

Investigation of the copolymerization of butyl acrylate (BA) with vinyl neononanoate (Veova-9)

By

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Declaration

I, the undersigned, hereby declare that the work contained in this thesis 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.



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Abstract

This study has the goal of illuminating structure-properties relationships for copolymers of vinyl neononanoate (Veova-9) and butyl acrylate (BA). The Veova-9/BA copolymers were prepared using solution free radical copolymerization and miniemulsion copolymerization. The free radical copolymerization of Veova-9/BA at different feed ratios in benzene at 80°C using 2,2'-azobis (2-methylpropionitrile) (AIBN) as initiator was investigated. The terminal model was used to describe the copolymerization of these monomers and the copolymer composition was determined using ^1H NMR spectroscopy. The reactivity ratios, estimated using the nonlinear least square method, and the 95% confidence interval giving values of the reactivity ratios, which were 0.042 (± 0.014) and 6.95 ($-0.53 / +0.65$) for the Veova-9 and BA respectively. The copolymerization kinetics for the Veova-9/BA was investigated by following individual monomer consumption rates by *in-situ* NMR. The use of this method provides useful information about the individual monomer concentration during the course of reaction. The copolymerization reaction shows a higher tendency for BA to react than the Veova-9.

The copolymerization of these monomers was also investigated in a heterogeneous system using the miniemulsion technique. In these investigations the effect of surfactant, initiator type and water solubility of the monomer on the batch and semi-batch miniemulsion behaviour was demonstrated. The rate of the miniemulsion polymerization increased with increasing surfactant concentration, while the final particle size of the latex decreased with increasing surfactant concentration in the miniemulsion mixture. Two types of initiators were used, water and oil-soluble initiators (ammonium persulphate (APS) and AIBN respectively). The rate of the batch miniemulsion polymerization showed dependency on the type of initiator used as the monomer conversion increased faster with APS than when using AIBN. The average final particle size was also larger when the AIBN was used than it was when the APS was used. The batch miniemulsion showed an increase in the nucleation (inhibition) period and a slower polymerization rate as the Veova-9 concentration increased. The increase in the Veova-9 concentration in both batch and semi-batch miniemulsions also led to an increase in the particle size.

The obtained copolymers were characterized in terms of their chemical composition via two-dimensional chromatography (2-D), and in terms of some of their physical properties using dynamic mechanical analysis (DMA) and contact angle measurement. The 2-D analysis showed that all the BA was incorporated in the copolymer; this result was also confirmed by ^1H NMR. The 2-D analysis also showed that the copolymer composition depends on the monomer addition mode in the semi-batch process. The copolymer glass transition temperature (T_g) value showed an increase as the VeoVa-9 concentration increased and the T_g values of the copolymers ranged between the two homopolymers' T_g values. The hydrophobicity of the copolymers increased as the VeoVa-9 concentration increased as was indicated by contact angle measurements.

Opsomming

Die doel van die studie is om die struktuur-eienskap verhoudings vir kopolimere van vinielneonanoaat (Veova-9) en butielakrylaat (BA) te bestudeer. Die Veova-9/BA kopolimere was gesintetiseer deur van oplossingsvryeradikaalkopolimerisasie en mini-emulsie kopolimerisasie gebruik te maak. Die vryeradikaalkopolimerisasie van Veova-9/BA met verkillende verhoudings Veova-9 tot BA in benseen, by 80°C, en met 2,2'azobis (2-metielpropionitriël) (AIBN) as afsetter, was ondersoek. Die reaktiwiteitsverhoudings van die monomere was skattings wat gemaak is deur van die terminale (endgroep)-model gebruik te maak. Die kopolimeersamestellings was bepaal deur van ¹H-KMR-spektroskopie gebruik te maak. Die reaktiwiteitsverhoudings, bepaal deur van die nie-lineêre minste vierkantsmetode, asook om van die 95% sekerheidsinterval gebruik te maak, was 0.042 (±0.014) en 6.95 (-0.53 /+0.65) vir Veova-9 en BA onderskeidelik. Die kopolimerisasiekinetika vir verskillende Veova-9/BA verhoudings was ondersoek deur die individuele tempos van monomeeropname d.m.v. *in-situ* KMR te volg. Hierdie metode verskaf nuttige inligting oor die konsentrasies van individuele monomere gedurende die verloop van die reaksie. Die kopolimerisasiereaksie dui op 'n hoër waarskynlikheid vir BA om te reageer as die Veova-9.

Die kopolimerisasie van hierdie monomere was ook ondersoek deur van 'n heterogene sisteem gebruik te maak, in samewerking met die mini-emulsie tegniek. In hierdie ondersoek is die effek van die seep-tipe, inisieerder-tipe en die wateroplosbaarheid van die monomeer op die lot- en op die semi-lot-mini-emulsie gedrag gedemonstreer. Die tempo van die mini-emulsiepolimerisasie neem toe met toenemende seepkonsentrasie, terwyl die finale partikelgrootte van die lateks dan afneem. Die twee tipes initieerders wat gebruik was, was water- en olie-oplosbare initieerders (ammonium persulfaat (APS) en AIBN, onderskeidelik). Die tempo van die lot mini-emulsiepolimerisasie het op die afhanklikheid van die tipe initieerder gedui. Die monomeeromskakelingstempo was hoër wanneer APS gebruik was. Die gemiddelde finale partikelgrootte was groter wanneer AIBN gebruik was. Die lot-mini-emulsiepolimerisasie het 'n toename in die inhibisie (inhibition/'nucleation')-periode getoon en 'n stadiger polimerisasiestempo soos wat die Veova-9 konsentrasie toegeneem het. 'n Toename in Veova-9 se konsentrasie het ook 'n groter partikelgrootte tot gevolg gehad.

Die gesintetiseerde kopolimere is gekarakteriseer in terme van hul chemiese samestelling deur twee-dimensionele chromatografie (2-D), en in terme van sekere fisiese eienskappe, deur van dinamiese meganiese analise (DMA) en kontakhoekmetings gebruik te maak. Die 2-D analises het gewys dat al die BA geinkorporeer was in die kopolimeer. Hierdie resultaat was bevestig met $^1\text{H-KMR}$. Die 2-D analise het ook gewys dat die kopolimeersamestelling afhanklik is van die addissiewyse in die semi-lot proses. Die kopolimeer se glasorgangstemperatuur (T_g) het toeneem soos wat die konsentrasie van VeoVa-9 toeneem het. Die T_g waardes van die kopolimere het gewissel tussen die van die twee homopolimere se T_g waardes. Die hidrofobisiteit van die kopolimere het toeneem namate die VeoVa-9 konsentrasie toeneem het, soos ook aangedui deur kontakhoekmetings.

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List of Abbreviations

AIBN	2,2'-azobis(2-methylpropionitrile)
APS	Ammonium persulphate
BA	Butyl acrylate
^{13}C NMR	Carbon-13 nuclear magnetic resonance
CA	Cetyl alcohol
CCD	Chemical composition distribution
CDCl_3	Deuterated chloroform
C_6D_6	Deuterated benzene
2-D	Two-dimensional chromatography
DDI	Distilled deionized water
DMA	Dynamic mechanical analysis
ELSD	Evaporative light scattering detector
FR	Fineman-Ross method
FTD	Functionality type distribution
FTIR	Fourier transform infrared
GC	Gas chromatographic
^1H NMR	Proton nuclear magnetic resonance
HD	Hexadecane
HPLC	High performance liquid chromatographic
H-S	1-dodecanethiol
IR	Infrared
KOH	Potassium hydroxide
KT	Kelen-Tüdös method
LAC	Liquid adsorption chromatographic
LC-CC	Liquid chromatography at the critical point of adsorption
LMA	Lauryl methacrylate
LS	Light scattering
MAD	Molecular architecture distribution
MeOH	Methanol
MMA	Methyl methacrylate
MMD	Molar mass distribution

RI	Refractive index
SDBS	Sodium dodecylbenzene sulfonate
SDS	Sodium dodecyl sulfate
SLS	Sodium lauryl sulfate
SEC	Size exclusion chromatography
SMA	Stearyl methacrylate
SS	Sum of the squares
St	Styrene
T_g	Glass transition temperature
THF	Tetrahydrofuran
US	Ultrasound
UV	Ultraviolet
Veova-9	Vinyl nononanoate
Veova-10	Vinyl neodecanoate
YBR	Yezrielev-Brokhina-Rosin method

Chapter 1

Introduction and aims

1.1. Introduction

Most people are not familiar with the word “polymers” although they use and see them almost every minute and everywhere in their daily lives. The word “polymer” is derived from the Greek words “poly” (meaning many) and “meros” (parts), meaning something of “many parts” formed from a “single part” or monomer. Such materials are prepared in “polymerization reactions”; in the case of only one monomer being used in the reaction the reaction is referred to as homopolymerization, while in the case of two or more monomers being used the reaction is referred to as copolymerization. Depending on the types of monomers there are a number of different methods that can be used to synthesize polymeric materials, including free-radical polymerization, ring-opening polymerization, and step-reaction (condensation) polymerization.

1.2. Free-radical polymerization

Free-radical polymerization is one of the oldest and most widely used techniques for the synthesis of polymeric materials. Its wide use is due to the numerous advantages it has, such as its suitability for use with a wide range of monomers, including vinyl esters and acrylate monomers, and it being tolerant to many impurities. Free-radical polymerization reactions can be performed by many different methods, including homogenous methods, such as bulk polymerization and solution polymerization, and heterogeneous methods, such as suspension, conventional emulsion and miniemulsion polymerizations^{1,2}.

Generally most of the commercial polymers produced via free-radical techniques are in fact copolymers, achieved by the inclusion of a second monomer in the polymerization reaction. The inclusion of a second monomer greatly complicates the reaction kinetics,

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and introduce additional requirements in order to control the copolymerization, and hence the copolymer composition. The most important factor is the difference in the monomers' reactivities in the copolymerization reaction (known as monomer reactivity ratios in a binary copolymerization reaction). The value of the reactivity ratios is that they can provide a statistical estimation about the copolymer composition, and about the sequence distribution of the different repeat units in the copolymer molecules. This is important in the industrial applications of polymeric materials, since the polymer properties are directly determined by the copolymer structure².

The control of polymer properties has been the major interest of many studies due to the diversity of polymer applications (different applications require different properties). These properties are usually affected by a number of factors, including the molecular weight and, more importantly, the chemical structure of the polymer, which in turn depends on the structure(s) of the monomer(s) used. An important property of polymers is their hydrophobicity and water resistance, especially in coatings applications^{3,4}. This property can be achieved by using monomers that have a high hydrophobicity, such as versatic acid derivatives⁵. Due to the strong hydrophobicity of such monomers a special synthetic method is needed in order to obtain required products, and have good control over the (co)polymer structure, especially in heterogeneous systems.

1.3. Miniemulsion polymerization

Oil and water are essentially non-miscible; they coexist as a water phase and an oil phase, with each phase containing only a trace of the respective immiscible components. This immiscibility can be overcome by the addition of a sufficient quantity of a so-called surfactant. The latter disperses the oil phase into the water phase or vice versa, which, upon stirring, forms a milky mixture known as an emulsion. Under stirring, the emulsion mixture usually consists of four components in the water phase: large monomer droplets (roughly 1 μm in size), monomer-swollen micelles in which the surfactant molecules aggregate with their hydrophobic tails as the core and hydrophilic heads as the shell, some monomer molecules, and free surfactant molecules dissolved in the water.

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In the emulsion system the oil phase tends to separate from the water phase with time, upon standing. This process is due to two main mechanisms. The first is the coalescence of the monomer droplets due to van der Waals force attraction. The second is the Ostwald ripening process, in which the small monomer droplets are degraded by monomer diffusion to the larger droplets. The stability of the emulsion against degradation by these processes is brought about by the use of a surfactant and the addition of an extremely hydrophobic component. Such a system is known as a miniemulsion⁶. In miniemulsions, small and stable nanodroplets of monomer in the size range of 50–500 nm are dispersed in the aqueous phase prior to the polymerization process. Such a system can be achieved by the combination of high shear treatment (high energy), a suitable surfactant, and the presence of an extremely water-insoluble compound, known as a costabilizer. The size of the monomer droplets can be tailored by a number of parameters in the system, including the type and amount of surfactant and the volume fraction of the dispersed phase.

The polymerization mechanisms of conventional emulsion and miniemulsion polymerizations are, in some ways, significantly different. In a conventional emulsion polymerization the reaction process can be divided into three intervals. (i) Particle nucleation occurs during Interval I, in which radicals generated in the aqueous phase enter the monomer-swollen micelles and initiate the polymerization. These radicals may also continue to grow until they become surface active to form polymer particles (this is known as homogeneous nucleation). (ii) Interval II involves polymerization within the monomer-swollen polymer particles, with the monomer supplied by diffusion from the monomer droplets. (iii) Interval III begins when the monomer droplets disappear or they reach a polymer fraction (if they capture a radical) similar to that of the particles and continues to the end of the reaction. In a miniemulsion, radicals generated in the aqueous phase, due to the large total droplet surface area, enter monomer droplets directly to form polymer particles. Interval II in an emulsion polymerization is limited when highly water-insoluble monomers are used. Alternatively, in a miniemulsion system each of the droplets can be regarded as an individual batch reactor, and highly water-insoluble monomers can be introduced, in order to synthesize a highly hydrophobic polymer. Such methods are important in the production of water-resistant coatings⁷.

1.4. Objectives

The objectives of this study are as follows:

- Determine the reactivity ratios for the homogeneous free radical copolymerization of vinyl neononanoate (VeoVa-9) with butyl acrylate (BA) in benzene at 80°C using 2,2'-azobisisobutyronitrile (AIBN) as an initiator.
- Investigate the copolymerization of VeoVa-9 and BA by an *in-situ* NMR analysis of the reaction kinetics in deuterated benzene at 70°C, using different monomer feed ratios.
- Investigate the miniemulsion copolymerization of VeoVa-9 and BA.
- Characterize the copolymer product from the miniemulsion copolymerization reactions in terms of:
 - i. chemical composition, using two-dimensional chromatography at critical conditions
 - ii. the copolymer properties, by dynamic mechanical analysis (DMA) and surface contact angle measurements

1.5. Thesis outline

Chapter 2: This chapter gives an overview of the free radical copolymerization kinetic methods for estimating the monomer reactivity ratios, and the miniemulsion technique.

Chapter 3: Experimental details pertaining to the synthesis and characterization of VeoVa-9/BA copolymers are given.

Chapter 4: The results obtained for the copolymerization of VeoVa-9 and BA are discussed.

Chapter 5: General conclusions and recommendations for future study are presented.

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Chapter 2

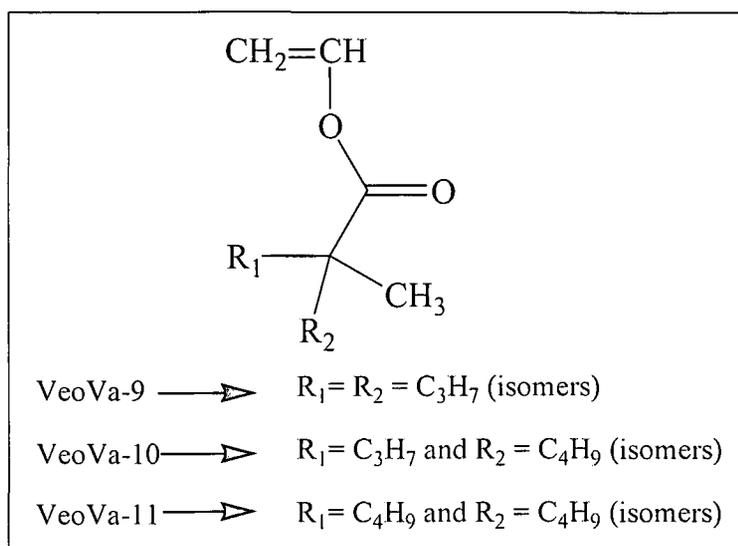
Theoretical background

2. Free-radical polymerization of vinyl monomers

2.1. Introduction

From the commercial point view, vinyl polymers are the most important of all polymer types. The polymerization reaction of vinyl monomers is commonly known as a chain-reaction process or addition polymerization, in which there is no by-product resulting from the polymerization reaction. In this type of polymerization reaction, the reaction is usually initiated by the decomposition of initiator or by the influence of light. The polymerization occurs only at the reactive end of a growing chain (unless a transfer reaction occurs), hence high molecular weight is achieved¹.

A wide variety of vinyl monomers are commercially used, including olefins, acrylates and vinyl esters. Due to the important applications of this type of monomer, e.g. in coating applications^{2,3}. The main focus of this study will be on investigating the copolymerization behaviour of vinyl ester and acrylate monomers as well as investigating some properties of the obtained copolymers. There are a number of different vinyl ester monomers, while vinyl acetate is the most industrially important monomer of this type, a number of other vinyl esters have also been used, such as vinyl propionate, vinyl oleate and the derivatives of versatic acid. The latter class of vinyl esters is known by the trade name VeoVa, which consists of vinyl nononanoate VeoVa-9, vinyl neodecanoate VeoVa-10 and VeoVa-11. These monomers represent a family of vinyl ester monomers with a unique highly branched carbon-rich structure (Scheme 2.1). Their principal use is as modifying comonomers in vinyl acetate and acrylic polymerization, to enhance some properties of the vinyl acetate and acrylic polymers, especially in terms of improving the water resistance and hydrolysis resistance^{3,4}.



Scheme 2.1: Different structures of versatic acid derivatives (VeoVa) monomers.

The main difference between these monomers is the degree of branching and the length of the hydrocarbon side groups, which vary the glass transition temperature T_g of their homopolymers. Due to this variation in the T_g , these monomers have been used as modifying comonomers and used to upgrade the performance of a wide range of copolymers. The most distinguishing features of these monomers are their resistance to hydrolysis, resistance to UV light, and they improve the copolymer hydrophobicity⁵. These features can be explained by the steric effect of the branched structure which functions as a shield that protects the main polymer chains against hydrolysis⁴. Another advantage of these monomers is that they can easily be copolymerized with wide range of monomers including ethylene, vinyl esters, acrylates and methacrylates⁴.

The synthesis of these polymers and copolymers with other types of monomers (e.g. acrylates) can be achieved via homogenous (bulk and solution) or heterogeneous (conventional emulsion, suspension and miniemulsion) systems. The use of the homogeneous methods in the production of vinyl ester polymers is limited due to viscosity and environment reasons. However, these methods still can be used, especially for the production of low molar mass polymers. Heterogeneous methods are considered the most industrially important technique when using vinyl ester monomers⁶. Due to the low water solubility of these monomers, conventional emulsion polymerization is difficult, and so the alternative method, namely miniemulsion polymerization has been used to eliminate the effect of low solubility problems^{7,8}. Due to the industrially important applications (especially coatings) of the vinyl ester and acrylate polymers, the copolymerization of BA with VeoVa-9 in miniemulsion

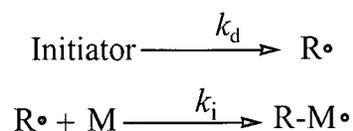
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will be investigated in this study. Some copolymer properties will also be investigated including the glass transition temperature using dynamic mechanical analysis, DMA, and the surface properties of the copolymers using contact angle measurements.

2.2. Free-radical polymerization

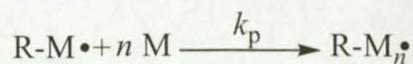
Free-radical polymerization is a technique that is widely used in the production of polymeric materials due to its advantages (fast process, high molecular weight polymer and no by-product resulting from the reaction) over other polymerization techniques. The compatibility of the free radical polymerization process with a wide range of monomers is an important advantage. Also there are many different methods by which the free radical reactions can be performed; these methods include homogenous methods such as bulk and solution polymerization, and heterogeneous such as suspension, emulsion and miniemulsion polymerization. Conventional emulsion and/or miniemulsion methods have major advantages of being environmentally friendly techniques, since the polymerization reaction is performed in a water medium^{6,9}.

The kinetics of free radical polymerization is dependent on three main steps: initiation, propagation, and termination^{6,9,10}. The initiation step involves the generation of primary radicals (R^\bullet), and the reaction of these radicals with a monomer unit. The generation of primary radicals can be achieved through the decomposition or dissociation of materials that are readily able to produce free radical species. Such materials decompose by various mechanisms, including thermal decomposition (e.g., azo compounds), photochemical (e.g. disulfides and benzil), and via a redox reaction (e.g., iron (II)/peroxide combinations) processes. The primary free radical may undergo addition to the double bonds of monomers (M). The decomposition and initiation processes can be described as follows:



k_d is the initiator decomposition rate coefficient, and k_i is the initiation rate coefficient.

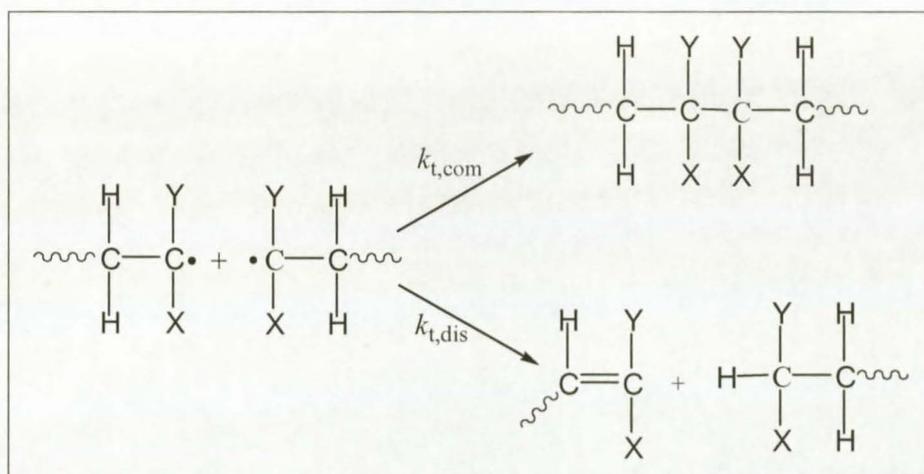
Following the initiation steps, the formed radicals propagate to form polymer chains by reacting with more monomer units; this stage is illustrated as follows:



k_p is the propagation rate coefficient.

