (**3**, Scheme 2.1) or trimeric α -olefin product after β -hydrogen elimination.



Scheme 2.1 Mechanism of α -olefin oligomerization⁶²⁻⁷¹.

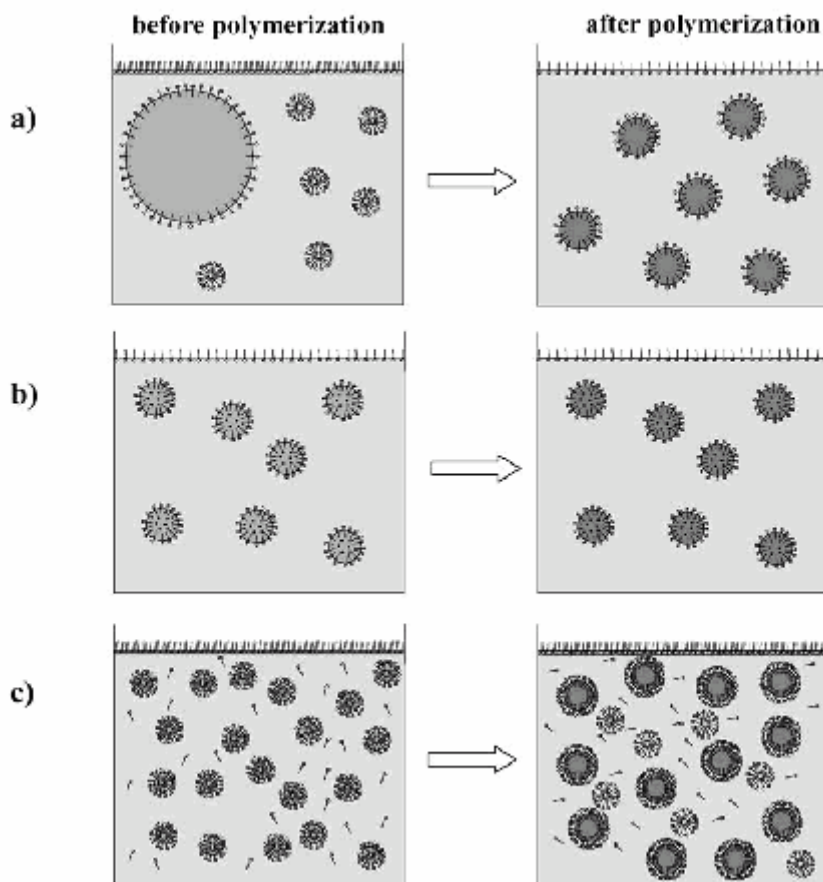
2.3 *Heterophase Systems*

2.3.1 Introduction

A mixture of at least three components (oil, water and surfactant; additional components: costabilizer/hydrophobe and initiator) can form an opaque (milky) or translucent polymer-dispersion (heterophase system) on polymerization. There are various ways of generating a polymer-dispersion. These include suspension polymerization, the generation of secondary dispersions by precipitation or polymerization of emulsions, inverse emulsions, mini-emulsions and micro-emulsions. The most common water-based heterophase systems for the generation of nanoscale polymer latexes are emulsion, mini-emulsion and micro-emulsion systems. The differences between these systems are illustrated in Scheme 2.2⁷³.

The following differences between the emulsion, mini-emulsion and micro-emulsion systems can be highlighted:

- *Conventional emulsions* produce latex particles in the size range of 50-300 nm. The size of the latex particles in conventional emulsion polymerization does not correspond to the size of the initial droplets.
- *Mini-emulsions* are colloidally stabilized by a surfactant and diffusionally stabilized by a costabilizer (hydrophobe). Particle sizes of between 30 and 100 nm have been reported. The latex particles in mini-emulsion polymerization are copies of the original droplets.
- *Micro-emulsions* are stabilized by high amounts of surfactant (15-50 wt % of monomer). Very small particles of between 10 and 30nm are characteristic of the final latex product.



Scheme 2.2 Differences between (a) emulsion, (b) mini-emulsion, and (c) micro-emulsion systems⁷³.

This study focuses on the technique of mini-emulsion polymerization for the synthesis of nanoscale polymer latexes for two major reasons. Firstly, conventional emulsions exhibit insufficient colloidal stability. Secondly, micro-emulsions require excessive amounts of surfactant.

The following section seeks to shed some light on the inner-workings of the mini-emulsion polymerization system.

2.3.2 Mini-emulsion polymerization

2.3.2.1 General

The generation of small (nanoscale), homogeneous and stable monomer droplets that undergo polymer reactions to form polymer latex particles identical to the initial monomer droplets are realized by the technique of mini-emulsion polymerization. Each monomer droplet behaves like a nanoreactor and becomes the predominant locus of nucleation. These nanoreactors are produced by subjecting a mixture of oil (monomer), water, emulsifier (surfactant), costabilizer (cosurfactant or hydrophobe) and initiator to a high shear force, for example by means of ultrasonication. Thus, a mini-emulsion can be defined as a dispersion of critically stabilized oil droplets (nanoreactors).

Antonietti and Landfester proposed the following checklist for the presence of a mini-emulsion⁷³:

- ❑ Steady-state dispersed mini-emulsions are stable against diffusional degradation, but critically stabilized with respect to colloidal stability.
- ❑ The interfacial energy between the oil and water phases is significantly larger than zero. The surface coverage of the droplets by surfactant molecules is incomplete.
- ❑ The formation of a mini-emulsion requires high mechanical agitation to reach a steady state, given by a rate-equilibrium of droplet fission and fusion.
- ❑ The stability of mini-emulsion droplets against diffusional degradation results from an osmotic pressure in the droplets, created by the addition of a component that has an extremely low solubility in the continuous phase.
- ❑ Polymerization of mini-emulsions occurs predominantly by droplet nucleation.
- ❑ The amount of surfactant required to form a polymerizable mini-emulsion is comparably small (between 0.25 and 25 weight % relative to the monomer), which is well below the surfactant amounts required for micro-emulsions.

The stability (kinetic or thermodynamic) of any mini-emulsion system depends on two major factors. Any mini-emulsion needs to be stabilized against coalescence, which is

brought about by the collision of the droplets or particles due to the attractive Van der Waals forces, and against Ostwald ripening (diffusional degradation), which entails the diffusion of monomer from smaller droplets to larger ones at the expense of the smaller droplets due to the Laplace pressure of the droplets (droplet pressure).

The use of an appropriate type and amount of surfactant (surface-active agent) provides colloidal stability to the droplets/particles by providing adequate coverage of the droplet/particle surface. Three types of surfactants have been successfully utilized: anionic, cationic and non-ionic surfactants. The ionic surfactants prevent extensive collision of droplets and particles by means of repulsive forces (like charges repel one another). Examples of ionic surfactants include sodium dodecyl sulphate (SDS) [Also known as sodium lauryl sulphate (SLS)] and cetyltrimethylammonium bromide (CTAB). The non-ionic surfactants provide colloidal stability due to steric hindrance. An example of a commonly used non-ionic surfactant is the polyethoxylated nonylphenol, with an average of 40 ethylene oxide units per molecule (NP40).

One of the major factors that distinguish mini-emulsions from conventional emulsions is the incorporation of a cosurfactant or hydrophobe. It must be noted that the term cosurfactant is only applicable in the case where the costabilizer has a polar group as part of its molecular structure. In other words, it has some surface activity associated with it in terms of further lowering the interfacial energy between the continuous and dispersed phases, but cannot form micellar aggregates by itself. An example of such a cosurfactant is cetyl alcohol. From this point onwards the author will refer to the costabilizer as a hydrophobe (or reactive hydrophobe, in the case where the costabilizer has the ability to be chemically incorporated into the final polymer product). The function of the hydrophobe is to significantly slow down the Ostwald ripening process by creating an osmotic pressure in the droplets that counteracts the droplet pressure. The droplet pressure (p_{Laplace}) is a function of the droplet size (Equation 2.1)⁷³.

$$p_{\text{Laplace}} = 2\gamma_{\text{LL}}/R \quad (2.1)$$

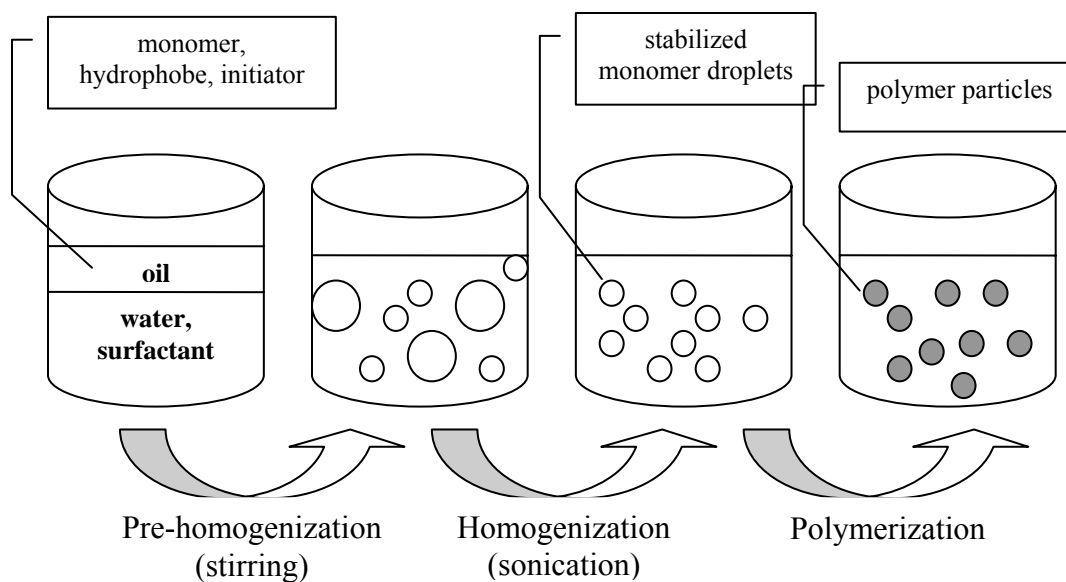
where R is the droplet radius and γ_{LL} is the surface tension of the droplets.

Thus, smaller droplets have a larger droplet pressure (or chemical potential) than larger droplets, making them susceptible to diffusional degradation due to the chemical potential gradient between the smaller and larger droplets. The incorporation of a low molecular weight, hydrophobic (water-insoluble) and monomer soluble hydrophobe serves to equalize the chemical potential of the droplets (in the general case of multi-dispersed droplet sizes) by equalizing (in the ideal case) the net pressure difference (the difference between the droplet and the osmotic pressure) between the droplets. Thus, diffusion of the monomer out of the droplets is retarded.

2.3.2.2 Principle of mini-emulsion polymerization

As previously mentioned (Section 2.3.2.1), mini-emulsions (nanoreactors) are prepared by subjecting a mixture of oil, water, surfactant and cosurfactant/hydrophobe to a high shear force. This results in the formation of two discrete phases: a continuous (water) phase and a dispersed (oil) phase. The mini-emulsion polymerization process consists of three major stages: (1) pre-homogenization, (2) homogenization, and (3) polymerization (Scheme 2.3).

Pre-homogenization involves of the mixing of the various suspension components via mechanical agitation (stirring), resulting in various droplet sizes (heterogeneous distribution). Subjecting this semi-stable suspension to ultrasonic homogenization results in the formation of smaller droplets, with a uniform droplet size distribution. Thereafter, a fast and minor equilibration process occurs and the effective net pressure in each droplet is equalized. The polymerization of these stable droplets results in the formation of polymer latex particles that are one-to-one copies of the original droplets.



Scheme 2.3 Schematic of the principle of mini-emulsion polymerization.

2.3.2.3 Role of the hydrophobe

As previously mentioned (section 2.3.2.1), conventional emulsions display extensive diffusional degradation of monomer from smaller droplets to larger ones due to the difference in the chemical potential of these droplets (Ostwald ripening). Monomer tends to diffuse from the small droplets, through the aqueous phase, to the large droplets, in order to relax the chemical potential gradient between two droplets with different sizes at the expense of the smaller droplets.

Higuchi and Misra originally proposed in 1962 that the incorporation of a largely hydrophobic component to the emulsion recipe could serve to impart diffusional stability to the monomer droplets⁷⁴. Webster and Cates theoretically described this stabilization effect⁷⁵. They considered an emulsion whose droplets contained a species insoluble in the continuous phase and studied its stability via the Lifshitz-Slezov theory. They concluded that the emulsion evolution is driven by the competition between the osmotic pressure of

the trapped species (hydrophobic component in the monomer droplets) and the Laplace pressure of the droplets.

As stated earlier (Section 2.3.2.1) I will refer to this hydrophobic, trapped species as the hydrophobe or reactive hydrophobe. Three characteristics qualify any compound as a good hydrophobe. They are: (1) extreme insolubility in the continuous phase, (2) good solubility in the dispersed phase, and (3) relatively low molecular weight (in the case of thermodynamic stable mini-emulsions).

Apart from the conventional hydrophobes like cetyl alcohol (CA) and hexadecane (HD), various other hydrophobes have been successfully used over the years to impart diffusional stability to polymerizable mini-emulsions. The use of other types of hydrophobes is mainly driven by the need to eliminate the low molecular weight cetyl alcohol and hexadecane, which serve as organic contaminants, from the final latex product. Polymeric hydrophobes like polystyrene and poly(methyl methacrylate) have been used to prepare kinetically stable mini-emulsions⁷⁶⁻⁷⁸. These polymers are highly water-insoluble and soluble in their own monomers. The drawback to using polymers as hydrophobes is their high molecular weight. The need for a good hydrophobe to be of low molecular weight is based on swelling experiments and theoretical swelling calculations⁷⁶. Thus, polymers are relatively poor hydrophobes that form mini-emulsions that are only stable over a very short period of time (hours or days).

Mini-emulsions with a high stability (months) have been successfully prepared with dodecyl mercaptan (DDM) acting as both hydrophobe and chain transfer agent⁷⁹⁻⁸⁰. The use of a blue dye (Blue 70) as hydrophobe by Chern and Chen resulted in relatively stable styrene mini-emulsions⁸¹. However, the rate of Ostwald ripening for the styrene mini-emulsions with Blue 70 as hydrophobe is faster than the mini-emulsions where the reactive hydrophobes lauryl methacrylate (LMA) and stearyl methacrylate (SMA) were used⁸². The effectiveness of LMA and SMA over Blue 70 as hydrophobe could be attributed to the fact that the reactive hydrophobes are more hydrophobic than Blue 70 and of a lower molecular weight than Blue 70. Alduncin and coworkers reported on the

use of a very low water soluble initiator as hydrophobe⁸². They compared the ability of lauroyl peroxide to stabilize the monomer droplets against diffusional degradation to that of benzoyl peroxide and azobis(isobutyronitrile). Only lauroyl peroxide was hydrophobic enough to stabilize the droplets against Ostwald ripening. Reimers and Schork also reported on the successful use of lauroyl peroxide as both initiator and hydrophobe in the mini-emulsion polymerization of methyl methacrylate⁸³.

Once again it must be highlighted that the effectiveness of any hydrophobe strongly depends on its water-solubility. Chern and Chen listed the following estimated values for the water-solubility of CA, HD, LMA and SMA, in decreasing order⁸¹.

CA (5.77×10^{-8} mL/mL) > DMA (1.38×10^{-8} mL/mL) > SMA (3.23×10^{-9} mL/mL) > HD (1.14×10^{-9} mL/mL)

A summary of the numerous types of alternative hydrophobes, hydrophobes other than hexadecane and cetyl alcohol, reported in literature is presented in Table 2.3⁷³.

Table 2.3

Summary of literature examples of alternative hydrophobes

Monomer	Hydrophobe	Surfactant	Initiator	Homogenization	References
Styrene	LPO	SDS	AIBN, BPO, LPO	Sonication	82, 84
Styrene	Blue 70	SDS	NaPS	Microfluidizer	85
Styrene	DMA	NP40	NaPS, AIBN	Microfluidizer	86
Styrene	SMA	NP40/SDS	NaPS	Microfluidizer	87
Styrene	DMA, SMA	SDS/NP40/NE40	NaHCO ₃	Microfluidizer	81
Styrene	PSt	SDS	KPS	Microfluidizer	88
MMA	DDM	SDS	KPS	Ultrasonication	79
MMA	PMMA	SDS	KPS	Sonication	78
MMA	LPO	SDS	LPO	Sonic dismembrator	83
MMA	PMMA	SDS	KPS	Sonication	89

MMA: methyl methacrylate; **LPO**: lauroyl peroxide; **DMA**: dodecyl methacrylate; **SMA**: stearyl methacrylate; **PSt**: polystyrene; **DDM**: dodecyl mercaptan; **PMMA**: poly(methyl methacrylate); **SDS**: sodium dodecyl sulphate; **NP40**: nonyl polyethoxylate with 40 ethylene oxides per molecule; **NE40**: polymerizable nonyl polyethoxylate with 40 ethylene oxides per molecule; **AIBN**: azobisisobutyronitrile; **NaPS**: sodium persulphate; **KPS**: potassium persulphate; **NaHCO₃**: sodium bicarbonate

2.3.2.4 *Kinetics of mini-emulsion polymerization*

a. Nucleation

Three major modes of nucleation are associated with heterophase polymerizations. These are micellar, homogeneous and droplet nucleation. Micellar nucleation can only occur in systems where the free surfactant concentration is above its critical micelle concentration (CMC). The micellar nucleation mechanism is typical for emulsion and micro-emulsion polymerizations started from the continuous phase. The use of a water-soluble initiator results in the formation of an oligomeric radical as a few monomer units are added. The water-insolubility of the oligomeric radical causes it to enter a monomer-swollen micelle, which results in chain-growth to form a polymer chain. Furthermore, monomer droplets and other monomer-swollen micelles act as reservoirs for the growing particles by freeing monomer to diffuse to the nucleated micelles. Thus, the polymerization rate is dependent on the water-solubility of a particular monomer in such systems.

Micellar nucleation is highly unlikely in mini-emulsion polymerization systems, due to the fact that very little (if any) free surfactant is available for the formation of micellar aggregates. In other words, the free surfactant concentration in the continuous phase of a mini-emulsion polymerization system will always be below its CMC.

Homogeneous (continuous phase) nucleation predominates in the surfactant-free emulsion polymerization systems. Various researchers have documented the occurrence of homogeneous nucleation in mini-emulsion polymerizations^{85-86,90-91}. The stabilization system seemed to be one of the major factors that determined the amount of homogeneous nucleation in a particular mini-emulsion system. The use of an oil-soluble initiator in the mini-emulsion system further promotes droplet nucleation over homogeneous nucleation.

Droplet nucleation predominates for an ideal mini-emulsion polymerization system. As explained above, micellar nucleation is non-existent and homogeneous nucleation can be limited to a large extent. Reimers and Schork reported a droplet nucleation of 95% in the

mini-emulsion polymerization of styrene using hexadecane as hydrophobe^{78,89}. It can generally be assumed that droplet nucleation is the predominant nucleation mechanism when there is no significant difference between the size of the droplets and the number of droplets compared to that of the particles. Fontenot and Schork made use of conductance data to support droplet nucleation as the main mechanism of particle formation in the mini-emulsion polymerization of styrene⁹².

b. Kinetics of polymer growth

Harkins defined three prominent intervals for emulsion polymerizations: nucleation (Interval I), an interval of constant reaction rate (Interval II) and a region of exponentially decreasing rate of reaction (Interval III)⁹³⁻⁹⁵. The only intervals of relevance in mini-emulsion polymerizations are intervals I and III. Furthermore, the presence of an interval with a marked gel-effect (Interval IV), due to the occurrence of auto-acceleration, is a possibility in glassy systems. Bechthold and Landfester obtained the calorimetric curve in Figure 2.2 for the mini-emulsion polymerization of styrene using hexadecane as hydrophobe⁹⁶. Figure 2.2 demonstrates the intervals applicable to the mini-emulsion polymerization system.

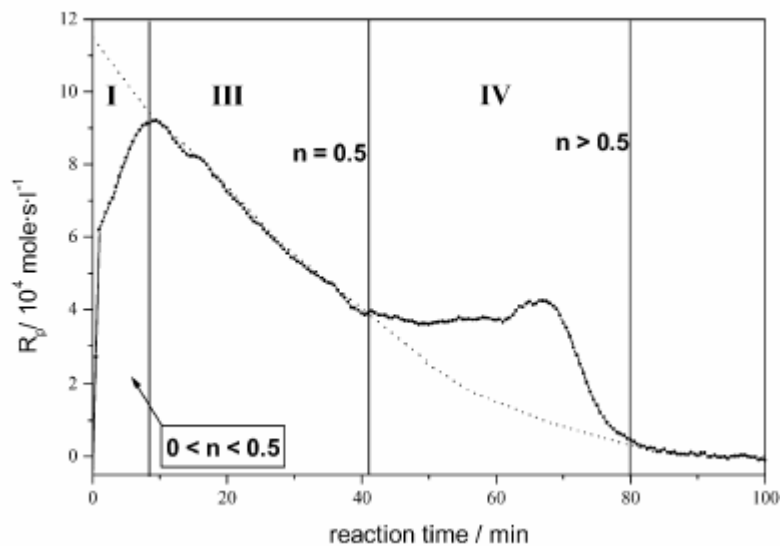


Figure 2.2 Calorimetric curve of a typical styrene mini-emulsion polymerization: surfactant: SDS, hydrophobe: hexadecane, initiator: KPS⁹⁶.

During the first interval (droplet nucleation) an equilibrium radical concentration is reached in every nucleated droplet. This interval ends at low conversions ($\leq 10\%$) so that every droplet is nucleated before unbalanced mass transfer can play a crucial role. The length of interval I depends on the type of initiator used (water-soluble or oil-soluble) and, in the case of a water-soluble initiator, the water-solubility of the monomer. Consequently, interval I is longer for water-soluble initiators due to the fact that these hydrophilic initiators have to add on a few monomer units before they are able to enter a monomer droplet. Interval I is further prolonged when a water-soluble initiator is used in conjunction with a monomer with poor water-solubility, like styrene. Alduncin and coworkers also demonstrated that the rate of nucleation is dependent on the size of the droplets⁸². They showed that the probability of droplet nucleation increased with increasing droplet size when a water-soluble initiator is employed.

The average number of active radicals per droplet slowly increases to approximately 0.5 during the initiation (nucleation) process. The primary maximum for the rate of polymerization at the end of interval I (Figure 2.2) is attributed to the formation and growth of polymer particles. The maximum rate of polymerization strongly depends on the size of the droplets, which is directly proportional to the number of droplets. The smaller the droplets are the faster is the rate of polymerization.

As is common in emulsion and suspension polymerization, an interval III corresponding to a decrease in the polymerization kinetics is also observed in mini-emulsion polymerization. The decrease in the polymerization kinetics is due to the exponential depletion of monomer from the reaction site, since only the monomer in the droplet is available for polymerization.

The secondary maximum for the rate of polymerization observed in interval IV (Figure 2.2) is ascribed to the gel effect, which is due to the viscosity increase inside the particles and the coupled kinetic hindrance of radical recombination. The presence of the gel peak depends on the size of the particles. The gel peak becomes more pronounced with an increase in particle size (Figure 2.3)⁹⁶. In addition, its onset also depends on the particle

size. It can be seen from Figure 2.3 that the onset of the gel peak for the 151 nm and 105 nm particles is at 45% and 60% conversion, respectively.

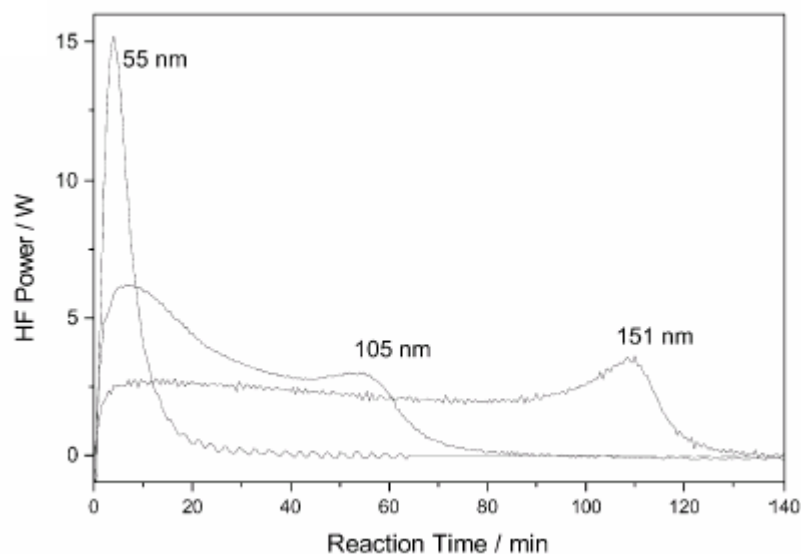


Figure 2.3 Calorimetric curves for styrene mini-emulsions with different particle sizes⁹⁶.

2.4 Polymer blends

2.4.1 Introduction

Blending of polymers for producing multiphase systems, either by the solvent-casting or the melt-mixing method, is less expensive than synthesizing block or graft copolymers. Early commercial work on polymer blending was largely focused on improving the impact strength of glassy polymers by the inclusion of elastomeric materials such as natural rubber⁹⁷. Most efforts were aimed at modifying polystyrene and have since expanded to include poly(vinyl chloride), poly(phenylene oxide), poly(methyl methacrylate), as well as various other thermoplastics and some thermosets⁹⁸.

A polymer blend can be classified as either a miscible or an immiscible blend. Both types of polymer blends are very useful. Examples of useful immiscible blends include high impact polystyrene (HIPS) and the poly(ethylene terephthalate)/poly(vinyl alcohol) blend used to make bottles for carbonated beverages.

2.4.2 Miscibility of polymer blends

The main problem associated with the blending of polymers is one of immiscibility. Very few polymers are miscible. Examples of miscible polymers include polystyrene/poly(phenylene oxide), poly(ethylene terephthalate)/poly(butylene terephthalate) and poly(methyl methacrylate)/poly(vinylidene fluoride). The majority of polymers are immiscible from a thermodynamic point of view due to the fact that the entropy contribution to the Gibbs energy of mixing is negligible⁹⁹. Therefore, mixing of two homopolymers often leads to a coarse heterogeneous phase structure with a low adhesion between phases.

Immiscible polymer blends are characterized by a two-phase morphology, a narrow interface and poor physical or chemical interactions across the phase boundaries¹⁰⁰. In such cases, the interfacial tension is high and adhesion between the two phases is low, which results in poor stress transfer across the interface. These shortcomings generally result in poor mechanical properties.

It was thus necessary to develop appropriate methods to address the compatibility-problem of polymer blends. The addition of a compatibilizer (interfacial agent) capable of physical or chemical interaction with the blend components is one such method that overcomes the compatibility-problem of polymer blends. The main function of the compatibilizer is to lower the interfacial tension between the two homopolymers and thereby promote adhesion between the homopolymers.

Moreover, the miscibility of polymer blends is affected by factors such as the processing method¹⁰¹⁻¹⁰⁵ and the processing parameters. The processing parameters of importance

are the temperature¹⁰⁶, mixing speed¹⁰⁷⁻¹⁰⁹, mixing time^{107,110-111}, type of solvent¹¹²⁻¹¹⁴ and the concentration of the dispersed phase¹¹⁵.

2.4.3 Polymeric compatibilizers

Various polymeric compatibilizers have been used over the last two decades. These compatibilizers may be classified into two types, depending on the method of addition. The two types are the separate addition type and the in situ formation type.

In the separate addition type, a block or a graft copolymer that is prepared in a separate step is added to the immiscible blend. The block or graft copolymer normally possesses segments with chemical structures that are identical or similar to those of the polymers being blended. In the in situ formation type, suitably functionalized polymers are melt-mixed with the immiscible polymer blend. The copolymer formed has segments that are identical or similar to the unreactive immiscible homopolymers.

Nakayama and coworkers made a direct comparison between a separately added and an in situ compatibilizer¹¹⁶. In their specific study, they reported that the compatibilization by in situ formed copolymers is more effective in reducing the domain size of the dispersed phase and stabilizing them than in the case of the separately added copolymers.

Styrene-butadiene-styrene block copolymer (SBS) is one of the most common compatibilizers used in immiscible polystyrene blends¹¹⁷⁻¹¹⁹. Other compatibilizers used in immiscible polystyrene blends include styrene-butadiene multiblock copolymers⁹⁹, styrene-ethylene/butylenes-styrene triblock copolymer (SEBS)^{118,120}, styrene/ethylene-propylene diblock copolymer (SEP)¹²¹ and polystyrene modified with maleic anhydride (MPS)¹⁰⁰. Polystyrene blends have been reportedly successfully prepared with polymers such as polypropylene (PP), high-density polyethylene (HDPE), low-density polyethylene (LDPE), polyamide 6 (PA6) and ethylene-propylene-diene terpolymer (EPDM) using the abovementioned polymeric compatibilizers.

2.4.4 Characterization of polymer blends by dynamic mechanical analysis

Dynamic mechanical analysis is one of the most useful tools available to study the behaviour of polymeric materials. Dynamic mechanical analysis gives valuable information regarding the visco-elastic (temperature- and time-dependent) properties of polymeric materials. The properties obtained from the dynamic mechanical analysis of polymers are the glass transition temperature (T_g), storage modulus (E'), loss modulus (E'') and loss tangent ($\tan \delta = E''/E'$).