During this step, a number of chain transfer reactions may occur in which the free radical activity from the propagating chain is transferred by a chain transfer reaction to other molecules. These molecules include solvent, formed polymer, or potentially any other component existing in the polymerization system. This reaction is an important side reaction in free-radical polymerization that limits the obtainable molecular weight in conventional free-radical polymerization reactions, and often plays an important part in the rate of reaction.

In the termination step two radicals are destroyed, thus preventing further addition of more monomer units to those chains. This may occur via either of two possible mechanisms (Scheme 2.2); in the first mechanism, two growing radicals link, leading to a single terminated chain, while in the second mechanism, hydrogen abstraction at the end of one of the growing radicals leads to two polymeric molecules, one of which contains an unsaturated end-group that is capable of further reaction.



Scheme 2.2: The two possible termination mechanisms in a conventional free-radical polymerization reaction: combination and disproportionation.

2.2.1. Free-radical polymerization techniques

Free-radical polymerization can be performed in homogeneous systems, or in heterogeneous systems. In this work, the focus will be only on solution polymerization and miniemulsion polymerization. The use of solution polymerization will be limited only to the calculation of the reactivity ratios for the monomers used.

2.2.1.1. Homogeneous techniques

Homogeneous systems include bulk, suspension, solution, and in the gas-phase. Free-radical polymerization in solution (usually organic solvents are used) is a well known process for the synthesis of polymers. A solvent may affect the polymer structure and molecular weight by acting as a modifier during the polymerization process, due for example, to chain transfer reactions to solvent and the possible solvent effects on the product properties. This should be considered when choosing a suitable solvent. In this regard the solvent can be chosen by its chain transfer constant, with a lower constant resulting in a higher potential molecular weight of the polymer.

The major advantage of solution polymerization is the efficiency of heat transfer and viscosity. In terms of the polymer properties, the use of solution polymerization is limited (for the need of specific properties such as low molecular weight, good flow behaviour and homogeneous film formation). This limitation is due to its environmentally unfriendly characteristics (e.g. the need for solvent disposal) and also due to the difficulty in removing the solvent from the resultant polymer. Nevertheless solution polymerization can still be used when the polymer solution is used directly (e.g. in solvent-based paints)^{6,11}.

2.2.1.2. Heterogeneous techniques

Polymer latexes are mostly made by emulsion polymerization, where the monomers are dispersed in a non-solvent continuous phase. The choice of this method is due to a number of advantages it has over the other methods. The major advantage of the process includes the use of an aqueous medium. It has, therefore become a popular process, to minimize the use of volatile organic solvents, and thus reduce the toxic effect and health risks associated with the use of organic solvents, since the non-solvent used in most cases is water. There are further reasons why the dispersion of a polymer in water is preferred: first, high molecular weight polymers can be obtained with good control over the polymerization kinetics; second, high solid content latexes can be achieved without viscosity problems; and third, the product of the polymerization can be directly applied (e.g. in coatings applications or adhesives). Also, efficiency of heat transfer and core-shell latices and other morphologies can only be readily made by emulsion techniques.

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There is a variety of heterogeneous techniques that can be used to produce polymer dispersions, such as conventional emulsion, microemulsion, and miniemulsion polymerizations¹². The latter technique will be used in this study due to its numerous advantages when using highly hydrophobic monomers.

2.3. Miniemulsion polymerization

2.3.1. Introduction

Miniemulsion polymerization has recently become the major focus of an increasing number of studies due to its unique features. It can be used to overcome the problems associated with the other dispersion techniques, such as hydrophobicity of the monomers. Miniemulsion polymerization can be defined as a heterophase polymerization in which small, stable homogeneous monomer droplets are generated and dispersed in a continuous water phase. These droplets can then be converted to polymer particles by means of polymerization reactions. If this is the case then this means that the droplets that are converted into particles remain the primary locus of the polymerization reaction. So the monomer droplets can be considered as nanoreactors dispersed in a continuous water phase, thus reducing heat transfer problems¹³.

2.3.2. History of miniemulsion polymerization

The history of the miniemulsion system goes back to the 1970s when Ugelstad *et al.*¹⁴ carried out the first polymerization of submicron droplets using styrene as the monomer and sodium lauryl sulfate (SLS) in addition to cetyl alcohol (CA). In those early years, the term 'miniemulsion' had not yet been given to such a system, although these polymerizations did generally fit the definition of miniemulsion polymerization, in which small monomer droplets (smaller than 1 micron) are created by stirring a solution of monomer and costabilizer into a mixture of the water and surfactant, followed by initiating the polymerization by the addition of the initiator.

Later, a number of studies focused on investigating the actual nucleation mechanism¹⁵⁻¹⁷. In these studies, styrene was used as the sole monomer and a number of different costabilizers were used, including hexadecane (HD), cetyl alcohol and dodecanol. Besides using simple

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stirring to prepare the miniemulsions, high shear and ultrasonic devices were also used. In general, those studies concluded that the smaller the droplets, the more likely it is that these droplets will be the nucleation sites, since the surface area of these droplets is large enough for significant radical absorption¹⁸.

Since the mid-1980s the miniemulsion technique has been the subject of many studies. Numerous different monomers have been used, including styrene, acrylates and methacrylates, vinyl esters, and also highly hydrophilic monomers such as vinyl 2-ethylhexanoate¹⁹. Miniemulsion copolymerizations have also been studied using different types of monomers with different water solubilities. The formulations of these miniemulsion systems were varied by using different types of surfactants, costabilizers and initiators. The miniemulsion states were achieved by using different shear devices, including Ultrasound (US) and a Microfluidizer²⁰⁻²³.

2.3.3. Nucleation mechanisms in heterogeneous systems

In general there are three types of nucleation mechanisms that exist in heterogeneous systems, and these mechanisms depend on the formulation and preparation process of the actual system. These mechanisms are (i) micellar nucleation, (ii) homogeneous nucleation and (iii) droplet nucleation²⁴.

In the micellar nucleation mechanism, radicals enter the micelles, where some monomer molecules exist. As the radicals enter the micelles, the polymerization reaction is initiated and polymer chains are formed. Further monomer molecules diffuse to the micelles from the monomer droplets, which serve as monomer reservoirs. This mechanism is the typical mechanism for microemulsion polymerization^{25,26}, since this process only occurs if the surfactant concentration is above the critical micelle concentration. It was assumed however that the micellar nucleation mechanism was very unlikely to occur in miniemulsion reactions since micelles usually do not exist, due to the low surfactant concentrations used in miniemulsion systems. The absence of micelles in the miniemulsion was proved by Landfester and coworkers²⁷, who showed that the surface tension of the miniemulsion is far above that of saturated surfactant solutions.

The second possible nucleation mechanism for both the conventional emulsion and miniemulsion systems is the so-called homogeneous nucleation. In this case the radicals in the

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aqueous phase polymerize to form oligomers, and these continue to grow until they reach a critical chain length at which they are no longer water-soluble, these oligomers then swell with monomer and adsorb surfactant, and eventually become polymer particles. Throughout the growth process of the oligomers, the monomers are brought to the reaction sites (polymer growing particles) by diffusion. This mechanism is typically sensitive to the overall initiator concentration and depends on the solubility of the monomers used in the aqueous phase.

The droplet nucleation mechanism (using water-soluble initiator) assumes that the small monomer droplets (0.01–0.5 μm) which form during the emulsification process are nucleated directly via the oligomeric radicals formed in the aqueous phase, which enter these droplets and react with the monomers present to form particles. For an ideal miniemulsion system, the droplet nucleation process is the most widely accepted mechanism^{14,27-30}. As a result of this mechanism, in an ideal system, all of the monomer droplets are nucleated, and thus the number and size of polymeric particles do not change during the polymerization process. This mechanism also explains the successful use of oil-soluble initiator as well as the use of extremely low-water-solubility monomers.

2.3.4. Mechanism of miniemulsion polymerization

The mechanisms of miniemulsion and conventional emulsion polymerizations are, in some ways, significantly different^{19,31,32}. In a conventional emulsion polymerization reaction the process can be divided into three intervals^{31,33} (e.g. I, II and III, see Figure 2.1). During interval I the nucleation of the particles occurs, and this usually only carries on until monomer conversion reaches about 10%, when most of the particles are nucleated. The nucleation process normally starts when the radicals that formed in the aqueous phase grow via propagation, enter into micelles, or continue to grow until they become large enough to form a primary particle by homogeneous nucleation, which may undergo limited flocculation until a stable particle population is obtained. Particle nucleation is usually much more significant than monomer droplet nucleation. This is attributed to the large size of the monomer droplets (1–10 μm) which have a much lower total surface area than that of the micelles^{31,32}.

Following the nucleation process, interval II takes place. This involves polymerization within the monomer-swollen polymer particles. In this step the large monomer droplets serve as monomer reservoirs, supplying monomer to the reaction sites. By diffusion through the aqueous phase, the monomer molecules migrate from the monomer droplets to the

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monomer-swollen polymer particles in which the polymerization reaction takes place. At this stage the rate of polymerization is relatively constant until most of the monomer in the droplets is consumed. Interval III begins when all of the monomer droplets disappear (or at least reach a polymer fraction similar to that of the particles (in the case they capture radicals)) and continues to the end of the reaction^{13,24}.

In the miniemulsion system, the monomer droplets are very small (0.01–0.5 μm) compared to most conventional emulsion systems. Hence the surface area of the droplets in this system is very large, and most of the surfactant molecules are adsorbed at the droplet surface. In the case of a water-soluble initiator, particle nucleation is mostly via radical (primary or oligomeric) entry into the monomer droplets, since little surfactant is present in the form of micelles, or as free surfactant available to stabilize particles formed in the continuous phase. The important feature is that the reaction proceeds by polymerization of the monomer in these small droplets, so there is no true Interval II. This allows the possibility of using both oil- and water-soluble initiators^{30,34,35}, as well as the successful incorporation of highly water-insoluble monomers in miniemulsion systems^{20,23}. The mechanisms of conventional emulsion and miniemulsion polymerization are schematically shown in Figure 2.1^{19,24}.

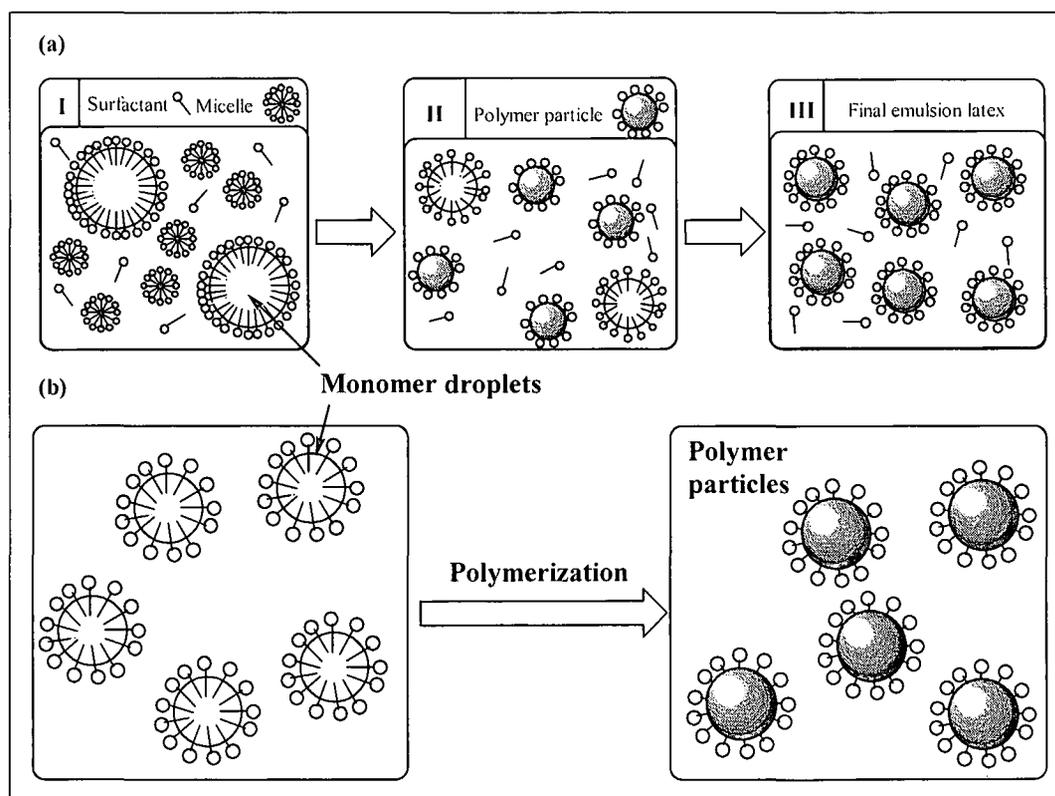


Figure 2.1: Conventional emulsion polymerization (a) and miniemulsion polymerization (b)

2.3.5. Miniemulsion formulation and preparation

Miniemulsion polymerization is a special formulated heterogeneous system in which submicron monomer droplets are dispersed and stabilized in the aqueous phase. In general, emulsion systems, before polymerization, degrade by two mechanisms (i) monomer diffusion from small to large droplets^{36,37} and (ii) monomer droplet coalescence. In the miniemulsion system, these mechanisms are suppressed by the addition of extremely hydrophobic, low molecular weight compounds (costabilizers) and a surfactant respectively. So the key issues in the preparation of a miniemulsion are the formulation as well as the method of preparation^{19,36}. These issues will be discussed below.

A typical formulation of a miniemulsion system is a continuous phase which is usually a solution of surfactant in water, and an oil phase which includes the monomer(s), and the costabilizer²⁹. In miniemulsion polymerization, different types of initiator systems are used, including redox systems³⁸ and water-or oil-soluble initiators³⁹⁻⁴¹. Due to its unique mechanism miniemulsion polymerization can be considered, with respect to the water solubility, as a suitable method for most monomers, including both highly water-soluble and highly water-insoluble monomers. The ability to use highly water insoluble monomers in a miniemulsion is a very important feature, since this feature is limited in a conventional emulsion, due to the need for highly hydrophobic monomers to be transported from the monomer droplets to the micelles through the water phase.

Such highly water insoluble monomers that have been used in miniemulsions, include stearyl methacrylate, dodecyl methacrylate, vinyl 2-ethylhexanoate and vinyl versate^{23,42}. In the present study, vinyl nonanoate (VeoVa-9) and butyl acrylate (BA) will be used in miniemulsion polymerization, to investigate the copolymerization kinetics. The product of this copolymerization will also be characterized in terms of chemical composition via two-dimensional chromatography (2-D), and in terms of physical properties, including thermal properties and surface properties using dynamic mechanical analysis and contact angle measurements respectively.

The preparation of a miniemulsion commences with the emulsification step, in which submicron-size monomer droplets are created and stabilized in the water phase, followed by the polymerization processes¹⁹. The preparation processes in miniemulsion polymerization can be schematically described by Figure 2.2¹⁸.

2.3.6. Emulsification and homogenization techniques

The emulsification process in a miniemulsion starts with premixing of the dispersed phase (monomer(s) and costabilizer) and continuous phase (water and surfactant). This process includes two mechanistic steps: first, deformation and disruption of the droplets, in which the size of the monomer droplets decreases and second, stabilization of the newly formed droplets by the surfactant molecules. Thereafter the mixture is then subjected to highly efficient homogenization.

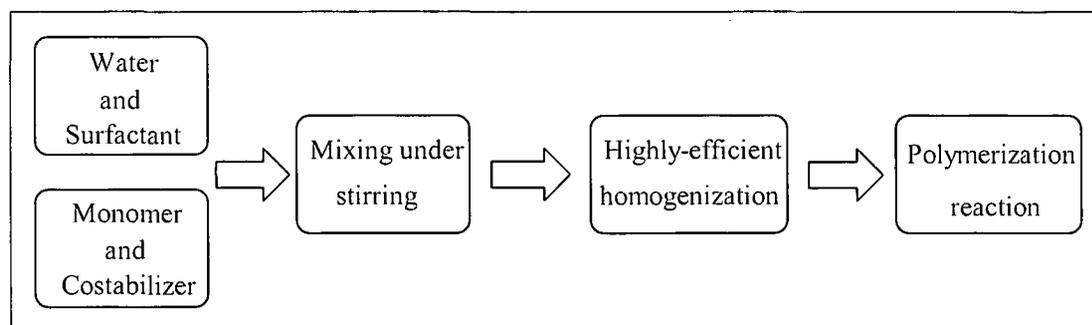


Figure 2.2: Schematic representation of a miniemulsion polymerization.

A number of homogenization techniques have been used for emulsification in miniemulsion. These methods vary, depending on their efficiency at breaking the monomer droplets. In early work, Ugelstad *et al.*¹⁴ used simple stirring to create droplets with sizes smaller than 1 micron by using a mixed emulsifier system of SLS and CA. More recently, more highly efficient equipment has become available, and is used; the most widely used now are rotor-stator systems, sonifiers and high-pressure homogenizers^{13,19}. Rotor-stator systems and other high-shear devices rely on turbulence to produce the emulsification. In these devices the minimum size of the droplets that can be obtained depends on the geometry of the rotor-stator system and on the rotation speed.

The sonifier device uses ultrasound waves, inducing cavitation in the medium, which causes the breakage of the monomer droplets, and hence small monomer droplets are obtained. The main disadvantage of the sonifier is that additional stirring is needed during the emulsification process, since only a small fraction of the fluid around the sonifier tip is directly affected by the ultrasound waves. The additional stirring is required to allow all of the fluid to pass through the ultrasound region and to thus ensure the break-up of the monomer droplets until a suitable small size is reached.

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A number of authors have reported that the size of the monomer droplets in miniemulsions prepared using a sonifier is a function in the sonication time^{27,29}. Landfester *et al.*²⁷ determined the effect of the ultrasonication time on the particle size by changing the time of the ultrasonication process between 15 s and 30 min. Results of those experiments showed that the droplet size decreased as the time of sonication increased, before a steady state was reached, where the droplet size is no longer a function of the sonication time. Figure 2.3 describes the sonication process where the size of the droplets first shows a pronounced decrease; however, as the time proceeds the droplet size reaches an equilibrium size, which depends on the initial formulation. This is due to two mechanistic steps: first, deformation and disruption of the monomer droplets, under the power of the ultrasound waves, which increase the specific surface area of the emulsion, and the second, the stabilization of the newly formed interfaces by surfactant. During the homogenization process, in the beginning, the polydispersity of the monomer droplets is still high, however, as time proceeds, the polydispersity decreases by the constant fusion and fission processes; thus, the miniemulsion reaches a steady state (Figure 2.3¹⁸)

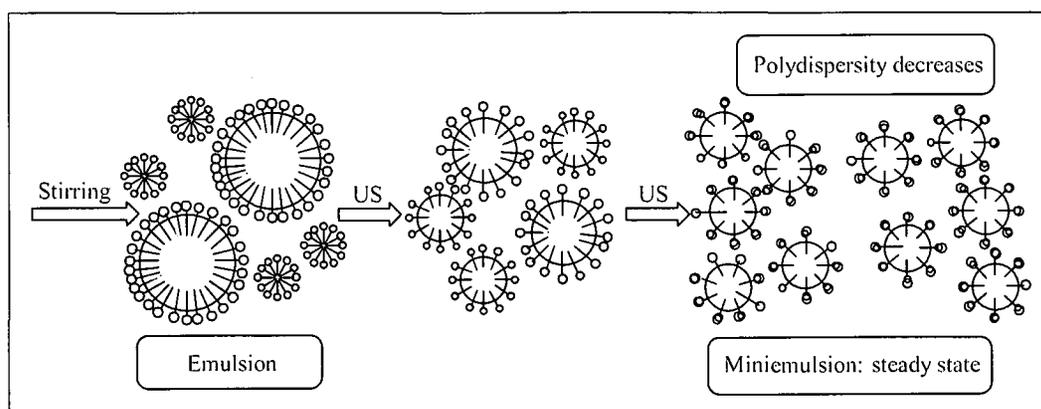


Figure 2.3: Schematic representation of the formation of a miniemulsion by ultrasound.

High-pressure homogenizers or microfluidizers are commonly used for processing large quantities. In these techniques, the break-up of the droplets occurs due to shear, impact and cavitation forces, which are focused on a small area in a very small volume of the emulsion fluid, resulting in a homogenized dispersed phase with stirring.

In a miniemulsion system, the droplet size is determined by the amount of monomer in water (solids content), monomer solubility, the amount of surfactant used and also droplet (emulsion) preparations as described above. It was reported by Landfester *et al.*²⁸ and Huang *et al.*^{27,43} that, as discussed above, the initial droplet size is also a function in the

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efficiency of the homogenizer. This means that the polydispersity of the droplets is quite high in the initial stage in the homogenization process; however the polydispersity of the droplets decreases as the droplets reach equilibrium size, where the miniemulsion is in a steady state (Figure. 2.3).