Dynamic mechanical analysis is commonly used to evaluate the miscibility of a polymer blend. The blending of any two, or more, polymers can produce one of three possibilities: an immiscible, a partially miscible or a highly miscible blend⁸⁻¹⁰. The loss tangent curve of a highly miscible blend displays a single peak between the transition temperatures of the individual polymers (Figure 2.4). The loss tangent curve of an immiscible blend of two polymers generally shows the presence of two dampening peaks, corresponding to the T_g values of the individual polymers (Figure 2.5). A broadening of the glass transition occurs in the case of a partially miscible blend (Figure 2.6). The T_g is shifted to lower or higher temperatures.

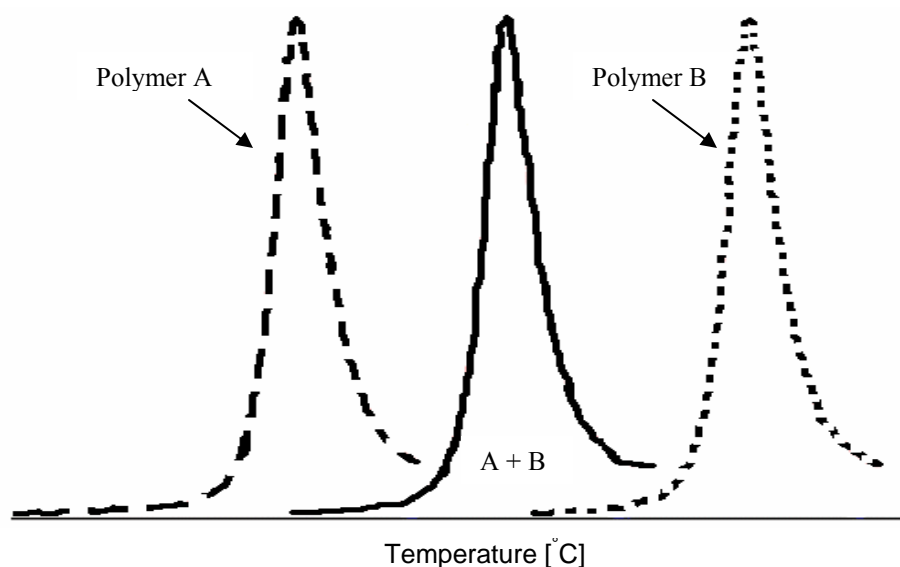


Figure 2.4 Graphic representation of the loss tangent curve of a miscible polymer blend (A + B).

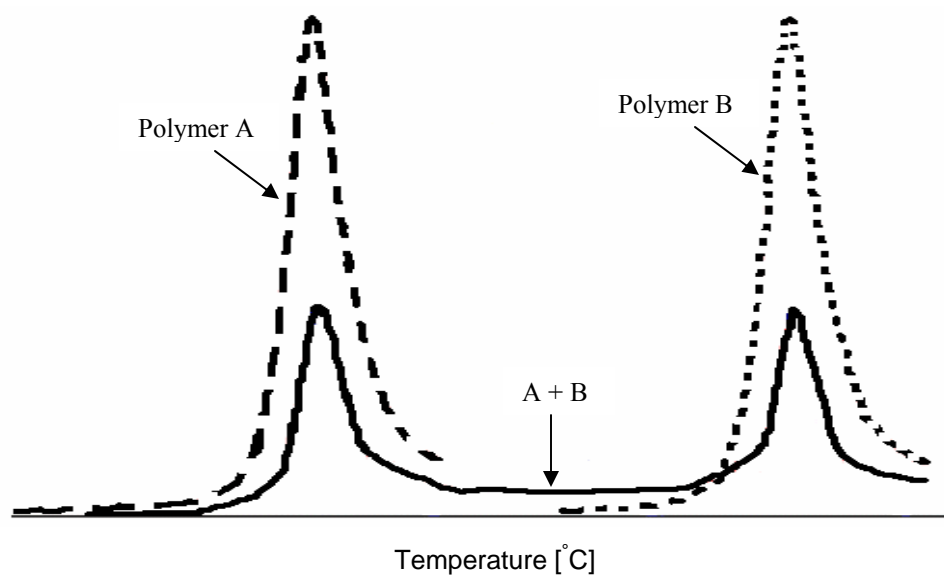


Figure 2.5 Graphic representation of the loss tangent curve of an immiscible polymer blend (A + B).

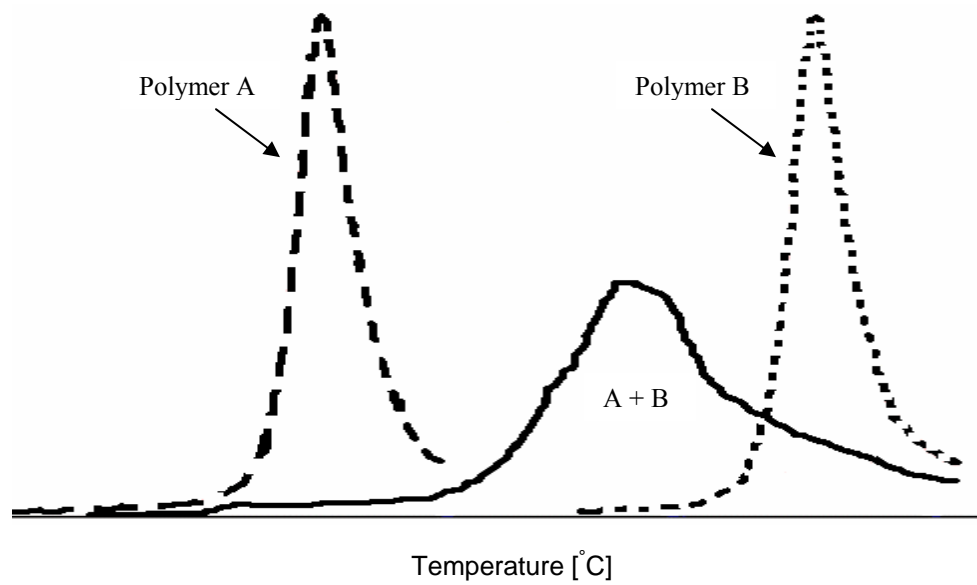


Figure 2.6 Graphic representation of the loss tangent curve of a partially miscible polymer blend (A + B).

2.5 References

1. D.I. Lee, **Macromolecular Chemistry**, Macromolecular Symposium, 33, 117 (1990)
2. A.W. McCaskie, J.B. Richardson, P.J. Gregg, **Journal of the Royal College of Surgeons of Edinburgh**, 43, 37 (February 1998)
3. H. Staudinger, **Angewandte Chemie**, 42, 37 (1929)
4. H. Staudinger, **Naturwissenschaften**, 17, 141 (1929)
5. G.G. Godwin, C.S.J. Selvamalara, A. Penlidis, S. Nanjundan, **Reactive and Functional Polymers**, 59, Issue 3, 197 (2004)
6. C.S.J. Selvamalar, T. Krithiga, A. Penlidis, S. Nanjundan, **Reactive and Functional Polymers**, 56, Issue 2, 89 (2003)
7. B.S.R. Reddy, **Journal of Polymer Materials**, 16, Issue 4, 271 (1999)
8. S. Balasubramanian, B.S.R. Reddy, **European Polymer Journal**, 32, No. 9, 1073 (1996)
9. B.S.R. Reddy, S. Balasubramanian, **European Polymer Journal**, 38, 803 (2002)
10. C.S.J. Selvamalar, T. Krithiga, A. Penlidis, S. Nanjundan, **Reactive and Functional Polymers**, 56, Issue 2, 89 (2003)
11. S. Nanjundan, C. Sreekuttan Unnithan, C.S.J. Selvamalar, A. Penlidis, **Reactive and Functional Polymers**, 62, Issue 1, 11 (2005)
12. I. Erol, C. Soykan, **Journal of Macromolecular Science: Pure and Applied Chemistry**, A39, Issue 9, 953 (2002)
13. P.S. Vijayanand, R. Arunprasath, R. Balaji, S. Nanjundan, **Journal of Applied Polymer Science**, 85, Issue 11, 2261 (2002)
14. P.S. Vijayanand, A. Penlidis, S. Radhakrishnan, S. Nanjundan, **Journal of Macromolecular Science: Pure and Applied Chemistry**, A39, Issue 6, 591 (2002)
15. R. Balaji, N. Sivakumar, P.S. Vijayanand, S. Nanjundan, **Journal of Macromolecular Science: Pure and Applied Chemistry**, A38, Issue 2, 159 (2001)
16. R. Balaji, K. Subramanian, S. Nanjundan, A.V.R. Reddy, **Journal of Applied Polymer Science**, 78, 1412 (2000)
17. M. Coskun, K. Demirelli, I. Erol, M. Ahmetzade, **Journal of Polymer Science: Part A: Polymer Chemistry**, 35, Issue 11, 2123 (1997)

18. M. Coskun, H. Erten, E. Ozdemir, M.A. Ahmedov, **Journal of Macromolecular Science: Pure and Applied Chemistry**, A34, Issue 1, 91 (1997)
19. T. Fukuda, Y. Ma, H. Inagaki, **Macromolecules**, 18, 17 (1985)
20. M.L. Coote, M.D. Zammit, T.P. Davis, G.D. Willett, **Macromolecules**, 30, 8182 (1997)
21. J.P.A. Heuts, D. Kukulj, D.J. Forster, T.P. Davis, **Macromolecules**, 31, 2894 (1998)
22. Y. Kotani, M. Kamigaito, M. Sawamoto, **Macromolecules**, 31, 5582 (1998)
23. E.V. Kolyakina, V.V. Polyanskova, M.A. Lopatin, T.I. Liogon'kaya, A.A. Shchepalov, L.L. Semenycheva, D.F. Grishin, **Russian Journal of Applied Chemistry**, 77, 136 (2004)
24. R.K. Yumagulova, S.V. Kolesov, Y.B. Monakov, **Russian Journal of Applied Chemistry**, 78, 291 (2005)
25. T.P. Davis, K.F. O'Driscoll, M.C. Piton, M.A. Winnik, **Macromolecules**, 23, 2113 (1990)
26. S.V. Arehart, K. Matyjaszewski, **Macromolecules**, 32, 2221 (1999)
27. T. Otsu, T. Ito, M. Imoto, **Journal of Polymer Science**, 3, 113 (1965)
28. E. Vidović, K. Sarić, Z. Janović, **Croatica Chemica Acta**, 75, 769 (2002)
29. J. Skupinska, **Chemical Reviews**, 91, 613 (1991)
30. R. Mülhaupt, T. Duschek, B. Rieger, **Macromolecular Chemistry**, Macromolecular Symposium, 48/49, 317 (1991)
31. K.D. Hungenberg, J. Kerth, F. Langhauser, H.J. Müller, P. Müller, **Angewandte Makromolekulare Chemie**, 227, 159 (1995)
32. C. Janiak, K.C.H. Lange, P. Marquardt, **Journal of Molecular Catalysis A: Chemical**, 180, 43 (2002)
33. C. Wörner, J. Rösch, A. Höhn, R. Mülhaupt, **Polymer Bulletin**, 36, 303 (1996)
34. R. Mülhaupt, T. Duschek, D. Fischer, S. Setz, **Polymer Advanced Technology**, 4, 439 (1993)
35. R. Mülhaupt, T. Duschek, J. Rösch, **Polymer Advanced Technology**, 4, 465 (1993)
36. W. Keim, E. Hoffmann, R. Lodewick, M. Pauckert, G. Schmitt, J. Fleischhauer, U. Meier, **Journal of Molecular Catalysis**, 6, 79 (1979)

37. Y.V. Kissin, **Journal of Polymer Science: Part A: Polymer Chemistry**, 27, 605 (1989)
38. H. Isa, H. Mandai, T. Ukiumi, Y. Tominaga, R. Taniyasu, S. Nagai, Japanese Patent 7912952 (1979)
39. J.A. Brennan, **Industrial Engineering Chemical Production Research Development**, 19, 2 (1980)
40. G.W. Schoenthal, L.H. Slaugh, European Patent Application EP 257695 (1988)
41. U.M. Wahner, R. Brull, H. Pasch, H.G. Raubenheimer, R. Sanderson, **Die Angewandte Makromolekulare Chemie**, 270, 49 (1999)
42. S. Mange, **Dissertation (PhD)**, University of Stellenbosch (2005)
43. D.L. Beach, T.P. Kobylinski, U.S. Patent 4293726 (1982)
44. H. Mandai, A. Timinaga, Y. Yoshimura, H. Isa, German Patent 2837235 (1979)
45. H. Isa, H. Mandai, T. Ukigai, A. Tominaga, M. Sato, Japanese Patent 76122002 (1977)
46. N.E. Morganson, A. V. Vayda, U.S. Patent 4409415 (1984)
47. R.L. Shubkin, M.S. Baylerian, A.R. Maler, **Preprint: American Chemical Society, Division Petroleum Chemistry**, 24, 809 (1979)
48. J.R. Anderson, Y.F. Chang, R.J. Western, **Journal of Catalysis**, 118, 466 (1989)
49. T.H. Johnson, U.S. Patent 4476343 (1985)
50. S.A. Tabak, U.S. Patent 4254295 (1981)
51. M. Bianchi, G. Menchi, U. Matteoli, F. Piacenti, **Journal of Organometallic Chemistry**, 526, 33 (1996)
52. R.G. da Rosa, M.O. de Souza, R.F. de Souza, **Journal of Molecular Catalysis A: Chemical**, 120, 55 (1997)
53. O. Stenzell, R. Brüll, U.M. Wahner, R.D. Sanderson, H.G. Raubenheimer, **Journal of Molecular Catalysis A: Chemical**, 192, 217 (2003)
54. Y. Chauvin, J.F. Gaillard, J. Leonard, P. Bonnifay, J.W. Andrews, **Hydrocarbon Processing**, 110 (1982)
55. B. Bogdanović, B. Henc, H. Karmann, H. Nüssel, D. Walter, G. Wilke, **Industrial and Engineering Chemistry Research**, 62, 34 (1970)

56. J.R. Briggs, **Journal of the Chemical Society: Chemical Communications**, 674 (1989)
57. J. Christoffers, R.G. Bergman, **Journal of the American Chemical Society**, 118, 4715 (1996)
58. B.L. Small, R. Schmidt, **Chemical European Journal**, 10, 1014 (2004)
59. P. Wasserscheid, S. Grimm, R.D. Kohn, M. Haufe, **Advanced Synthesis and Catalysis**, 343, Issue 8, 814 (2001)
60. A. Ranwell, M.A. Tshamano, **ACS Symposium Series**, 818, 147 (2002)
61. O.N. Tsvetkov, R.L. Toporishcheva, S.K. Bogdanov, USSR Patent 711044 (1980)
62. B.L. Cupples, A.M. Madgavkar, U.S. Patent 4213001 (1980)
63. N.L. Allphin, F.S. Valentine, G.W. Grams, U.S. Patent 4239930 (1981)
64. N.E. Morganson, U.S. Patent 4365105 (1983)
65. A. Onopchenko, B.L. Cupples, A.N. Kreage, **Industrial Engineering Chemical Production Research Development**, 22,182 (1983)
66. J.M. Larkin, U.S. Patent 4434309 (1984)
67. R.L. Bobsein, U.S. Patent. 4436948 (1984)
68. F.C. Loveless, A.V. Merijanian, D.J. Smudin, W. Nudenberg, European Patent EP 139343 (1985)
69. F.C. Loveless, U.S. Patent 4642410 (1987)
70. F.H. Dressler, S. Vermaire, **Macromolecular Chemistry, Macromolecular Symposium**,13, 271 (1988)
71. S. Akatau, Japan Kokai 0195108, **Chemical Abstracts**, 111, 195622v (1989)
72. J.S. Rogers, R.J. Lachicotte, G.C. Bazan, **Journal of the American Chemical Society**, 121, 1288 (1999)
73. M. Antonietti, K. Landfester, **Progress in Polymer Science**, 27, 689 (2002)
74. W.I. Higuchi, J. Misra, **Journal of Pharmaceutical Science**, 459 (1962)
75. A.J. Webster, M.E. Cates, **Langmuir**, 14, 2068 (1998)
76. C.S. Chern, Y.C. Liou, **Journal of Polymer Science: Part A: Polymer Chemistry**, 37, 2537 (1999)
77. K.J.J. Fontenot, F.J. Schork, **Fourth International Workshop on Polymer Reaction Engineering**, 127, 429 (1992)

78. J.L. Reimers, F.J. Schork, **Journal of Applied Polymer Science**, 60, 251 (1996)
79. D. Mouran, J.L. Reimers, F.J. Schork, **Journal of Polymer Science: Part A: Polymer Chemistry**, 34, 1073 (1996)
80. S. Wang, G.W. Poelein, F.J. Schork, **Journal of Polymer Science: Part A: Polymer Chemistry**, 35, 595 (1997)
81. C.S. Chern, T.J. Chen, **Colloids and Surfaces A: Physicochemical and Engineering Aspects**, 138, 65 (1998)
82. J.A. Alduncin, J. Forcada, J.M. Asua, **Macromolecules**, 27, 2256 (1994)
83. J.L. Reimers, F.J. Schork, **Industrial Engineering and Chemistry Research**, 36, 1085 (1997)
84. J.A. Alduncin, J.M. Asua, **Polymer**, 35, 3758 (1994)
85. C.S. Chern, T.J. Chen, Y.C. Liou, **Polymer**, 39, 3767 (1998)
86. C.S. Chern, Y.C. Liou, **Polymer**, 40, 3763 (1999)
87. C.S. Chern, Y.C. Liou, **Macromolecular Chemistry and Physics**, 199, 2051 (1998)
88. P.J. Blythe, A. Klein, E.D. Sudol, M.S. El-Aasser, **Macromolecules**, 32, 6952 (1999)
89. J.L. Reimers, F.J. Schork, **Journal of Applied Polymer Science**, 59, 1833 (1996)
90. C.S. Chern, Y.C. Liou, T.J. Chen, **Macromolecular Chemistry and Physics**, 199, 1315 (1998)
91. Y.T. Choi, M.S. El-Aasser, E.D. Sudol, J.W. Vanderhoff, **Journal of Polymer Science: Part A: Polymer Chemistry**, 23, 2973 (1985)
92. K.J.J. Fontenot, F.J. Schork, **Journal of Applied Polymer Science**, 49, 633 (1993)
93. W.D. Harkins, **Journal of Chemistry and Physics**, 13, 381 (1945)
94. W.D. Harkins, **Journal of the American Chemical Society**, 69, 1428 (1947)
95. W.D. Harkins, **Journal of Polymer Science**, 5, 217 (1950)
96. N. Bechthold, K. Landfester, **Macromolecules**, 33, 4682 (2000)
97. C.E. Locke, D.R. Paul, **Journal of Applied Polymer Science**, 17, 2791 (1973)
98. S.W. Shalaby, H.E. Bair, **Thermal Characterization of Polymeric Materials**, Academic Press: New York, p 408 (1981)
99. D. Hlavata, Z. Horak, F. Lednický, J. Hromádková, A. Pleska, V. Zanevskii, **Journal of Polymer Science: Part B: Polymer Physics**, 39, 931 (2001)
100. C.D. Park, W.H. Jo, M.S. Lee, **Polymer**, 37, 3055 (1996)

101. S. Cimmino, F. Coppola, L. D'orazio, R. Greco, G. Maglio, M. Maliuconico, C. Man Cavella, E. Martuscelli, G. Ragosta, **Polymer**, 27, 1874 (1986)
102. C. Qin, J. Yin, B. Huang, **Rubber Chemistry Technology**, 63, 77 (1989)
103. J.M. Willis, B.D. Favis, **Polymer Engineering Science**, 28, 1416 (1988)
104. L.H. Chu, S. Guo, W. Chiu, H. Tseng, **Journal of Applied Polymer Science**, 49, 1791 (1993)
105. F.P. La Mantia, **Advanced Polymer Technology**, 12, 47 (1993)
106. I. Fortelny, D. Michalkova, **Polymer Networks and Blends**, 3, 125 (1997)
107. B.D. Favis, **Journal of Applied Polymer Science**, 39, 285, (1990)
108. C.S. Ha, **Journal of Applied Polymer Science**, 37, 317 (1989)
109. A.P. Plachocki, S.S. Dagli, R.D. Andrews, **Polymer Engineering Science**, 30, 741 (1990)
110. C.E. Scott, C.W. Macosko, **Polymer**, 35, 5425 (1994)
111. J.M. Willis, B.D. Favis, J. Lunt, **Polymer Engineering Science**, 30, 1073 (1990)
112. M. Bank, J. Leffingwell, C. Thies, **Macromolecules**, 4, 43 (1971)
113. Z. Oommen, M.R.G. Nair, S. Thomas, **Polymer Engineering Science**, 36, 151 (1996)
114. C.K. Park, C.S. Ha, J.K. Lee, W.J. Cho, **Journal of Applied Polymer Science**, 50, 1239 (1993)
115. T. Kunori, P.H. Geil, **Journal of Macromolecular Science and Physics**, 8, 93 (1980)
116. A. Nakayama, T. Inoue, P. Guegan, C.W. Macosko, **Polymer Preprints**, 34, 840 (1993)
117. J. Li, C.M. Chan, B. Gao, J. Wu, **Macromolecules**, 33, 1022 (2000)
118. P.H.P. Macaubas, N.R. Demarquette, **Polymer**, 42, 2543 (2001)
119. Z. Fang, Z. Guo, L. Zha, **Macromolecular Materials and Engineering**, 289, 743 (2004)
120. B.K. Hong, W.H. Jo, **Polymer**, 41, 2069 (2000)
121. J.J. Crevecoeur, L. Nelissen, M.C.M. van der Sanden, P.J. Lemstra, H.J. Mencer, A.H. Hogt, **Polymer**, 36, 753 (1995)
122. D.J. Walsh, J.S. Higgins, **Polymer**, 23, 336 (1982)

123. S. George, N.R. Neelakanthan, K.T. Varughese, S. Thomas, **Journal of Polymer Science: Polymer Physics Edition**, 35, 2309 (1997)
124. K.T. Varughese, G.B. Nando, P.P. De, S.K. De, **Journal of Material Science**, 23, 3894 (1988)

CHAPTER 3

Selective Dimerization of 1-Decene

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ABSTRACT

The selective dimerization of 1-decene with the metallocene-based bis(cyclopentadienyl)zirconium dichloride (Cp_2ZrCl_2 , zirconocene) catalyst and methylaluminoxane (MAO) as cocatalyst was investigated in this study. The effect of various factors on the dimerization of 1-decene, such as temperature, cocatalyst concentration and reaction time is reported. The efficiency of Cp_2ZrCl_2 catalyst, in terms of the final product-composition for the amount of catalyst used and the reaction time, compared to bis(cyclopentadienyl)hafnium dichloride (Cp_2HfCl_2 , hafnocene) catalyst for the dimerization of 1-decene is also reported.

Keywords: 1-decene, metallocene-based catalytic systems, dimerization

3.1 Introduction

In most reported cases for the oligomerization of α -olefins, the obtained products are normally a distribution of oligomers, under various reaction conditions, such as temperature and the type of catalytic system¹⁻³. Very few oligomerization conditions for selective α -olefin oligomerization, to a single α -olefin, have been reported^{4,5}. For examples of α -olefins that have been successfully selectively oligomerized to a single α -olefin see Section 2.2.5.

The successful selective trimerization of 1-decene has been reported by Wasserscheid and coworkers⁵; 1-decene was selectively trimerized by making use of homogeneous chromium catalysts. However, there is no available literature on the selective dimerization of 1-decene. Thus, I was faced with the challenge of selectively dimerizing 1-decene, in order to avoid the harsh conditions required for the separation of the higher oligomers of 1-decene from the dimeric product, due to the relatively high boiling points of the 1-decene higher oligomers.

In an attempt to selectively dimerize 1-decene using the bis(cyclopentadienyl)zirconium dichloride (zirconocene)/methylaluminoxane (MAO) catalytic system, the effect of various factors, such as co-catalyst concentration, reaction temperature and time, on the oligomerization of 1-decene were investigated. The efficiencies of the metallocene-based catalytic systems, zirconocene/MAO and bis(cyclopentadienyl)hafnium dichloride (hafnocene)/MAO, for the oligomerization of 1-decene were also investigated and reported on. The fact that these metallocene-based catalytic systems are homogeneous systems, and that they oligomerize α -olefins at moderate temperatures (energy efficient conditions) and at atmospheric pressure (no costly reactors are required), makes them ideal candidates for this study.

The oligomerization of α -olefins such as 1-pentene, 1-hexene and 1-heptene has been successfully carried out with the abovementioned metallocene-based catalytic systems^{2,4}.

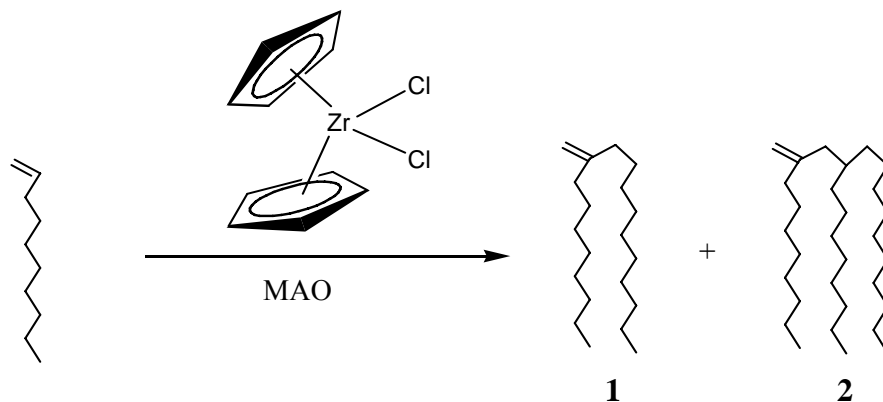
3.2 Experimental

3.2.1 Reagents

All the reagents were used as received without any further purification. The monomer, 1-decene (95%), and the catalyst, bis(cyclopentadienyl)zirconium dichloride (zirconocene, Cp_2ZrCl_2 , 98%), were purchased from ACROS (Labchem). The cocatalyst, methylaluminoxane (MAO) (10 wt% solution in toluene), was purchased from Aldrich. The catalyst, bis(cyclopentadienyl)hafnium dichloride (hafnocene, Cp_2HfCl_2 , >97%), was purchased from Fluka.

3.2.2 Selective dimerization of 1-decene

The general procedure used for the dimerization of 1-decene was based on that used by Wahner and coworkers². A Schlenk-tube was charged with N_2 gas, before the addition of 1-decene (22.2 g, 0.16 mol) and MAO (2.90 g, 0.050 mol). The catalyst (zirconocene, 15 mg, 0.050 mmol) was then added. Molar ratios of 500, 1000, 2000, 4000 and 8000:1 of MAO:catalyst were used. The Schlenk-tube was sealed. The reaction mixture was heated, or cooled in ice, to the desired temperature (5, 35, 70 or 90 °C) and allowed to react for the pre-determined duration (1, 3, 6 or 24 h). The Schlenk-tube was opened and methanol was added to the reaction mixture to quench the reaction. Hydrochloric acid (20 ml, 5.0% solution) was used to dissolve the aluminium hydroxide formed after quenching. The two layers that formed were separated. Toluene was evaporated from the product-containing layer. A colourless solution consisting of a mixture of 1-decene, the dimer of 1-decene (2-octyl-1-dodecene) (**1**) and the trimer of 1-decene (2, 4-octyl-1-tetradecene) (**2**), as determined by GCMS, was obtained. Thereafter the dimer (**1**) and trimer (**2**) were separated using a micro-distillation system. This was achieved at a pressure of 10mbar and a temperature of 140 °C. The respective purities of the dimer and trimer were 98.0% and 96.0%, as determined by GC.



Scheme 3.1 Reaction scheme for the oligomerization of 1-decene.

3.2.3 Characterization

GCMS analyses of the final reaction mixtures were carried out on a Finnigan MAT GCQ system fitted with a 30 m x 0.25 mm non-polar column (0.25 μm film thickness). Each sample was dissolved in dichloromethane (1.0 μl sample/ml DCM). A heating rate of 4.0 $^{\circ}\text{C}/\text{min}$, starting from an initial temperature of 40 $^{\circ}\text{C}$ was used. The helium flow rate was 40 cm/s. In all instances the final reaction mixtures were found to comprise residual monomer, the dimer and the trimer of 1-decene.

The isolation of the dimer and trimer of 1-decene was carried out under reduced pressure at 140 $^{\circ}\text{C}$ with a Buchi GKR-50 ball-tube micro-distillation apparatus.

The determination of the purity of the dimer and trimer of 1-decene, after isolation, was performed on a Perkin Elmer Autosystem XL fitted with a 30 m x 0.2 mm fused silica, Supelco SPB-1 column with a 0.20 μm film thickness.

The ^1H -NMR spectra were run on a VarianVXR 300 MHz spectrometer. The samples were dissolved in CDCl_3 and TMS was used as internal standard.

Quantitative ^{13}C -NMR analysis was carried out using a Varian Inova 600 MHz spectrometer with a triple resonance HCN probe with pulsed field gradient (PFG). Based on the T1 measurements for quantitative conditions, a 45 degree pulse angle was used with a 1.3 s acquisition time at a 3 s pulse delay. Inverse gated decoupling was applied. The sample was dissolved in CDCl_3 and TMS was used as internal standard.

3.3 Results and Discussion

3.3.1 Identification of the reaction products

Figure 3.1 is a typical gas chromatogram of the colourless reaction product obtained after the evaporation of toluene. It shows that the reaction product contains residual monomer (**a**), the dimer (**b**) and the trimer (**c**) of 1-decene.