2.3.7. Role of surfactants (function, concentration and type)

In miniemulsions there are two mechanisms by which the monomer droplets degrade, as discussed above; the first is by Ostwald ripening, and the second is by coalescence of the monomer droplets. In general, the colloidal stability against coalescence can be achieved by the addition of surfactant molecules. The stability is due to the presence of charged groups (or steric stabilization, in the case of non-ionic surfactants) of the surfactant molecules on the surface of the monomer droplets; these charges provide strong electrostatic repulsion between droplets, thus providing stability for the droplets against coalescence⁷.

The type and amount of surfactant are crucial parameters in terms of droplet stability, polymerization rate and size in a miniemulsion system. In this regard, Bechthold and Landfester³⁰ reported that the polymerization rate of a styrene miniemulsion, prepared with SDS surfactant, increased as the surfactant concentration increased, and that the higher the surfactant concentration is the smaller the particle size will be, thus inducing a higher particle number (e.g. small particle sizes cause a high particle number).

In a miniemulsion system, the size of the monomer droplets can be controlled by a number of factors, including the ultrasonication time as well as the amount of surfactant used^{27,44}. At constant ultrasonication time, the monomer droplet size is a function of the ability to increase the stability of newly created interfacial areas (new droplets). The ability to stabilize these droplets is therefore dependent on the amount of surfactant, and hence the area per surfactant molecule becomes an important parameter in determining the droplet stability. Landfester⁴⁵ has reported that for SDS surfactant, only one SDS molecule per 5.5 nm² is needed to stabilize a monomer droplet with a diameter of about 180 nm. This value will decrease to a value of 0.4 nm² for droplets of 50 nm diameter. This result was similar to that found by van Zyl *et al.*⁴⁴ who studied the role of surfactant concentration on controlling the particle size.

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In terms of the type of surfactant, the majority of miniemulsion polymerizations reported in the literature are based on anionic surfactants, however cationic and non-ionic surfactants have also been used to produce stable miniemulsions with droplets that have similar sizes to those produced by anionic surfactants⁴⁶⁻⁴⁸. Examples of such surfactants are SDS for anionic surfactants and cetyltrimethyl ammonium bromide and cetyltrimethyl ammonium tartrate for cationic surfactants. Wang and Schork⁴⁹ used poly(vinyl alcohol) in the miniemulsion polymerization of vinyl acetate. They showed that a stable miniemulsion was produced when (HD) was added, but this miniemulsion was no longer stable when the HD was removed. A stable miniemulsion of styrene and methyl methacrylate (MMA) has been obtained using the polymerizable vinyl benzyl sulphosuccinic acid sodium salt as a surfactant with HD⁵⁰.

2.3.8. The role of co-stabilizer (hydrophobe)

In miniemulsion systems, the monomer droplets can also degrade by monomer diffusion from small to large droplets, and this process is also known as Ostwald ripening. Because of the contribution of the surface energy of the small and large droplets, the chemical potential of the monomer in small droplets is higher than in large droplets, which leads the monomer molecules to diffuse from small to large droplets^{7,36}.

Stability against this process can be achieved by the addition of a highly water insoluble compound, which minimizes the degradation of small droplets by monomer diffusion. The use of small amounts of the hydrophobe leads to a build-up of an osmotic pressure (Π) in the monomer droplets, which suppresses the monomer diffusion and hence small stable droplets are obtained. If the costabilizer (hydrophobe) molecules are confined in the monomer droplets, the change in the droplet size by the diffusion of monomer molecules results in an increase in the osmotic pressure with a decrease in the droplet radius (R) ($\Pi \sim R^{-3}$)²⁷. This increase in the osmotic pressure in the small monomer droplets prevents growth of the large droplets by stopping the monomer diffusion process, and hence the small monomer droplets have increased stability.

In terms of the solubility of the costabilizer, a number of different costabilizers have been used in miniemulsion systems⁵¹, including HD³⁰, CA³⁹, and also highly water insoluble monomers such as lauryl methacrylate (LMA) and stearyl methacrylate (SMA). It was found that the efficiency of the costabilizer depends on its solubility in both the water phase and oil

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phase (monomers)^{22,47,52}; the higher its water insolubility, the more stable are the monomer droplets¹⁹.

Polymeric materials, such as polystyrene and polymethylmethacrylate PMMA⁵²⁻⁵⁶ have also been used as costabilizers in miniemulsion systems. Using a miniemulsion of styrene stabilized with polystyrene, the effect of the molecular weight and the end-groups of the added polymer were investigated, and it was found that neither the molar mass nor the end-group type had an effect on the miniemulsion kinetics⁵⁴. In general, the rate of the polymerization reaction was much faster when the polymer was used than without polymer. In another study of miniemulsions, Yu *et al.*⁵⁷ used vinyl siloxane rubber as a hydrophobe to investigate the effect of the molecular weight of the rubber on both the stability and kinetics of the miniemulsion. The rate of polymerization was found to decrease with an increase in the molecular weight of the rubber and, in terms of the stability, these miniemulsions were not as stable as those using HD or CA.

With respect to droplet stability in the minemulsion, it was often found that the most stable miniemulsion was obtained when HD was used. This explains the large number of miniemulsions that are described in the literature in which hexadecane is used as costabilizer. Hexadecane does however affect the properties of the final polymer, which usually limits its use to laboratory studies only.

2.3.9. Batch and semi-batch processes in miniemulsion polymerization

The procedure by which miniemulsion polymerization is carried out has a profound effect on the properties of the resulting latex and polymer. Generally, there are two polymerization processes, each of which results in different polymer performance (composition and properties), even when the same reaction formulations are used. These processes are batch and semi-batch polymerizations. The main difference between the two processes is that in the batch process all of the reagents are added to the reactor at the beginning of the polymerization reaction, while in the semi-batch process (also known as a semi-continuous batch processes) only some of the reagents are added to the reactor at the beginning of the reaction, and the remaining material is added during the polymerization process¹³.

According to the polymer characteristics desired, the addition of the respective components can either be done continuously or at certain time intervals throughout the polymerization

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reaction. Industrially, the use of the batch processes is limited due to a number of reasons, such as the lack of control over the polymer structure; hence the semi-batch process is the more widely used method, where greater control over the polymer structure and polymerization process and hence better polymer properties can be achieved.

Miniemulsion homopolymerization and copolymerization have been carried out using both (batch^{22,23,58} and semi-batch^{23,42}) processes, to investigate the effect of the polymerization conditions on the polymerization kinetics and polymer properties. Reimers *et al.*⁵¹ carried out batch copolymerizations in miniemulsions; MMA was used as the main monomer and a number of other monomers with different water solubilities as the comonomers. They reported that the chemical composition of obtained polymer was affected by the water solubility of the comonomers used. Again the semi-batch process resulted in better control in terms of the polymer structure than the batch processes.

In a miniemulsion system, the main nucleation mechanism is the droplet nucleation mechanism, which gives this system advantages over the microemulsion and conventional emulsion systems, as there is no need for monomer transport through the monomer phase.

These characteristics of miniemulsions provide a number of advantages in the production of latexes with special properties including high solid content latexes with low viscosity^{59,60}. Due to the nucleation mechanism of the miniemulsion, highly hydrophobic monomers can be introduced^{20,42}. This is an important feature in the production of hydrophobic polymers, especially in the manufacture of coatings in which water resistance is the major interest¹³.

In the present study, the batch and semi-batch miniemulsion polymerization techniques will be used in the copolymerization of VeoVa-9 and butyl acrylate. The obtained copolymers will be characterized in terms of chemical composition using ¹H-NMR spectroscopy and 2-D chromatography. Some of the copolymer properties will also be investigated, including thermal and surface properties (hydrophobicity) using dynamic mechanical analysis (DMA) and contact angle measurement respectively.

2.4. Free-radical copolymerization

Most commercial polymers prepared by free-radical polymerization are in fact copolymers formed by the simultaneous polymerization of two or more monomers, this usually results in

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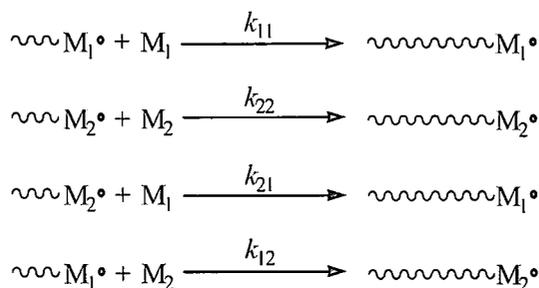
polymers with unique properties that lie between those of the corresponding homopolymers. Several different types of copolymers can be made, depending on the sequence of repeating units along the chains and the process used to prepare these copolymers. The main copolymer types known are random copolymers, alternating copolymers, block copolymers, graft copolymers and star copolymers.

The distribution of the different monomeric units along the final copolymer chain is usually known as the chemical composition distribution (CCD). This distribution plays an important role in determining the copolymer properties. The CCD may vary between two different polymer chains that result from the same polymerization reaction. Therefore an understanding of the incorporation of each monomeric unit in the copolymerization reaction may provide some control over the CCD, which leads to control of the polymer properties⁶¹. In this regard, a number of models have been applied to describe the copolymerization process, including: (i) terminal unit model⁶²⁻⁶⁴, (ii) penultimate unit model⁶⁵⁻⁶⁷, (iii) antepenultimate unit model⁶⁸, (iv) complex participation model⁶⁹, (v) complex dissociation model⁷⁰ and (vi) the Comppen model⁷¹.

The terminal model was proposed by Alfrey (1944), Mayo and Lewis (1944), and Walling (1957)^{62,63}. This model can be used to describe the free radical copolymerization of most conventional monomers, including vinyl esters and acrylate monomers. This model assumes that the reactivity of the propagating species towards free monomer units is only affected by the monomeric unit at the end of the growing chain (active side). In this study, the terminal model will be used, since it adequately describes the copolymerization behaviour of vinyl neononanoate (Veova-9) with butyl acrylate (BA).

In the binary free-radical copolymerization reaction of two monomers (M_1) and (M_2), there are two types of propagating species involved: (i) a propagating chain that ends with a M_1 unit and (ii) a propagating chain that ends with a M_2 unit. By assuming that the kinetics obeys the terminal model⁷², four different propagation reactions are possible for copolymerization reactions. During the propagation step, the growth of radicals may occur either by adding a monomeric unit that is the same as the end unit (homo-propagation) or by adding the other monomeric type (cross-propagation), as shown below.

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Where k_{ij} is the rate coefficient of the respective reactions of the propagating chain.

Since only the terminal unit of the growing chain is important, the reaction rate is assumed to be chain-length independent, and interactions between monomer and solvent, and the possible chain transfer reactions, are negligible⁶⁴.

If steady-state conditions are assumed for the propagating centers⁷³ (i.e. concentrations of $[M_1]$ and $[M_2]$ remain constant) and that the rate of addition of M_1 to M_2 is equal to the rate of addition of M_2 to M_1 then:

$$k_{12}[M_1^\bullet][M_2] = k_{21}[M_2^\bullet][M_1] \quad (2.1)$$

Then the rates of monomer consumption can be represented as the following equations:

$$-\frac{d[M_1]}{dt} = k_{11}[M_1^\bullet][M_1] + k_{21}[M_2^\bullet][M_1] \quad (2.2)$$

and

$$-\frac{d[M_2]}{dt} = k_{22}[M_2^\bullet][M_2] + k_{12}[M_1^\bullet][M_2] \quad (2.3)$$

In order to find the rate at which the two monomers are incorporated into the copolymer, Equation 2.2 is divided by Equation 2.3 to give the copolymerization equation, which is expressed in the following equations:

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[M_1^\bullet][M_1] + k_{21}[M_2^\bullet][M_1]}{k_{12}[M_1^\bullet][M_2] + k_{22}[M_2^\bullet][M_2]} \quad (2.4)$$

or

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} \quad (2.5)$$

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where:

$$r_1 = \frac{k_{11}}{k_{12}}, \text{ and } r_2 = \frac{k_{22}}{k_{21}} \quad (2.6)$$

This (Equation 2.5) is the most familiar form for the copolymerization composition.

The ratio of the rates of the addition of each monomer can also be considered to be the ratio of the molar concentrations of the two monomers incorporated in the copolymer, which is denoted by $(\frac{m_1}{m_2})$. Using this ratio, the copolymer composition can be expressed as the following:

$$\frac{m_1}{m_2} = \frac{[M_1] (r_1[M_1] + [M_2])}{[M_2] ([M_1] + r_2[M_2])} \quad (2.7)$$

The copolymer composition equation defines the molar ratios of the two monomers M_1 and M_2 that are incorporated into the copolymer. As can be seen in the equation, this term is directly related to the concentration of the monomers that are in the feed at any time and also to the monomer reactivity ratios, r_1 and r_2 , which are the ratios of the rate coefficients for the addition of its own type of monomer to the rate coefficient for the addition of the other monomer. When RM_1^\bullet prefers to add the monomer M_1 instead of monomer M_2 , this means that the r_1 value is greater than one. When RM_1^\bullet prefers to add monomer M_2 instead of monomer M_1 , then the r_1 value is less than one. When the r_1 value is equal to zero, the monomer M_1 is not capable of adding to itself, which means that homopolymerization is not possible^{6,72}.

The copolymer equation can also be expressed in terms of mole fractions instead of concentration, which is useful in experimental studies. The concentration expression can be converted to mole fractions according to the following equations:

$$f_1 = \frac{[M_1]}{[M_1] + [M_2]} = 1 - f_2 \quad (2.8)$$

and

$$F_1 = \frac{d[M_1]}{d[M_1] + d[M_2]} = 1 - F_2 \quad (2.9)$$

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where F_i and f_i are the mole fractions of monomer $[M_i]$ in the copolymer and in the feed respectively.

The combination of these equations and the copolymerization equation yields another common form of the copolymerization equation (Equation 2.10)

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \quad (2.10)$$

This equation gives the mole fraction of monomer M_1 incorporated into the copolymer¹. The values of the reactivity ratios are an indication of the tendency of the propagating radicals, bearing M_1 or M_2 as the terminal unit, to either homopropagate or cross-propagate and hence they give an indication of the copolymer structure. The values of the reactivity ratios in a copolymerization system may be affected by a number of factors, including the reaction temperature, the reaction solvent and more importantly the chemical structure of the two monomers.

Since reactivity ratios are important parameters in any copolymerization reaction for estimating the chemical structure of the resultant copolymer, many methods have been applied to determine these parameters in binary copolymerization systems. These methods are briefly discussed in the following section.

2.4.1. Determination of reactivity ratios

Estimation of reactivity ratios of any copolymerization system is an important task to both academia and industry, as evidenced by the number of publications that focus on this. Various methods exist to estimate the reactivity ratios in binary copolymerization reactions. These methods can be theoretical or experimental^{6,72}.

2.4.1.1. Theoretical method

The theoretical method is based on the Q-e scheme⁷⁴ which is a semi-empirical model that eliminates the need for experimental work, and this is where its popularity stems from. The Q-e scheme assigns characteristic constants to monomers. These constants are independent of the comonomer involved in the copolymerization reaction. The Q-value is a measure of the general reactivity of a monomer and is determined by the resonance stabilization of a

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monomer. The e -value is related to the polarity of the monomer. Thus, for a binary free radical copolymerization of monomers M_1 and M_2 , the corresponding reactivity ratios are given by the following expressions:

$$r_1 = \left(\frac{Q_1}{Q_2} \right) \exp[-e_1(e_1 - e_2)] \quad (2.11)$$

and

$$r_2 = \left(\frac{Q_1}{Q_2} \right) \exp[-e_2(e_2 - e_1)] \quad (2.12)$$

where Q_1 and Q_2 are indicative of the reactivity of M_1 and M_2 respectively, and e_1 and e_2 are measures of the polarity of M_1 and M_2 respectively. These values of reactivity ratios can not be considered as accurate values since the Q and e value do not take into account the bulkiness of the side groups of the monomer which affect the monomer reactivity of certain monomers; however these values of the reactivity ratios are still very useful to indicate possible behaviour of copolymerization reactions^{6,73}.

2.4.1.2. Experimental methods

A number of experimental methods have been used to estimate the reactivity ratios of a large number of monomers. These methods include linear methods and nonlinear methods. The linear methods include (i) intersection method⁷⁵, (ii) Fineman-Ross method (FR)⁷⁶, (iii) inverted Fineman-Ross method⁷⁶, (iv) Kelen-Tüdös method (KT)⁷⁷, (v) Yezrielev-Brokhina-Rosin method (YBR)⁶⁴ and (vi) analyzing dyad ($-A-A-$, $-A-B-$ and $-B-A-$), triad ($-A-A-A-$, $-B-A-A-$, $-B-A-B-$, and $-A-A-B-$ for A centred) and higher order distributions by using NMR spectrometry⁷⁸.

The linear methods apply to some linear forms of the copolymer composition equation (Equation 2.5). Here some statistical limitations are inherent in these linearization methods. O'Driscoll *et al.*⁷⁹ determined that the dependent variable does not truly have a constant variance and the independent variable in any form of the linear copolymer equation is not truly independent. Therefore, analyzing the composition data using a non-linear method has come to be the most statistically reliable technique.

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The nonlinear methods include (i) curve-fitting method, (ii) Tidwell-Mortimer method⁸⁰, (iii) Kuo-Chen method, (iv) error-in-variables method⁸¹ (v) optimization method. The non-linear methods use the non-linear form of the copolymerization equation (Equation 2.10) for the calculation of the reactivity ratios of given monomers. In these methods, a graph is generated by plotting the monomer concentration that was incorporated into the polymer chain versus the monomer concentration in the feed at different monomer concentrations in the feed. In this regard, the Tidwell-Mortimer or nonlinear least squares method is the most widely used approach of these methods to obtain accurate values of reactivity ratios. For selected values of r_1 and r_2 , the sum of the squares (SS) of the differences between the experiment F_i^{exp} and theoretical F_i^{cal} mole fractions in the copolymer (Equation 2.13) for all different points is minimized.

$$SS = \sum_{i=1}^n (F_i^{\text{exp}} - F_i^{\text{cal}})^2 \quad (1.13)$$

The use of the Gauss-Newton nonlinear least squares procedure predicts the reactivity ratios for a given set of data after repeating the calculations so that the difference between the experimental data points and the calculated data points on a plot of mole fraction of comonomer incorporated into the copolymer (e.g. F_1) versus comonomer in the feed (e.g. f_1) is reduced to a minimum value^{82,16}. The Tidwell-Mortimer method uses a good first estimation of the reactivity ratios which can be obtained using any technique (FR or KT) for the system and experimental data of the amounts of comonomers charged in the feed and comonomer amounts that have been incorporated into the copolymer, in terms of mole fractions.

For more accurate values of the reactivity ratios (r_1 and r_2) the 95% joint confidence limit is used, where an interval in which r_1 and r_2 are likely to be found with a 95% probability. On a plot of the reactivity ratio of monomer one (r_1) versus the reactivity ratio of monomer two (r_2), the joint confidence limits are, in general, elliptical figures due to the nonlinear calculations that were performed.

The copolymer composition may not be independent of conversion, which means that the disappearance of one type of monomer (e.g. M_1) may be faster than the other and for example, the rate of incorporation of M_1 into the copolymer is faster than M_2 . In order to

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determine the amount of the comonomer that has been incorporated into the copolymer, various analytical methods may be used. Nuclear magnetic resonance (^1H NMR, and ^{13}C NMR) and Fourier transform infrared (FTIR) spectroscopy are sensitive techniques that can be used to determine the copolymer composition.

2.5. Copolymer composition and properties

2.5.1. Introduction

The properties of a polymer material are directly related to its chemical nature, morphology, formulation, processing and chemical composition. The complexity of polymers arises from the distribution of the different monomeric units along the polymer chains and from polymer architecture. The heterogeneity of polymers can be described depending on the monomers used and the polymerization reaction, by using different aspects such as molar mass distribution (MMD), distribution in chemical composition (CCD), also the functionality type distribution (FTD), and molecular architecture distribution (MAD). The characterization of these different types of molecular heterogeneity is complicated, requiring the use of a wide range of sophisticated analytical techniques. These techniques should also be selective towards a specific type of heterogeneity, e.g. molar mass distribution and chemical composition. Combinations of techniques can provide two-dimensional information on the molecular heterogeneity⁸³. Since the properties of polymers are highly dependent on all of their distributions, the analysis of such polymers must be capable of describing the polymer heterogeneities.

Polymer scientists have used numerous analytical methods to analyze synthetic polymers, including spectroscopic techniques such as ultraviolet (UV), IR, and NMR spectroscopy. Such techniques can provide information about the type of monomers present in a polymer sample. However, the limitation of these methods is that they do not provide information about how differently the functional groups are distributed along the polymer chains; they also do not provide information about the molecule size (molar mass). In other words these methods will only provide one feature of the polymer complexity, namely polymer functionality. To overcome these limitations, chromatographic methods have been developed to characterize the polymers in terms of either their size or functionality. In this regard, size exclusion chromatography (SEC) is a well known method for the analysis of the molar mass

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distribution of a polymer; this method however still provides only one characteristic of the polymer heterogeneity (i.g. molecular weight).

For a complete analysis of a complex polymer, two analytical techniques must be coupled with respect to its heterogeneity. This can be achieved by using two analytical methods, where one is sensitive towards one type of heterogeneity (e.g. molar mass), while the other method is sensitive toward other types of heterogeneity (functional groups). Many such analytical methods have been used, including the coupling of chromatographic with spectroscopic techniques, coupling of chromatographic with two spectroscopic techniques, and also coupling of two different chromatographic techniques⁸³⁻⁸⁶.