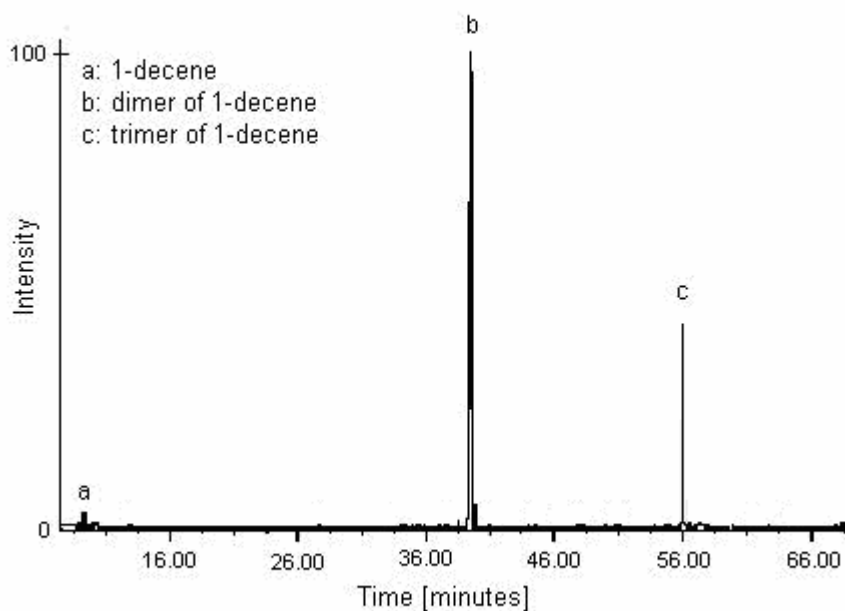


Figure 3.1 Typical gas chromatogram of the final reaction mixture of the oligomerization of 1-decene.

The aforementioned is supported by the MS and NMR data. Figure 3.2(a) shows the mass spectrum obtained for **a**.

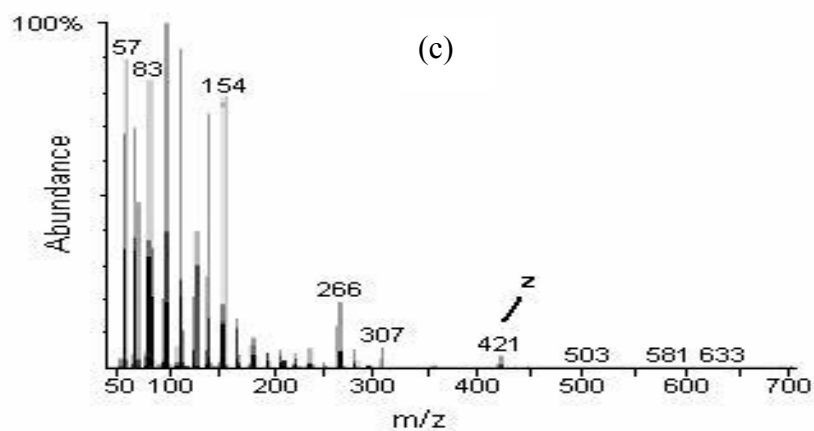
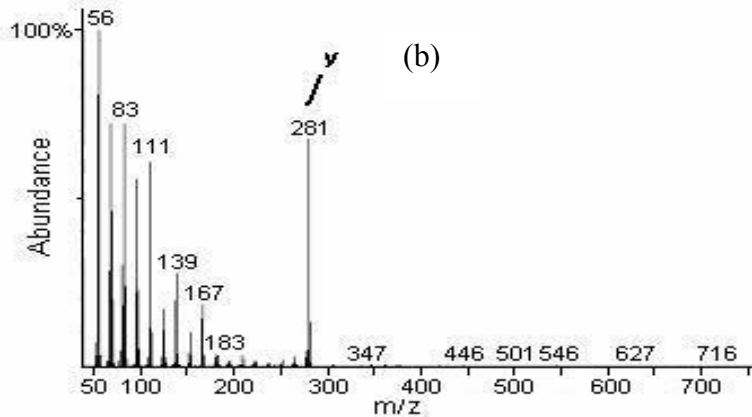
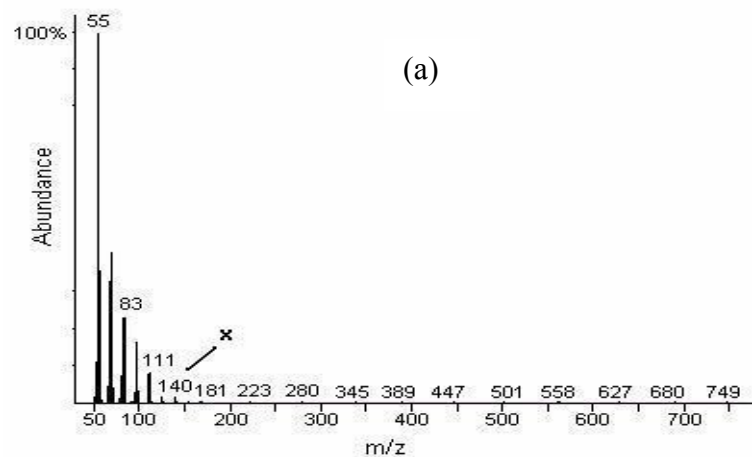


Figure 3.2 Mass spectra of the (a) residual 1-decene, (b) 1-decene dimer and (c) 1-decene trimer in the final reaction mixture.

The mass fragment for 1-decene is indicated by **x**. Figure 3.2(b) shows the mass spectrum obtained for **b**. The mass fragment for the dimer of 1-decene is indicated by **y**. Figure 3.2(c) shows the mass spectrum obtained for **c**. The mass fragment for the trimer of 1-decene is indicated by **z**. The mass fragments **x**, **y** and **z** correspond to the fragments for 1-decene, the dimer of 1-decene and trimer of 1-decene, respectively.

The formation of the 1-decene dimer was further confirmed by $^1\text{H-NMR}$ spectroscopy. Figure 3.3 and Figure 3.4 show the $^1\text{H-NMR}$ spectra of 1-decene and the 1-decene dimer, respectively.

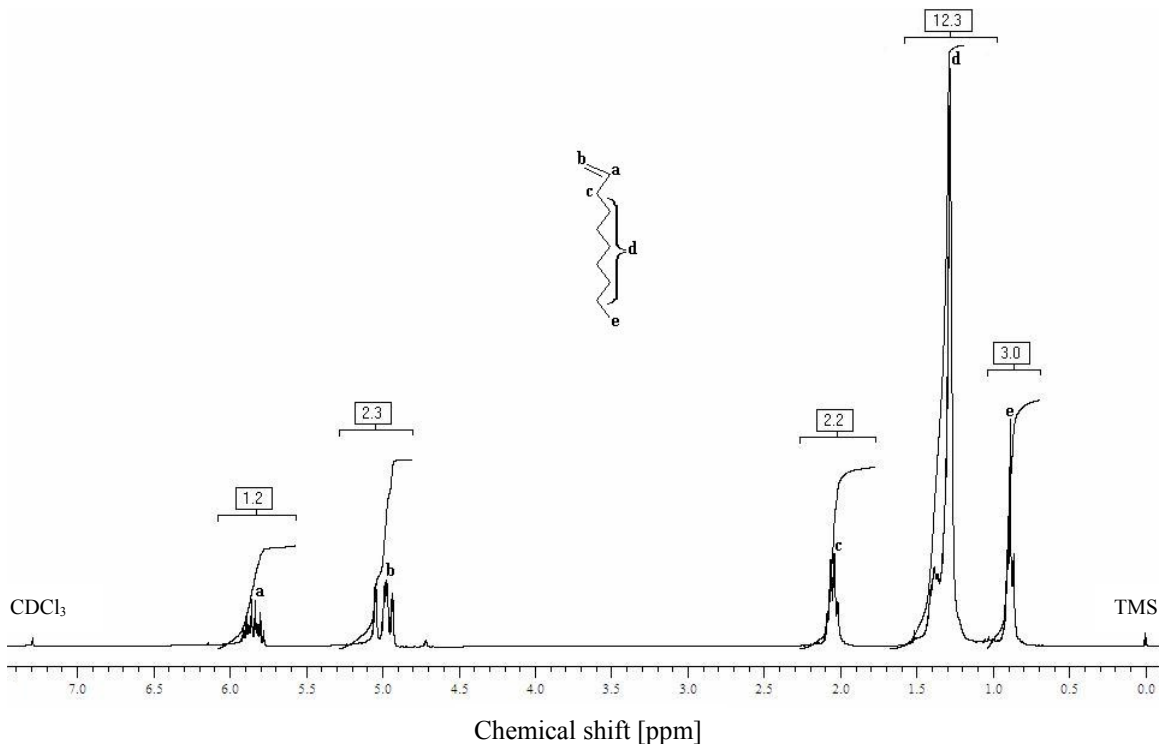


Figure 3.3 $^1\text{H-NMR}$ spectrum of 1-decene in CDCl_3 with TMS as internal standard.

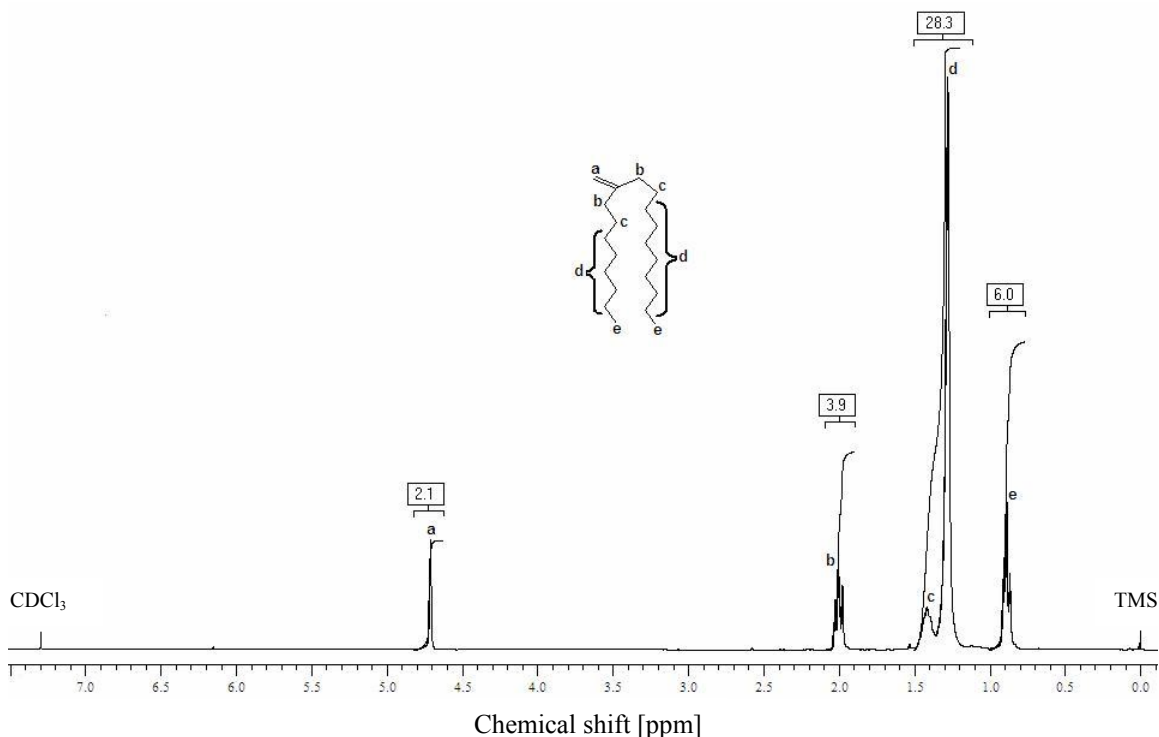


Figure 3.4 $^1\text{H-NMR}$ spectrum of the 1-decene dimer in CDCl_3 with TMS as internal standard.

In Figure 3.3, the peaks due to the vinylic protons appear at about 5.0 ppm and 5.9 ppm. The absence of the peak at about 5.9 ppm in Figure 3.4 confirms the formation of the 1-decene dimer. The other peaks are as assigned.

Figure 3.5 shows the quantitative $^{13}\text{C-NMR}$ spectrum of 2-octyl-1-dodecene (1-decene dimer). It can be seen from Figure 3.5 that a small amount of impurities (any species other than 2-octyl-1-dodecene) is present in the product. The labeled peaks in Figure 3.5 correspond to a 1-decene dimeric product, 3-methyl-2-octyl-1-undecene, resulting from a 2,1-insertion followed by a 1,2-insertion. The aforementioned byproduct constitutes approximately 3.0% percent of the total of 4.2% (as calculated from NMR integration values) impurities in the 2-octyl-1-dodecene product. The remaining impurities consist of traces of 1-decene, 1-decene trimer and toluene.

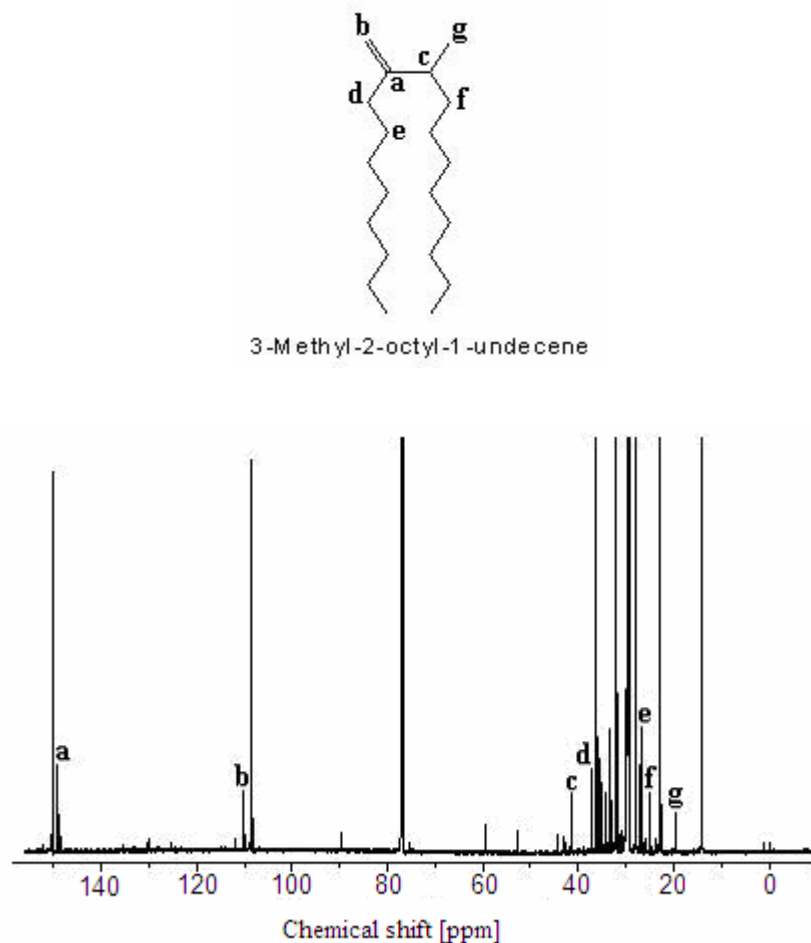


Figure 3.5 Quantitative ¹³C-NMR spectrum of 2-octyl-1-dodecene in CDCl₃ with TMS as internal standard. Peaks associated with 3-methyl-2-octyl-1-undecene are as assigned.

3.3.2 The effect of various factors on the dimerization of 1-decene

Determinations of the relative percentages of the residual monomer, dimer and trimer of 1-decene in each final reaction mixture were based on the relative peak areas of these different components in the different reaction mixtures, as determined by GCMS. The reliability of using these relative peak areas was verified with known ratios of a mixture of 1-decene and 1-octadecene. Within acceptable experimental scatter margins, the expected relationships were obtained.

3.3.2.1 The effect of co-catalyst to catalyst ratio on the dimerization of 1-decene at 35 °C

Figure 3.6 shows the effect of the co-catalyst to catalyst molar ratio on the final reaction product composition for the dimerization of 1-decene at 35 °C when using Cp_2ZrCl_2 as catalyst. The percentage residual monomer in the final reaction mixture decreased from about 15% at $\text{MAO}:\text{Cp}_2\text{ZrCl}_2 = 500:1$, to about 1.0% at $\text{MAO}:\text{Cp}_2\text{ZrCl}_2 = 8000:1$. For $\text{MAO}:\text{Cp}_2\text{ZrCl}_2$ ratios of 500:1, 2000:1, 4000:1 and 8000:1, the percentage of dimer in the final reaction mixture was about 70%. For $\text{MAO}:\text{Cp}_2\text{ZrCl}_2$ ratios of 250:1 and 1000:1, the percentage of dimer in the final reaction mixture was 81% and 79%, respectively. The percentage of trimer in the reaction mixture increased from 13% to 29% over this co-catalyst to catalyst concentration range. The higher co-catalyst concentrations (2000:1, 4000:1 and 8000:1) promote the formation of a greater fraction of the 1-decene-trimer at 35 °C. The same amount of trimer (29%) was obtained in all three instances.

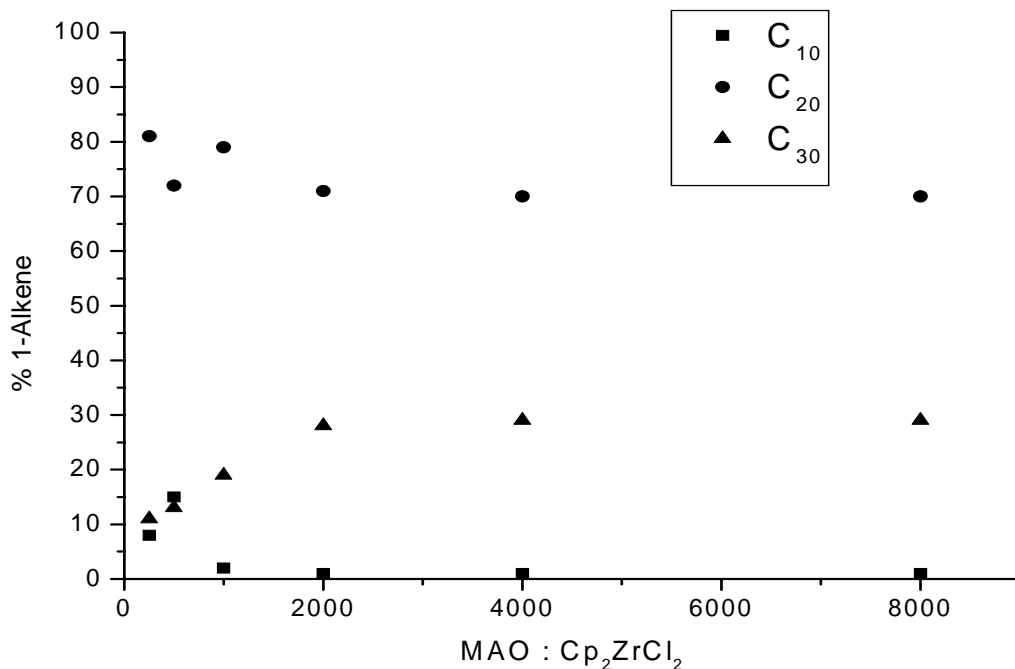


Figure 3.6 Effect of co-catalyst to catalyst molar ratio on product composition for the dimerization of 1-decene (22.2 g) using Cp_2ZrCl_2 (15 mg) as catalyst. Reaction conditions: 35 °C, 24 hours.

3.3.2.2 The effect of temperature on the dimerization of 1-decene at a co-catalyst to catalyst ratio of 1000:1

Figure 3.7 shows the effect of temperature on the final product composition for the dimerization of 1-decene at a co-catalyst to catalyst molar ratio of 1000:1, using Cp_2ZrCl_2 as catalyst. The same amount of unreacted monomer (2.0%) was left after 24 hours at 35, 70 and 90 °C, and about 3.0% at 5 °C. The amount of dimer produced at 5 °C and 35 °C was 70% and 79%, respectively. The same amount of dimer (87%) was obtained at 70 °C and 90 °C.

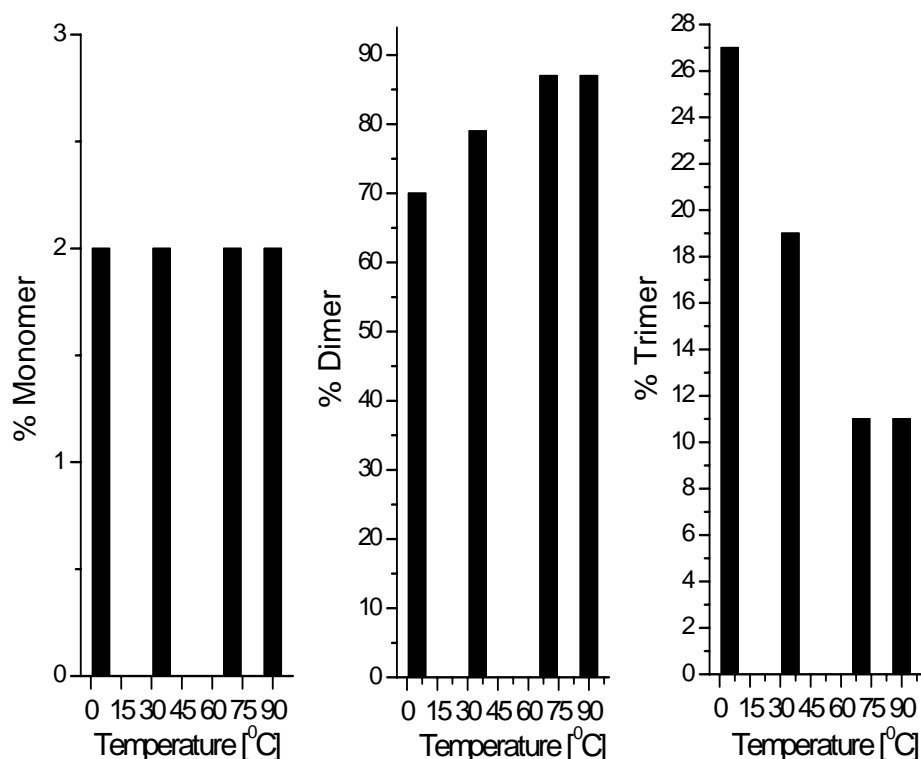


Figure 3.7 Effect of temperature (5, 35, 70 and 90 °C) on product composition for the dimerization of 1-decene (22.2 g). Reaction conditions: molar ratio of MAO: Cp_2ZrCl_2 = 1000:1; 24 hours.

The percentages of trimer in the reaction mixtures at 5, 35, 70 and 90 °C were 27, 19, 11 and 11%, respectively. The above results show that higher temperatures (70 °C and 90 °C) facilitate the formation of the shorter oligomers (dimers of 1-decene) when Cp_2ZrCl_2 (MAO: $\text{Cp}_2\text{ZrCl}_2 = 1000:1$) is used as catalyst, whereas more of the trimer of 1-decene is obtained at the lower temperatures (5 °C and 35 °C)^{3,4}.

In all of the abovementioned instances, approximately 2.0% of residual monomer was present in the final reaction mixtures.

3.3.2.3 The effect of different reaction times on the product composition for the dimerization of 1-decene

Figure 3.8 shows the effect of different reaction times on the dimerization of 1-decene at 35 °C using Cp_2ZrCl_2 as catalyst and a co-catalyst to catalyst ratio of 1000:1.

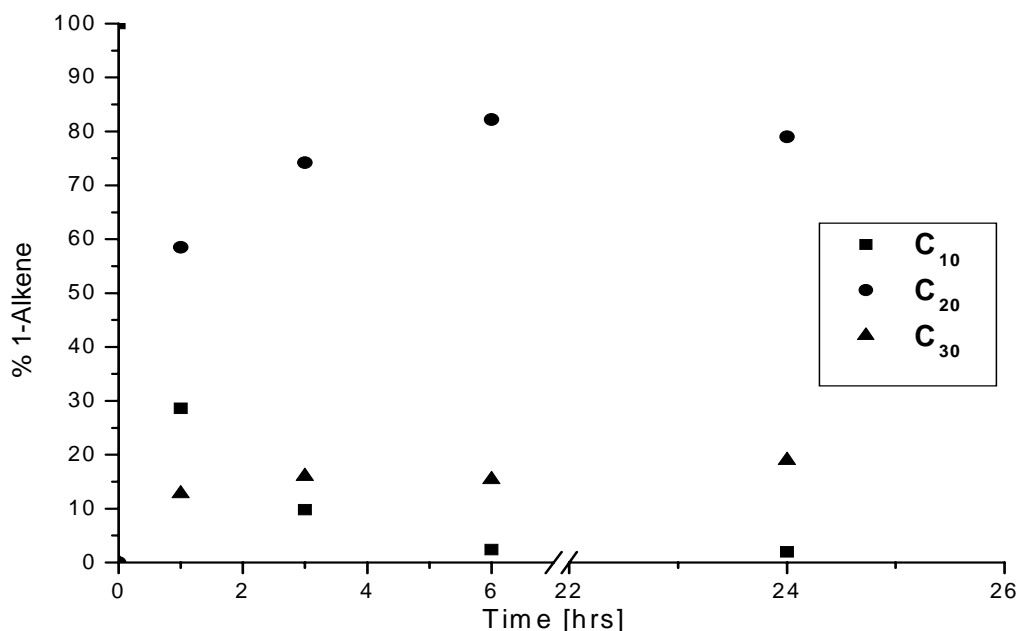


Figure 3.8 Comparison of the relative amounts of dimer and trimer of 1-decene produced after reaction times of 1, 3, 6 and 24 hour(s), respectively. Reaction conditions: molar ratio of MAO: $\text{Cp}_2\text{ZrCl}_2 = 1000:1$, reaction temperature 35 °C.

The percentages of 1-decene in the reaction mixtures were 29, 9.8, 2.4 and 2.0% after reaction times of 1, 3, 6 and 24 hour(s), respectively. The percentages of dimer in the reaction mixtures were 59, 74, 82 and 79% after 1, 3, 6 and 24 hour(s), respectively. The percentages of trimer in the reaction mixture were 13, 16, 15 and 19% after 1, 3, 6 and 24 hour(s), respectively. The results obtained for a reaction time of 6 hours compare very well with those obtained for the longer reaction time of 24 hours at 35 °C for a molar ratio of MAO:Cp₂ZrCl₂ = 1000:1. A reaction time of 6 hours is thus preferred to one of 24 hours.

3.3.2.4 Comparison of the efficiency of zirconocene and hafnocene as catalysts for the dimerization of 1-decene

The efficiency of zirconocene (Zr) and hafnocene (Hf) as catalysts for the dimerization of 1-decene was compared in terms of the amount of oligomer(s) produced in the same time period (24 h). In all instances 0.05 mmol of catalyst was used. A comparison of the efficiency of zirconocene and hafnocene as catalysts for the dimerization of 1-decene at 35 °C, for a co-catalyst to catalyst molar ratio of 1000:1 and a reaction time of 24 hours, is shown in Figure 3.9.

A large percentage of monomer (88%) was left in the final reaction mixture after 24 hours when hafnocene was used as catalyst compared to 2.0% of monomer in the case of the zirconocene catalyst.

A comparison the efficiency of zirconocene and hafnocene as catalysts for the dimerization of 1-decene at 70 °C, for a co-catalyst to catalyst molar ratio of 1000:1 and a reaction time of 24 hours, is shown in Figure 3.10. An amount of 59% of monomer, 23% of dimer and 18% of trimer remained in the final reaction mixture when hafnocene was used as catalyst. When zirconocene was used as catalyst, the final reaction mixture consisted of 2.0% monomer, 87% dimer and 11% trimer.

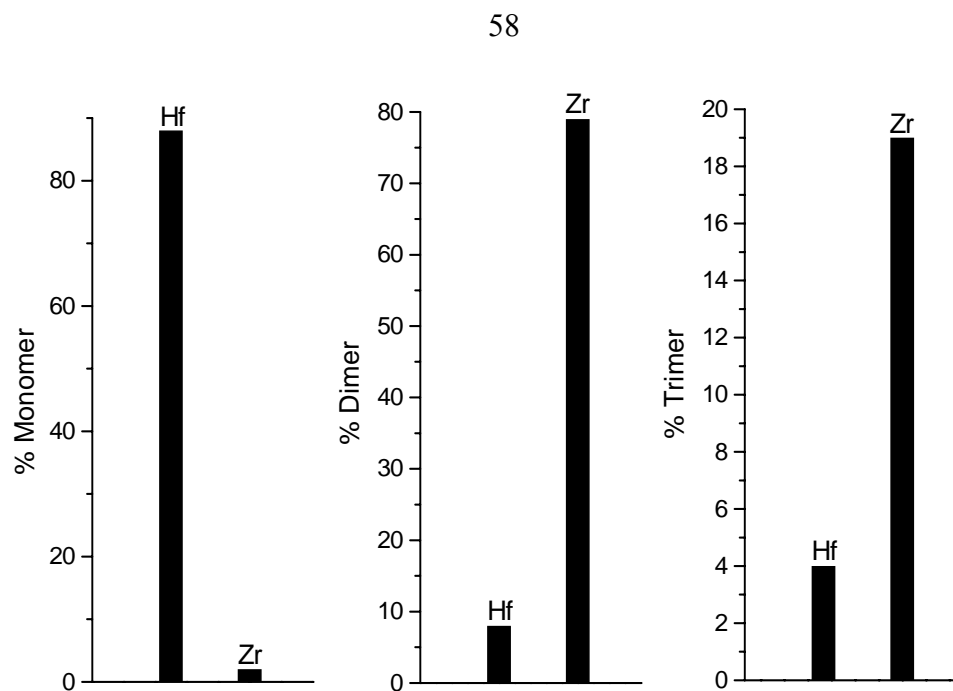


Figure 3.9 Comparison of the efficiency of zirconocene (Zr) (15 mg) and hafnocene (Hf) (15 mg) as catalysts for the dimerization of 1-decene (22.2 g). Reaction conditions: molar ratio of MAO:catalyst = 1000:1, reaction temperature 35 °C, reaction time 24 hours.

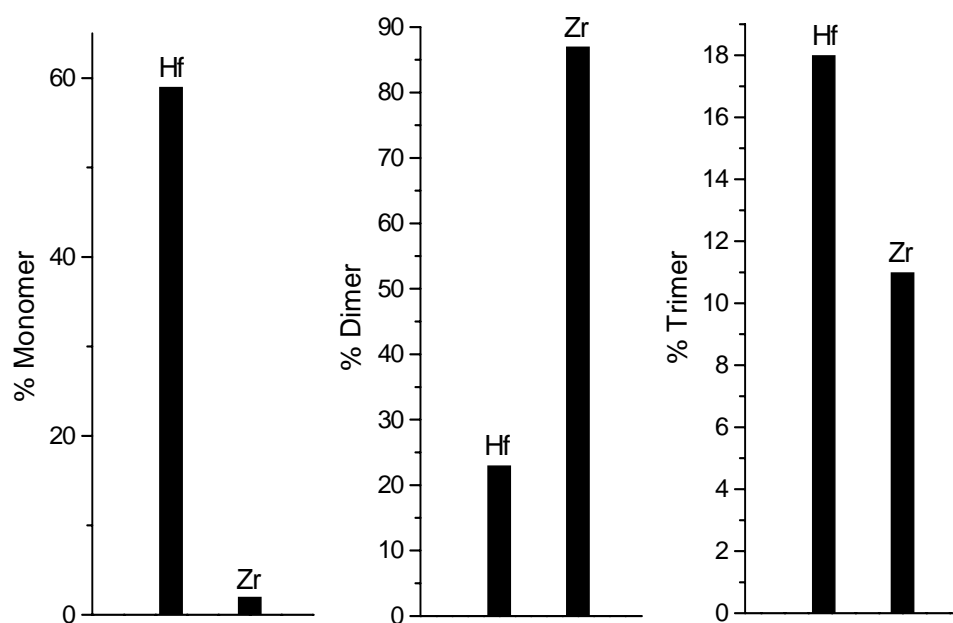


Figure 3.10 Comparison of the efficiency of catalysts of zirconocene (Zr) (15 mg) and hafnocene (Hf) (15 mg) for the dimerization of 1-decene (22.2 g). Reaction conditions: molar ratio of MAO:catalyst = 1000:1, reaction temperature: 70 °C, reaction time: 24 hours.

These results suggest that zirconocene is a more efficient catalyst for the production of 1-decene dimers than hafnocene is. Large concentrations of residual monomer (>50% of initial monomer concentration) were still present in the final reaction mixtures when hafnocene was used as catalyst for a reaction time of 24 hours⁵. The greatest concentrations of dimer and trimer of 1-decene in the final reaction mixture were obtained with zirconocene, at a reaction temperature of 35 °C. At a reaction temperature of 70 °C, zirconocene produced the largest concentration of the dimer of 1-decene and hafnocene the largest concentration of the trimer of 1-decene in the final reaction mixture.

3.4 Conclusions

Oligomers of 1-decene with a high percentage of the dimeric product were successfully synthesized with the metallocene catalyst, zirconocene, under various reaction conditions. The results indicate that zirconocene is the preferred catalyst over hafnocene for the dimerization of 1-decene. Reaction times of 24 hours seemed to be excessive, as a comparable composition of the final reaction mixture was obtained after only 6 hours.

The various reaction conditions that were used in this study did not result in the selective dimerization of 1-decene. The reaction product, in all instances, consisted mostly of the dimeric product. Further purification of the main product of interest, the 1-decene dimer, was thus necessary.

The general trends observed for the oligomerization of 1-decene agree with previously reported trends for α -olefins such as 1-pentene and 1-hexene^{2,3}. Namely, lower temperatures and higher co-catalyst concentrations facilitate the formation of the higher oligomers of α -olefins.

3.5 References

1. G.W. Schoenthal, L.H. Slaugh, European Patent Application EP 257695 (1988)
2. U.M. Wahner, R. Brull, H. Pasch, H.G. Raubenheimer, R. Sanderson, **Die Angewandte Makromolekulare Chemie**, 270, 49 (1999)
3. S. Mange, **PhD Dissertation**, University of Stellenbosch (2005)
4. J. Christoffers, R.G. Bergman, **Inorganica Chimica Acta**, 270, 20 (1998)
5. P. Wasserscheid, S. Grimm, R.D. Kohn, M. Haufe, **Advanced Synthesis and Catalysis**, 343, Issue 8, 814 (2001)

CHAPTER 4

The Synthesis of a Novel Hydrophobic Acrylic Monomer

CONTENTS

4.1 Introduction

4.2 Experimental

4.2.1 Oxymercuration-demercuration of 2-octyl dodecene

4.2.2 Synthesis of 2-octyl dodecyl acrylate

4.2.3 Characterization

4.3 Results and Discussion

4.4 Conclusions

4.5 References

ABSTRACT

The synthesis and characterization of a new tertiary alcohol (2-octyl-2-dodecanol) and acrylic monomer (2-octyl-dodecyl acrylate) from a 1-decene dimer precursor (2-octyl-1-dodecene), which was synthesized with a metallocene-based catalytic system, is reported. The newly synthesized acrylic monomer was characterized via infra red (IR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy.

Keywords: oxymercuration-demercuration, esterification of alcohols, hydrophobic acrylic monomer

4.1 Introduction

The synthesis and characterization of a new tertiary alcohol, 2-octyl-2-dodecanol, and a novel hydrophobic acrylic monomer, 2-octyl-dodecyl acrylate, from the purified 1-decene dimer precursor, 2-octyl-1-dodecene, is reported here. The synthesis and purification of the 2-octyl-1-dodecene is detailed in the previous chapter.

The highly hydrophobic nature of 2-octyl-1-dodecene necessitated the introduction of some slight modifications, as explained in the following paragraphs, to the existing literature procedures for the oxymercuration-demercuration of alkenes and esterification of alcohols with acryloyl chloride¹⁻⁴.

The oxymercuration-demercuration of short chain alkenes normally only requires a 1:1 volume ratio of water to THF for significant yields. Brown and Geoghegan reported on the need for an increased volume of THF with increased alkene chain length to facilitate the solubility of the longer chain alkenes and thus the reaction between the water-soluble mercurial salt and the oil-soluble alkene¹. In the present case, no more than a 1:2 volume ratio of water to THF was sufficient for a satisfactory yield of 2-octyl-2-dodecanol.

For the esterification of 2-octyl-2-dodecanol, a 10% excess of acryloyl chloride to the alcohol, as reported in literature²⁻⁴, was insufficient for a high yield of the acrylate. Also, where short chain alcohols or relatively water-soluble alcohols are used, it is normally sufficient to wash the final reaction mixture with a NaOH solution to remove any residual alcohol. Due to the very low water solubility of 2-octyl-2-dodecanol, the aforementioned procedure for the removal of any residual 2-octyl-2-dodecanol would not be very efficient. It was thus necessary to use an increased excess of acryloyl chloride (30%) for optimum conversion of 2-octyl-2-dodecanol to 2-octyl-dodecyl acrylate.

4.2 Experimental

4.2.1 Oxymercuration-demercuration of 2-octyl dodecene

4.2.1.1 Reagents

The 2-octyl-1-dodecene (98%, as determined by GC) was synthesized and purified as in chapter 3.2.2. The mercury acetate (98.5%) and sodium borohydride (minimum 95%) were obtained from Saarchem and used as received. The solvent (THF, 99.5%) was purchased from Saarchem. The sodium hydroxide pellets (97%) were purchased from Associated Chemical Enterprises.

4.2.1.2 Procedure

The synthetic procedure followed in the hydration of 2-octyl-1-dodecene was as reported by Brown and Geoghegan¹. Mercuric acetate (11.4 g, 35.7 mmol) together with 50 ml of water was placed in a 500 ml flask and stirred until it dissolved. This was followed by the addition of 50 ml of THF and 2-octyl-1-dodecene (10.0 g, 35.7 mmol) in 50 ml of THF. The reaction mixture was stirred for 4 hours at 25 °C to complete the oxymercuration step. The addition of 50 ml of 3.0 M sodium hydroxide, followed by a 50 ml solution of 0.50 M sodium borohydride in 3.0 M sodium hydroxide, resulted in the reduction of the mercurial intermediate with the separation of elemental mercury. The reaction mixture was stirred for 1h to complete the demercuration process. The elemental mercury was allowed to settle. The organic and aqueous layers were separated. The aqueous layer was extracted with three 30 ml portions of ether. The ether extract and organic layer were combined. The 2-octyl-2-dodecanol (yield: 10.1 g, 95%) (**3**, Scheme 4.1) was obtained after evaporation of the volatiles.

separated and the resulting product, 2-octyl-dodecyl acrylate (**4**, Scheme 4.1), was obtained in good yield (9.8 g, 92%) after the evaporation of the diethyl ether.

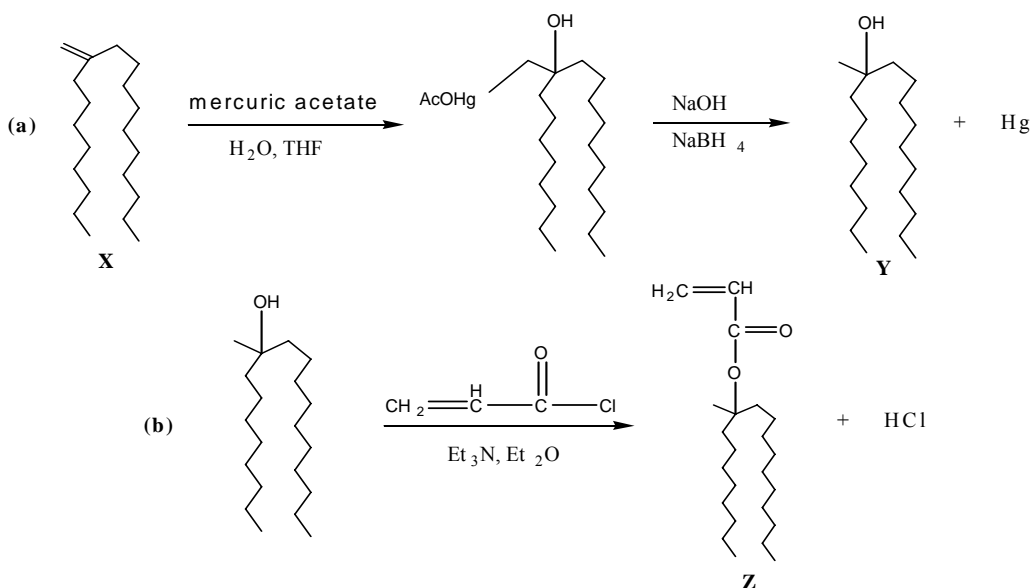
4.2.3 Characterization

The FT-NMR spectra of 2-octyl-2-dodecanol and 2-octyl-dodecyl acrylate were run on a Varian VXR 300 MHz spectrometer. The samples were dissolved in CDCl_3 using TMS as internal standard.

The FT-IR spectra were recorded on a Perkin Elmer Paragon 1000 PC spectrometer.

4.3 Results and Discussion

The synthesis of the new acrylic monomer, 2-octyl dodecyl acrylate [**Z**, Scheme 4.2(b)], was preceded by the synthesis of the tertiary alcohol, 2-octyl-2-dodecanol [**Y**, Scheme 4.2(a)], by means of the oxymercuration-demercuration procedure.



Scheme 4.2 The (a) oxymercuration-demercuration of 2-octyl-1-dodecene and (b) esterification of 2-octyl-2-dodecanol.

The successful synthesis of the tertiary alcohol [**Y**, Scheme 4.2(a)] and acrylic monomer [**Z**, Scheme 4.2(b)] were confirmed by IR, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectroscopy.

It can be seen from Figure 4.1b that the tertiary alcohol absorbs near 3400 cm^{-1} . The absence of the typical double bond absorption of the dimeric alkene [**X**, Scheme 4.2 (a)] in the region of 1620 cm^{-1} (Figure 4.1a) further confirms the synthesis of **Y** (Figure 4.1b). Furthermore, the absence of the vinyl group is indicated by the absence of the peak at around 4.7 ppm in Figure 4.2. The singlet at 2.2 ppm is associated with the hydroxyl proton.

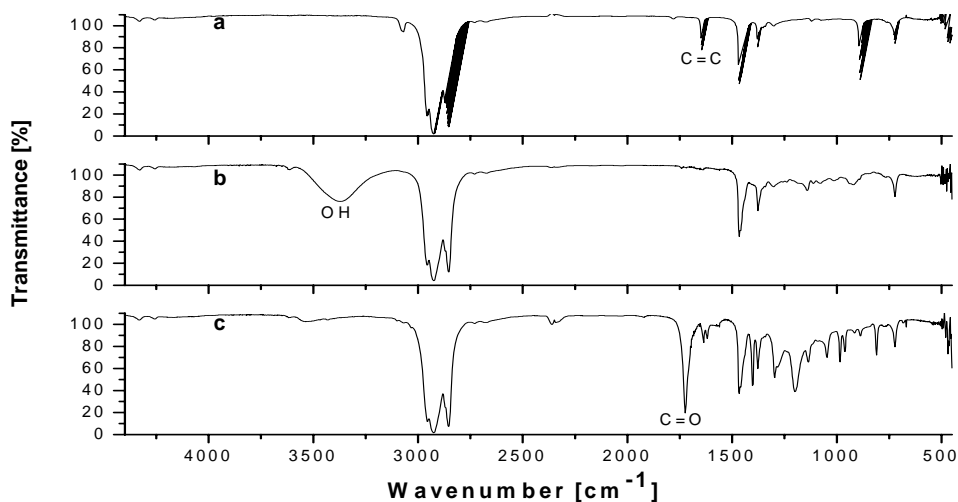


Figure 4.1 IR spectra of (a) 2-octyl-1-dodecene, (b) 2-octyl-2-dodecanol and (c) 2-octyl-dodecyl acrylate.

Figure 4.1c shows the typical carbonyl peak at around 1720 cm^{-1} and the carbonyl overtone band (generally of low intensity) in the region of 3550 cm^{-1} due to the $\text{C}=\text{O}$ stretching⁵. The reappearance of the peak in the region of 1620 cm^{-1} (Figure 4.1c), associated with the vinyl group, further confirms the synthesis of the acrylate [**Z**, Scheme 4.2(b)]. The peaks due to the vinylic protons appear at $5.7\text{-}6.4\text{ ppm}$ in the $^1\text{H-NMR}$ spectrum (Figure 4.3).

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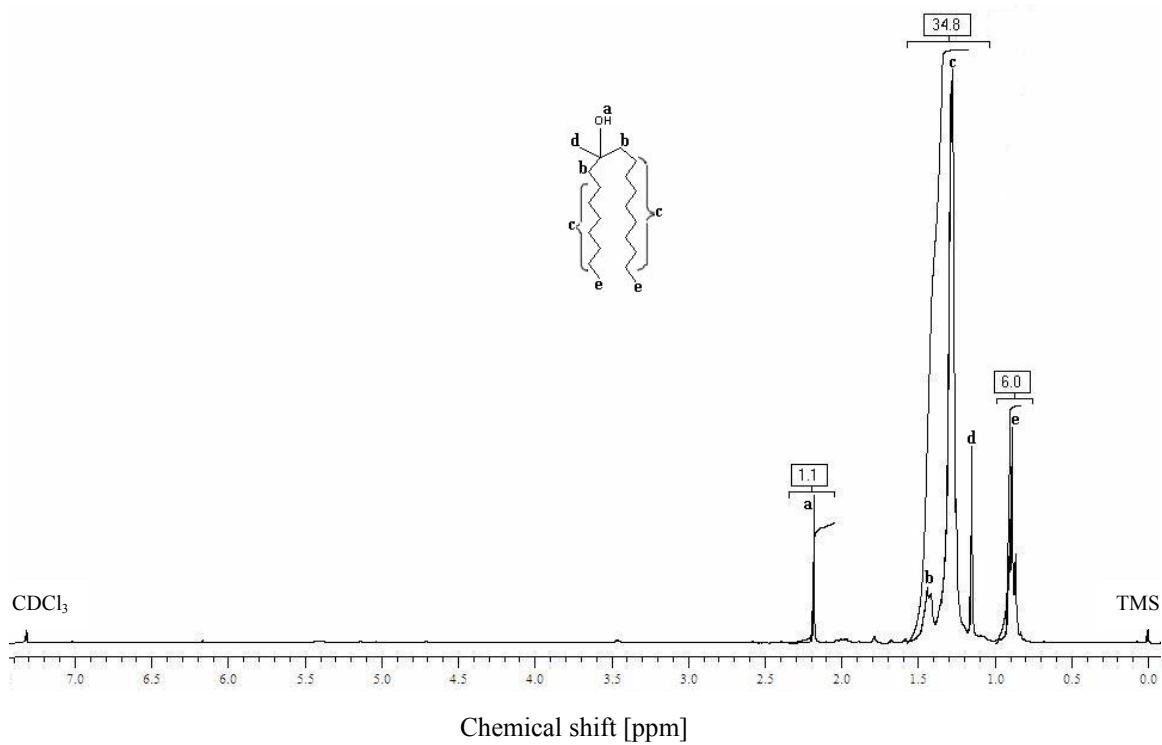


Figure 4.2 ¹H-NMR spectrum of 2-octyl-2-dodecanol in CDCl₃ with TMS as internal standard.

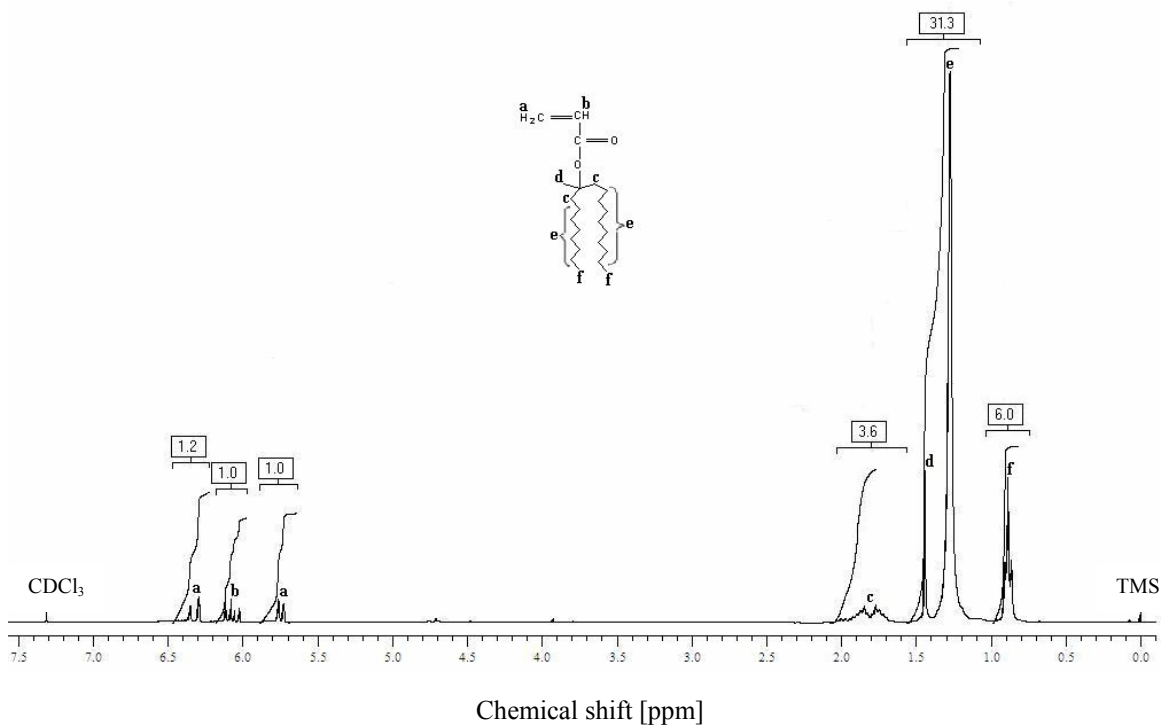


Figure 4.3 ¹H-NMR spectrum of 2-octyl-dodecyl acrylate in CDCl₃ with TMS as internal standard.

The synthesis of 2-octyl-1-dodecene, 2-octyl-2-dodecanol and 2-octyl-dodecyl acrylate is further confirmed by the ^{13}C -NMR spectra presented in Figure 4.4, Figure 4.5 and Figure 4.6, respectively.

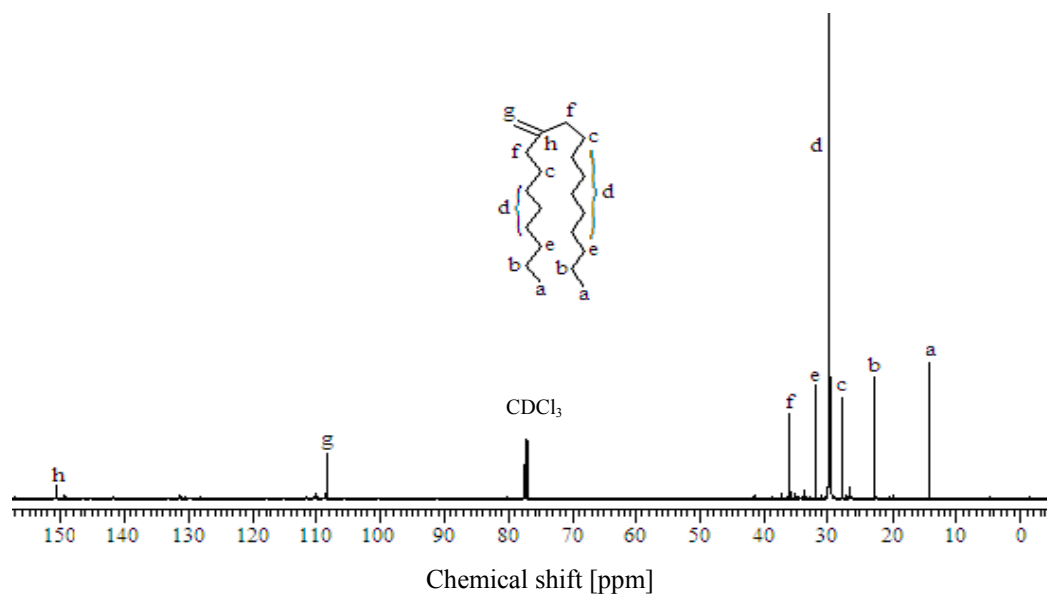


Figure 4.4 ^{13}C -NMR spectrum of 2-octyl-1-dodecene in CDCl_3 .

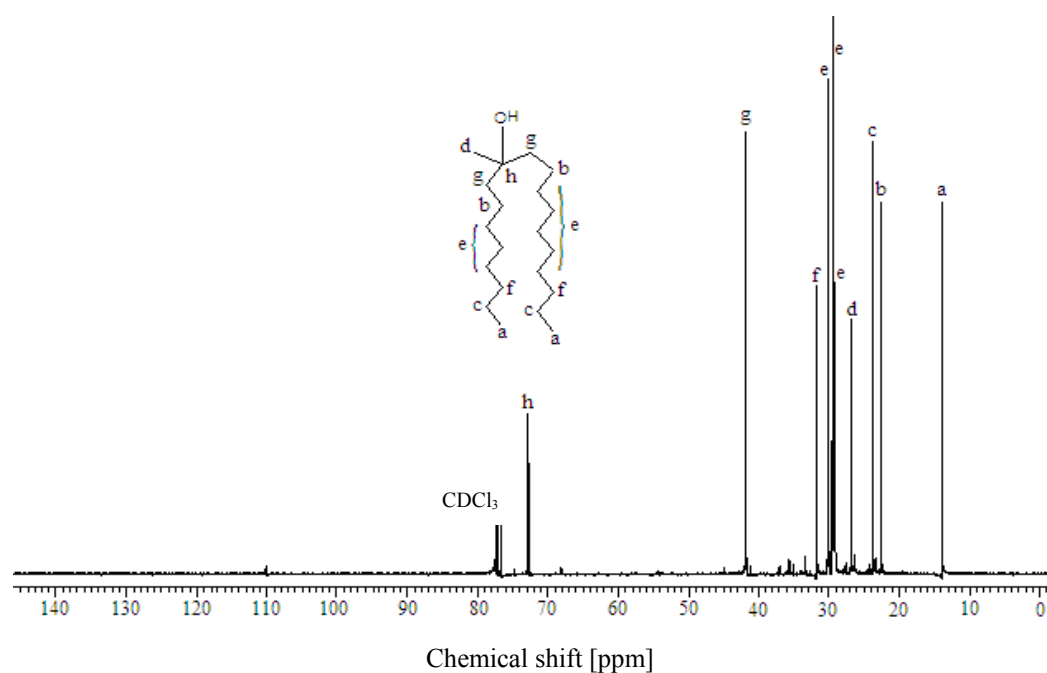


Figure 4.5 ^{13}C -NMR spectrum of 2-octyl-2-dodecanol in CDCl_3 .

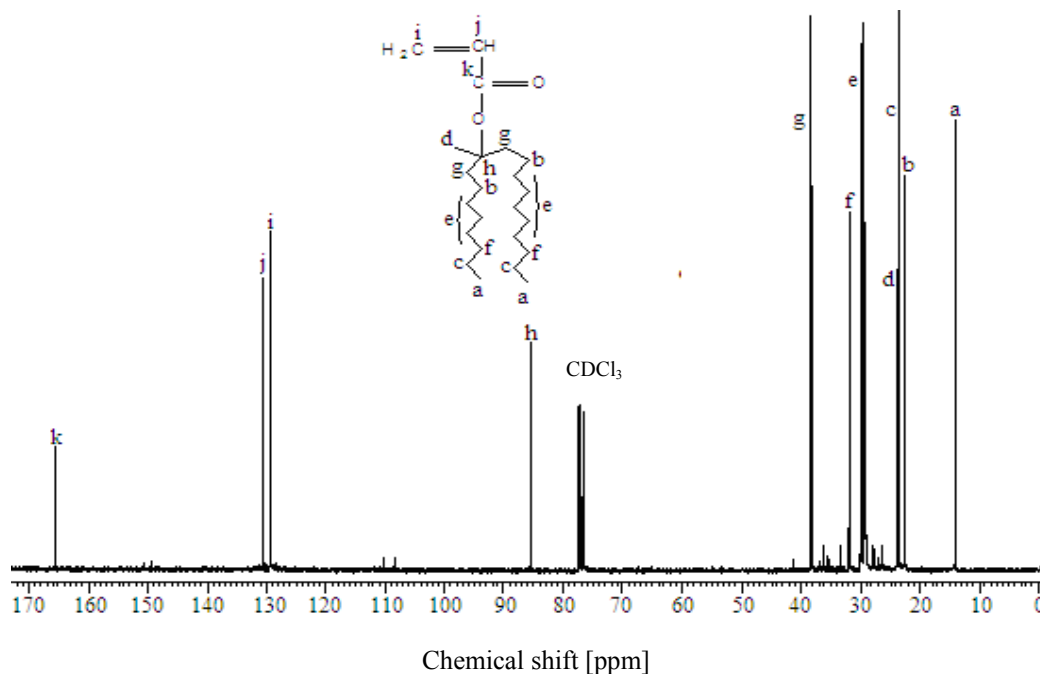


Figure 4.6 ¹³C-NMR spectrum of 2-octyl-dodecyl acrylate in CDCl₃.

4.4 Conclusions

The tertiary alcohol, 2-octyl-2-dodecanol, and the novel acrylic monomer, 2-octyl-dodecyl acrylate, were successfully synthesized and characterized. The preliminary usefulness of the newly synthesized hydrophobic acrylic monomer is the focus of the chapters that follow. Is 2-octyl-dodecyl acrylate useful as a reactive hydrophobe in the mini-emulsion polymerization of various monomers? How effective is 2-octyl-dodecyl acrylate as an internal (reactive) plasticizer?

4.5 References

1. H.C. Brown, P.J. Geoghegan Jr., **Journal of Organic Chemistry**, 35, 6 (1970)
2. B.S.R. Reddy, **Journal of Polymer Materials**, 16, Issue 4, 271 (1999)
3. S. Balasubramanian, B.S.R. Reddy, **European Polymer Journal**, 32, No. 9, 1073 (1996)
4. B.S.R. Reddy, S. Balasubramanian, **European Polymer Journal**, 38, 803 (2002)
5. G. Socrates, **Infrared Characteristic Group Frequencies**, John Wiley and Sons, Second Edition, p204 (1994)

CHAPTER 5

Conventional Mini-emulsion Polymerizations Stabilized with SDS and 2-Octyl-dodecyl acrylate

CONTENTS

5.1 Introduction

5.2 Experimental

5.2.1 Reagents

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5.3.4 Comparison of the reactive hydrophobes 2-octyl-dodecyl acrylate, lauryl methacrylate and stearyl methacrylate

5.4 Conclusions

5.5 References

ABSTRACT

Mini-emulsions of butyl acrylate, methyl methacrylate and styrene with sodium dodecyl sulphate as surfactant and 2-octyl-dodecyl acrylate (2-ODA) as costabilizer were prepared and polymerized. The ability of 2-ODA to stabilize the polymer latexes against Ostwald ripening was investigated.