2.5.2. Hyphenation in polymer analysis

Synthetic polymers are typically highly complex mixtures in which the composition depends on the polymerization kinetics, mechanism, and process by which the polymers were prepared. To keep pace with the large number of developments in polymerization reactions, characterization methods capable of analyzing these polymers must be used. Modern analytical methods use multidimensional analytical approaches. The combination of analytical techniques has been widely applied in the characterization of polymers for a long time⁸³. These combinations can be performed, for example, by coupling different liquid chromatography methods with different spectroscopy methods, as well as by the combination of chromatographic techniques which may be more efficient in separating polymer materials of different complexity types. An overview of the combination techniques used in the characterization of polymers will be discussed in the following section.

2.5.2.1. Combination of chromatographic and spectroscopic techniques

The most widely used chromatographic method in the analysis of polymeric materials is size exclusion chromatography, which can be considered as one of the premier characterization methods in polymer science. The use of this technique is limited to the determination of the molar mass of polymers. This limitation is due to the actual separation mechanism of this method.

The combination of size exclusion chromatography and spectroscopic methods is one such development to improve characterization efficiency. In this regard, SEC has been coupled

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with many spectroscopic detectors, including refractive index (RI), and light scattering (LS), NMR, FT-IR, UV and mass spectroscopic detectors⁸⁷. This combination of detectors can provide very useful information about both the molar mass and the chemical composition. However, for a successful characterization, the number of detectors should preferably be at least equal to the number of different heterogeneity types, and, in the case UV, the combination can only be used if at least one of the monomers used in the copolymerization reaction adsorbs at a suitable wavelength, and when the UV spectra of both monomers are sufficiently different to be distinguished.

2.5.2.2. Combination of two chromatographic techniques

There are a number of chromatographic methods that have been developed and applied in the characterization of polymeric materials, including capillary gas chromatographic (GC), and different types of liquid chromatographic techniques, such as gradient high performance liquid chromatographic (HPLC), SEC, liquid adsorption chromatographic (LAC), and liquid chromatography at the critical point of adsorption (LC-CC)⁸⁴.

The combination of these techniques can be considered as the most adequate approach in polymer characterization, which is true when two chromatographic techniques have different separation mechanisms. Such combinations can be performed by (on-line or off-line) coupling of the different methods. In this system, which also known as two-dimensional (2-D) chromatography, each of the used techniques or dimensions must operate in a mode that is sensitive towards one type of molecular heterogeneity. Due to the different separation mechanisms of the different chromatographic techniques, one may use this combination to separate a complex polymer into its different heterogeneity types. In order to do so, the understanding of the separation mechanism is essential.

In SEC, the separation mechanism is based on the molecular size. When a polymer solution passes through the chromatographic column which contains porous particles, the polymer molecules in the solution (eluent) can experience penetration of/exclusion from the pores of the particles (controlled by entropy effects) based on the difference in molar mass or hydrodynamic volume. These effects cause the smaller molecules to enter into the pores of the particles, and when the polymer molecules are bigger than the pores they only partially enter. The result of this is a retention difference between the small and big molecules, by which the

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largest molecules elute first from the column, and thus separation according to molecular size and hence molar mass, is achieved. The separation mechanism here assumes that no specific interactions occur between the polymer and the column.

The other type of chromatographic method is liquid adsorption chromatography. Here the separation mechanism is based on enthalpy effects. Polymer molecules consist of many groups that can interact with the column material; these interactions are normally the result of interaction between the chemical groups in the polymer and the column packing material. Thus, the separation mechanism here depends on the chemical structure of the polymer molecules. Since large polymer molecules have a larger number of chemical groups than the small ones, so the large molecules experience a longer retention in the column than the small molecules, thus, partial separation according to molar mass is also achieved here. These interactions (enthalpy effects) are controlled by a number of factors, such as the column (which depends on the material in the column), eluent combination (solvent) used, and temperature; all play important roles in the actual separation mechanism.

Liquid chromatography at the critical condition of adsorption (LC-CC) is the chromatographic state where the entropic and enthalpic interactions between the polymer molecules and the column materials compensate each other. From the thermodynamic point of view, the Gibbs free energy is equal to zero ($\Delta G = 0$), and the polymer molecules will elute independently of the molar mass of the polymer, and hence all of the molecules (different molar masses) elute at the same time. Using such conditions, it is possible to analyze a complex polymer, to determine its heterogeneity type with high efficiency, independent of the chain length⁸⁶.

For complex polymers that consist of more than one heterogeneity type, a combination of separation methods must be used for complete characterization. This combination may be on-line or off-line (these terms refer to the actual connection between the two methods). Regardless of the separation order (e.g. LL-CC to SEC or SEC to LL-CC), the only difference between these two coupling methods is that in the off-line coupling mode, fractions from the first method are collected, isolated, and then transferred to the second method. Using this procedure important information is obtained; however, this procedure is very time consuming and the accuracy of the obtained information largely depends on the skills of the operator. In the on-line coupling mode, the two separation methods are connected via a storage loop system, in which fractions from the first method are transferred automatically to the second

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method via an injection valve. Recently, most of the papers published in this regard use coupling in the order of LC-CC in the first dimension and SEC as the second dimension. The major advantage of this ordered combination is the molar mass independence in the first dimension. Furthermore, the on-line approach is preferred due to the use of computer software, which usually operates the system automatically⁸⁴.

In terms of characterization, the critical conditions can be obtained by changing the solvent mixture⁸⁷ or by controlling the temperature⁸⁸. Using temperature profiling, Lee and Chang⁸⁸ separated a mixture of PS and PMMA in terms of their chemical nature and molecular weight simultaneously; however a number of authors used solvent mixtures to obtain the critical point. Such combinations have been widely used to characterize several complex polymers, including graft copolymers^{87,89}, block copolymers⁹⁰ and star type copolymers⁹¹. Critical conditions have also been used to separate polymers according to their tacticity⁹².

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Chapter 3

Experimental

3.1. Introduction

The control of polymer properties has been the major interest of many studies due to the diversity of polymer applications. These properties are usually affected by a number of factors including the molecular weight and, more importantly, the chemical structure of the polymer. In other words, controlling the polymer properties can be achieved by controlling the polymer structure, which depends on the structure of the monomer(s) used. One of the most important properties of polymers is their hydrophobicity and water resistance, especially in coatings applications. These properties can be achieved by using monomers that have strong hydrophobicity, such as stearyl methacrylate and versatic acid derivatives. Due to the strong hydrophobicity of these monomers, a special synthetic method is needed in order to obtain a suitable product and have good control over the (co)polymer structure.

The synthesis of such copolymers by conventional methods may result in a low molecular weight polymer, such as in the case of solution polymerization, or poor control over the polymer structure (especially when highly hydrophobic monomers are used), such as in the case of emulsion polymerization, due to the mechanisms of these methods. To overcome these problems, miniemulsion polymerization has been developed; it offers the possibility to synthesise co-polymers without any hydrophobicity limitations. In this study the copolymerization of vinyl neonanoate (Veova-9) and n-butyl acrylate (BA) will be investigated in solution and miniemulsion polymerization (Scheme 3.1) to study the copolymerization kinetics as well as the copolymer composition and some of the copolymer properties. This chapter deals with the synthesis and characterization of the copolymers. It is divided into two sections, each of which divided into two parts: miniemulsion polymerization (batch and semi-batch processes) and solution polymerization (*in-situ* process and benchmark bench-scale process).

3.2. Materials

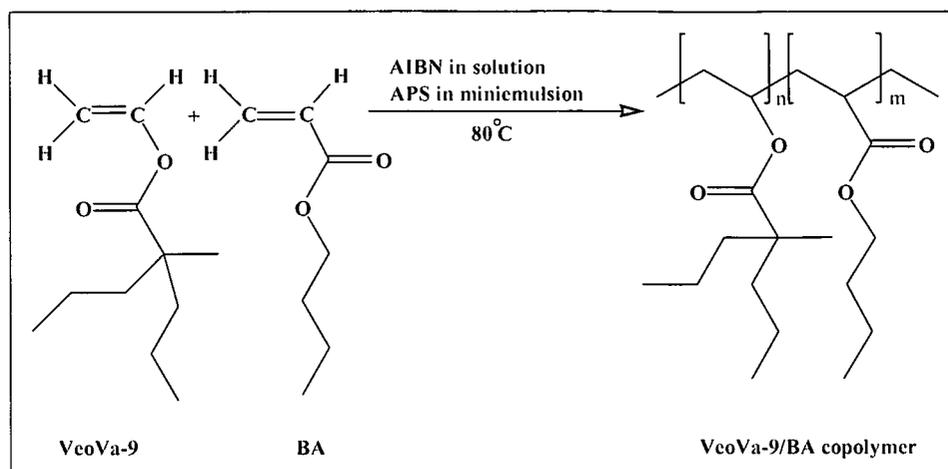
The materials that were used in this study of both the solution and miniemulsion polymerizations are given in Table 3.1.

Table 3.1: materials used in the study of the copolymerization

Material	Material Abbreviation	Supplier
vinyl neononanoate (isomers)	Veova-9	Aldrich
butyl acrylate	BA	Aldrich, 98%
sodium dodecyl benzenesulphonate	SDBS	Fluka, 80%
hexadecane	HD	Aldrich, 99%
ammonium persulphate	APS	uniLAB, 98 %
2,2'-azobis(2-methylpropionitrile)	AIBN	Aldrich, 98%
deuterated chloroform	CDCl ₃	Aldrich, 99.8% atom D
benzene		Fluka, 99.5%
deuterated benzene	C ₆ D ₆	Aldrich, 99.6% atom D
1-dodecanethiol	H-S	Aldrich, 98%
1,4-dioxane		Saarchem
potassium hydroxide	KOH	Associated Chemical Enterprises, 85%
magnesium sulphate (anhydrous)	MgSO ₄	Merck, 70%
distilled deionized water	DDI	Millipore Milli-Q purification system
Sodium hydrogen carbonate (buffer)	NaHCO ₃	R & S Scientific, 99.5%

Prior to any polymerization, all monomers were purified in order to remove the stabilizers (hydroquinone). The monomers were washed with 0.3 M KOH solution (33.6 g in 2 L of DDI water) three times, in a separation funnel, followed by washing with water to remove the remaining KOH. The monomers were then dried by stirring with MgSO₄ for 30 min followed by filtration under vacuum; before they were stored in a fridge at about ±3°C (the purity of the monomers was checked by NMR analysis). The AIBN was recrystallized from methanol, and the other materials were used as received.

Chapter 3: Experimental



Scheme 3.1: Reaction scheme for the synthesis of the VeoVa-9/BA copolymers in miniemulsion and solution. Note that the distribution of monomers units in the copolymer is expected to be random, and that these are not diblock copolymers.

3.3. Equipment

3.3.1. Proton nuclear magnetic resonance spectroscopy (^1H NMR)

^1H NMR spectra were recorded on a Varian *Unity*Inova 400 MHz spectrometer. The 400MHz spectrometer is equipped with an Oxford magnet (9.39 T) and a 5 mm dual broadband PFG probe. Standard pulse sequences were used to obtain the ^1H spectra.

3.3.2. Particle size

The particle size of the latexes was determined at room temperature using a dynamic light scattering instrument (Malvern Instruments Zetasizer 1000 HAS) with a fixed scattering angle of 90° , assuming a mono-modal distribution.

3.3.3. Chromatography

3.3.3.1. Size-exclusion chromatography (SEC)

The polymer molecular weights were estimated by using size-exclusion chromatography (SEC). The SEC system was equipped with a Waters 610 Fluid Unit Pump, Waters 600E System Controller, Waters 410 Differential Refractometer at 30°C , and a Waters 717_{plus} Autosampler. The GPC column was first calibrated with 10 samples of polystyrene standards, prior to analysis; samples were vigorously stirred in THF for a week (to ensure all components were in solution). The samples were then filtered through a $0.45\text{-}\mu\text{m}$ -filter

Chapter 3: Experimental

membrane, three times, thus only the THF soluble components was analyzed.

3.3.3.2. Two-dimensional chromatography

Chromatograph 1 consists of a Waters 2690 Alliance separation (including the pump) module using a combination of two columns, Supelco Nuclecril Si 300 Å 25 cm×6.2 mm 5 µm and Supelco Nucleosil 100 Å Silica 250 mm×4.6 mm. Chromatograph 2 consists of a Waters model 515 HPLC pump and PSS SDV linear M column, 50 mm×20 mm 5 µm. Detection was carried out using an evaporative light scattering detector (ELSD), model PL-ELS 1000 from Polymer Labs.

3.3.4. Dynamic mechanical analysis (DMA)

The glass transition temperature (T_g) of the obtained copolymer from the miniemulsions were measured by using a Perkin Elmer model DMA 7e using a 3 mm diameter parallel plate. The frequency was 1 Hz and the heating rate was 5°C/min.

3.3.5. Surface contact angle

Static and dynamic contact angle measurements on the copolymer surfaces were performed using a contact angle goniometer (DGD-ADR, TELI-CS8620Ci, France). Ten contact angle measurements were performed for each copolymer film at a humidity between 55 to 60%, with temperature at 20 ±1°C.

3.4. Synthesis of the VeoVa-9/BA copolymer

3.4.1. Solution polymerization

3.4.1.1. Benchmark experiments

The copolymerization experiments were performed in a clean, three-neck, round-bottom flask (250 mL) equipped with a condenser, nitrogen inlet, and septum. The VeoVa-9 and BA and solvent (less than 2 g, which was used to dissolve the initiator to be added later) were added to the flask, under stirring. The mixture was flushed with nitrogen through a submerged needle for about 25 min prior to the copolymerization reaction, in order to remove all oxygen,

Chapter 3: Experimental

which can affect the polymerization kinetics. Thereafter the flask was immersed in an oil bath which was pre-heated to the reaction temperature (80°C), on a hot plate. When the temperature of the reaction mixture reached 80°C, the initiator solution, having been flushed with nitrogen for about 7 min, was added to the reaction mixture through the septum, using a glass syringe. The reaction temperature was constant throughout the polymerization. The nitrogen flushing was maintained throughout, although at slower flow rate, to ensure no oxygen contamination.

Samples were withdrawn frequently for determining the conversion. The sampling was performed by removing about 5 g of the polymerization solution by means of glass syringe. The solution was then poured into a pre-weighed aluminium pan and then weighed. Thereafter, the pans were kept in an open place to dry and then further dried in a vacuum oven at 25°C before weighing. Thus the dry weight of the polymer was determined, and the percent conversion calculated. The obtained copolymers in the first 10% conversion were analyzed by ¹H NMR spectroscopy in order to determine the copolymer composition for calculation of the reactivity ratios.

In these experiments, eighteen copolymerization reactions were performed in which the ratios of VeoVa-9 and BA in the feed were changed in a systematic manner. The total number of moles of the monomer was kept constant at 0.05 moles and the solids content of the polymerizations was kept at 20% of the total mixture mass. The amount of initiator was 0.5 mole% (0.041 g) of the total monomers amount. The reaction formulations of all experiments are given in Table 3.2.

3.4.1.2. *In-situ* determination of reaction kinetics copolymerization in an NMR tube.

The use of the *in-situ* NMR approach is a relatively new technique to study the kinetics of free radical polymerization reactions. The advantage of this approach is that a large amount of data can be obtained from only one experiment. In this study the copolymerization processes were followed by NMR spectroscopy to determine the disappearance of the vinylic peaks of both monomers (VeoVa-9 and BA) throughout the reaction. The vinyl peaks of the monomers used in the NMR spectrum are well separated, which led to simple analysis of the polymerization process.

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The *in-situ* ^1H NMR spectrometry data were obtained by conducting a series of reactions with reaction mixtures that contained different mole percentages of VeoVa-9 and BA in a sealed glass NMR tube. Ten different mole percentages of the monomers were used, and the formulations of these experiments are given in Table 3.3. The polymerizations were performed in 5-mm diameter NMR tubes in benzene- d_6 as polymerization solvent, and using 1,4-dioxane as an internal reference.

Table 3.2: Feed ratios for the VeoVa-9/BA in solution copolymerization.

VeoVa-9 mol%	BA mol%	VeoVa-9 # mol	BA # mol	AIBN 10^{-4} mol	Monomer (g)	Solvent (g)
90	10	0.0450	0.005	2.5	8.92	35.68
85	15	0.0425	0.007	2.5	8.78	35.12
80	20	0.0400	0.01	2.5	8.64	34.56
75	25	0.0375	0.012	2.5	8.50	34.00
70	30	0.035	0.015	2.5	8.36	33.44
65	35	0.0325	0.017	2.5	8.22	32.88
60	40	0.0300	0.02	2.5	8.08	32.32
55	45	0.0275	0.022	2.5	7.94	31.76
50	50	0.0250	0.025	2.5	7.80	31.20
45	55	0.0225	0.027	2.5	7.66	30.64
40	60	0.0200	0.03	2.5	7.52	30.08
35	65	0.0175	0.032	2.5	7.38	29.52
30	70	0.0150	0.035	2.5	7.24	28.96
25	75	0.0125	0.037	2.5	7.10	28.40
20	80	0.0100	0.04	2.5	6.96	27.84
15	85	0.0075	0.042	2.5	6.82	27.28
10	90	0.0050	0.045	2.5	6.68	26.72
5	95	0.0025	0.047	2.5	6.54	26.16

A representative example of the preparation of the reaction mixture is as follows: The reaction mixtures were prepared by dissolving VeoVa-9 (0.4 g), BA (0.28 g) AIBN (0.0039 g) and 1,4-dioxane (0.04 g) in benzene- d_6 (2.72 g) in a small 5-mL, vial. This mixture was then flushed with nitrogen for about 10 min, under stirring. Thereafter a volume (about 0.2 mL) of the mixture was transferred to an NMR tube by a clean glass syringe. The tube was then

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flushed with nitrogen before sealing to ensure no loss of the contents during the reaction. The tube was then placed in the NMR instrument.

Table 3.3: Feed ratios for the VeoVa-9/BA in-situ copolymerizations.

VeoVa-9 mol%	BA mol%	AIBN wt%	VeoVa-9 (mol)	BA $\times 10^{-4}$ (mol)	AIBN $\times 10^{-5}$ (mol)	Benzene (g)	Dioxane (g)
90	10	0.5	0.00391	04.35	2.17	3.102	0.023
80	20	0.5	0.00348	08.69	2.17	3.004	0.030
70	30	0.5	0.00304	13.04	2.17	2.908	0.048
60	40	0.5	0.00261	17.40	2.17	2.808	0.05
50	50	0.5	0.00217	21.74	2.17	2.712	0.04
40	60	0.5	0.00174	26.10	2.17	2.616	0.04
30	70	0.5	0.00130	30.43	2.17	2.516	0.035
20	80	0.5	0.00087	34.78	2.17	2.420	0.03
10	90	0.5	0.00043	39.13	2.17	2.324	0.025

The NMR spectra were collected on a 400 MHz Varian *Unity*Inova spectrometer operating at 400 MHz for ^1H . A 5 mm dual broadband PFG probe was used for the experiments and the sample cavity in the probe was calibrated in the manner suggested by the NMR instrument manufacturer. For the ^1H NMR kinetic experiments, samples were inserted into the magnet at 25°C and the magnet fully shimmed on the sample. A spectrum was collected at 25°C to serve as a reference. The sample was then removed from the magnet and the cavity of the magnet raised to the required temperature. Once the magnet cavity had stabilised at the required temperature, the sample was re-inserted and allowed to equilibrate for approximately 5 min. Additional shimming was then carried out to fully optimise the system and the experiments started between 5 and 10 min after the sample was inserted in the magnet, the exact time being noted and a spectrum recorded every minute in the first hour of the reaction time and every ten minutes for the remaining polymerization time.

3.4.2. Miniemulsion and polymerization

This section discusses the process by which the miniemulsion polymerization was performed; these experiments were divided to two parts: batch and semi-batch processes.

3.4.2.1. Batch miniemulsion polymerization

Homo- (only for VeoVa-9) and copolymers were synthesized via miniemulsion polymerization. These experiments were performed in a fume hood with a clean, three necked round bottom flask (100 mL) equipped with a condenser in one neck, nitrogen needle and septum in the other necks. A representative example of the miniemulsion preparation for the latex synthesis is as follows:

Butyl acrylate (4.8 g), VeoVa-9 (6.9 g) and hexadecane (0.351 g) were premixed with the SDBS (0.117 g)/water (44.8 g)/buffer (0.1 g) solution (2 g from the total water mass (46.8 g) was used to dissolve the initiator) for about one hour. Thereafter the mixture was transferred to a water-cooled jacketed vessel where the emulsification was performed. When an oil-soluble initiator (AIBN) was used, the same procedure was followed, except that the initiator was dissolved in the monomers before premixing with aqueous solution. The homogenization procedure was also modified in terms of the temperature profile, to avoid the initiator decomposition during the homogenization process¹.

The miniemulsion state was then obtained by ultrasonicing the mixture for 11 min at 50°C (in the case of AIBN 30°C) at 90% amplitude using a Sonics & Materials Inc, Vibra cell 750 VCX ultrasonicator to create the submicron droplets. The total energy was in the range of 70 to 73 kJ. The water-cooled jacketed vessel was used to avoid polymerization due to the heat generated during the sonication process. Additional stirring was used during the sonication process to facilitate homogeneous sonication. The emulsified mixture was then transferred immediately after emulsification to the reactor flask that was suspended in a thermostatted oil bath. The miniemulsion mixture was then purged with nitrogen for 30 min while it was stirred at 300 rpm. Thereafter the flask was immersed in a heated oil bath; the polymerization was initiated by adding the initiator solution (0.006 g/mL) at 80°C. For all of the experiments, sampling was performed throughout for the evolution of the monomer conversion^{2,3}. In this part, a number of miniemulsion reactions were performed with different

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objectives; the formulations of each series are given in Chapter four. The total monomer weight in all of these experiments was kept constant at 20 wt% and initiator concentration at 0.1 wt% relative to the monomers.