Keywords: mini-emulsion, reactive hydrophobe, diffusional degradation

5.1 Introduction

Science is not just the pursuit of novel concepts, but also the pursuit of novel alternatives, whether it is more economical alternatives and/or more effective alternatives. This study focused on the use of an effective novel alternative to the conventional hydrophobe (costabilizer) hexadecane in a mini-emulsion formulation.

The use of reactive acrylates and methacrylates as costabilizers (hydrophobes) in the mini-emulsion polymerization of various monomers is motivated by the need to eliminate low molecular weight hydrophobes, such as hexadecane, from the final polymer product. The presence of these unreactive low molecular weight costabilizers is undesirable for commercial applications as they are low molecular weight contaminants. The use of a reactive hydrophobe ensures that the hydrophobe becomes chemically incorporated into the final polymer product. Although the reactive hydrophobe is consumed during the polymerization process, the hydrophobic polymer formed should still act as an effective Ostwald ripening (diffusional degradation) suppressant.

Chern and Chen¹ successfully used the hydrophobic monomers lauryl methacrylate and stearyl methacrylate as reactive hydrophobes in the mini-emulsion polymerization of styrene. Alduncin and coworkers² and Reimers and Schork³ successfully used lauryl peroxide as reactive hydrophobe in the mini-emulsion polymerization of styrene and methyl methacrylate, respectively.

It must be noted that the effectiveness of the reactive hydrophobe strongly depends on its solubility in water (or lack thereof). The effectiveness of the reactive hydrophobe in suppressing Ostwald ripening increases as its water-solubility decreases.

The aim of this chapter is to show that 2-octyl-dodecyl acrylate can be used as an effective (reactive) hydrophobe, and equivalent to the model hydrophobe hexadecane, in the conventional mini-emulsion polymerizations of butyl acrylate, methyl methacrylate and styrene.

Does 2-octyl-dodecyl acrylate meet all the necessary criteria for a good (reactive) costabilizer? A good costabilizer should have a very low water-solubility, be monomer-soluble and of low molecular weight. All of the aforementioned criteria are met by 2-octyl-dodecyl acrylate. Thus, in theory, 2-octyl-dodecyl acrylate should be able to serve as a good costabilizer.

Four different experiments were performed for each monomer:

- *Experiment 1*: Formulation and polymerization of the mini-emulsion with the conventional hydrophobe hexadecane
- *Experiment 2*: Formulation and polymerization of the mini-emulsion with 2-octyl dodecyl acrylate as reactive hydrophobe
- *Experiment 3*: Formulation and polymerization of the mini-emulsion with no hydrophobe present, but with shearing (sonication)
- *Experiment 4*: Conventional emulsion polymerization of the three monomers^ψ

In all instances sodium dodecyl sulphate (SDS) was used as the surfactant.

The ability of 2-octyl-dodecyl acrylate to stabilize the mini-emulsions against Ostwald ripening was evaluated on the basis of the visual onset of phase separation for the different systems and their long-term stability. It was anticipated that the use of 2-octyl-dodecyl acrylate as reactive hydrophobe would result in final polymer latexes of at least comparable stability to those latexes where hexadecane was used as hydrophobe.

In addition, the ability of 2-octyl-dodecyl acrylate to stabilize the mini-emulsion formulations against Ostwald ripening was compared to that of the hydrophobic monomers lauryl methacrylate and stearyl methacrylate.

^ψ The conventional emulsion is defined here as an emulsion where no hydrophobe and no high shear force was used.

5.2 Experimental

5.2.1 Reagents

The monomers butyl acrylate, methyl methacrylate and styrene were purified by washing with a 10% KOH solution to remove the inhibitor and then distilled under reduced pressure. The oil-soluble initiator, azobisisobutyronitrile (AIBN), was recrystallized from methanol. The sodium dodecyl acrylate (SDS) [90%, BDH Laboratory Supplies] and hexadecane [99%, Aldrich] were used as received. The 2-octyl-dodecyl acrylate was synthesized as described in Section 4.2.2.2. Distilled and deionized (DDI) water was used in all the formulations.

5.2.2 Typical formulations

5.2.2.1 Mini-emulsions

The water (continuous) phase consisted of approximately 40 g DDI water and 1.0 g SDS (10 wt% of monomer). The oil (dispersed) phase consisted of approximately 10 g monomer, 16 mg AIBN and 500 mg hydrophobe (where applicable). The oil phase was added to the water phase in a beaker and stirred for 1 hour (prehomogenization). Thereafter, the reaction mixture was subjected to 10 minutes of ultrasonication at 80% amplitude (homogenization). This resulted in an average energy input of 98 kJ. The reaction mixture was then transferred to a 100-ml three-necked flask equipped with a magnetic stirrer bar. The reaction mixture was purged with argon gas for 15 minutes and thereafter immersed in an oil bath at 75 °C. The reactions were allowed to run for 2 hours with continuous stirring. Samples were taken at regular intervals. Monomer conversion was followed by means of gravimetric analysis.

5.2.2.2 *Emulsions*

A typical emulsion polymerization was as follows. Approximately 40 g DDI water, 1.0 g SDS, 10 g monomer and 16 mg AIBN were placed in a 100-ml three-necked flask equipped with a magnetic stirrer bar. The reaction mixture was purged for 15 minutes with argon gas and then immersed in an oil bath at 75 °C. The reaction was run for 2 hours. Samples were taken at regular intervals. Monomer conversion was followed by means of gravimetric analysis.

5.2.2.3 *Phase-separation studies*

All of the formulations for the phase-separation studies were prepared as described in Sections 5.2.2.1 and 5.2.2.2. The reaction mixtures were placed in sample vials at 25 °C and the rate of phase-separation before polymerization was observed. The average rate of phase-separation (given in cm/min) was determined by recording the time it took to visually observe a separation of 2.0 cm.

5.2.3 Characterization

All droplet and particle size analyses were done on a Malvern Zetasizer 1000 HS at a wavelength of 633 nm and a detector angle of 90°. The samples were diluted with a 1.0 mM NaCl solution.

For transmission electron microscopy (TEM) analysis, the latex was diluted to a ratio of 1:50 with water. The solution was transferred to a gold grid by means of a pipette. The grid was stained with uranyl acetate. Analyses were done on a Leo 912 TEM.

Capillary hydrodynamic fractionation (CHDF) analysis was performed using a Matec Applied Science CHDF 1100. The instrument was calibrated using polystyrene standards. The Key Centre for Polymer Colloids, University of Sydney, generously provided machine time. The samples were diluted with a 1.0 mM NaCl solution.

^{13}C -NMR analysis was done on a Varian Inova 400 MHz spectrometer with a 5-mm dual broadband probe with pulsed field gradient (PFG). The sample was dissolved in CDCl_3 and TMS was used as internal standard.

5.3 Results and Discussion

5.3.1 Mini-emulsion polymerization of butyl acrylate with 2-octyl-dodecyl acrylate as reactive hydrophobe

5.3.1.1 Rate of polymerization studies

Figure 5.1 shows the progression of the conversion with time for the mini-emulsion and emulsion polymerization of butyl acrylate. In the case of the mini-emulsion polymerizations, the stabilization system was one of the following: either hexadecane/SDS or 2-ODA/SDS. All formulations were as given in Table 5.1.

It can be seen from Figure 5.1 that all of the polymerizations were very fast. After only 20 minutes, conversions of 85, 80, 91 and 87% were obtained for reactions 1, 2, 3 and 4, respectively. The amount of surfactant (10 wt % of monomer) used in the various reactions could be responsible for these fast reaction rates. The amount of surfactant determines the size of the particles, and hence, the number of particles produced in a mini-emulsion system, for an optimally homogenized system. This in turn affects the rate of polymerization. The more particles formed, the faster the rate of polymerization.

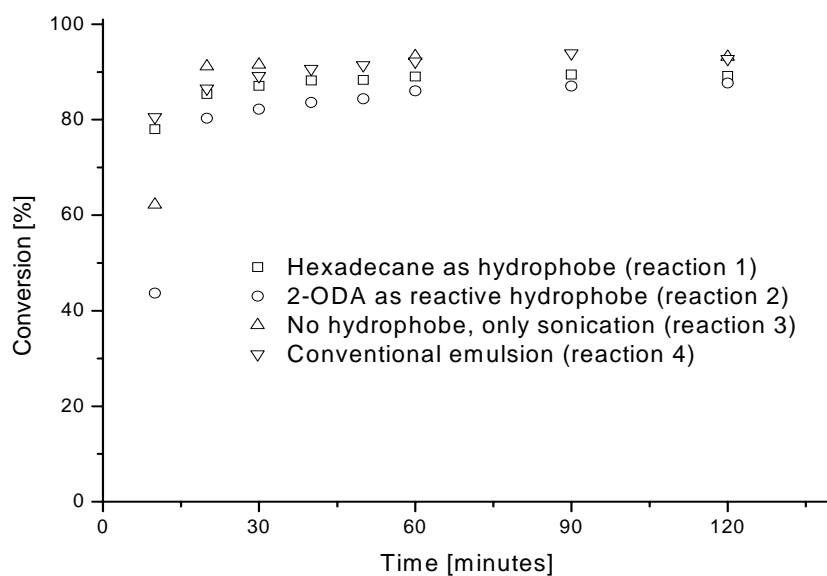


Figure 5.1 Graph of conversion versus time for the emulsion and mini-emulsion polymerizations of butyl acrylate.

Table 5.1

Formulations for the emulsion and mini-emulsion polymerizations of butyl acrylate

Reaction	1	2	3	4
<i>Water phase</i>				
SDS (g)	1.00 ^a	1.00 ^a	1.00 ^a	1.00
DDI water (g)	40.3	41.7	40.2	40.6
<i>Oil phase</i>				
BA (g)	10.0	10.0	10.0	10.0
HD (g)	0.46			
2-ODA (g)		0.47 ^b		
AIBN (g)	0.015	0.015	0.016	0.016
<i>Sonication</i>				
Sonication time (min)	10	10	10	
Sonication amplitude (%)	80	80	80	
Sonication energy (kJ)	101	98	98	

^a Approximately 2.5 wt % of continuous phase

^b 1.65 mol % in feed relative to BA

5.3.1.2 *Particle size studies*

Table 5.2 shows the average particle sizes of the emulsion and mini-emulsion poly(butyl acrylate) latexes. It can be seen from Table 5.2 that the average particle sizes of the prepared emulsion and mini-emulsions ranged from 73 nm to 103 nm, as determined by dynamic light scattering.

An average particle size of $73.0 \text{ nm} \pm 0.7 \text{ nm}$ was obtained for the mini-emulsion with 2-ODA as reactive hydrophobe (reaction 2), as determined by dynamic light scattering. The average particle size obtained for the mini-emulsion with 2-ODA as reactive hydrophobe was confirmed by TEM (Image 5.1) and CHDF analysis (Figure 5.2). The average particle size, from the TEM image, was calculated by making use of a weighted average of the values obtained via TEM. The average particle size was calculated to be $71.0 \text{ nm}^{\#}$. The average particle sizes as determined by CHDF analysis were $66.8 \text{ nm} \pm 18.9 \text{ nm}$ (by number) and $72.6 \text{ nm} \pm 19.1 \text{ nm}$ (by weight).

The average particle size data for reactions 1, 3, and 4 are as listed in Table 5.2^Y.

Table 5.2

Average particle sizes of poly(butyl acrylate) latexes

Reaction ^a	1	2	3	4
Hydrophobe	Hexadecane	2-ODA	None	None
Particle size [nm] ^b	89 ± 0.4	73 ± 0.7	94 ± 1.2	103 ± 0.5
Particle size [nm] ^c	83.0 ± 24.2	66.8 ± 18.9	85.3 ± 24.2	89.3 ± 24.5
Particle size [nm] ^d	87.9 ± 18.8	72.6 ± 19.1	90.9 ± 20.6	94.9 ± 21.4

^a Reactions are defined in Table 5.1

^b Average particle sizes as determined by dynamic light scattering

^c Average particle size (by number) as determined by CHDF

^d Average particle size (by weight) as determined by CHDF

[#] See Appendix A

^Y See Appendix B for CHDF results.

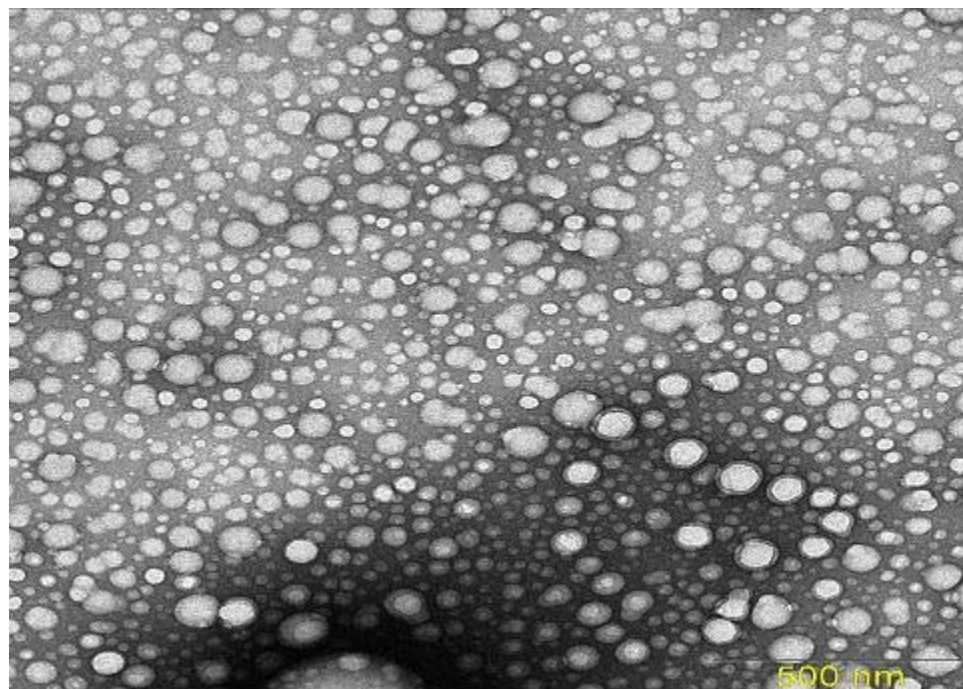


Image 5.1 TEM image of poly(butyl acrylate) latex particles with 2-octyl-dodecyl acrylate as hydrophobe in the mini-emulsion polymerization of butyl acrylate.

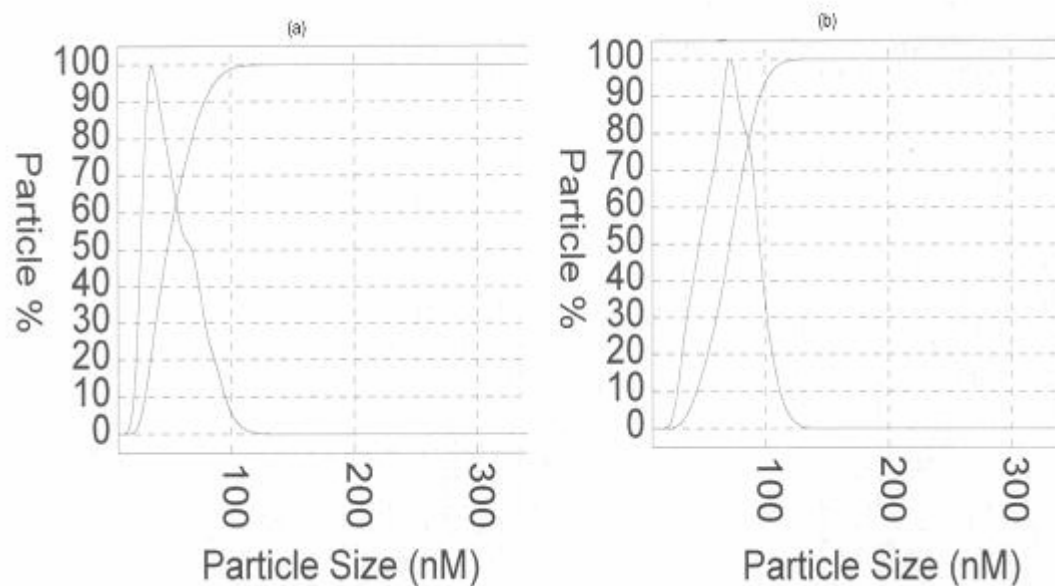


Figure 5.2 CHDF results of poly(butyl acrylate) latex particles with 2-octyl-dodecyl acrylate as hydrophobe in the mini-emulsion polymerization of butyl acrylate: (a) number average particle size and (b) weight average particle size.

The amount of surfactant used in this study (approximately 2.5 wt % of the continuous phase) is one of the major factors responsible for the obtained particle sizes, besides the sonication time. It must be noted that in the case of optimally homogenized systems the particle size is only dependent on the surfactant concentration. There are three major advantages of using high concentrations of surfactant. The first is a corresponding decrease in particle size. It is well documented that the particle size decreases with an increasing amount of surfactant. Van Zyl and coworkers reported a decrease in particle size from 87.8 nm to 36.0 nm by increasing the surfactant concentration from 0.10 to 2.0 wt % of the continuous phase in the mini-emulsion polymerization of butyl acrylate⁴. Landfester and Antonietti reported a similar trend for the mini-emulsion polymerization of styrene⁵. They showed that by varying the concentration of surfactant from 0.30 to 50 wt % relative to styrene the particle size decreased from 182 nm to 32 nm. The authors reported that only in the case of the highest surfactant load (50 wt % SDS of styrene) did they observe a dense surface layer and a surface tension value typical for a micellar phase.

The second major advantage is an increase in the number of particles, which translates into faster polymerization rates (as stated above). The third major advantage is that the steady-state dispersed mini-emulsions are critically stabilized with respect to colloidal stability.

The aforementioned results indicate that dynamic light scattering gives reliable average particle size data compared to TEM and CHDF. Thus, only dynamic light scattering (DLS) was used in Sections 5.3.2 and 5.3.3 for the determination of the average particle sizes, due to the fact that the DLS equipment was more readily available than the TEM and CHDF equipment.

5.3.1.3 Phase-separation and stability studies

It was envisaged that the use of the novel reactive hydrophobe, 2-octyl-dodecyl acrylate, would result in a mini-emulsion that was not only kinetically stable (stable for the polymerization time), but thermodynamically stable, in other words, that it would exhibit long-term stability. Hence, it was necessary to compare the rate of phase-separation of the various emulsion and mini-emulsion formulations.

Looking at the rate of phase-separation for the different butyl acrylate emulsion and mini-emulsion formulations used in this study, the following observations were made. The rate of phase-separation for the conventional emulsion (no hydrophobe and no high shear) was determined to be 0.24 cm/min. The mini-emulsions with hexadecane and 2-ODA as hydrophobes exhibited rates of phase-separation of $< 5.0 \times 10^{-5}$ cm/min (no visible signs of phase-separation after 4 weeks). In the case where only sonication, and no hydrophobe, was used, the rate of phase-separation was 0.12 cm/min. In other words, phase-separation was at least a 2400 times faster in the mini-emulsion in which a hydrophobe was absent (Figure 5.3 and Image 5.2).

The mini-emulsions in which hexadecane and 2-ODA were used as hydrophobes exhibited long-term stability (longer than 4 months). The results indicate that 2-ODA retards Ostwald ripening and allows the production of stable mini-emulsions.

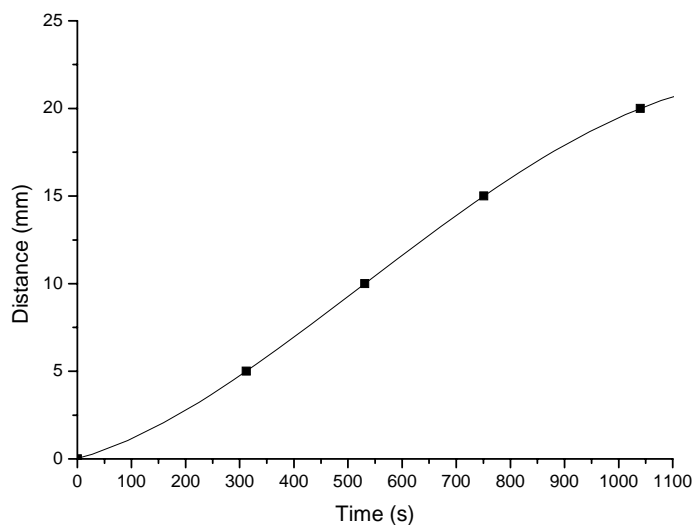


Figure 5.3 Graph of distance versus time for the phase-separation of the butyl acrylate mini-emulsion formulation with no hydrophobe present. [An observation distance of 20 mm was chosen.]

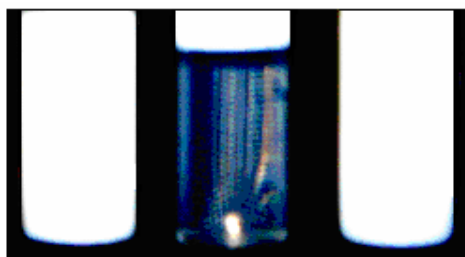


Image 5.2 Butyl acrylate mini-emulsion formulations. Left to right: hexadecane as hydrophobe (stable mini-emulsion), no hydrophobe (extensive phase-separation observed) and 2-octyl-dodecyl acrylate as hydrophobe (stable mini-emulsion).

5.3.1.4 Investigation of the incorporation of 2-octyl-dodecyl acrylate

Figure 5.4 shows the 0 to 40 ppm region of in the ^{13}C -NMR spectrum of the butyl acrylate/2-octyl-dodecyl acrylate copolymer. The signals labelled a, b and c have chemical shifts of 14.2, 22.6 and 31.9 ppm, respectively, corresponding to carbon atoms contained in 2-octyl-dodecyl acrylate. No peaks were observed in the region of 129.3 and

130.5 ppm. Such peaks would have corresponded to the vinylic carbons of 2-octyl-dodecyl acrylate. It can thus be concluded that 2-octyl-dodecyl acrylate does indeed become chemically incorporated, and therefore acts as a reactive hydrophobe.

The amount of 2-octyl-dodecyl acrylate incorporated into the copolymer was quantified by making use of ^{13}C -NMR. Based on the T1 measurements for quantitative conditions, a 60 degree pulse width was used with a 2.3 s acquisition time at a 1 s pulse delay. Inverse gated decoupling was used. The sample was run overnight. Integration of the obtained quantitative ^{13}C -NMR spectrum was performed. The quantity of 2-octyl-dodecyl acrylate incorporated into the butyl acrylate/2-octyl-dodecyl acrylate copolymer was calculated to be 0.8 mol % (0.22 g).

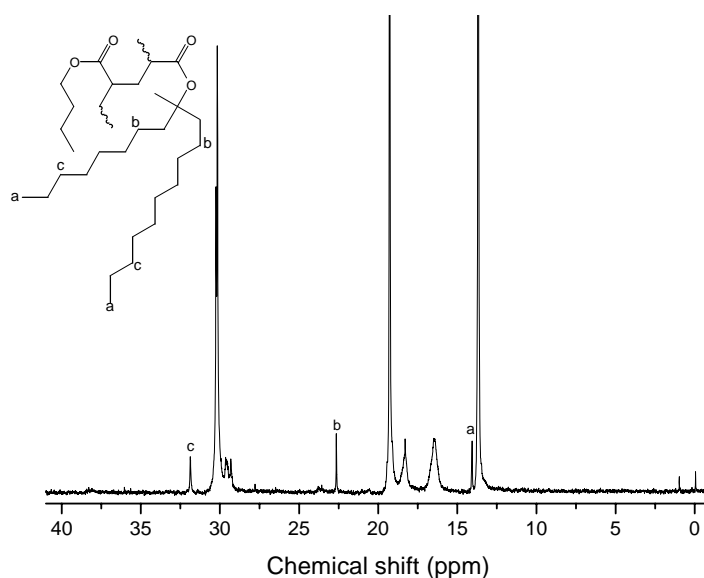


Figure 5.4 ^{13}C -NMR spectrum of the butyl acrylate/2-octyl-dodecyl acrylate copolymer, in deuterated chloroform, in the region 0 ppm to 40 ppm.

5.3.2 Mini-emulsion polymerization of methyl methacrylate with 2-octyl-dodecyl acrylate as reactive hydrophobe

5.3.2.1 Rate of polymerization studies

Figure 5.5 shows the progression of the conversion with time for the mini-emulsion and emulsion polymerization of methyl methacrylate. Either hexadecane/SDS or 2-ODA/SDS was used to stabilize the mini-emulsions. All formulations were as tabulated in Table 5.3.

Figure 5.5 shows that, again, the polymerization rates for the different systems are fast. Conversions were 82%, 59%, 76% and 77% after 30 minutes for reactions 1, 2, 3 and 4, respectively.

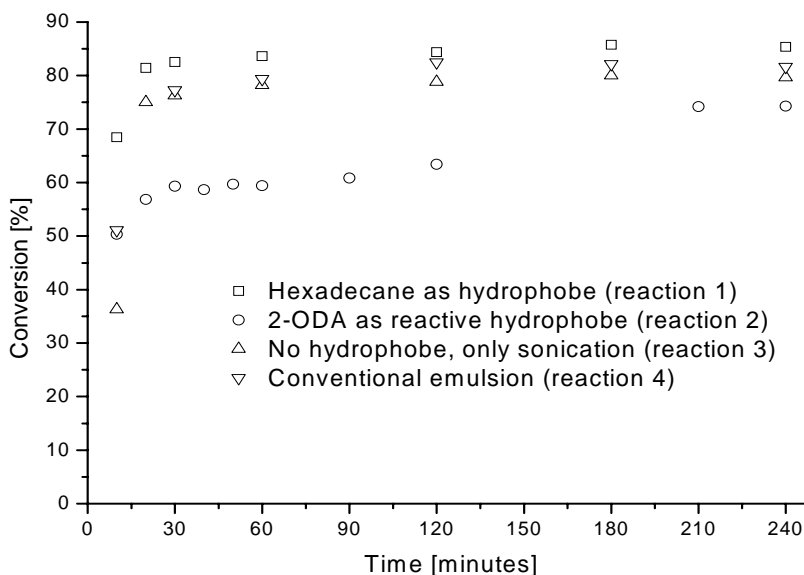


Figure 5.5 Graph of conversion versus time for the emulsion and mini-emulsion polymerizations of methyl methacrylate.

Table 5.3

Formulations for the emulsion and mini-emulsion polymerizations of methyl methacrylate

Reaction	1	2	3	4
<i>Water phase</i>				
SDS (g)	1.00 ^a	1.00 ^a	1.00 ^a	1.00
DDI water (g)	41.2	40.2	40.2	40.1
<i>Oil phase</i>				
MMA (g)	10.0	10.0	10.0	10.1
HD (g)	0.45			
2-ODA (g)		0.48 ^b		
AIBN (g)	0.015	0.015	0.016	0.015
<i>Sonication</i>				
Sonication time (min)	10	10	10	
Sonication amplitude (%)	80	80	80	
Sonication energy (kJ)	97	98	98	

^a Approximately 2.5 wt % of continuous phase^b 1.65 mol % in feed relative to MMA

5.3.2.2 *Particle size studies*

The average particle sizes for the poly(methyl methacrylate) latexes, as determined by dynamic light scattering, ranged from 54 nm to 84 nm (Table 5.4). The obtained particle sizes can, once again, be mainly ascribed to the surfactant concentration (Section 5.3.1). Once again smaller particles were obtained with 2-octyl-dodecyl acrylate as hydrophobe due to its possible surface activity.

Table 5.4

Average particle sizes of poly(methyl methacrylate) latexes

Reaction ^a	1	2	3	4
Hydrophobe	Hexadecane	2-ODA	None	None
Particle size [nm] ^b	67.2 ± 1.5	54.1 ± 1.1	83.8 ± 2.1	83.6 ± 1.7

^a Reactions are defined in Table 5.3^b Average particle sizes as determined by dynamic light scattering

5.3.2.3 *Phase-separation and stability studies*

The rates of phase-separation for the different methyl methacrylate emulsion and mini-emulsion formulations were as follow. The rate of phase-separation for the conventional emulsion (no hydrophobe and no high shear) was determined to be 0.22 cm/min. In the case where only sonication, and no hydrophobe, was used the rate of phase-separation was 0.13 cm/min. The mini-emulsions in which hexadecane and 2-ODA were used as hydrophobes exhibited rates of phase-separation of $< 5.0 \cdot 10^{-5}$ cm/min (no visible signs of phase-separation after 4 weeks). In other words, phase-separation was at least 2400 times faster in the mini-emulsion where a hydrophobe was absent (Figure 5.6 and Image 5.3).

As expected from the results obtained with butyl acrylate (Section 5.3.1), the mini-emulsions containing hexadecane and 2-ODA as hydrophobes displayed long-term stability (months).

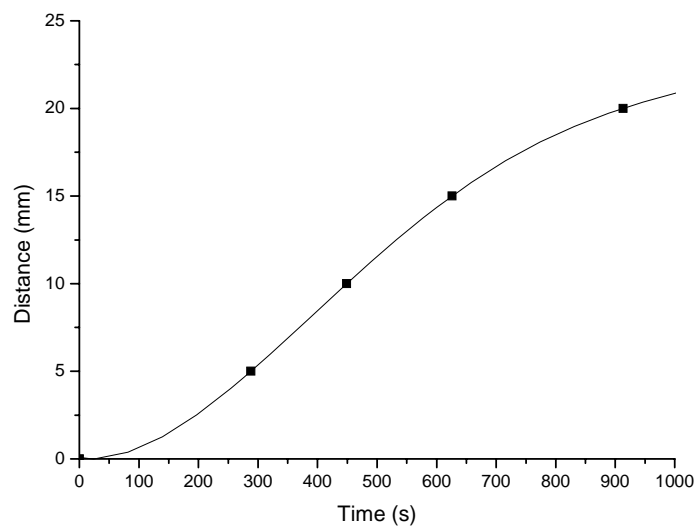


Figure 5.6 Graph of distance versus time for the phase-separation of a methyl methacrylate mini-emulsion formulation with no hydrophobe present. [An observation distance of 20 mm was chosen.]

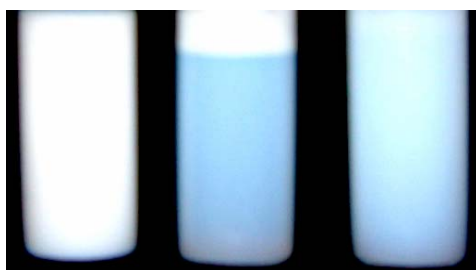


Image 5.3 Methyl methacrylate mini-emulsion formulations. Left to right: hexadecane as hydrophobe (stable mini-emulsion), no hydrophobe (extensive phase-separation observed) and 2-octyl-dodecyl acrylate as hydrophobe (stable mini-emulsion).

5.3.3 Mini-emulsion polymerization of styrene with 2-octyl-dodecyl acrylate as reactive hydrophobe

5.3.3.1 Rate of polymerization studies

Figure 5.7 shows the progression of the conversion with time for the mini-emulsion and emulsion polymerization of styrene. Either hexadecane/SDS or 2-ODA/SDS was once again used to stabilize the mini-emulsions. All formulations were as given in Table 5.5.

The respective conversions for the different reactions after 1 hour were 87.8% (reaction 1), 87.9% (reaction 2), 82.8% (reaction 3) and 55.4% (reaction 4) (see Figure 5.7). As to be expected, the polymerization rate for the conventional styrene emulsion is much slower than that of all the other reactions. The observed difference in the polymerization rates is related to the local monomer and radical concentrations in the droplets versus the particles.

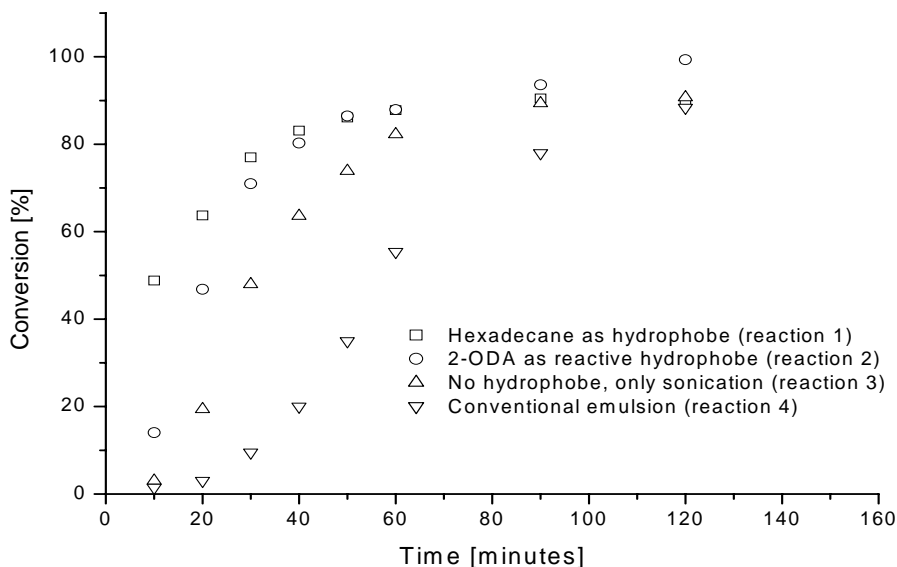


Figure 5.7 Graph of conversion versus time for the emulsion and mini-emulsion polymerizations of styrene.

Table 5.5

Formulations for the emulsion and mini-emulsion polymerizations of styrene

Reaction	1	2	3	4
<i>Water phase</i>				
SDS (g)	1.03 ^a	1.00 ^a	1.04 ^a	1.00
DDI water (g)	40.8	40.0	40.6	40.4
<i>Oil phase</i>				
Styrene (g)	10.0	10.0	10.1	10.0
HD (g)	0.49			
2-ODA (g)		0.48 ^b		
AIBN (g)	0.019	0.020	0.019	0.018
<i>Sonication</i>				
Sonication time (min)	10	10	10	
Sonication amplitude (%)	80	80	80	
Sonication energy (kJ)	98	98	98	

^a Approximately 2.5 wt % of continuous phase^b 1.65 mol % in feed relative to styrene

The polymerization rate of the conventional emulsion polymerization of styrene is much slower compared to that of methyl methacrylate (Figure 5.5, reaction 4) and butyl acrylate (Figure 5.1, reaction 4). The polymerization rates for the methyl methacrylate and butyl acrylate emulsions are much faster due to their higher propagation rate coefficients compared to styrene and the difference in the radical concentrations. Comparing the polymerization rate of the styrene mini-emulsion polymerizations to those of the methyl methacrylate and butyl acrylate, it is once again noticeable that the polymerization rates of the styrene mini-emulsion polymerizations are much slower. The lower reactivity of the styrene compared to methyl methacrylate and butyl acrylate is largely responsible for the observed slower polymerization rate.

5.3.3.2 *Particle size studies*

The average particle sizes for the polystyrene latexes, as determined by dynamic light scattering, ranged from 65.4 nm to 92.2 nm (Table 5.6). Once again, the obtained particle sizes could largely be ascribed to the concentration of the surfactant.

Table 5.6

Average particle sizes of polystyrene latexes

Reaction ^a	1	2	3	4
Hydrophobe	Hexadecane	2-ODA	None	None
Particle size [nm] ^b	64.7 ± 0.6	65.4 ± 2.1	88.8 ± 1.8	92.2 ± 1.8

^a Reactions are defined in Table 5.5

^b Average particle sizes as determined by dynamic light scattering

5.3.3.3 *Phase-separation and stability studies*

The rates of phase-separation for the different styrene emulsion and mini-emulsion formulations were as follow. The rate of phase-separation for the conventional emulsion (no hydrophobe and no high shear) was determined to be 0.28 cm/min. The mini-emulsions in which hexadecane and 2-ODA were used as hydrophobes exhibited rates of phase-separation of $< 5.0 \times 10^{-5}$ cm/min (no visible signs of phase-separation after 4 weeks). In the case where only sonication, and no hydrophobe, was used the rate of phase-separation was 0.13 cm/min. In other words, phase-separation was at least 2400 times faster in the mini-emulsion in which a hydrophobe was absent (Figure 5.8 and Image 5.4).

A comparison of the shelf-life (stability) of the aforementioned styrene mini- emulsion polymerization latexes reveals that the use of 2-octyl-dodecyl acrylate as reactive hydrophobe imparts long-term stability (months) to the latex particles.

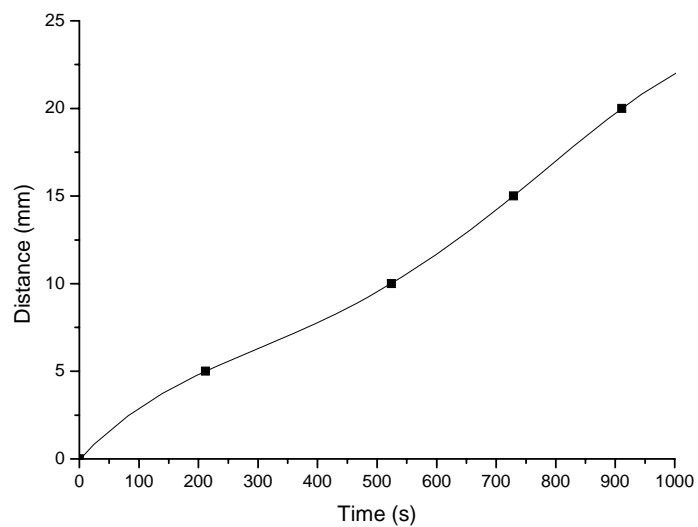


Figure 5.8 Graph of distance versus time for the phase-separation of the styrene mini-emulsion formulation with no hydrophobe present. [An observation distance of 20 mm was chosen.]

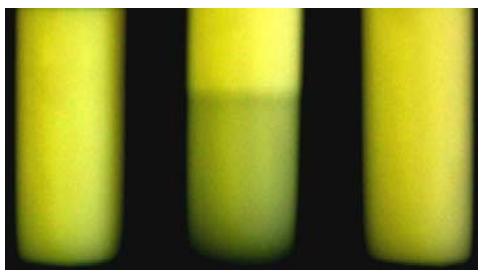


Image 5.4 Styrene mini-emulsion formulations. Left to right: hexadecane as hydrophobe (stable mini-emulsion), no hydrophobe (extensive phase-separation observed) and 2-octyl-dodecyl acrylate as hydrophobe (stable mini-emulsion).

5.3.4 Comparison of the reactive hydrophobes 2-octyl-dodecyl acrylate, lauryl methacrylate and stearyl methacrylate

Mini-emulsion formulations of butyl acrylate, methyl methacrylate and styrene with the reactive hydrophobes 2-octyl-dodecyl acrylate, lauryl methacrylate and stearyl methacrylate were prepared as described in Section 5.2.2.3. An observation period of one month was chosen for the phase-separation experiments. No phase-separation was observed for all of the formulations with 2-octyl-dodecyl acrylate and stearyl methacrylate. In the case of lauryl methacrylate, phase-separation was observed after approximately three weeks for all of the formulations.

Do the mini-emulsions with 2-octyl-dodecyl acrylate as hydrophobe qualify as true mini-emulsions?

The average particle sizes (as determined by dynamic light scattering) for the poly(butyl acrylate), poly(methyl methacrylate) and polystyrene latexes were $73 \text{ nm} \pm 0.7 \text{ nm}$, $51.9 \text{ nm} \pm 0.5 \text{ nm}$ and $65.4 \text{ nm} \pm 2.1 \text{ nm}$, which is typical of mini-emulsions. These particle sizes correspond very well with previously reported particle sizes by Landfester and Antonietti for similar mini-emulsion systems⁵. The obtained small particle sizes, and hence large surface areas, give an indication that most (if not all) of the surfactant is adsorbed onto the surface of the particles. Thus, very little (if any) free surfactant would have been available for micelle-formation or to stabilize aqueous-phase polymerization. Consequently, micellar and homogeneous nucleation would be limited to a large extent. In addition, the use of an oil-soluble (hydrophobic) initiator also limits the existence of radicals in the aqueous phase. As a result, we have to assume that droplet nucleation predominates.

A one-to-one copy of droplet size compared to particle size was obtained for all the mini-emulsions in which 2-octyl-dodecyl acrylate was used as reactive hydrophobe. No major discrepancies between the droplet sizes and particle sizes of the various mini-emulsions

were observed. Table 5.7 tabulates the droplet sizes and particle sizes of the mini-emulsions prepared with 2-octyl-dodecyl acrylate as reactive hydrophobe.

Table 5.7

Comparison of the droplet sizes and particle sizes of the mini-emulsions prepared with 2-octyl-dodecyl acrylate as reactive hydrophobe

Monomer	Butyl acrylate	Methyl methacrylate	Styrene
Droplet size [nm] ^a	69.8 ± 0.6	50.4 ± 1.6	77.0 ± 1.6
Particle size [nm] ^b	73.0 ± 0.7	54.1 ± 1.1	65.4 ± 2.1

^a Average droplet sizes as determined by dynamic light scattering

^b Average particle sizes as determined by dynamic light scattering

Furthermore, 2-octyl-dodecyl acrylate qualifies as a very good hydrophobe due to its chemical nature. Chern and Chen¹ reported the estimated values for the water-solubility of hexadecane and stearyl methacrylate to be 1.14×10^{-9} mL/mL and 3.23×10^{-9} mL/mL, respectively. The water solubility of 2-octyl-dodecyl acrylate can be estimated to be at least comparable to that of stearyl methacrylate, based on chemical structure comparisons. It is thus safe to assume that 2-octyl-dodecyl acrylate will exhibit poor water solubility due to its ultra-hydrophobic component. The other criteria for a good hydrophobe, such as low molecular weight and monomer-solubility, are also met by 2-octyl-dodecyl acrylate.

5.4 Conclusions

The presence of 2-octyl-dodecyl acrylate in the dispersed phase resulted in a sufficient osmotic pressure that significantly retarded Ostwald ripening. This is evidenced by the results obtained from the phase-separation studies. The average rates of phase-separation for the butyl acrylate, methyl methacrylate and styrene mini-emulsion formulations were at least 2400 times slower than for the formulations with no hydrophobe present. It must

be noted that after 4 weeks no visible sign of phase-separation was observable for the mini-emulsion formulations in which 2-octyl-dodecyl acrylate was used as hydrophobe.

Finally, the results show that 2-octyl-dodecyl acrylate is capable of producing stable latex products. In all instances where 2-octyl-dodecyl acrylate was used as hydrophobe, the obtained mini-emulsions displayed long-term stability (months).

5.5 References

1. C.S. Chern, T.J. Chen, **Colloid Surfaces A: Physiochemical and Engineering Aspects**, 138, 65 (1998)
2. J.A. Alduncin, J. Forcada, J.M. Asua, **Macromolecules**, 27, 2256 (1994)
3. J.L. Reimers, F.J. Schork, **Industrial Engineering and Chemistry Research**, 36, 1085 (1997)
4. A.J.P. Van Zyl, D. De Wet-Roos, R.D. Sanderson, B. Klumperman, **European Polymer Journal**, 40, 2717 (2004)
5. K. Landfester, M. Antonietti, **Progress in Polymer Science**, 27, 689 (2002)

CHAPTER 6

Preparation of Polystyrene/Poly(styrene-co-2-octyl-dodecyl acrylate) Blends: Investigation of the Thermo-mechanical Behaviour of the Blends

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- 6.1 Introduction**
- 6.2 Experimental**
 - 6.2.1 Reagents
 - 6.2.2 Copolymerization
 - 6.2.3 Blending studies
 - 6.2.4 Characterization
- 6.3 Results and Discussion**
 - 6.3.1 Synthesis of high molecular weight styrene/2-octyl-dodecyl acrylate copolymers
 - 6.3.2 Thermo-mechanical behaviour of blends of polystyrene with high molecular weight styrene/2-octyl-dodecyl acrylate copolymers
 - 6.3.3 Synthesis of low molecular weight styrene/2-octyl-dodecyl acrylate copolymers
 - 6.3.4 Thermo-mechanical behaviour of blends of polystyrene with low molecular weight styrene/2-octyl-dodecyl acrylate copolymers
- 6.4 Conclusions**
- 6.5 References**

ABSTRACT

The novel acrylic monomer, 2-octyl-dodecyl acrylate, was copolymerized with styrene via conventional free-radical polymerization. Blends of virgin polystyrene and the synthesized low- and high-molecular-weight copolymers were prepared. The thermo-mechanical properties of the obtained copolymers and blends were investigated.

Keywords: copolymerization, glass transition temperature, loss modulus, blends, toughening, plasticization

6.1 Introduction

The ongoing need for new polymeric materials has warranted the development of different methods of preparation for such polymeric materials to meet this demand. The three main methods, in use today, for the creation and development of new polymeric materials include the synthesis of new polymers from new monomers, copolymerization (random, alternating, gradient, block or graft) and physical blending of polymers.

Blending of two or more polymers, whether to make new materials or to improve the properties of an existing polymer, is a widely used practice due to its cost-effectiveness. However, the blending of polymers is most often plagued by the problem of the compatibility of the blended components. Immiscibility of the blended polymers leads to weak interaction of the different phases, resulting in a product with poor mechanical properties. Various researchers have made use of polymeric compatibilizers to overcome the compatibility problem. Examples of these are given in Chapter 2 (Section 2.4.3). In addition, the modification of the properties of a homopolymer by blending it with a copolymer (block, grafted or random), with one of its constituents being the homopolymer in question, is another possible approach that can be used to minimize the incompatibility of the different phases^{1,2}. In this study the previously mentioned approach was used to modify the thermo-mechanical properties of polystyrene. Glassy polymers, like polystyrene, are generally characterized as having poor toughness, which limits the application of these polymers. Over the last three decades, extensive research has gone into improving the toughness of glassy polymers.

In an effort to synthesize new polymeric materials with improved damping properties (viscous dissipation) and toughness (which is a combination of tensile strength and ductility) properties, the synthesis of various styrene copolymers and blends are reported. Applications for which materials with low-temperature flexibility and toughness as well as moisture resistance are required, are ideal markets for these materials. Dynamic mechanical analysis was used to monitor any changes in the damping and toughness properties of the copolymers and blends.

The purpose of this study was to investigate the ability of the novel hydrophobic, 'bushy-tailed' acrylic monomer, 2-octyl-dodecyl acrylate, to serve as a reactive modifier³⁻⁶. Due to the nature of the newly synthesized acrylic monomer it was expected that an increased flexibility and extensibility would be introduced into the obtained copolymers. How much (or how little) of the novel monomer would be adequate to modify the thermo-mechanical properties of the glassy polystyrene appreciably was investigated.

'Random' copolymers of styrene and 2-octyl-dodecyl acrylate with high (targeted \overline{M}_w between 50 000 and 100 000 g/mol) and low (targeted \overline{M}_w between 5 000 and 20 000 g/mol) molecular weights were prepared via conventional free-radical copolymerization.

¹H-NMR spectroscopy was used to determine the level of incorporation of 2-octyl-dodecyl acrylate into the various copolymers when starting with a specific feed ratio of styrene to 2-octyl-dodecyl acrylate.

Blends of polystyrene with the newly synthesized high- and low-molecular-weight copolymers were prepared. The thermo-mechanical properties of the blends were investigated.

Important note: Realizing the importance of knowing the reactivity ratios of any monomer pair, an attempt was first made to calculate the reactivity ratios for the monomers used in this study. However, this attempt was unsuccessful. This was due to the fact that it was not possible to form a true copolymer at low conversions under the experimental conditions used here. Future study might shed some light on this current unknown.

6.2 Experimental

6.2.1 Reagents

The 2-octyl-dodecyl acrylate was synthesized as described in Section 4.2. The styrene was washed with a 10% KOH solution and distilled under reduced pressure prior to use. The AIBN (initiator) was recrystallized from methanol. THF (99%) was received from Saarchem and used as received. Chloroform (99.8%) was received from ProChem and used as received. Polystyrene ($\overline{M}_w = 137\ 000$ g/mol, PDI = 2.15) was obtained from BDH Laboratory Reagents.

6.2.2 Copolymerization

6.2.2.1 High molecular weight copolymers

A typical copolymerization was carried out as follows. The monomers, solvent and initiator (0.1 wt%) were added to a three-neck flask. The reaction mixture was degassed with argon for approximately 15 minutes. The reaction vessel was placed in an oil bath at 65 °C for 24 hours. The overall conversion was determined via $^1\text{H-NMR}$ spectroscopy, using 1,3,5-trioxane as internal standard. The copolymers were repeatedly precipitated in methanol, dried and then redissolved in chloroform to remove the unreacted monomers.

6.2.2.2 Low molecular weight copolymers

The monomers, solvent and initiator (5 wt % of total monomer content) were added to a three-neck flask. The reaction mixture was degassed with argon for approximately 15 minutes. The reaction vessel was placed in an oil bath at 65 °C for 24 hours. Samples were taken at predetermined intervals. The overall conversion was determined via $^1\text{H-NMR}$ spectroscopy, using 1,3,5-trioxane as internal standard. The copolymers were repeatedly precipitated in methanol, dried and then redissolved in chloroform to remove the unreacted monomers.

6.2.3 Blending studies

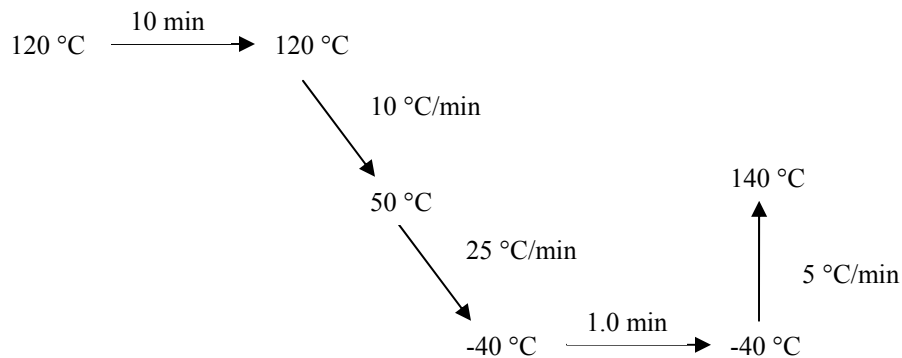
A typical blending procedure was as follows for a 100-mg sample. The virgin polystyrene and the appropriate fraction of either the low- or high-molecular-weight copolymer were dissolved in chloroform and mixed. The chloroform was allowed to evaporate at a temperature of 40 °C and a pressure of 200 mbar for 48 hours. Thereafter each sample was further dried at 130 °C for 24 hours at 200 mbar to ensure that all of the solvent was removed.

6.2.4 Characterization

The ¹H-NMR spectra of the copolymers were run on a VarianVXR 300 MHz spectrometer. The samples were dissolved in CDCl₃ and TMS was used as internal standard.

The molecular weights and molecular weight distributions of all samples (sample concentration: 5 mg/mL; injection volume: 100 μL) were determined on a Waters 600E instrument, fitted with a Waters 610 fluid unit, Waters 410 differential refractometer and a Waters 717_{plus} autosampler. THF (purged with IR-grade helium) was used as mobile phase, at a flow rate of 1.0 mL/min, and the column temperature was 30 °C. Four Phenogel columns, with respective pore sizes of 100, 10³, 10⁴ and 10⁵ Å, were used in series. The system was calibrated using narrow molecular weight polystyrene standards.

Dynamic mechanical analysis (DMA) was performed on a Perkin-Elmer DMA 7e instrument fitted with an intercooler. Analyses were performed in a nitrogen atmosphere, using a flow rate of 28.5 mL/min. The following DMA temperature gradient (heat-cool-heat cycle) was used:

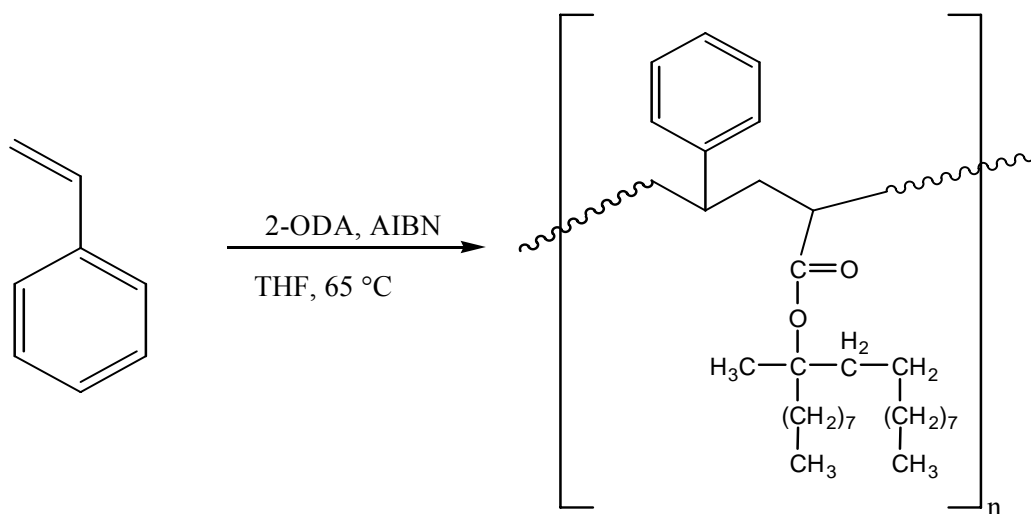


Scheme 6.1 Temperature gradient used for dynamic mechanical analysis.

6.3 Results and Discussion

6.3.1 Synthesis of high molecular weight styrene/2-octyl-dodecyl acrylate copolymers

Several high-molecular-weight copolymers of styrene and 2-octyl-dodecyl acrylate were synthesized (Scheme 6.2). The feed compositions consisted of 1.0, 3.0, 5.0 and 7.0 mol % of 2-ODA. The syntheses of the copolymers were confirmed by $^1\text{H-NMR}$ spectroscopy (see Figure 6.1).



Scheme 6.2 Schematic representation of the copolymerization of styrene and 2-octyl-dodecyl acrylate.

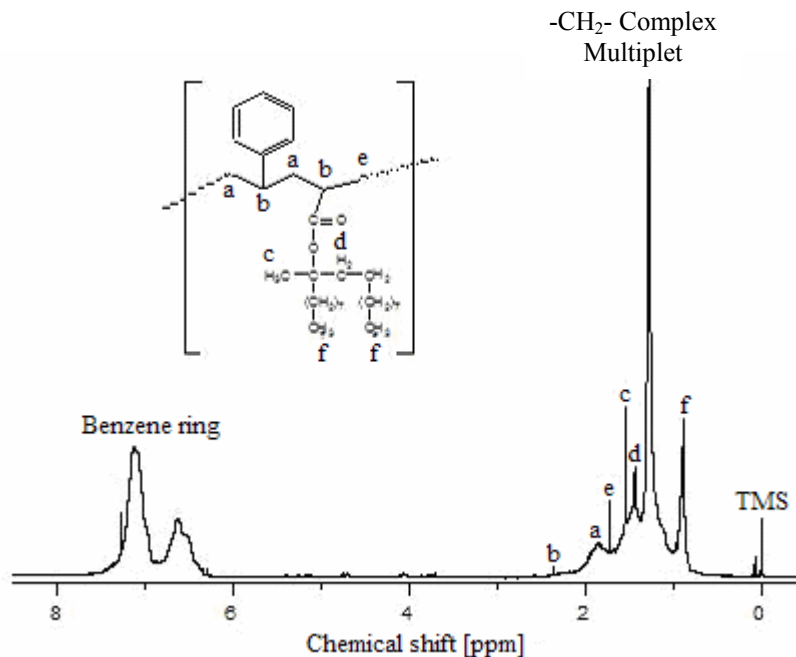


Figure 6.1 ¹H-NMR spectrum of poly(styrene-co-2-ODA) in CDCl₃ with TMS as internal standard; 7.0 mol % of 2-ODA in copolymer.

Due to the fact that acrylic monomers are generally more reactive than styrenic monomers, it could be predicted that 2-octyl-dodecyl acrylate would be incorporated into the copolymer at a higher rate than styrene. Thus, it could be assumed that 'blocky' random copolymers were formed.

The compositions, overall conversions, average molecular weights, molecular weight distributions (PDI) and glass transition temperatures (T_g) of the copolymers are presented in Table 6.1. It must be noted that the copolymers were 'random' copolymers. Table 6.1 shows that average molecular weights (\overline{M}_w) of between 50 000 and 80 000 g/mol and polydispersities ranging from 1.73 to 1.79 were obtained for the styrene/2-octyl-dodecyl acrylate copolymers synthesized. The overall conversions for the copolymers were above 80%.

The T_g values of the styrene/2-octyl-dodecyl acrylate copolymers, as determined by DMA analysis, were measured as the onset temperature of the loss tangent ($\tan \delta$) peaks. A shift of the T_g values to lower temperatures was observed for all of the copolymers. Glass transition temperatures of 74.5 °C, 57.4 °C, 50.0 °C and 47.9 °C were observed for copolymers A, B, C and D, respectively. A difference of 52.1 °C between the T_g of the virgin polystyrene (assuming a T_g of 100 °C) and copolymer D (7.0 mol % 2-ODA incorporated) was observed. The difference in the T_g values of the copolymers with 1.0 mol % and 7.0 mol % 2-ODA incorporated is 26.6 °C (see Figure 6.2). Figure 6.2 also shows that the $\tan \delta_{\max}$ for copolymer D is higher than that of copolymer A. This implies an increase in the main chain mobility with increasing 2-ODA content⁷. The area under the respective loss modulus curves supports the abovementioned observation. Any restriction in the main chain mobility in the polymer is expected to decrease the area under the loss modulus curve and vice versa. Figure 6.3 demonstrates this.