3.4.2.2. Semi-batch experiments

In the semi-batch process, an amount of VeoVa-9 was initially charged into the reactor as miniemulsion mixture. The BA was fed into the reactor drop-wise during the time of polymerization, the addition of the BA started as soon as the initiator solution was added at about 0.2 mL/min. (the BA addition mode was first added after 20 min after the initiator solution, however due to the 2-D results this mode was changed as shown above). The mole percentage of the VeoVa-9 was varied from 10 mol% to 90 mol%, keeping the predicted final solids content constant (at 20% relative to the aqueous phase). Furthermore, the surfactant, costabilizer and initiator concentrations were kept constant relative to the overall monomer concentration, as in the batch process. As a result of the addition mode the solids content might not be the same at the start and the end of the polymerization, since the VeoVa-9 concentration was varied.

3.5. Characterizations

The polymer bulk was obtained by precipitating it from the latex in order to remove the surfactant. The procedure by which the surfactant was removed is as follows: the latex (10 mL) was added drop wise to approximately 30 mL of methanol (MeOH) that had been previously mixed with a few drops of HCl (5 drops). The precipitated polymer was dissolved in a minimum amount of chloroform and reprecipitated in MeOH again. This procedure was repeated three times. The obtained polymer was then washed with MeOH and DDI water before it was dried in a vacuum oven at 30°C.

3.5.1. Two-dimensional chromatography

The critical conditions for the PBA were obtained using a solvent mixture consisting of cyclohexane/THF (15.5/84.5 v/v%) at 30°C. A combination of liquid chromatography at the critical point of adsorption as the first dimension (chromatograph 1) and size exclusion chromatography as the second dimension (chromatograph 2) was used for the analysis of the copolymers that were prepared in miniemulsion. These instruments were connected via one

Chapter 3: Experimental

electrically driven eight-port injection valve (VICI-Valco instruments, model EMMA), and two storage loops used for the analysis.

3.5.3 Particle size

Latex samples were prepared by diluting a drop of the respective latex in distilled deionized water (~4 mL). The dynamic light scattering instrument was first calibrated with a nano-standard solution with a particle size of 220 nm, before any measurement was run.

3.5.4 Contact angle measurements

Static and dynamic contact angles of water were measured on the copolymers films, the copolymers films were prepared from 12.5% copolymer/THF solutions using spin casting on microscope glass slides at 2250 rpm for 2 minutes. The air-water (Figure 3.1) contact angle was then measured by capturing a drop of water as soon as it was in contact with the copolymer surface. The measurements were repeated 10 times for each sample in order to minimize the experimental error. In the case of dynamic measurements, the air-water contact angle was measured by first capturing the water drop as it was advancing and receding on the polymer surface and then determining the advancing and receding contact angles using the instrument software. These measurements were also repeated for 10 times for each sample.

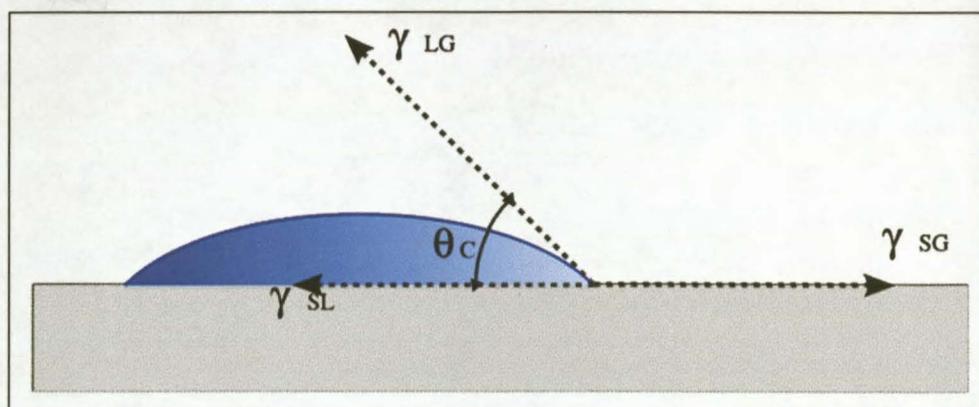


Figure 3.1: Static contact angle on a smooth surface.

3.6 References

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Chapter 4:

Results and discussions

4. Synthesis and characterization of VeoVa-9/BA copolymers

4.1. Introduction

In this chapter, the copolymerization of vinyl neonanoate (VeoVa-9) and butyl acrylate (BA) was investigated. These investigations were divided into two main sections. The first was also divided to two parts: estimation of the reactivity ratios of the copolymerization of the two monomers in benzene at 80°C using the nonlinear least squares method¹, and investigation the of copolymerization kinetics using *in-situ* NMR spectroscopy. The copolymerization kinetics were investigated by quantifying the consumption of the individual monomers during the course of the copolymerization reaction using the *in-situ* NMR approach. In the second section, the copolymerization of these monomers was investigated using miniemulsion techniques.

Due to the industrial importance and popularity of VeoVa-9 and BA, monomers, especially in coating applications^{2,3}, were chosen in order to study their copolymerization using the miniemulsion technique. In this method, due to the high overall surface area of monomer droplets, the main nucleation mechanism is assumed to be the monomer droplet nucleation mechanism, in which most of the monomer droplets are converted to particles by capturing radicals generated in the aqueous phase. Due to this mechanism, the use of the miniemulsion method would be an advantage in the production of a copolymer latex of highly water-insoluble monomers. Exclusive monomer droplet nucleation could provide good control over the copolymer structure, especially when the monomers used have large differences in their water solubility. Another advantage of the miniemulsion system is the ability to control the particle size, which is an important parameter of the resulting latex. The properties of the

produced polymer materials are directly related to its microstructure and chemical composition. The complexity of polymers arises from the distribution of the different monomeric units along the polymer chains and from differences in polymer architecture. The chemical composition of the copolymers can be determined by the combination of two or more analytical methods; each of these methods provides information about a particular heterogeneity type, such as molecular weight or chemical structure.

The chemical composition of the copolymers that were obtained from miniemulsion polymerization was studied by two dimensional chromatography (2-D) using liquid chromatography at critical conditions of adsorption (LC-CC) of PBA in the first dimension, and size exclusion chromatography (SEC) in the second dimension. Physical properties of the obtained copolymers from the miniemulsion were investigated, including the thermal properties and surface contact angle measurements. These investigations are discussed below.

4.2. Synthesis of VeoVa-9/BA copolymer in benzene at 80°C.

Investigation of the VeoVa-9 and BA copolymerization behaviour was done by assuming the terminal model^{4,5} describes the copolymerization. As discussed earlier (Section 2.4), the terminal model culminates in the copolymer equation, which uses the monomer mole fractions in both feed and copolymer (f_i and F_i) to estimate the reactivity ratios of these monomers. The experimental investigations were based on determining the amount of each monomer incorporated into the copolymer by ¹H NMR, by isolating the copolymers at less than 10% conversion for different starting monomer feed ratios.

4.2.1. Copolymerization conversion

Throughout the entire range of monomer conversion, the copolymer composition may not be the same, which means the copolymer composition may not be independent of conversion⁶. This will be the case for a copolymerization system of two monomers that have different reactivity ratios. When one of the monomers has a higher reactivity than the other, this monomer will be consumed more rapidly in the copolymerization reaction, and hence the concentration of this monomer in the solution becomes very low towards the end of the polymerization reaction. This also means that the copolymerization rate may give an indication about the reactivity of the monomers in the copolymerization system. For instance,

Chapter 4: results and discussions

when one of the monomers has a higher reactivity than the other, the copolymerization rate will be affected by the concentration of each monomer, and hence the higher the concentration of the monomer that has a higher reactivity, the faster the copolymerization rate will be. In this study, the copolymerization conversion was used to describe the copolymerization rate by following the monomer conversion at time intervals throughout the copolymerization reaction. The monomer conversions of the copolymerization reaction for different comonomer feed ratios were determined as shown in the experimental part (see Section 3.4.1.1); the total comonomer conversions as a function of time are given in Figure 4.1.

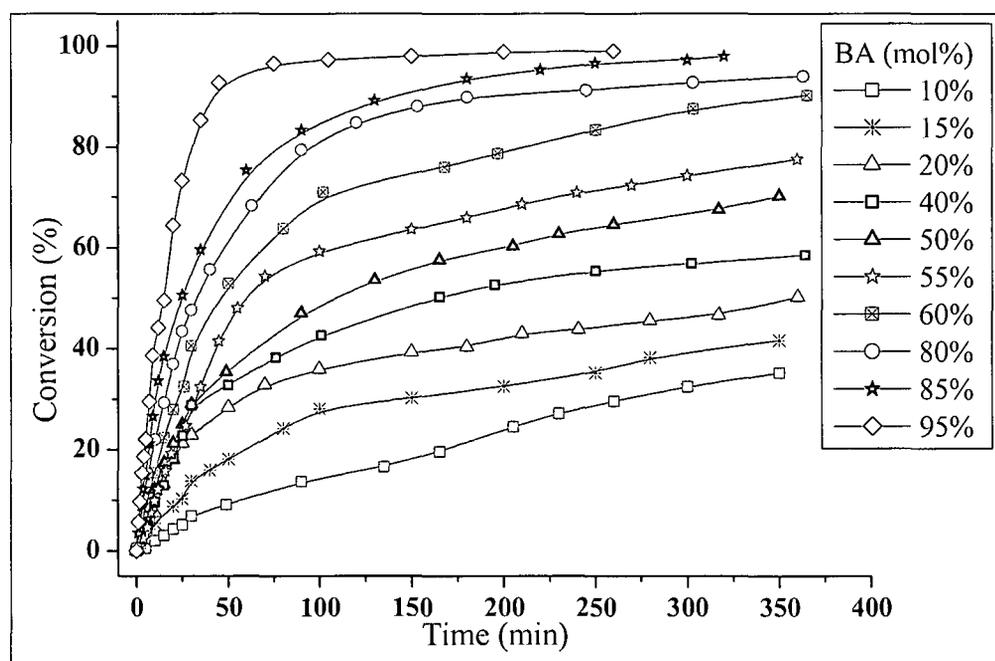


Figure 4.1: Monomer conversions for VeoVa-9/BA solution copolymerization of different starting monomer feed ratios at 80°C in benzene as a function of time.

Figure 4.1 shows the percentage monomer conversion as a function of time for ten different monomer feed ratios. As the BA concentration in the starting feed increases, the rate of monomer conversion increases and hence copolymerization reactions were faster at higher BA concentrations, which can be seen from the gradient of the curves in the first 50 minutes.

Due to this difference in the reactivity of the monomers during the copolymerization, the composition of the obtained copolymer must be determined in the first 5-10% of monomer conversion⁶, where the concentration of both monomers in the solution will not change appreciably. Therefore the copolymer composition at this range of conversion reflects the nearly correct values of reactivity ratios of both monomers.

4.2.2. Determination of copolymer composition by ^1H NMR analysis

^1H NMR spectroscopy was used to determine the amount of each monomer that was incorporated into the copolymer. A representative example of the ^1H NMR analysis for the VeoVa-9/BA copolymer (85/15 mol%) is shown in Figure 4.2.

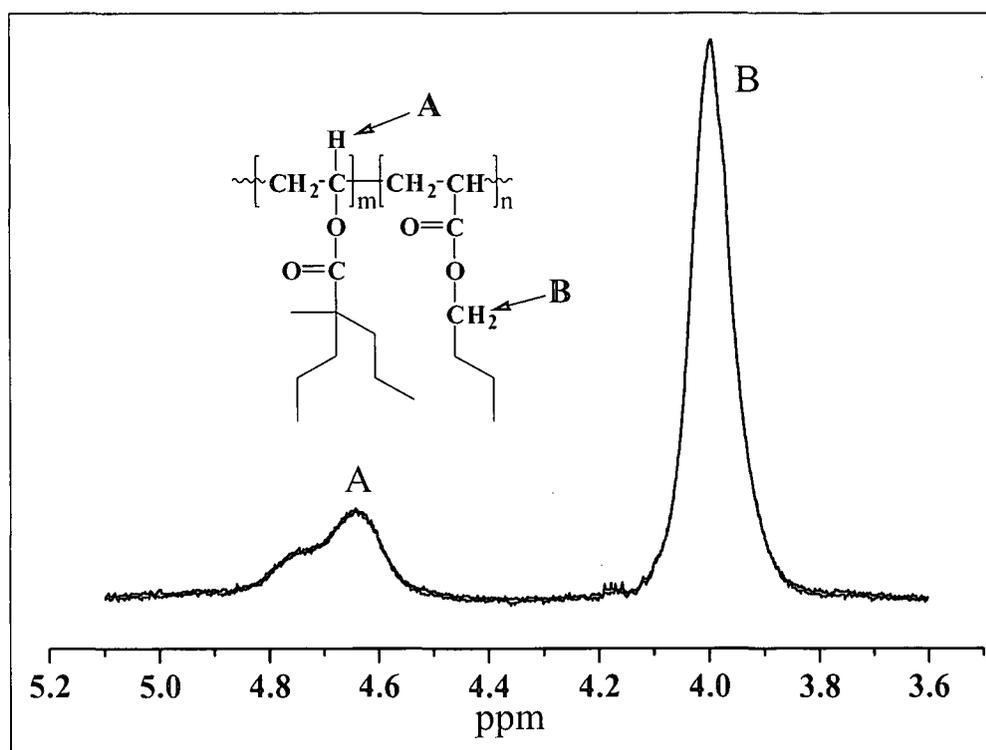


Figure 4.2: ^1H NMR spectrum of VeoVa-9/BA copolymer (85/15 mol% in the feed). Note that the distribution of monomers units in the copolymer is expected to be random, and that these are not diblock copolymers.

From the ^1H NMR spectrum, using the well-separated peaks of the secondary methoxy group ($\text{CH}_2\text{-O}$ between 3.8 to 4.18 ppm) for the BA and the tertiary methoxy group (CH-O between 4.5 to 4.9 ppm; note that the broadness of the peak could be due to the different environments around the proton), the amount of each monomer incorporated into the copolymer was calculated according to Equation 4.1⁷.

$$(\text{VeoVa-9})\% = \frac{A_{\text{VeoVa-9}}}{A_{\text{VeoVa-9}} + \frac{B_{\text{BA}}}{2}} \times 100\% \quad (4.1)$$

Where: $A_{\text{VeoVa-9}}$ is the integration of the tertiary methoxy proton of the VeoVa-9 (proton A, in Figure 4.2) and B_{BA} is the integration of the secondary group of the BA (proton B, in Figure 4.2).

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Table 4. 1: Concentrations and mole fractions of the monomers BA and VeoVa-9 in the feed and copolymers.

Veova-9 f_1	BA f_2	Veova-9 F_1	BA F_2
0.90	0.10	0.45	0.55
0.85	0.15	0.36	0.64
0.80	0.20	0.28	0.72
0.75	0.25	0.25	0.75
0.70	0.30	0.20	0.80
0.65	0.35	0.19	0.81
0.60	0.40	0.15	0.85
0.55	0.45	0.14	0.86
0.50	0.50	0.12	0.88
0.45	0.55	0.11	0.89
0.40	0.60	0.11	0.89
0.35	0.65	0.07	0.93
0.30	0.70	0.06	0.94
0.25	0.75	0.04	0.96
0.20	0.80	0.03	0.97
0.15	0.85	0.02	0.98
0.10	0.90	0.02	0.98
0.05	0.95	0.02	0.98

The mole percentages of each monomer in the copolymer for all different feed ratios were calculated and converted to mole fractions using Equations 4.2 and 4.3; these results are given in Table 4.1.

$$f_1 = \frac{[M_1]}{[M_1] + [M_2]} = 1 - f_2 \quad 4.2$$

$$F_1 = \frac{d[M_1]}{d[M_1] + d[M_2]} = 1 - F_2 \quad 4.3$$

Where: F_i and f_i are the monomer mole fractions in the copolymer and feed respectively, $[M_1]$ and $[M_2]$ are monomer concentrations in feed, and $d[M_1]$ and $d[M_2]$ are monomer concentrations in the copolymer.

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The reactivity ratios, as discussed in Chapter 2 (Section 2.4), are an indication of the tendency of the growing macroradicals, bearing the M_1 or M_2 as terminal units, to either homopropagate or cross-propagate⁸. This can be illustrated by a compositional diagram that gives the compositional changes in the copolymer chains with changes in the feed composition; this diagram for the VeoVa-9-BA copolymerization is shown in Figure 4.3.

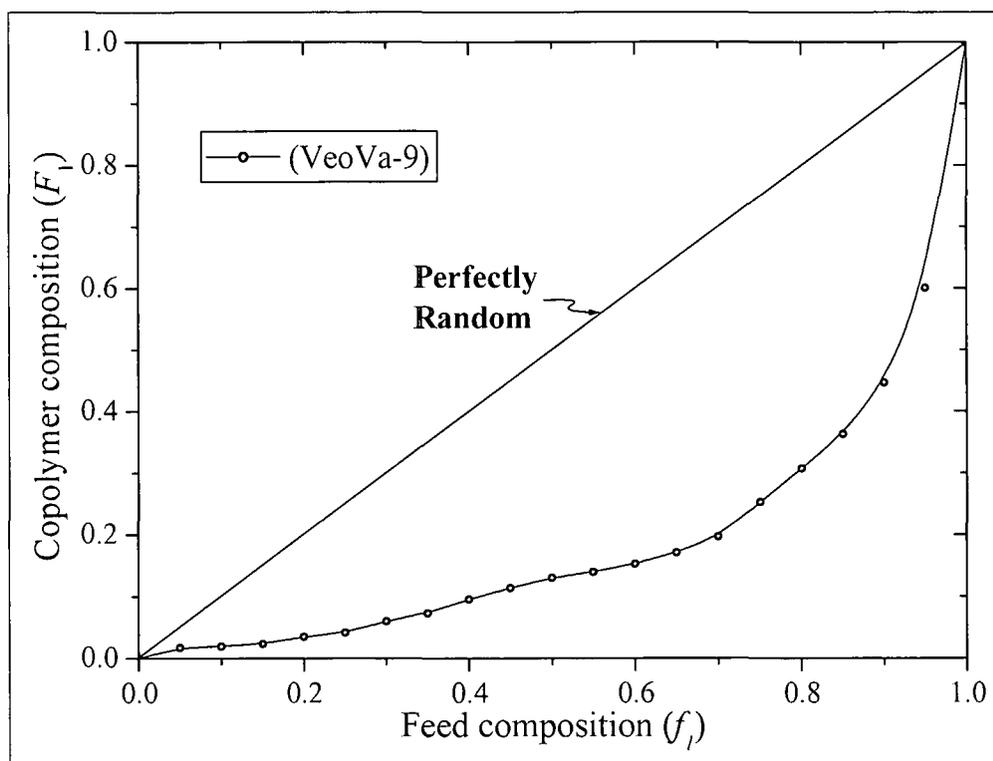


Figure 4.3: Composition diagram of VeoVa-9 and BA copolymerization showing the copolymer composition as a function of VeoVa-9 feed.

Figure 4.3 shows the mole fraction of VeoVa-9 in the copolymer ($F(\text{VeoVa-9})$) as a function of the mole fraction of VeoVa-9 composition in the feed ($f(\text{VeoVa-9})$). It would appear that at the feed compositions used for this monomer, the amount of VeoVa-9 that was charged in the feed is higher than that incorporated into the copolymer. This means that the amount of VeoVa-9 monomer incorporated into the copolymer is less than the BA, and hence the copolymer structure is rich with BA units. These results indicate that the reactivity of the VeoVa-9 monomer in this system is less than that of the BA. The reactivity ratios of both monomers were calculated, as will be discussed below.

4.2.3. Determination of reactivity ratios

From the copolymer equation (Equation 4.4) the theoretical value for the mole fraction F_1 of the monomer that was incorporated into the copolymer (e.g. VeoVa-9) can be determined.

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This was done by using estimated values of r_1 and r_2 , by fitting experimental copolymer composition data for a range of feed compositions. In order to estimate the reactivity ratios by this method, the experimental mole fractions of the monomer (e.g. VeoVa-9) in the copolymer were plotted versus the mole fractions of the monomer in the feed for the entire range of the monomer concentrations in the experiments. Then, by using the copolymer equation (Equation 4.4), a curve could be drawn through the points for selected r_1 and r_2 values. The validity of the chosen values could be checked by changing the selected r_1 and r_2 values until the theoretical data and the experimental data gave the best fit⁹.

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \quad 4.4$$

A nonlinear least squares method was then used¹, in which the sum of the squares (SS) of the difference between the experimental and theoretical mole fractions in the copolymer (Equation 4.5) was minimized. This was done by using Microsoft/Excel's "Solver" function.

$$SS = \sum_{i=1}^n (F_i^{\text{exp}} - F_i^{\text{cal}})^2 \quad 4.5$$

Using this program the sum of the squares (SS) of the difference between the experimental and the theoretical was found to be 0.0021 for the nineteen points. Using the code developed by Alex van Herk¹⁰, a 95% joint confidence interval was calculated and accurate reactivity ratios of the monomers was obtained to be $r_{\text{VeoVa-9}} = 0.042 (\pm 0.014)$, and $r_{\text{BA}} = 6.95 (-0.53/+0.65)$ as shown in Figure 4.4.