Table 6.1

Copolymerization and glass transition temperature data for high molecular weight styrene/2-octyl-dodecyl acrylate copolymers

Copolymer	Mol % 2-ODA in copolymer [*]	Overall conversion [*] [%]	Average molecular weights			PDI	T_g [°C]
			[g/mol]				
			M_w	M_p	M_n		
A	1.0	89.6	52747	51158	29668	1.78	74.5
B	3.0	89.1	59150	47212	33865	1.75	57.4
C	5.0	80.7	56420	52791	32670	1.73	50.0
D	7.0	82.4	75987	57873	42370	1.79	47.9

^{*}Determined from ¹H-NMR spectroscopy data

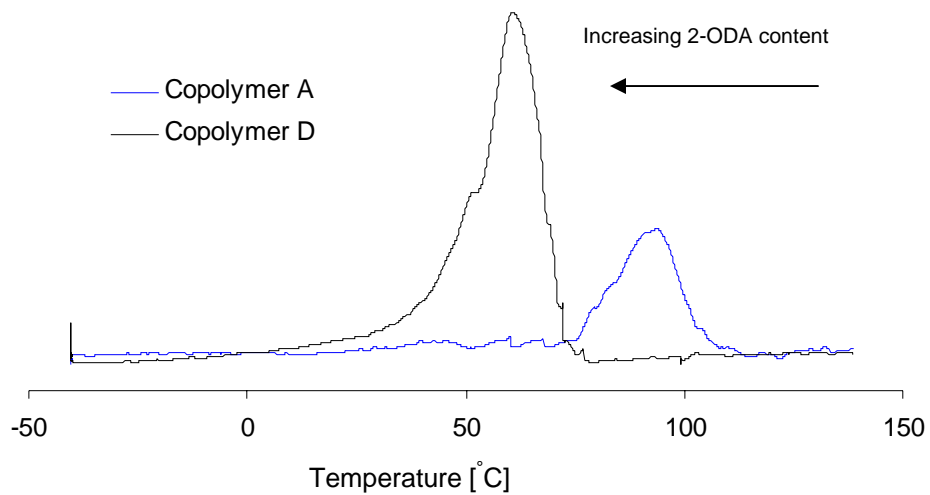


Figure 6.2 Loss tangent ($\tan \delta$) curves of copolymers A and D to illustrate the decrease in the glass transition temperature with increasing 2-ODA content.

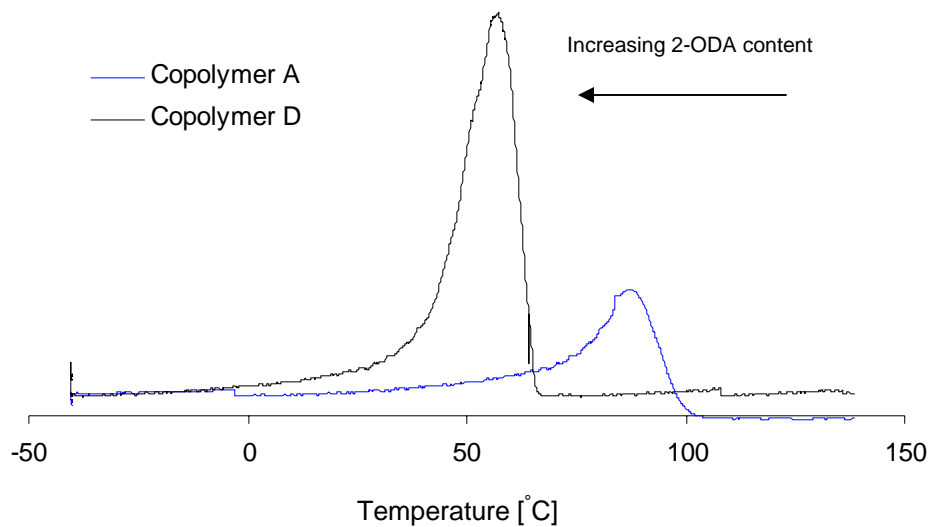


Figure 6.3 Loss modulus curves of copolymers A and D, illustrating the increase in the main chain mobility with increasing 2-ODA content.

6.3.2 Thermo-mechanical behaviour of blends of polystyrene with high molecular weight styrene/2-octyl-dodecyl acrylate copolymers

The toughening ability of the copolymers and the compatibility of the blends were assessed, based on considerations such as the molecular weight of the copolymers and the amount of copolymer added. The toughening of any polymer, by whatever means, generally manifests itself as a broadening of the $\tan \delta$ peak of the polymer, without a significant change in stiffness.

Two copolymers were chosen for this study: copolymer C (Table 6.1: $T_g = 50.0\text{ }^\circ\text{C}$, $\overline{M}_w \approx 56\ 000\text{ g/mol}$) and copolymer D (Table 6.1: $T_g = 47.9\text{ }^\circ\text{C}$, $\overline{M}_w \approx 76\ 000\text{ g/mol}$). Glass transition temperatures of $111.7\text{ }^\circ\text{C}$ (onset of $\tan \delta_{\max}$ curve) and $103.7\text{ }^\circ\text{C}$ (onset of loss modulus peak) were obtained for the commercial virgin polystyrene (see Figure 6.4).

Blends of the commercial polystyrene with 5 wt % to 20 wt % of the abovementioned copolymers were prepared and analyzed. The blends are defined as follows:

blend 1: polystyrene + copolymer D

blend 2: polystyrene + copolymer C.

The T_g values of the blends were taken as the onset temperatures of the loss tangent peaks.

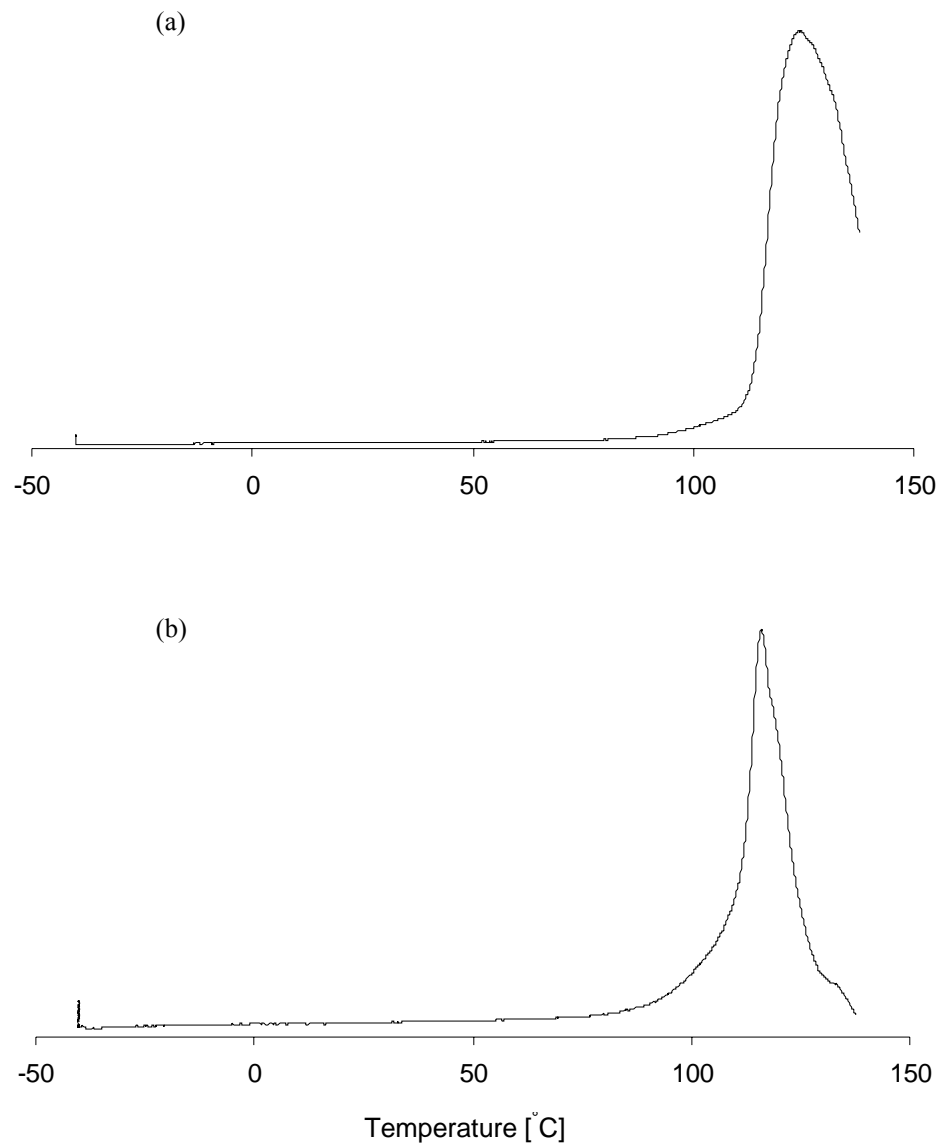


Figure 6.4 (a) Tan δ and (b) loss modulus curve of the commercial virgin polystyrene used in this study.

The results for blend 1 are presented in Table 6.2. (Figure 6.5 shows the loss tangent curves of polystyrene and copolymer D.)

Table 6.2

Glass transition temperatures of blend 1 as determined by DMA

Blend ratio [wt %]	95/5	90/10	85/15	80/20
T_g [°C]	52.8	53.5	52.9	77.5

Table 6.2 shows that the T_g values of the polystyrene/copolymer D blends are shifted to lower temperatures compared to the virgin polystyrene. The blends that contained the lower amounts of copolymer D (5-15 wt %) had the lowest T_g values. Approximately the same T_g (≈ 53.0 °C) was obtained for the blends with 5-15 wt % of copolymer D mixed into the virgin polystyrene. The T_g values of these blends differed from the T_g of the virgin polystyrene by approximately 58.2 °C. Although the T_g of the polystyrene/20 wt % copolymer D blend (T_g = 77.5 °C) is 34.2 °C lower than the virgin polystyrene, it is relatively much higher than the T_g values of the other polystyrene/copolymer D blends.

There seems to be an optimum amount of copolymer D (20 wt %) at which the temperature of onset of molecular motion of the polystyrene/copolymer D blend increases again. This could be due to the formation of entanglements at specific copolymer D amount in the blend, which would lead to restricted mobility of the chains.

The decrease in the amount of chain mobility with increased amounts of copolymer D can be seen from the decrease in the tan δ_{max} in Figure 6.6. This is supported by the decrease in the area under the loss modulus curves (Figure 6.7). Furthermore, restriction in the amount of chain mobility in the blends compared to the commercial polystyrene is also evident from Figures 6.6 and 6.7. This is seen from the difference in the peak maxima.

Figure 6.6 shows that the polystyrene/copolymer D blends were partially miscible. The broadening of the loss tangent curves can be related to a certain degree of dynamic heterogeneity (micro-phase separation) in the blends.

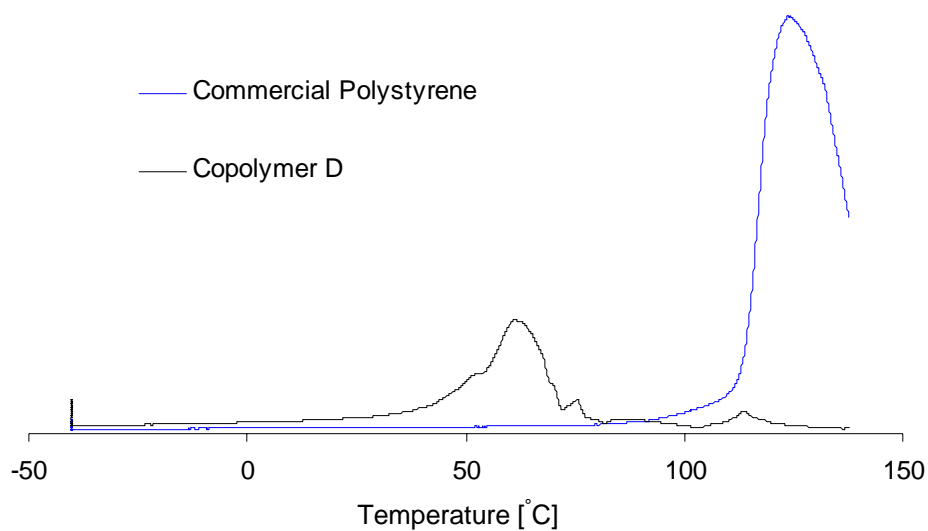


Figure 6.5 Loss tangent curves of commercial polystyrene and copolymer D.

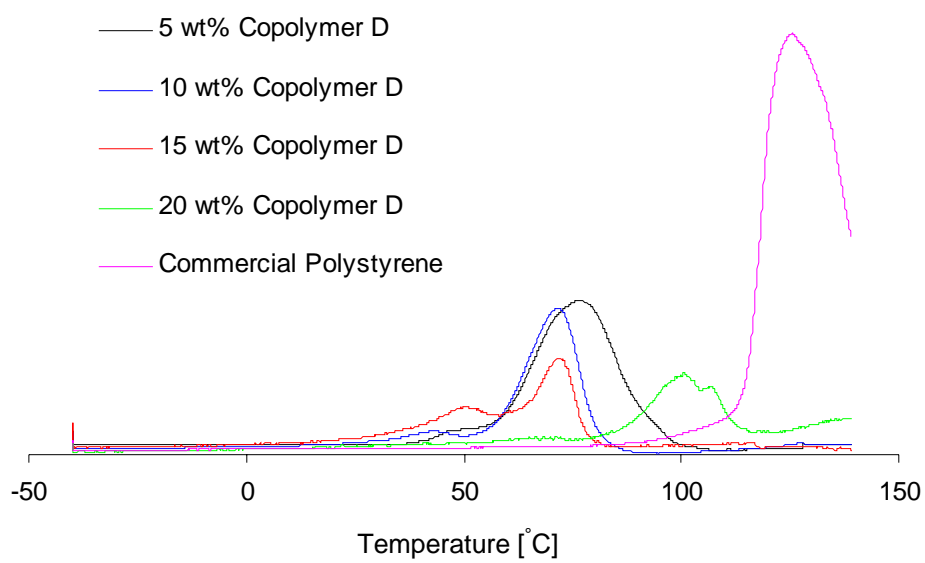


Figure 6.6 Loss tangent curves of commercial polystyrene and polystyrene/copolymer D blends.

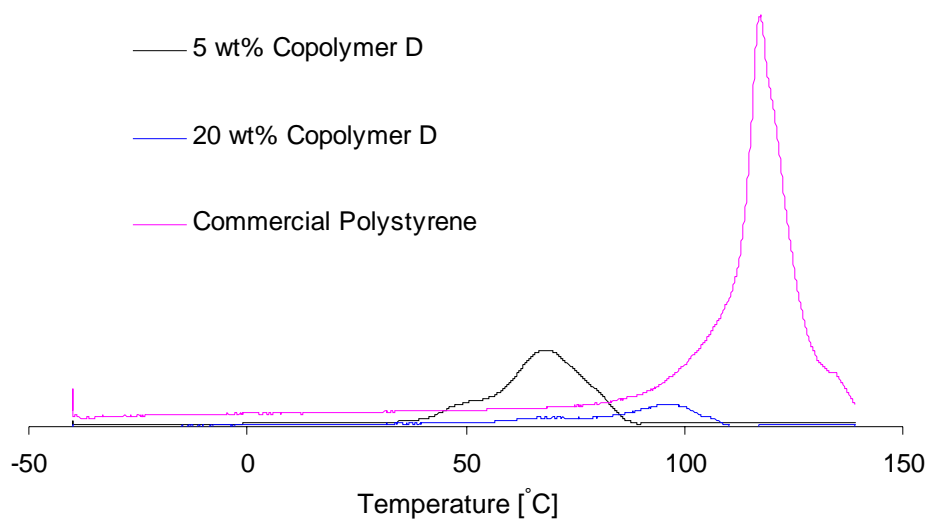


Figure 6.7 Loss modulus curves of commercial polystyrene, polystyrene/5 wt % copolymer D and polystyrene/20 wt % copolymer D blends.

The results for blend 2 are presented in Table 6.3. (Figure 6.8 shows the loss tangent curves of polystyrene and copolymer C.)

Table 6.3

Glass transition temperatures of blend 2 as determined by DMA

Blend ratio [wt%]	95/5	90/10	85/15	80/20
T_g [°C]	49.1	53.1	48.3	70.9

The T_g values of the blends decreased considerably compared to the commercial virgin polystyrene. A minimum decrease in the T_g of 40.8 °C and a maximum of 63.4 °C were observed. Similar trends for the T_g values of the polystyrene/copolymer C blends as for the polystyrene/copolymer D blends were observed. Approximately the same T_g was obtained for the blends with 5-15 wt % of copolymer C mixed into the virgin polystyrene.

The T_g of the polystyrene/copolymer C blend increased when 20 wt % of copolymer C was mixed into the virgin polystyrene.

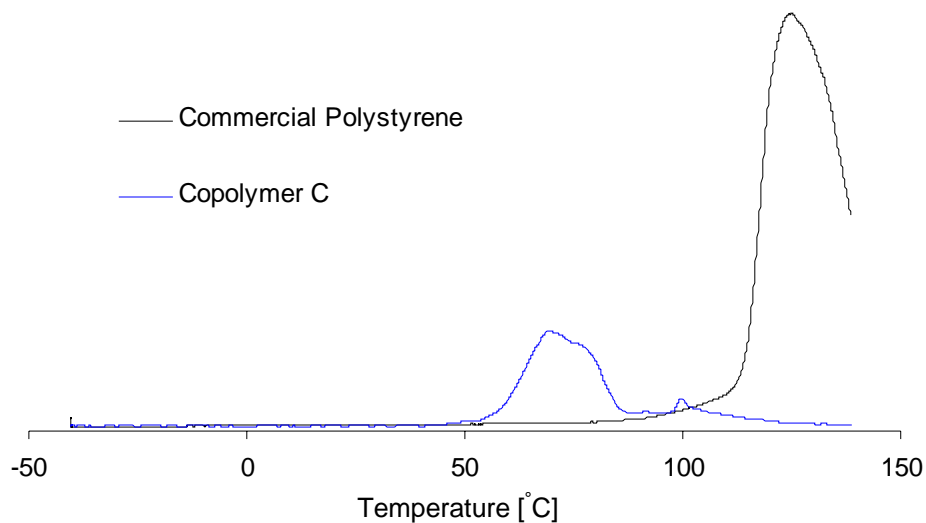


Figure 6.8 Loss tangent curves of commercial polystyrene and copolymer C.

The observed increase in the T_g could once again be ascribed to a restriction in the mobility of the chains due to entanglements. This is confirmed by Figures 6.9 and 6.10. The $\tan \delta_{\max}$ of the polystyrene/20 wt % copolymer C blend is lower than that of the polystyrene/5 wt % copolymer C blend (Figure 6.9). In addition, the area under the loss modulus curve is greater for the polystyrene/5 wt % copolymer C blend than for the polystyrene/20 wt % copolymer C blend (Figure 6.10). Moreover, a decrease in the amount of chain mobility of the blends compared to the virgin polystyrene was observed (Figures 6.9 and 6.10).

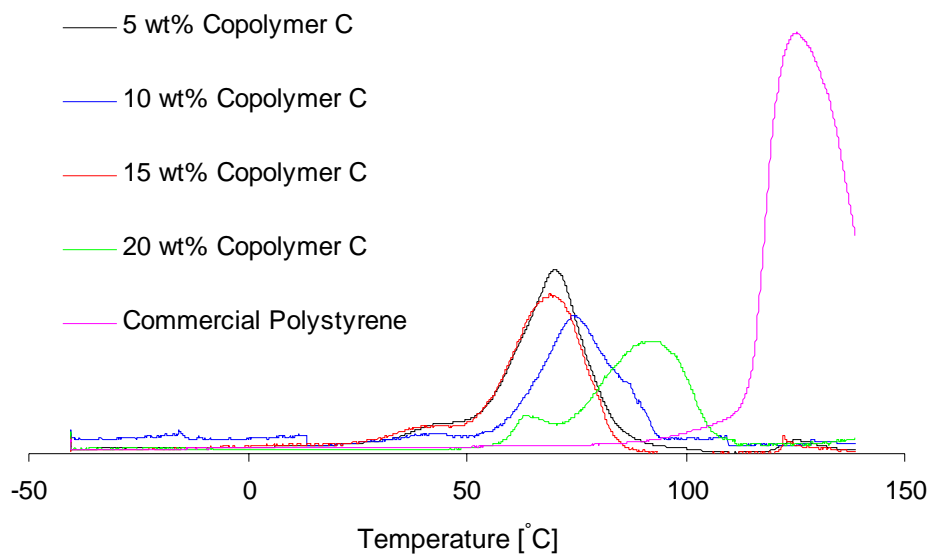


Figure 6.9 Loss tangent curves of commercial polystyrene and polystyrene/copolymer C blends.

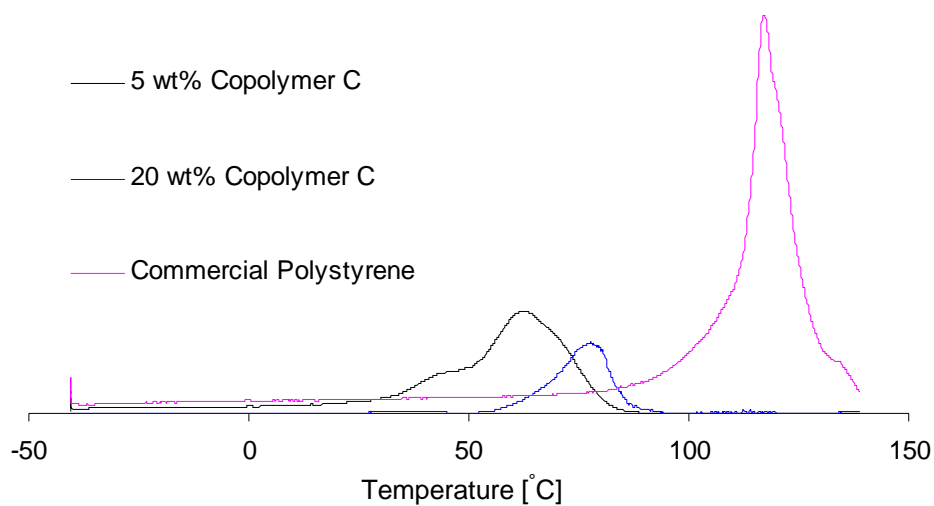


Figure 6.10 Loss modulus curves of commercial polystyrene, polystyrene/5 wt % copolymer C and polystyrene/20 wt % copolymer C blends.

Figure 6.9 shows that the formed blends were once again partially miscible. A certain amount of phase-separation was present in all of the blends as evidenced by the broadening of the loss tangent peaks.

The difference in the weight average molecular weight of 20 000 g/mol, between copolymer C and D, did not result in a significant difference in the thermo-mechanical behaviour of the polystyrene blends. In addition, the blending of the commercial virgin polystyrene with copolymers C and D did not result in a toughening, but only a plasticizing, of the commercial virgin polystyrene. The temperature at which the blends lose their stiffness is considerably lower than the temperature at which the virgin polystyrene loses its stiffness. Moreover, substantial differences in the maximum stiffness of the virgin polystyrene compared to the blends were observed[†].

The effect of a low molecular weight polystyrene/2-octyl-dodecyl acrylate copolymer on the thermo-mechanical behaviour of polystyrene was investigated, as described in the following sections. How will the low molecular weight additive affect the mobility of the chains in the blends? Does it introduce a toughening and/or plasticizing effect?

6.3.3 Synthesis of low molecular weight styrene/2-octyl-dodecyl acrylate copolymers

Several low molecular weight copolymers of styrene and 2-octyl-dodecyl acrylate were synthesized. The feed compositions comprised 1.0-7.0 mol % 2-ODA. The syntheses of the copolymers were confirmed by ¹H-NMR spectroscopy (See Figure 6.1). The results are also presented in Table 6.4. It can once again be assumed that the copolymers were 'blocky' random copolymers.

The overall conversions for copolymers 1 and 2 were above 95%. The overall conversions for copolymers 3 and 4 were above 80%. Average molecular weights (\overline{M}_w) of between 7 000 and 18 000 g/mol and polydispersities ranging from 2.5 to 3.5 were obtained for the synthesized copolymers.

[†] See Appendix C, Figures C.1 and C.2

Table 6.4

Copolymerization and glass transition temperature data for low molecular weight styrene/2-octyl-dodecyl acrylate copolymers

Copolymer	Mol % 2-ODA in copolymer *	Overall conversion * [%]	Average molecular weights [g/mol]			PDI	T _g [°C]
			M _w	M _p	M _n		
			0	-	80.5		
1	1.0	98.7	9057	8684	2928	3.1	77.0
2	3.0	97.6	17933	15626	7160	2.5	66.0
3	4.5	80.9	9131	8386	3291	2.8	52.0
4	7.1	84.2	9034	8035	3456	2.6	35.8

* Determined from ¹H-NMR spectroscopy data

The glass transition temperature values of the styrene/2-octyl-dodecyl acrylate copolymers, as determined by DMA analysis, were measured as the onset temperature of the loss tangent peak. It must be noted that two factors are responsible for the obtained T_g values: the low average molecular weights of the copolymers and the incorporation of 2-ODA.

The decrease in the T_g of the synthesized copolymers with increasing 2-ODA content is not directly illustrated in Table 6.4. It can be seen that the copolymers with 1.0 and 3.0 mol % 2-ODA content have T_g values that are higher than that of the virgin, low molecular weight polystyrene. This can be directly related to the obtained molecular weights for the copolymers, due to the fact that the T_g of a polymer is a function of its molecular weight (up to a limiting molecular weight). Chartoff⁸ reported on the molecular weight dependence of the T_g for polystyrene; a T_g of 62 °C is reported for the virgin low molecular weight polystyrene, which corresponds very well with the data reported by the abovementioned author.

However, it can be seen from the results in Table 6.4 that for copolymers 1, 3 and 4, with comparable \overline{M}_w values, that the T_g values decreased from 77.0 °C to 35.8 °C when increasing amounts of 2-ODA were incorporated into the copolymers (Figure 6.11).

Although molecular motion set in at lower temperatures, the amount of mobility of the chains decreased with increasing amounts of 2-ODA, as evidenced by the lower $\tan \delta_{\max}$ of copolymer 4 (Figure 6.11). Additionally, the broader molecular weight distribution associated with copolymer 1 could mean that copolymer 1 contains more short chains, which would contribute to the amount of chain mobility.

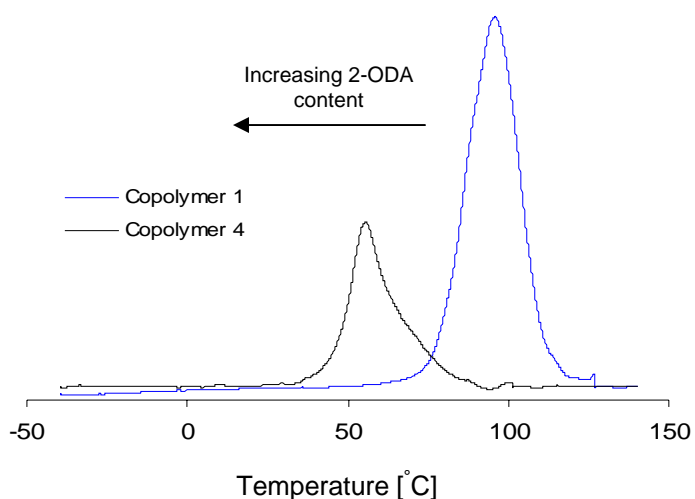


Figure 6.11 Loss tangent curves of copolymers 1 and 4, illustrating the decrease in the glass transition temperature with increasing 2-ODA content.

6.3.4 Thermo-mechanical behaviour of blends of polystyrene with low molecular weight styrene/2-octyl-dodecyl acrylate copolymers

Copolymer 3 (Table 6.4; $\overline{M}_w \approx 9\,000$ g/mol, $T_g = 52.0$ °C), with a glass transition temperature comparable to that of copolymers C and D, was chosen for this study. Various polystyrene/copolymer 3 blends were prepared and analyzed. The glass transition temperature results for the blends are presented in Table 6.5. (Figure 6.12 shows the loss tangent curves of polystyrene and copolymer 3.)

Table 6.5

Glass transition temperatures of polystyrene/copolymer 3 blends
as determined by DMA

Blend ratio [wt%]	95/5	90/10	85/15	80/20
T_g [°C]	93.5	99. 7	85. 9	79. 0

Table 6.5 shows that the T_g values of the blends generally decreased from 99.7 °C to 79.0 °C as the amount of copolymer 3 in the blend increased. The blend that contained 20 wt % of copolymer 3 had the lowest T_g . A difference of 32.7 °C between the T_g of the virgin polystyrene and this particular blend was observed. It is generally expected that the addition of a low molecular weight additive to a polymer causes a significant decrease in the T_g . This was not observed in this particular instance. The effect of the high molecular weight additives on the T_g of the virgin polystyrene (Section 6.3.2) was more pronounced than that of the low molecular weight additive (copolymer 3). It is possible that nano-phase separation plays a significant role in the case of the high molecular weight additives. This would influence the free volume in the 2-ODA-enriched phase, leading to lower T_g values compared to a more compatible polystyrene/copolymer 3 blend above.

Figure 6.13 shows that the $\tan \delta_{\max}$ of the polystyrene/copolymer 3 blends generally decreased with increasing amounts of copolymer 3. This indicates a decrease in the amount of chain mobility with increasing amounts of copolymer 3 in the blends. In addition, a decrease in the amount of chain mobility of the blends compared to the commercial polystyrene was also observed (Figure 6.13). The $\tan \delta_{\max}$ of the commercial polystyrene is significantly higher than that of the blends.