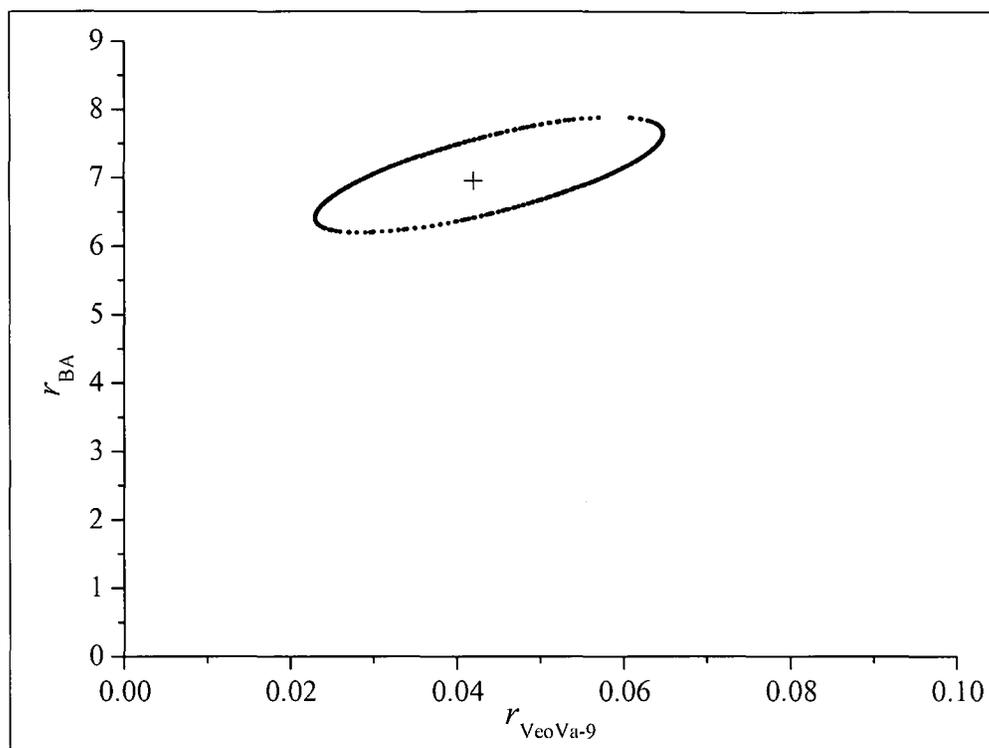
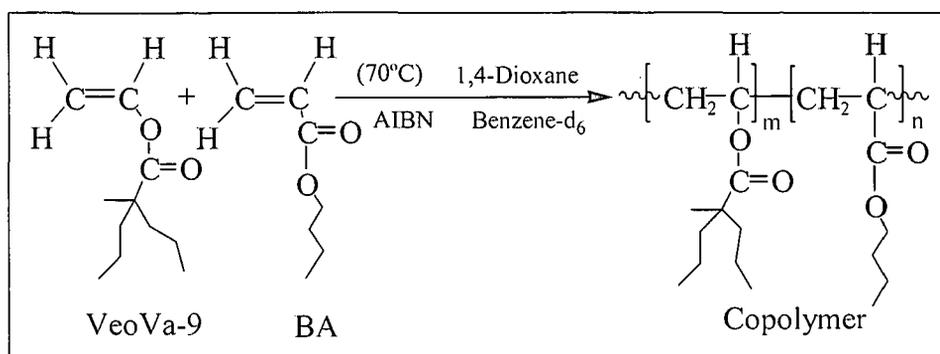


Figure 4.4: 95% joint confidence interval associated with the obtained final values for the reactivity ratios for the copolymerization of VeoVa-9/BA in benzene at 80°C using AIBN as initiator.

4.3. Copolymerization kinetics via *in-situ* ^1H NMR spectroscopy

The copolymerization behaviour was further investigated by *in-situ* ^1H NMR spectroscopy. An advantage of using the *in-situ* approach is that the consumption of each monomer during the polymerization reaction can be monitored. Additionally, the amount of instantaneous data that can be obtained from only one experiment is greater than in the bench-scale experiments, in which the resultant copolymer must first be isolated and purified^{11,12}.

The kinetics of the radical copolymerization of VeoVa-9 and BA was monitored *in-situ* at 70°C, by 400-MHz ^1H NMR spectroscopy (Scheme 4.1), using the vinylic region in the NMR spectrum of the monomers (between 3.5 and 7.5 ppm). As shown in Figure 4.5, the vinyl signals of the BA and VeoVa-9 are well separated for each monomer's double bond protons, simplifying the analysis of the individual vinyl peaks. Hence accurate calculations of each monomer concentration in the copolymerization, at any time during the course of copolymerization reaction, can be made. A number of different mole ratios (see experimental Section, 3.4.1.2) of the monomers were used in each copolymerization reaction and the total monomer concentration in the solution was kept constant at 20 wt%.



Scheme 4.1: Reaction scheme for the copolymerization of VeoVa-9 with BA at 70°C in benzene-d₆.

The underlying assumption of this approach is that monomer not present in the reaction mixture as free monomer is incorporated into the polymer chain. In other words, there is a direct relationship between the reduction of the double bond proton peak intensities in the ¹H NMR spectrum and the production of the copolymer. This assumption permits a direct quantitative measurement of the amount of each monomer incorporated into the copolymer¹³.

The disappearance of each individual monomer was monitored by the decrease in the intensity of the double bond proton signals relative to the 1,4-dioxane reference signal. Figure 4.5 shows the NMR spectra of the double bond signals of both monomers at the start and at the end of the reaction. From the integration of the peaks during the course of the reaction, the decreases in monomer concentrations were calculated. The AIBN consumption at 70°C in dioxane-d₈ was studied by Ito and Miller¹¹, who found that about 70% of the AIBN was consumed after 24 hours; the longest reaction time here was 7.5 hours.

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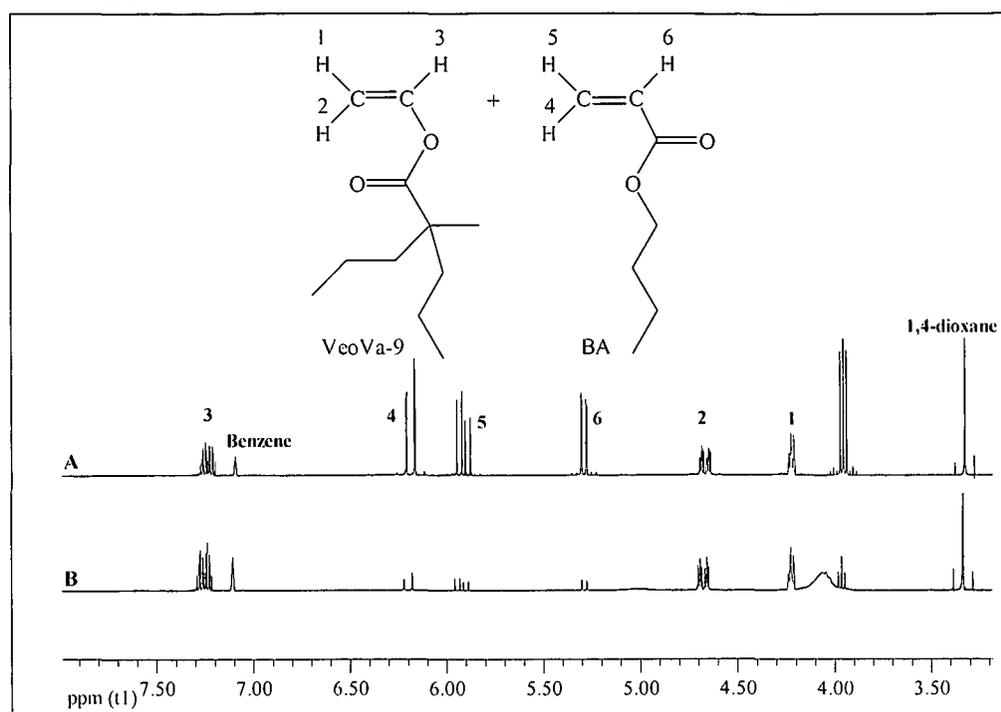


Figure 4.5: ^1H NMR spectra of copolymerization of VeoVa-9 and BA at 70°C , in benzene- d_6 : A, before polymerization, and B, after polymerization.

Monomer concentrations were calculated as follows. First, the peak areas (integrations) were normalized. This was done by dividing the peak integration at any given time by the peak integration of the reference. Figure 4.6 shows the normalized (integrated) peak intensities, which reflect the consumption of each monomer during the reaction time for the 50/50 mol% ratio of the VeoVa-9/BA in the feed. In order to determine the initial monomer concentrations, the double bond protons (protons 3 and 5 in Figure 4.5) of the monomer were used. The initial concentrations of the monomers in the feed were 0.657 mol/L and 0.634 mol/L for VeoVa-9 and BA, respectively, which agreed with the actual mole percentage of the monomers that were charged into the reaction mixture (50.91% and 49.09% for the VeoVa-9 and BA respectively).

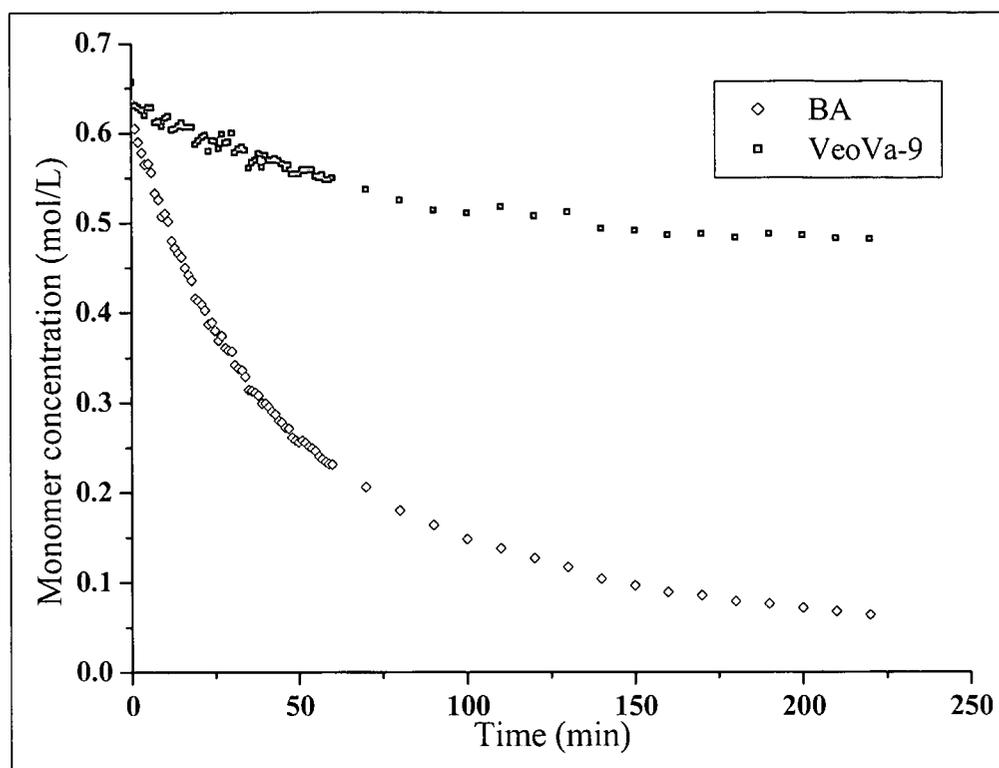


Figure 4.6: Monomer consumption curves for the VeoVa-9/BA (50/50 mol%) copolymerization at 70°C in benzene-d₆ (20% final solid contents).

Figure 4.6 shows that the BA reacts much faster than the VeoVa-9, which indicates that the copolymer structure will be rich in the BA monomer, since about 90% of the BA that was charged into the reaction mixture had reacted.

The amounts (mol%) of each monomer incorporated into the copolymer was also calculated, using Equations 4.6 and 4.7.

$$(\text{VeoVa-9})_i \% = \left(\frac{[\text{VeoVa-9}]_t}{[\text{VeoVa-9}]_0 + [\text{BA}]_0} \right) \times 100 \quad 4.6$$

$$(\text{BA})_i \% = \left(\frac{[\text{BA}]_t}{[\text{VeoVa-9}]_0 + [\text{BA}]_0} \right) \times 100 \quad 4.7$$

The result of these calculations is shown in Figure 4.7, where the mol% of each individual monomer, incorporated into the copolymer, as well as the overall conversion of the copolymerization (wt%), are plotted versus time.

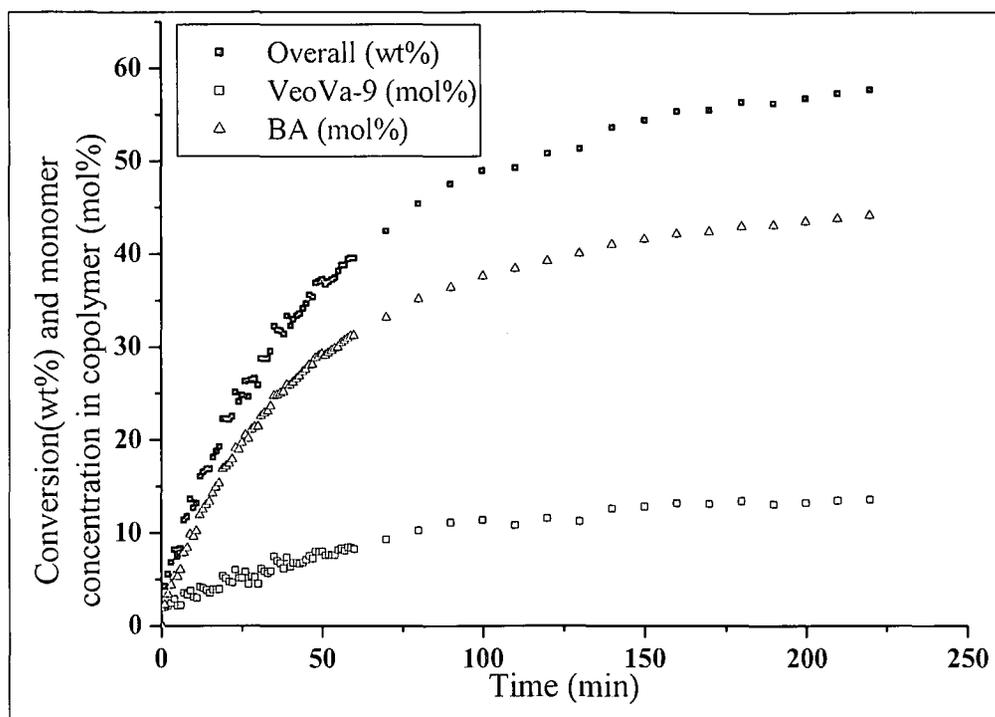


Figure 4.7: Copolymer conversion and monomer concentration in the VeoVa-9/BA (50/50 mol%) copolymerization at 70°C in benzene- d_6 as a function of time.

Statistically, from Figure 4.7 and under these conditions, the mole percentage of each monomer in the copolymer was calculated at different intervals throughout the reaction. The calculations show that about 77 mol% of the copolymer structure consists of BA units and about 23 mol% of the copolymer structure consists of VeoVa-9 units, i.e. there is about one VeoVa-9 unit for every three BA units. These calculations also show that about 88% of the BA (of the total BA feed fraction) was incorporated into the copolymer, while about 27% of the VeoVa-9 (of the total VeoVa-9 in the feed fraction) was incorporated into the copolymer, at about 58% overall monomer conversion.

The percentage conversion during the polymerization was calculated for the entire range of mole ratios of the monomers, using Equation 4.8.

$$\text{Conversion \%} = \left(\frac{[\text{VeoVa-9}]_t + [\text{BA}]_t}{[\text{VeoVa-9}]_0 + [\text{BA}]_0} \right) \times 100 \quad 4.8$$

Where: $[\text{VeoVa-9}]_t$ is the concentration of the VeoVa-9 in the copolymer at time t .

$[\text{BA}]_t$: Concentration of the BA in the copolymer at time t .

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$[VeoVa-9]_0$: Initial concentration of the VeoVa-9 in the reaction mixture.

$[BA]_0$: Initial concentration of the BA in the reaction mixture.

The monomer conversions from Equation 4.8 for the entire range of initial mole ratios are given in Figure 4.8. Once again, the final overall monomer conversion increased by increasing the concentration of BA, because of the higher reactivity of the BA in the copolymerization reaction.

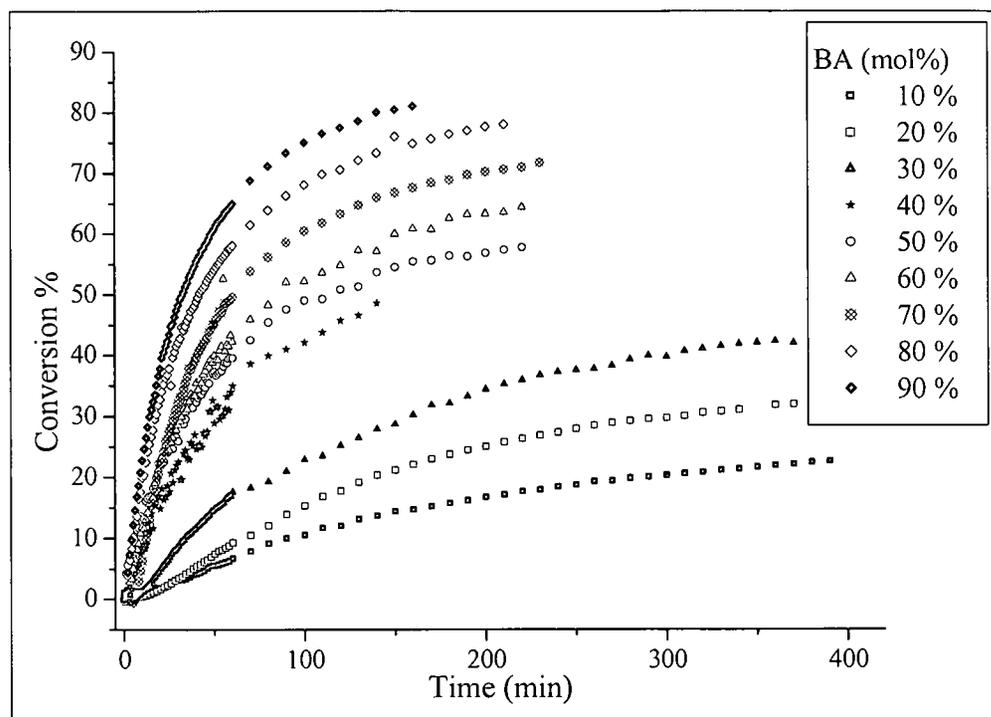


Figure 4.8: Overall monomer conversions for the copolymerization of VeoVa-9 with BA at 70°C in benzene- d_6 as a function of time for the different feed ratios.

These results could be related to the monomer structures, which plays an important role in determining the monomer reactivity during copolymerization⁸. There is a large difference between the two monomer structures, as shown in Scheme 4.1. Due to electronic effects, it is apparent that the acrylate radicals are very reactive whereas the VeoVa-9 chain end radicals are less stable. In general, the copolymerization behaviour of acrylates with vinyl esters shows a strong composition drift during the copolymerization reaction, due to the wide differences in the reactivity of those monomers. For instance, the copolymerization reaction of VeoVa-9 with ethyl acrylates¹⁴ is characterized by reactivity ratios of $r_{EA} = 5.9$ and $r_{VeoVa-9} = 0.1$, and also in the copolymerization of BA and vinyl acetate¹⁵ the reactivity ratios were estimated at $r_{BA} = 5.94$ and $r_{VA} = 0.026$. The obtained results in this system and the above examples show

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that the reactivity of acrylate monomers in copolymer systems is generally higher than the vinyl ester monomers; this difference in the reactivity of the radical and monomer results in a difficulty in production of uniform copolymers, as it affects the copolymer properties.

Table 4.2 Summarizes the initial molar ratios, initial monomer concentrations $[M]_0$, monomer conversions and percentages of monomers incorporated into the copolymers $\%(M_{incorp})$ for the entire range of monomer feed ratios.

Table 4.2: Feed and copolymer compositions and monomer conversions for the VeoVa-9/BA copolymerization reactions in benzene- d_6 at 70°C for different initial monomer feed ratios.

Ratio in feed (mol%)		$[M]_0$ (mol/L)		$\%(M_{incorp})$	
VeoVa-9	BA	VeoVa-9	BA	VeoVa-9	BA
90	10	1.01	0.11	32.0	10.5
80	20	0.98	0.25	14.5	19.0
70	30	0.92	0.40	14.2	27.8
60	40	0.67	0.66	15.6	32.9
50	50	0.66	0.63	13.6	44.2
40	60	0.49	0.72	11.5	52.3
30	70	0.42	0.99	08.2	63.6
20	80	0.28	1.12	06.3	71.8
10	90	0.17	1.38	02.9	78.0

The *in-situ* NMR procedure was also carried out using higher monomer concentrations in the solution to attempt to minimize the effects of solvent. In this copolymerization, the total monomer concentration was 90% of the polymerization mixture and the initial mole ratio of the two monomers was 50/50 (mol%). Since high monomer concentration was used, the polymerization was carried out at 70°C for only 15 min, with a scan every 30 seconds to collect enough data before viscosity-related problems, such as line broadening occurred. Figure 4.9 shows the monomer consumption during the copolymerization reaction. The initial measured VeoVa-9 and BA concentrations were 0.425 mol/L and 0.412 mol/L respectively, thus the actual mole percentage of the monomers in the feed was 51% for the VeoVa-9 and 49% for the BA, which is similar to the charged ratio.