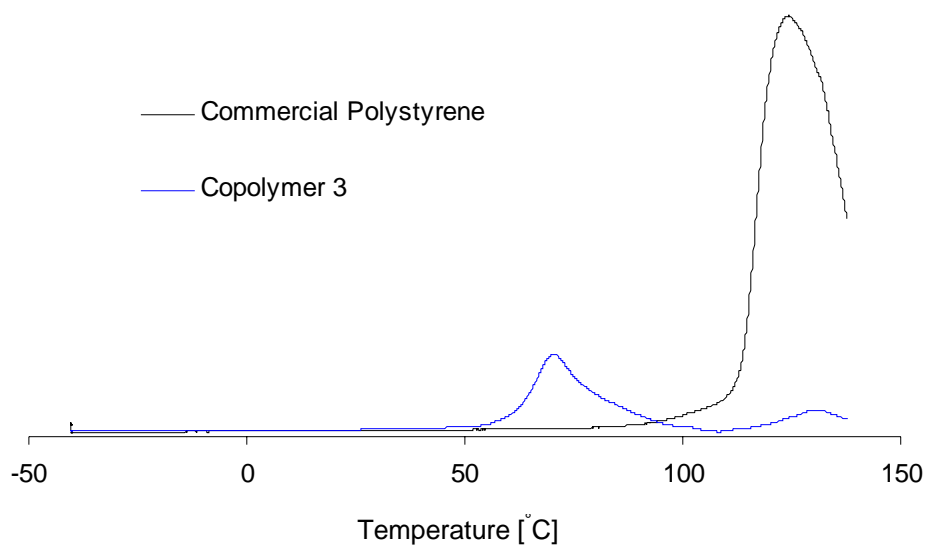


Figure 6.12 Loss tangent curves of commercial polystyrene and copolymer 3.

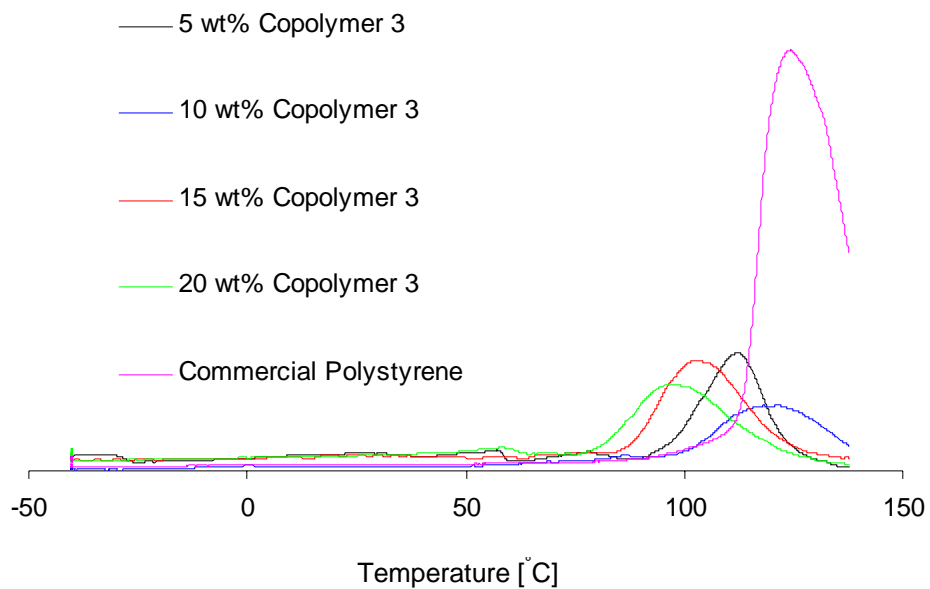


Figure 6.13 Loss tangent curves of commercial polystyrene and polystyrene/copolymer 3 blends.

Partial miscibility of the blends is indicated by the broadening of the loss tangent curves (Figure 6.13). Furthermore, as in the case of the blends (Section 6.3.2), the commercial polystyrene is plasticized rather than toughened by the addition of copolymer 3. A substantial drop in stiffness of the blends compared to the commercial polystyrene was observed^κ.

6.4 Conclusions

Low- and high-molecular-weight ‘random’ styrene/2-octyl-dodecyl acrylate copolymers were successfully prepared. The incorporation of 2-octyl-dodecyl acrylate into the various copolymers significantly decreased the glass transition temperatures of the synthesized copolymers. A difference in T_g of 52.1 °C between polystyrene (assuming a T_g of 100 °C) and the high molecular weight styrene/2-octyl-dodecyl acrylate copolymer with 7.0 mol % 2-octyl-dodecyl acrylate incorporated was observed. In the case of the low molecular weight styrene/2-octyl-dodecyl acrylate copolymer with 7.0 mol% 2-octyl-dodecyl acrylate incorporated, the T_g decreased by 64.2 °C.

The obtained results indicate that the novel ‘bushy-tailed’ monomer, 2-octyl-dodecyl acrylate, has the ability to serve as an internal plasticizer, and thereby serves to enhance the damping properties of the commercial polystyrene at low temperatures.

The blending of commercial polystyrene with the high molecular weight copolymers C and D that were synthesized showed similar thermo-mechanical results. Partially miscible blends with significantly decreased glass transition temperatures compared to the commercial virgin polystyrene were obtained. Furthermore, approximately the same glass transition temperatures were observed for 5 to 15 wt % of the copolymers mixed into the commercial polystyrene. An increase in the glass transition temperature of the blends was observed when 20 wt % of the copolymers were mixed into the commercial polystyrene.

^κ See Appendix C, Figure C.3

The blending of commercial polystyrene with the low molecular weight copolymer 3 produced partially miscible blends with less significant differences in the glass transition temperatures compared to the commercial virgin polystyrene.

In all instances, the commercial virgin polystyrene was plasticized by the copolymers. Significant differences in the stiffness of the blends compared to the commercial polystyrene were observed.

It was observed from the DMA results that the blends were partially miscible. A second technique is required to study possible micro-phase separation, but this is not easy with 2-octyl-dodecyl acrylate, which is difficult to stain or to see in neutron or low angle X-ray scattering. Furthermore, factors like the method of blending, the mixing time and the type of casting solvent might play a possible role in further enhancing the compatibility of the blends.

6.5 REFERENCES

1. S. Jacob, M.D. Sefcik, E.O. Stejskal, R.A. Mckay, **Macromolecules**, 14, 188 (1981)
2. T.A. Huy, R. Adhikari, T. Lupke, G.H. Michler, K. Knoll, **Polymer Engineering and Science**, 44, 1534 (2004)
3. Z. Zhang, S. Fang, **Electrochimica Acta**, 45, 2131 (2000)
4. M. Kono, E. Hayashi, M. Watanabe, **Journal of the Electrochemical Society**, 145, 1521 (1998)
5. J. Greener, J. R. Gillmor, R. C. Daly, **Annual Technical Conference - Society of Plastics Engineers (53rd)**, 2, 1964 (1995)
6. J. S. Wrana, L. A. Monroe, S. W. Shalaby, **Book of Abstracts, 215th ACS National Meeting (Dallas)**, March 29-April 2 (1998)
7. M.C. Senake Perera, U.S. Ishiaku, Z.A. Mohd Ishak, **European Polymer Journal**, 37, 167 (2001)
8. R.P. Chartoff, **Thermal Characterization of Polymeric Materials**, 2nd Edition, Academic Press: New York, 1, 513 (1997)

CHAPTER 7

Conclusions and Recommendations

CONTENTS

- 7.1 Introduction
- 7.2 Summary of Conclusions
- 7.3 Recommendations for Future Work

ABSTRACT

All of the results of this study are summarized, conclusions are drawn, and possible future directions are suggested.

Keywords: oligomerization, novel hydrophobic acrylic monomer, reactive hydrophobe, copolymerization, reactive plasticizer

7.1 Introduction

As the need for new materials and innovative applications continues to be an ongoing scientific pursuit, I trust that the work presented in this dissertation on the synthesis and applications of a new hydrophobic acrylic monomer (2-octyl-dodecyl acrylate) has contributed to this pursuit and opened up avenues for future exploration. I believe that this study has hardly scratched the surface as far as the synthesis of novel ultra-hydrophobic, 'bushy-tailed' monomers and their applications are concerned. Section 7.3 highlights a few likely research directions.

7.2 Summary of Conclusions

Selective dimerization of 1-decene

Although the selective dimerization of 1-decene was not achieved in this study, the oligomerization of 1-decene with the bis(cyclopentadienyl)zirconium dichloride (catalyst)/methyl aluminoxane (cocatalyst) catalytic system did result in reaction products with a large dimeric fraction (a minimum of 70% and a maximum of 87%). Use of a cocatalyst to catalyst ratio of 1000:1 and reaction temperatures of 70 °C and 90 °C resulted in the optimum (87%) 1-decene dimer concentration in the reaction product. The obtained dimeric product, 2-octyl-1-dodecene, resulted from the 1,2-insertion mechanism. It must be noted that a very small percentage (3.0%) of dimer from a 2,1-misinsertion was obtained, 3-methyl-2-octyl-1-undecene.

Synthesis of a novel hydrophobic acrylic monomer

The tertiary alcohol, 2-octyl-2-dodecanol, and the novel uniquely branched hydrophobic acrylic monomer, 2-octyl-dodecyl acrylate, were successfully synthesized from 2-octyl-1-dodecene. Characterization of the reaction products by means of ¹H-NMR and IR spectroscopy confirmed this.

The effectiveness of 2-octyl-dodecyl acrylate as a reactive hydrophobe in mini-emulsion polymerizations

Stable polymer latex particles of butyl acrylate, methyl methacrylate and styrene were successfully synthesized with the novel reactive hydrophobe 2-octyl-dodecyl acrylate. Phase-separation experiments showed that the presence of 2-octyl-dodecyl acrylate in the dispersed phase retarded Ostwald ripening. A one-to-one copy of droplet size compared to particle size was obtained from all the mini-emulsions in which 2-octyl-dodecyl acrylate was used as reactive hydrophobe. The ^{13}C -NMR data showed that 2-octyl-dodecyl acrylate does indeed become chemically incorporated into the latex particles.

Preparation of polystyrene/poly(styrene-co-2-octyl-dodecyl acrylate) blends

Low- and high-molecular-weight styrene/2-octyl-dodecyl acrylate copolymers were successfully prepared and characterized. ^1H -NMR data confirmed the chemical incorporation of 2-octyl-dodecyl acrylate.

Dynamic mechanical analysis results indicated that the novel 'bushy-tailed' monomer, 2-octyl-dodecyl acrylate, has the ability to serve as an internal plasticizer, and thereby serves to enhance the damping properties of the obtained copolymers.

Blends of commercial virgin polystyrene and the synthesized low- and high-molecular-weight copolymers were prepared. Decreases in the glass transition temperatures of the blends compared to the virgin polystyrene were observed. This was more pronounced in the case of the blends with the high molecular weight copolymers. Furthermore, phase-separation was evident in the blends.

7.3 Recommendations for Future Work

I submit the following spin-offs as viable options for further research.

- The synthesis of a vinyl ester monomer derived from 2-octyl-1-dodecene that is equivalent to the commercial VEOVA (vinyl ester of versatic acid) monomer, and the investigation of its possible applications.
- The synthesis and characterization of a 1-decene trimer derived acrylic monomer and investigating its uses. The synthesis procedure of Wasserscheid and coworkers (Reference 5, Chapter 3) is recommended as the method to be used for the highly selective trimerization of 1-decene.
- The controlled mini-emulsion polymerization of various monomers using 2-octyl-dodecyl acrylate as a reactive hydrophobe in combination with a polymerizable surfactant.
- The use of 2-octyl-dodecyl acrylate modified styrene copolymers as opposed to virgin polystyrene in blends with (meth)acrylic polymers, to facilitate the miscibility of polystyrene with otherwise immiscible polymers.
- The synthesis of well-controlled 2-octyl-dodecyl acrylate/maleic anhydride copolymers via the radical addition fragmentation transfer (RAFT) polymerization process and the application of these copolymers as polymeric reactive soaps.

APPENDIX A: Calculation of weight average particle size of poly(butyl acrylate) latex from TEM results

Table A.1

Measured poly(butyl acrylate) latex particle sizes

Measured particle sizes [nm]	Weighted value [nm]
36.50	1.446 ^φ
19.74	0.4232
72.37	5.686
72.55	5.715
76.39	6.335
81.17	7.153
79.45	6.853
59.28	3.815
61.11	4.055
65.28	4.627
85.28	7.896
89.56	8.709
74.54	6.033
47.84	2.485

Sum of measured particle sizes = 921.05 nm

^φ Weighted value = $(36.50/921.05) \times 36.50 = 1.446$ nm

Calculated weight average particle size = Sum of weighted values = 71 nm

APPENDIX B: Capillary hydrodynamic fractionation (CHDF) results of poly(butyl acrylate) latexes

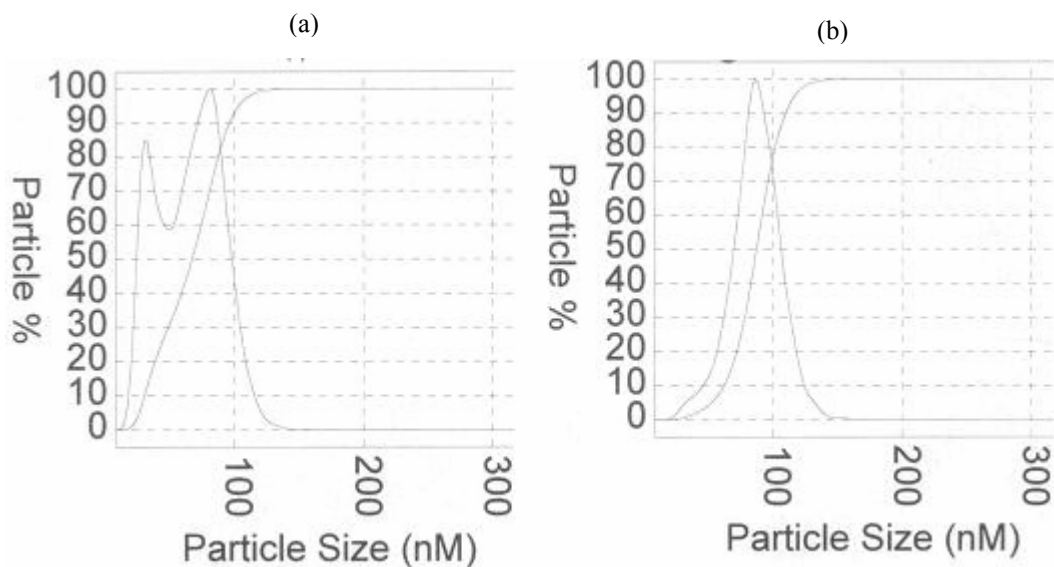


Figure B.1 CHDF results of mini-emulsion polymerization of butyl acrylate with hexadecane as hydrophobe; (a) number average particle size and (b) weight average particle size.

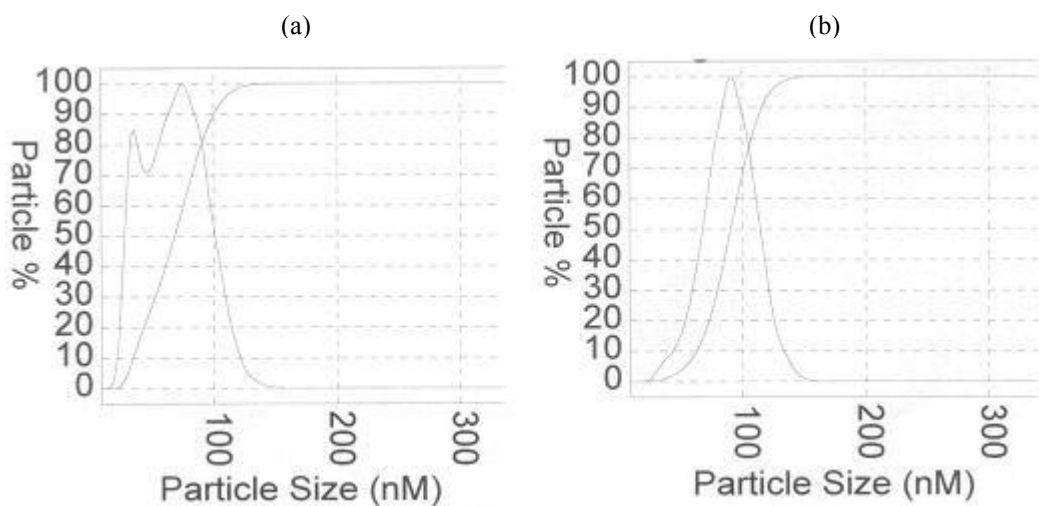


Figure B.2 CHDF results of mini-emulsion polymerization of butyl acrylate with no hydrophobe (only high shear); (a) number average particle size and (b) weight average particle size.

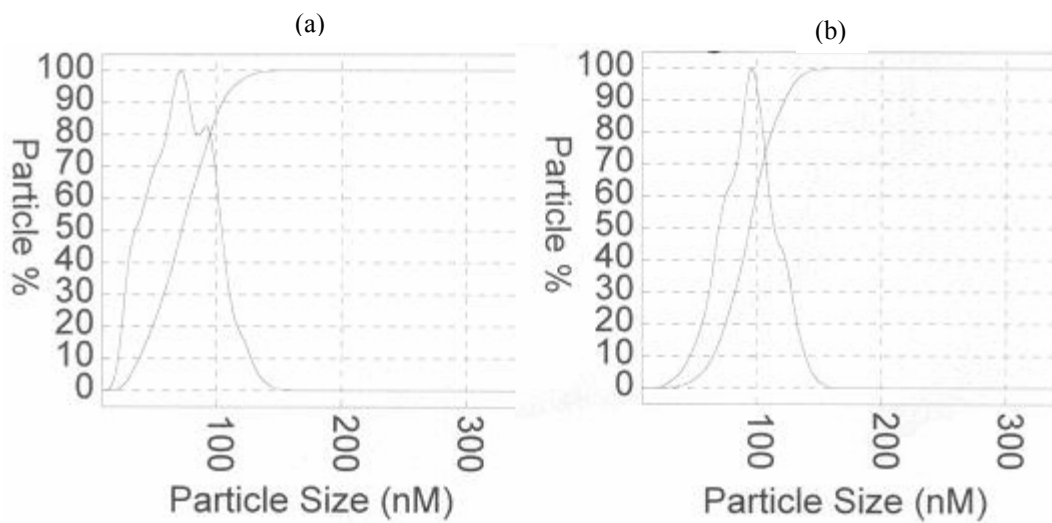


Figure B.3 CHDF results of emulsion polymerization of butyl acrylate; (a) number average particle size and (b) weight average particle size.

APPENDIX C: Stiffness of the various polystyrene/poly(styrene-co-2-octyl-dodecyl acrylate) blends compared to the commercial virgin polystyrene

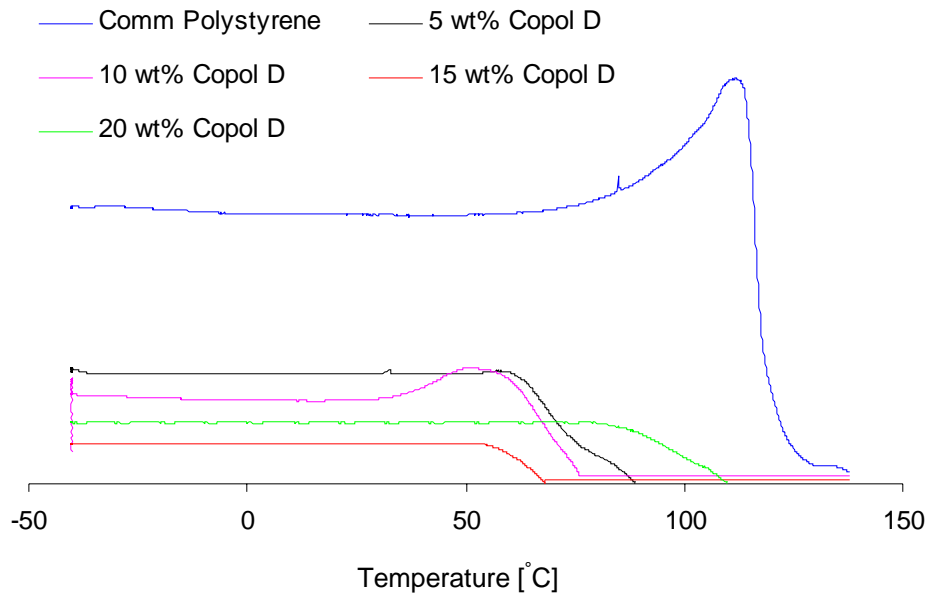


Figure C.1 Storage modulus curves illustrating the difference in the stiffness of the commercial polystyrene and polystyrene/copolymer D blends.

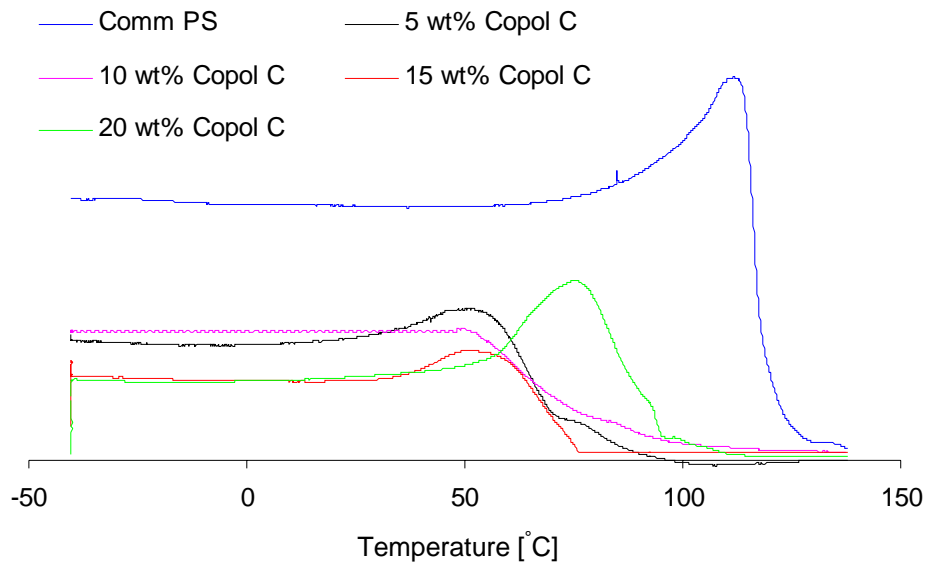


Figure C.2 Storage modulus curves illustrating the difference in the stiffness of the commercial polystyrene and polystyrene/copolymer C blends.

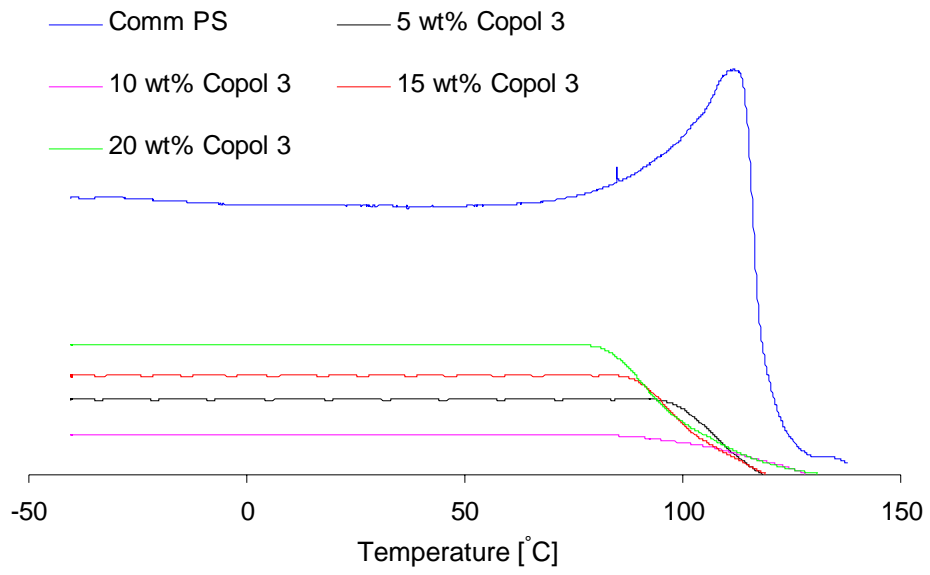


Figure C.3 Storage modulus curves illustrating the difference in the stiffness of the commercial polystyrene and polystyrene/copolymer 3 blends.

APPENDIX D: Loss modulus curves of the various polystyrene/poly(styrene-co-2-octyl-dodecyl acrylate) blends compared to the commercial virgin polystyrene

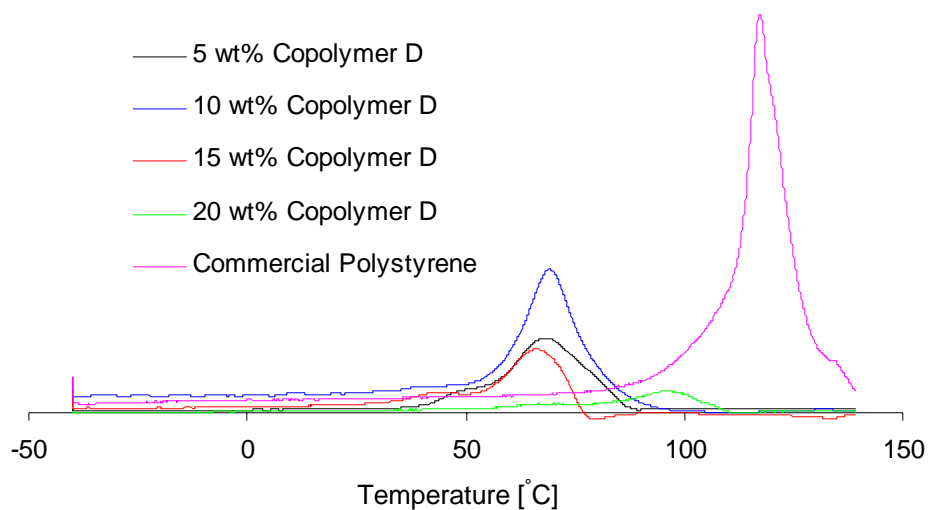


Figure D.1 Loss modulus curves of commercial polystyrene and polystyrene/copolymer D blends.

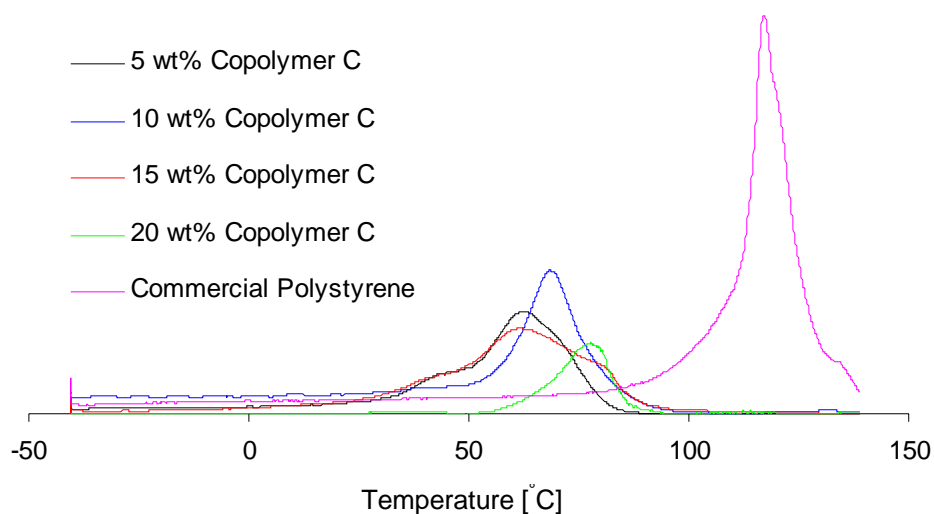


Figure D.2 Loss modulus curves of commercial polystyrene and polystyrene/copolymer C blends.

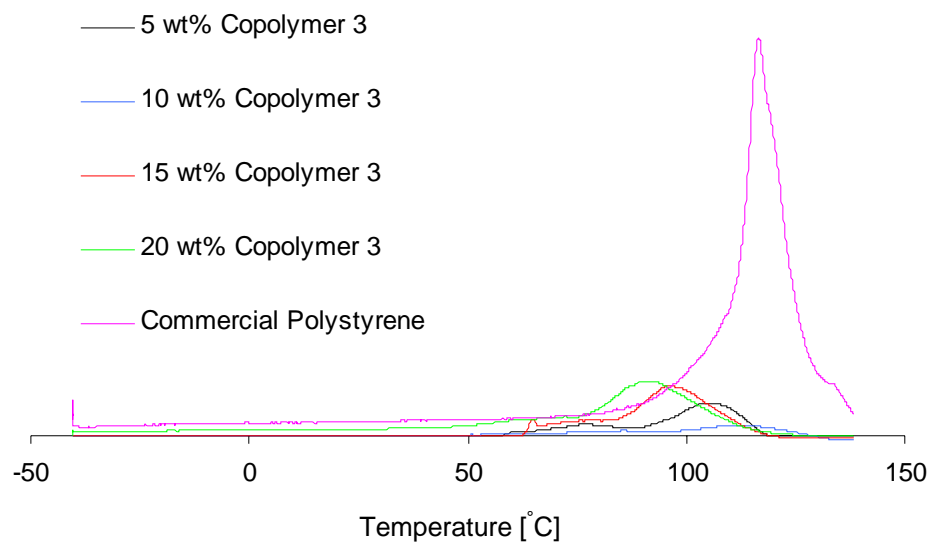


Figure D.3 Loss modulus curves of commercial polystyrene and polystyrene/copolymer 3 blends.