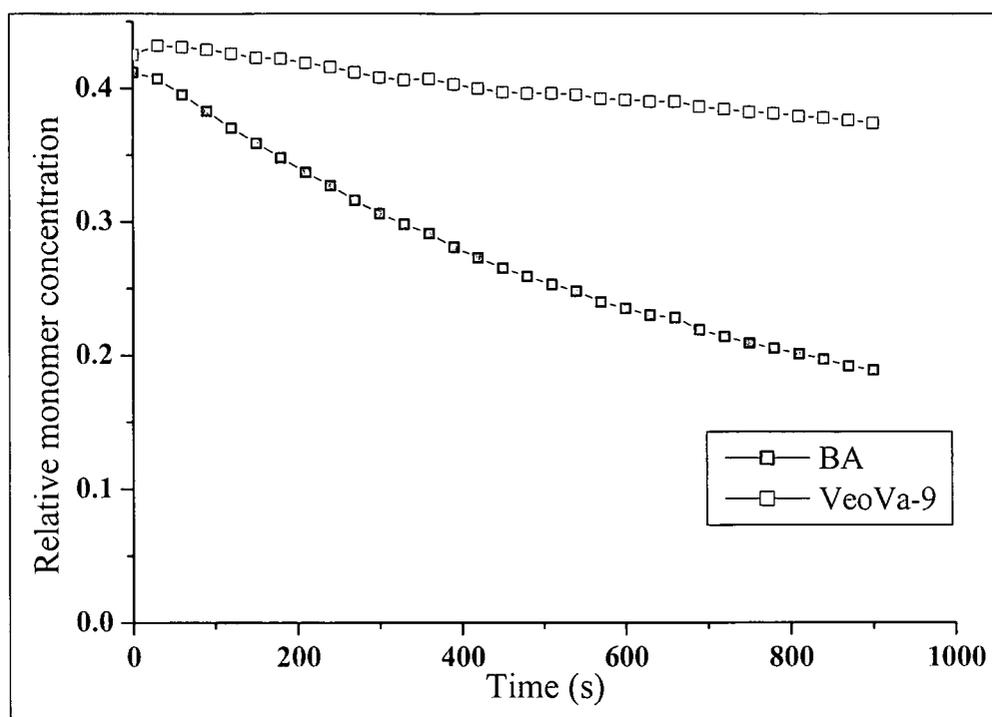


Figure 4.9: Monomer consumption curves for the VeoVa-9/BA (50/50 mol%) copolymerization at 70°C in benzene- d_6 , at 90% final solids content. Note that the monomer concentration is relative to the 1,4-dioxane concentration.

The amounts (mol%) of each monomer incorporated into the copolymer and the overall monomer conversion were calculated using Equations 4.6, 4.7 and 4.8. The results of these calculations are shown in Figure 4.10. Note that in Figure 4.9 the initial rise of the curves is probably due to temperature stabilisation. Comparing the two experiments (Figures 4.6 and 4.9), the monomer concentrations in Figure 4.9 tend to be lower than in Figure 4.6, which is because the monomer concentrations are relative to the internal standard concentration in the reaction mixture.

Figure 4.10 shows the conversion of each monomer during the copolymerization reaction. From Figure 4.10, about 21% of the copolymer structure consists of VeoVa-9 units. These calculations also show that about 53% of the BA in the feed was incorporated into the copolymer at the end of the reaction, while about 14% of the VeoVa-9 was incorporated into the copolymer at about 33% overall monomer conversion.

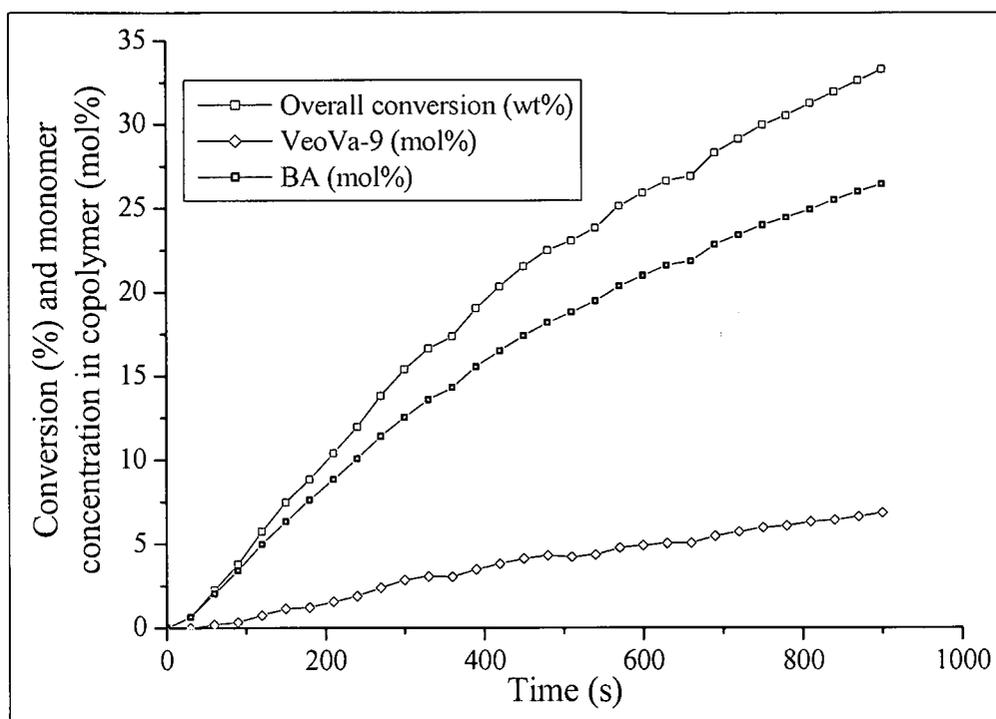


Figure 4.10: Copolymer conversion and monomer concentration in the copolymerization of VeoVa-9/BA (50/50 mol%) feed as function of time at 70°C in benzene-d₆, 90% final solids content.

Upon comparison of the two in-situ processes, namely 20% or 90% monomer concentration in the reaction, the rate of the copolymerization was faster when an overall 90% monomer concentration was used, as was expected since the monomer concentration is much higher. In terms of monomer incorporation into the copolymer, the difference between the two processes at the same overall conversion (10%) was investigated. For instance in the 90% concentration the copolymer structure consisted of 15% VeoVa-9 and 85% BA, while in the 20% monomer concentration the copolymer structure consisted of 31% VeoVa-9 and 69% BA. From the above discussion the monomer/solvent concentration only affects the copolymerization reaction rate; since the reaction was much faster when higher monomer concentration was used.

4.4. Copolymerization of VeoVa-9/BA miniemulsions

4.4.1. Introduction

Generally, monomer emulsions tend to degrade by two main mechanisms, which are coalescence of monomer droplets due to the attractive van der Waals forces between these droplets, and Ostwald ripening or monomer diffusion from small to large droplets^{16,17}. The first of these mechanisms can be retarded by the addition of a sufficient quantity of surfactant which stops the degradation of the monomer droplets via coalescence, by providing sufficient electrostatic repulsion or steric repulsion forces^{17,18}. The Ostwald ripening mechanism is stopped by the addition of an extremely water insoluble component (costabilizer), which leads to a build-up of an osmotic pressure in the small monomer droplets which competes with the driving force for Ostwald ripening¹⁹. Thus the monomers will diffuse back from the large to the small droplets (or not migrate to the large droplets), to balance the osmotic pressure in the droplet resulting in relatively stable monomer droplets. A system in which sub-micron monomer droplets are post-stabilized is usually known as a miniemulsion¹⁶. The miniemulsion can be obtained by dispersing an oil phase that consists of monomer(s) and costabilizer in a solution of surfactant and water using a high-shear device such as an ultrasonic device.

Due to the high overall surface area of monomer droplets in the miniemulsion, the main nucleation mechanism is monomer droplet nucleation and hence the monomer droplets become particles and are the main polymerization sites. The total surface area of the monomer is a function of the droplet size, which is a function of a number of factors including the surfactant and costabilizer concentrations in the miniemulsion. Due to this mechanism, the water solubility of the monomer is no longer a limitation in oil-in-water emulsions. Because of this feature, the miniemulsion technique was used in this study for the copolymerization of VeoVa-9 and BA to study the miniemulsion behaviour, as well as some of the resultant copolymer properties.

4.4.2. Influence of the amount of surfactant

A very important factor for the formulation of stable miniemulsions is the surfactant content, which provides stability against droplet degradation via coalescence, and later preventing

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coagulation of particles. However, its importance not only determines the miniemulsion stability, but also determines the final particle size and number, which in turn affects the film formation process and the subsequent film properties. Moreover, the surfactant concentration also affects the rate of the polymerization reaction.

In this study, the effect of the surfactant concentration in the miniemulsion and the impact of surfactant concentration on the surface properties of the copolymer films were investigated. In order to study these effects, various surfactant concentrations relative to monomer were used in the miniemulsions, keeping all other miniemulsion components' concentrations constant. The miniemulsions were prepared, using sodium dodecylbenzene sulfonate (SDBS) surfactant, as discussed in Section 3.4.2. These concentrations, as well as the applied sonication energy, are given in Table 4.3. Note that the stability of the miniemulsion was checked using only (the very hydrophobic) VeoVa-9 as costabilizer; however, the system tends to phase separate a few minutes after the sonication process. This is due to the water solubility of the VeoVa-9 not being low enough to function as a costabilizer (the water solubility of the costabilizer must be in the order of 10^{-7} mL mL⁻¹ or lower²⁰ and the water solubility of VeoVa monomers is in the order of 10^{-4} wt%²¹). Thus, HD was used to stabilize the miniemulsions. The results of these experiments will be discussed in terms of the influence of the surfactant concentration on both the copolymerization reaction rate and the resultant particle size.

Table 4. 3 Surfactant concentration and the applied energy in miniemulsions (at 80°C) of VeoVa-9/BA (50/50 mol%), using HD (3 wt%) and APS (0.1 wt%) relative to monomer at 20% solids.

Exp.	SDBS (wt%)	SDBS mass (g)	Applied energy (kJ)
WH1,1M	0.5	0.058	69.56
WH1,2M	1	0.117	72.21
WH1,3M	1.5	0.176	70.35
WH1,4M	2	0.234	69.64
WH1,5M	2.5	0.293	70.49
WH1,6M	3	0.351	71.98

4.4.2.1. Influence of the surfactant concentration on the polymerization rate

The effect of surfactant concentration on the rate of polymerization was studied by measuring the conversion at time intervals during the course of the polymerization. In these miniemulsions, the surfactant concentration was varied relative to the monomer concentration, as shown in Table 4.3. The effect of surfactant on the rate of polymerization is shown in Figure 4.11.

Figure 4.11 shows that the rate of the polymerization increases with increasing surfactant concentration. Comparing the miniemulsion rate of reaction using 0.5 and 3 wt% surfactant relative to monomer, the copolymerization reaction reached 98% conversion within 300 minutes in the case of 0.5 wt% surfactant; while it only took about 65 minutes to reach 98% when 3 wt% of surfactant was used.

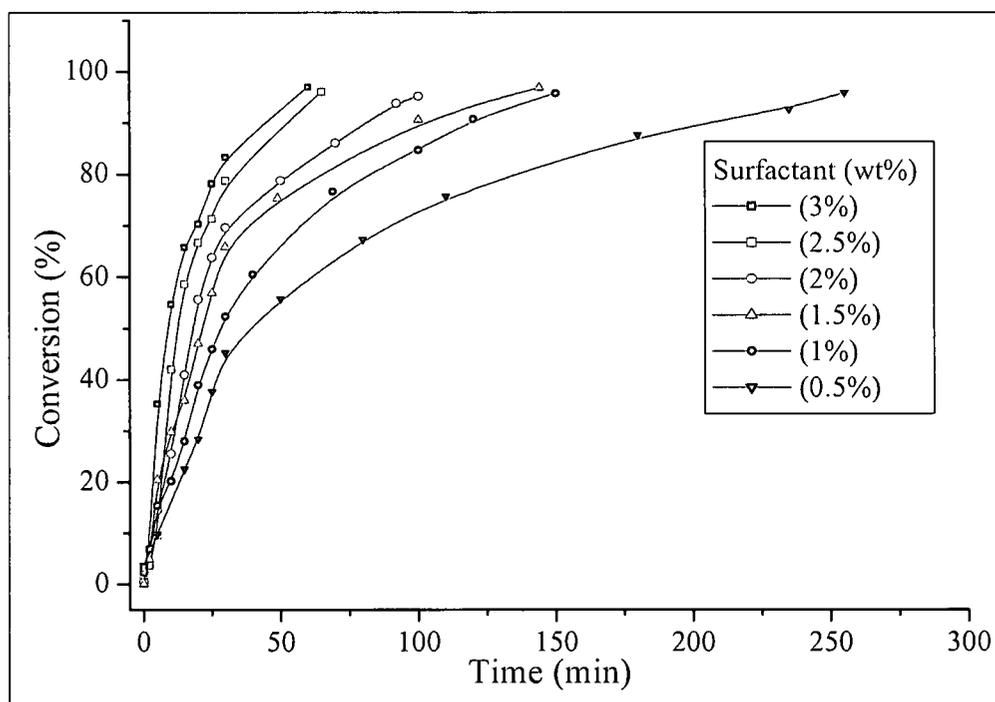


Figure 4.11: Conversion-time curves of VeoVa-9/BA (50/50 mol%) miniemulsions in which different surfactant concentrations were used.

These results were attributed to the particle size and more importantly the resulting particle number. It was found, as will be discussed later in this section, that the higher the surfactant concentration, the smaller the particles and the higher the particle number. The rates in Figure 4.11 are quite different, showing the strong dependency on the amount of surfactant.

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In terms of the particle size dependency (which is related to the monomer droplet size), it was shown by Bechthold *et al.*²² that as the monomer droplet size decreases, the overall efficiency of capturing radicals increases (in fact, this is not the case for an individual monomer droplet, since its surface area decreases). Decreasing the droplet size increases the droplet number, so the total surface area increases, leading to higher efficiency of radical adsorption, but more importantly, results in more particles giving more radical sites (i.e. more radicals for the same amount of monomer). This miniemulsion behaviour has been observed by Bechthold *et al.*²² for the miniemulsion polymerization of styrene using sodium dodecyl sulfate (SDS) as surfactant; they found that the rate of the polymerization strongly depends on the particle size. They also showed that there was no particle size dependence in the first interval (interval I), in which the droplets are nucleated. The effect of droplet size on the rate of polymerization is significant in the second interval of polymerization.

They also found that there was no gel peak corresponding to the “Trommsdorff-Norrish effect” in the case of the smallest particles; the effect became observable, and then more pronounced as the particle size increased appreciably. The gel peak arises from the drastic increase in the polymerization rate as the rate of conversion increases due to the increase in viscosity in the locus of polymerization. As the viscosity increases, the mobility of radical species is retarded in these sites, and hence their rate of diffusion reduces so that a second radical can enter the particle without causing termination (which is more likely as particles get larger). As a result, the rate coefficient for termination drops rapidly, leading to an increase in the propagation rate^{8,23}. The gel effect was more noticeable as the particle size increases; this was attributed to the difference between the monomer concentrations in the small and large monomer swollen particles.

Decreasing the droplet size leads to an increase in the droplet number in a miniemulsion system since all of the surfactant molecules are used to stabilize the monomer droplets^{17,20}. According to Equation 4.9, the rate of polymerization in the miniemulsion increases as the number of monomer droplets (and hence particles) increases²⁴⁻²⁶.

$$R_p = \frac{k_p [M]_p \bar{n} N_p}{N_A} \quad 4.9$$

Where R_p is the polymerization rate, k_p is the propagation rate coefficient, $[M]_p$ is the

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monomer concentration in the monomer swollen particles, \bar{n} is the average number of free radicals per particle, N_p is the number of monomer swollen particles and N_A is Avogadro's number. Assuming that the initiation rate is constant while the number of particles increases (since the only variable parameter in these experiments is the surfactant concentration), the interval between the entry of successive radicals into particles is lengthened²⁵ (i.e. more particles giving more radical sites). In other words \bar{n} does not change quickly with N_p , so increasing N_p increases the rate of the reaction.

4.4.2.2. Influence of the surfactant concentration on the particle size

An increase in the particle size with decreasing surfactant concentration was observed. As shown in Figure 4.12, the size of the particles observed for these miniemulsions decreased from about 200 nm to about 80 nm as the surfactant concentration increases from 0.5 to 3 wt% (relative to monomers). Assuming that all of the surfactant molecules are used to stabilize the droplets, the monomer droplets at the steady-state are "critically stable with respect to collisions²⁰" (the droplets are at the critical borderline between stability and instability) and their size is directly dependent on the surfactant concentration¹⁷. Accordingly, these results could be attributed to the actual droplet stability during the homogenization process and to surface coverage of the droplets with surfactant molecules.

As was shown by Landfester²⁰ *et al.*, during the ultrasonication process, the droplet size changes with time until the droplets reach an equilibrium size (steady state). However, the size of these minidroplets at this steady state is a function of the surfactant concentration while the time that is required reach the steady state is a function of the total shear applied to the system²⁰.

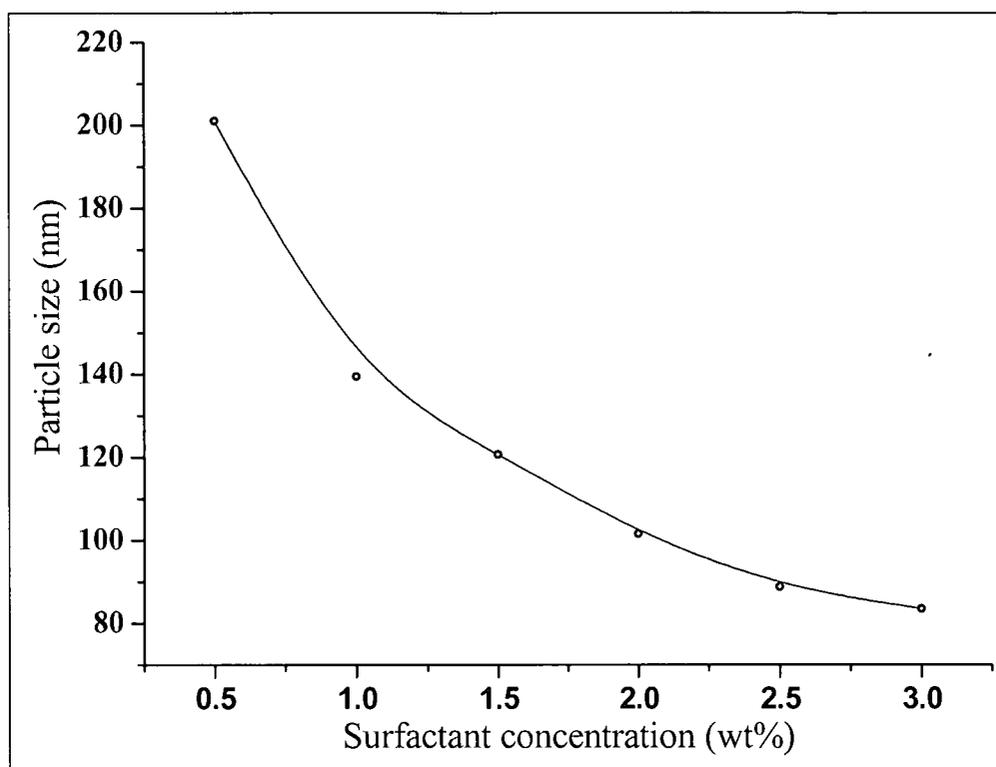


Figure 4.12: Final particle size as a function of surfactant concentration for VeoVa-9/BA (50/50 mol%) miniemulsions using SDBS as surfactant and APS as an initiator at 80°C.

During the emulsification process, the monomer droplets are dispersed into the aqueous phase by breaking the large droplets into smaller droplets. However, these small droplets may undergo degradation via aggregation and collision until they reach the steady-state. According to the surface coverage of the monomer droplets with surfactant molecules, the aggregation rate of the small droplets is faster than the large ones²⁰. As was found by a number of authors,^{20,27} small droplets require high coverage with surfactant molecules in order to be stable and hence a high surfactant concentration is needed to create small and stable droplets. This could be explained, as during the homogenization process, the smaller droplets that are generated in this process undergo a fast aggregation to form larger droplets. However, at high surfactant concentration, the aggregation of these small droplets can be retarded and stable small monomer droplets can be obtained, since the amount of surfactant available is enough to cover a large area on the droplets' surface.

In conclusion, the dependency of the particle size on the amount of the surfactant is due to the droplet stability against collision, which was found to be faster for the small droplets than for the large droplets. In other words, increasing the oil/water interfacial area (small monomer droplets) requires more surfactant in order to obtain stable droplets.

4.4.3. The influence of the VeoVa-9 fraction in the feed

Miniemulsion copolymerization of VeoVa-9 and BA using both batch and semi-batch processes was carried out with varying monomer ratios (see Table 4.4).

Table 4.4: Miniemulsion feed ratios for the VeoVa-9/BA copolymerizations.

Experiment ID	VeoVa-9 (mol%)	BA (mol%)	Initiator APS (g)	Surfactant SDBS (g)	Hexadecane HD (g)	Water (g)
WH3,1M	100	0	0.014	0.14	0.41	55.20
WH3,2M	90	10	0.013	0.13	0.40	53.52
WH3,3M	70	30	0.013	0.13	0.38	50.78
WH3,4M	50	50	0.012	0.12	0.35	46.80
WH3,5M	30	70	0.011	0.11	0.33	43.44
WH3,6M	20	80	0.010	0.10	0.31	41.76
WH3,7M	10	90	0.010	0.10	0.30	40.08

The effect of VeoVa-9 content on the miniemulsion behaviour, in terms of particle size and conversion, was investigated. The copolymer composition was studied by using 2-D chromatography at the critical point of adsorption. The effect of the VeoVa-9 on the copolymer properties (including the glass transition temperature (T_g) and surface properties of the copolymer) was also investigated. In both processes (batch and semi-batch), the mole percentage of the VeoVa-9 was varied, keeping the total monomer concentration in the miniemulsion (solids content) constant. The surfactant (SDBS), costabilizer (HD) and initiator (APS) concentrations were also kept constant relative to the total monomer mass (1 wt%, 3 wt% and 0.1 wt% respectively). The results of these studies are discussed below.

4.4.3.1. The influence of the VeoVa-9 feed fraction on the copolymerization conversion

The amount of VeoVa-9 was varied (Table 4.4) relative to the amount of BA in order to study the effects of the monomer feed ratio on the copolymerization conversion. The copolymerization conversion was measured at time intervals during the course of the copolymerization. The monomer conversions for different VeoVa-9 mole percentages as a function of time are shown in Figure 4.13.

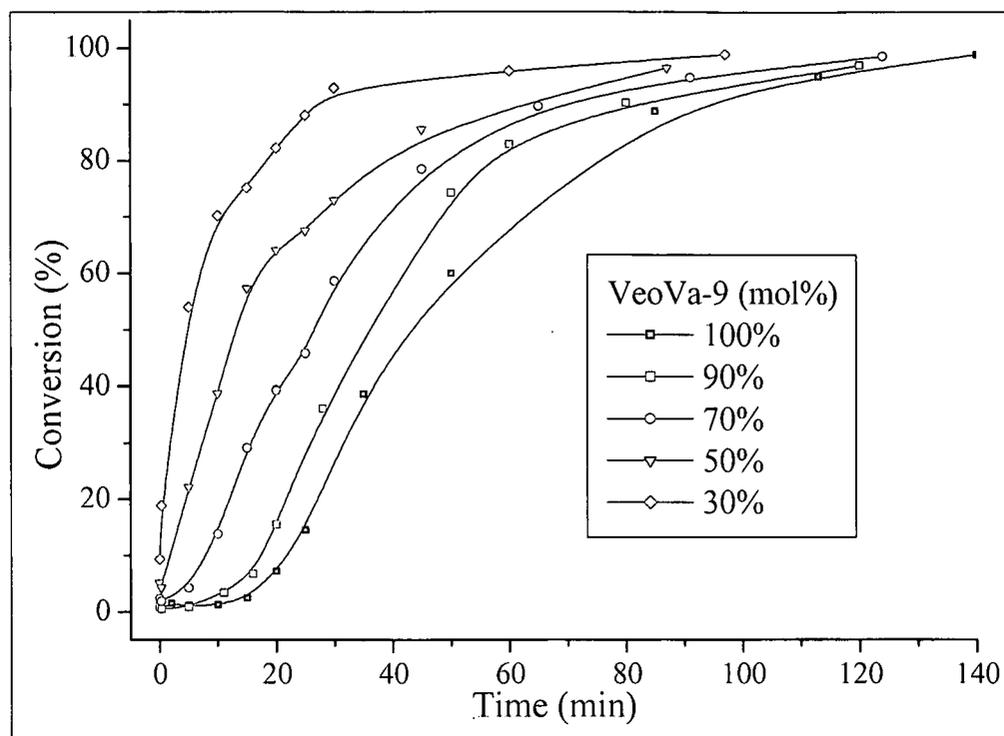


Figure 4.13: Monomer conversion as a function of time in the miniemulsion copolymerization of VeoVa-9/BA using different VeoVa-9 concentrations and using APS as an initiator at 80°C.

Figure 4.13 shows that the rate of polymerization increases as the amount of VeoVa-9 decreases. Increasing the amount of VeoVa-9 in the reaction leads to a longer induction period (e.g. 100% VeoVa-9 curve). This behaviour could be attributed to two possible factors; the first factor is that as shown earlier, the reactivity of VeoVa-9 is much lower than that of BA. Therefore an increasing BA fraction leads to an increase in the polymerization rate. Using the monomer droplet nucleation mechanism as the main particle formation mechanism, the above results could be explained also by the difference in the solubility of the monomers in the aqueous phase^{17,28}.

The rate of radical entry into the polymerization sites (monomer droplets/particles) has a partial dependence on the availability of the monomer in the aqueous phase. Hence the higher the aqueous (to a certain extent) phase monomer solubility, the faster the radical entry into the monomer droplets/particles. The entry rate and particle formation are strongly linked during the droplet nucleation phase, since the rate at which droplets are nucleated is proportional to the rate at which the radicals are entered, when the aqueous phase entry is the dominant nucleation process. Thus, if entry is slow, the droplet nucleation will be slow (unless exit and re-entry is very fast). This is where the monomer concentration (monomer solubility) in the aqueous phase is significant and affects the critical degree of polymerization. The critical

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degree of polymerization refers to the critical size (number of monomer units in the oligoradicals) of the radicals in the aqueous phase beyond which they become surface active and hence enter the polymerization sites (also known as z -mer or z_{entry}). The lowest critical degree of polymerization for entry is normally considered to be 1 (i.e. $z_{\text{entry}} \geq 1$), so, the initiator fragment must add at least one monomer unit to enter the droplets/particles. The rate of this process (per initiator fragment) is a function of the monomer concentration in the aqueous phase and the aqueous-phase propagation rate coefficient of the oligoradicals ($[M]_{\text{aq}}$ and k_p^{aq})^{29,30}.

From the above discussion, the entry of the radicals to the polymerization sites in the VeoVa-9/BA copolymerization is likely to be more efficient (faster) for the higher BA feed fraction, since the water solubility of the BA is higher than that of the VeoVa-9 (0.2% for BA and in the order of 10^{-4} wt% for the VeoVa-9²¹). In the case of 100% BA, although z_{entry} is probably higher, $[BA]_{\text{aq}}$ and k_p^{aq} are much higher than in the case of VeoVa-9 (100% VeoVa-9) so the entry efficiency is likely to be much higher. Thus, droplet nucleation will be faster, hence the induction period, which is probably due to particle formation, will be shorter at higher BA fractions; this might also be reflected in the particle size as will be discussed later. These arguments are only strictly true for 100% of either monomer, while the situation for the mixed (all other feeds) are complex, and mostly lie between those limits. These results are similar to that found by Huang *et al.*²⁸ for miniemulsion copolymerization of styrene with BA. They showed that increasing the BA concentration leads to a faster copolymerization rate; they also attributed their results to the difference in the water solubility.

Initiation in the droplet or particle phase could be achieved by the use of an oil-soluble initiator¹⁷. Due to the nucleation mechanism (droplet nucleation) in the miniemulsion system, the use of an oil-soluble initiator will allow radicals to form in the droplets, thus possibly nucleating them. This could reduce the dependency of the polymerization nucleation rate on the monomer water solubility. The effect of oil-soluble initiator on the copolymerization behaviour of VeoVa-9 and BA at different feed ratios was thus also investigated. In this set of experiments, the mole percentage of the VeoVa-9 was varied, keeping the solids content constant (at 20%); also the surfactant, costabilizer and initiator concentrations were kept constant relative to the monomer as when the APS initiator was used (see Section 4.4.3). The usual emulsification process was modified slightly in this set of experiments. The oil-soluble

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initiator azobis(isobutyronitrile) (AIBN) was first dissolved in the monomers prior to emulsification. In order to prevent polymerization during the ultrasonication process, the emulsification process was carried out at 30°C, instead of 50°C for APS-initiated miniemulsions, for about 11 min. The copolymerization conversion-time curves of this set of experiments are given in Figure 4.14.

The miniemulsion copolymerizations using oil-soluble initiator gave a similar result in terms of the maximum polymerization rate to those using a water-soluble initiator. However, in the presence of the oil-soluble initiator, the monomer conversion tended to decrease as the concentration of VeoVa-9 increased; in contrast this behaviour was not observed in the case of the water-soluble initiator. The decrease in the apparent final conversion was probably due to the coagulation of some of the polymer out of the latex, which was significant for the highest VeoVa-9 concentrations (100% VeoVa-9) and decreased (coagulation) as the VeoVa-9 concentration decreased in the feed. The increase in the amount of coagulation could be due to the increase in the particle size with increasing VeoVa-9 fraction in the feed, as will be discussed in the next section (Section 4.4.3.2).

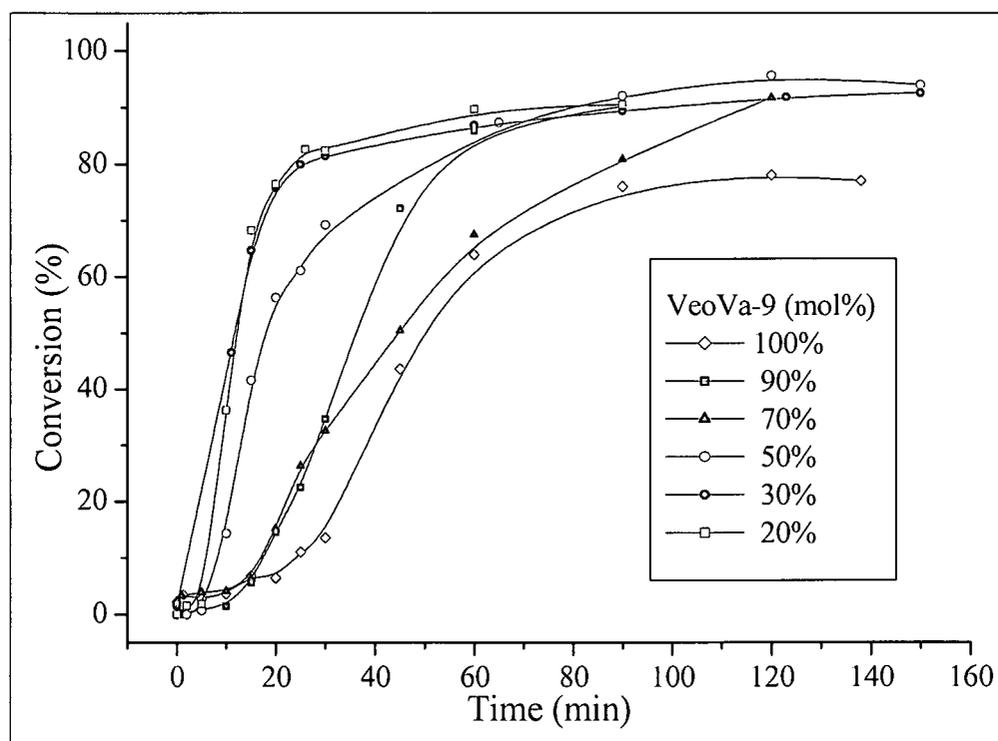


Figure 4.14: Monomer conversion-time curves for miniemulsion copolymerization of VeoVa-9/BA (20% solids) using the oil-soluble initiator 0.1 wt% (AIBN) at 80°C.

This behaviour could be attributed to the initiation mechanism of the oil-soluble initiator in the miniemulsion, which depends on the solubility of the initiator in both the monomer and

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water³¹. The initiation mechanism of an oil-soluble initiator is different from that of water-soluble ones. As was discussed earlier, when a water-soluble initiator is used, the polymerization will be initiated from the water phase via the entry process. However, in the case of an oil-soluble initiator, and depending on the solubility in water, a fraction of the polymerization is initiated in the monomer droplets (note that the aqueous phase may still be dominant). In this case AIBN initiator was used (which has limited water solubility 0.04 g/100 mL³²), and upon heating cyanoisopropyl radicals are formed in the monomer droplets and (to a lesser extent) in the aqueous phase; some of these radicals (since termination by geminate recombination is usually very likely, often one of the pair of radicals generated needs to exit for this process to be efficient) can react with the monomer to form a long chain polymer. The addition of these radicals to the VeoVa-9 is likely to be very slow, as it is for the addition to the analogous VAc (the rate coefficient for this process is 41 M⁻¹ s⁻¹ at 42°C³³). Thus, the particle formation rate is probably very low, leading to enhanced coagulation, and as a result large particles might form as will be discussed in the next section.

Inside the droplets when a pair of radicals forms in a droplet, one of the following processes may occur (i) one (or both) might exit the droplet before recombination can occur, or (ii) the formed radicals recombine and terminate. If significant propagation does not occur quickly enough, termination becomes quite probable (shorter growing radicals are very mobile, thus they terminate rapidly). Cyanoisopropyl radicals probably desorb quite well to the aqueous phase^{17,34} (which also depends on other factors such as particle size), so in order to form polymer chains in the droplets, they need to propagate faster than they desorb or terminate (which is a very likely scenario). However, as stated earlier, addition to the VeoVa-9 is probably very slow, so desorption or termination are thus likely fates, which could explain the decline in the rate of polymerization after the initial increase, which might correspond to either lower $\langle k_p \rangle$, the average propagation rate coefficient, or/and to a lower initiator efficiency. The addition of BA will improve the propagation rate of the radicals since the copolymerization is faster once a monomer unit is added (100% VeoVa-9 curve Figure 4.14).

An important observation in the case of reaction with the water-soluble initiator APS is that the polymerizations reach maximum rate faster than in the cases of the oil-soluble initiator AIBN. Furthermore, in the case of AIBN, the apparent conversion was lower than the APS polymerization, which, as was stated earlier, is due to coagulation (the final solids content as measured is 17.5% and the mass of the coagulated polymer is 2.5 g). This

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behaviour could also be due to the difference in the initiator efficiency, in which water-soluble initiators tend to be more efficient at higher conversion. This can be seen in Figure 4.15, which gives the monomer conversion curves of VeoVa-9 using both oil- and water-soluble initiators.

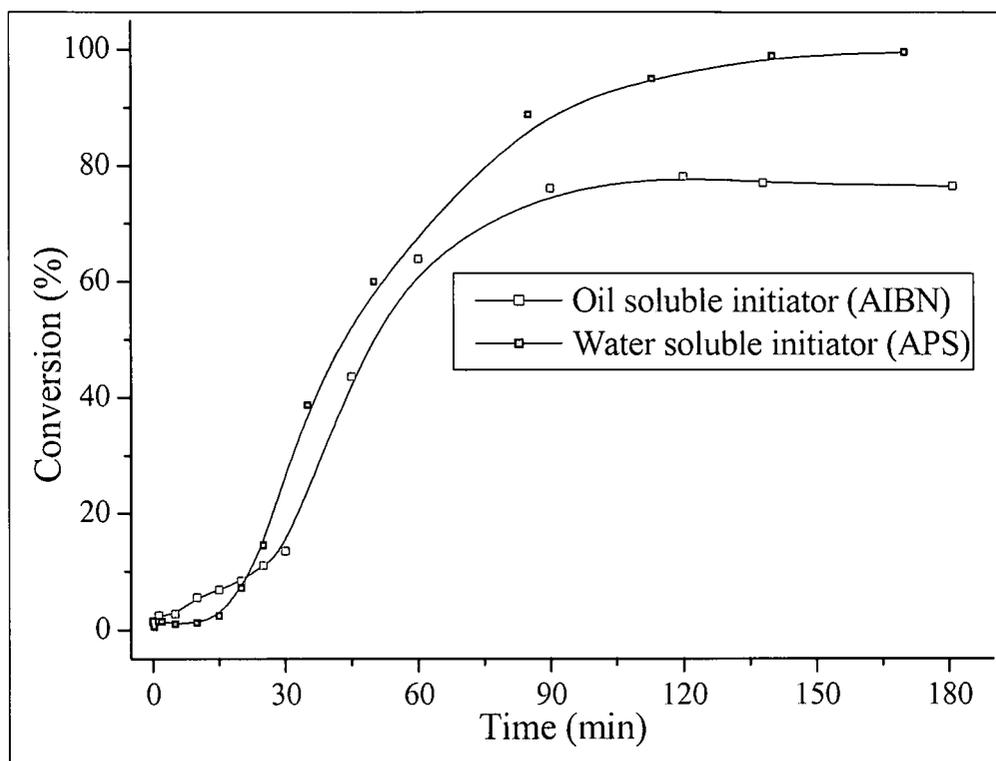


Figure 4.15: Monomer conversion as a function of time for the miniemulsion polymerization of VeoVa-9 using oil- and water-soluble initiators (AIBN and APS) at 80°C.

These results are due to differences in the initiation and mechanisms in which the monomer droplets are nucleated for each initiator (AIBN or APS). In the case of an oil-soluble initiator, the radicals are mainly generated in the monomer droplets and only to a lesser extent, in the water phase due to the low AIBN solubility in water. The probability of nucleation is closely related to the probability of formation of a long chain polymer in the monomer droplets. This long chain polymer will only usually be formed when a single free radical exists in a monomer droplet^{17,31}. Considering that pairs of radicals are formed by initiator decomposition, a single radical situation can be the result of desorption of one of the radicals generated from initiator decomposition, or by entry of a radical from the aqueous phase (either to terminate one of the two formed radicals or to initiate the polymerization)³¹. Above 60% conversion the droplets become very viscous, therefore when AIBN decomposes into two radicals it becomes difficult for one to exit. There is rather mutual termination and this limits future conversion.

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In the case of APS, the polymerization (particle formation) will only start when the radical in the aqueous phase reaches the critical length (*z*-mer) and enters/or nucleates the droplets, which could explain the faster particle formation when the AIBN initiator was used. However, due to the decomposition process of the AIBN, a growing free radical may undergo a termination reaction (between a radical in the droplet and an entering radical). Also, as stated earlier, the addition of cyanoisopropyl radicals to the VeoVa-9 is slow; this is probably not the case for the APS fragments. As a result, single radical nucleation and entry rates are expected to be very low in the case of AIBN, and hence large particles are formed, leading to enhanced coagulation of these large particles as will be discussed in the next section (Section 4.4.3.2).

Overall, this result shows that the monomer solubility in the aqueous phase and the type of initiator plays an important role in determining the polymerization kinetics in the miniemulsion. This can be seen by the difference in the curves, for both types of initiators, during the first 10% monomer conversion in Figure 4.15.

In a comparison between the miniemulsion and solution processes, the copolymerization of these monomers shows a faster copolymerization reaction when the miniemulsion technique was used. As shown in Figures 4.1 and 4.13 the copolymerization reaction in the miniemulsion took only about 125 minutes at maximum VeoVa-9 fraction (100% VeoVa-9) to reach 98% conversion. For the corresponding solution process, the copolymerization reaction proceeded for about 350 minutes and the monomer conversion reached only about 40%. The difference between the results is likely to be due to the reduced overall termination rate due to compartmentalisation³⁵. In the solution polymerization, any radical generated has equal access to others and hence has a high termination probability. However, in a miniemulsion system, the polymerization site is the latex particles, so the radical in a particle has no direct access to a radical in another particle, without the intervention of a phase-transfer event. In other words, the radical concentration in miniemulsion is much higher than it is in solution and hence the higher polymerization rate. The initiator efficiency could be also an important factor in determining the rate of polymerization. This could be due to the difference between the nature of the two processes, where in solution the monomer concentration is lowered by the solvent³⁶; in contrast, in the miniemulsion the highest monomer concentration is in the polymerization sites (monomer droplets/particles) which can be considered to be nanoreactors^{17,19}.

4.4.3.2. Influence of the VeoVa-9 concentration on the particle size

In the miniemulsion system, the diameter of the obtained particles is a function of a number of variables, including the surfactant concentration^{20,27,37-39}, the type and concentration of the hydrophobe^{20,38,40}, monomer solubility^{21,41}, and the solids content^{17,42}. In this study, most of these factors were held constant, and, depending on the process used, only one parameter was changed at a time. For instance, in the case of a batch process, the overall solubility of the monomer (by varying the feed ratio), was changed, since the VeoVa-9 has lower water solubility than the BA. However, in the case of a semi-batch process, besides varying the overall monomer solubility (according to the feed ratio), the solids content might also change; therefore the surfactant-to-monomer ratio might change, and hence affect the particle size. The effect of the VeoVa-9 concentration on the particle size was investigated in both processes (batch and semi-batch), the results are discussed below.

In the batch process, all of the starting materials were added at the beginning of the reaction which means that the final predicted solids content of the miniemulsion was constant throughout the reaction. Differences in the water solubility of the VeoVa-9 and BA may affect the obtained particle size. Changing the VeoVa-9 concentration in the polymerization mixture led to a change in the solubility of the mixture in the aqueous phase, which as a result could affect the nucleation efficiency of the monomer droplets, and hence change the particle diameter. It was found that increasing the VeoVa-9 concentration leads to increasing particle diameter. As shown in Figure 4.16 (batch miniemulsion), the particle diameter decreases from about 156 nm to about 110 nm as the VeoVa-9 concentration decreases from 90 to 10 (mol%) in the miniemulsion mixture.

In the semi-batch process, the amount of VeoVa-9 was initially charged into the reactor as a miniemulsion mixture. While the BA was fed into the reactor drop-wise during the time of polymerization, the addition started as soon as the initiator solution was added. The mole percentage of the VeoVa-9 was varied from 10 mol% to 90 mol%, keeping the predicted final solids content constant (at 20% relative to the aqueous phase). Furthermore, the surfactant, costabilizer and initiator concentrations were kept constant relative to the overall monomer concentration, as in the batch process. As a result of the addition mode, the solids content might not be the same at the start and the end of the polymerization, since the VeoVa-9 concentration was varied.

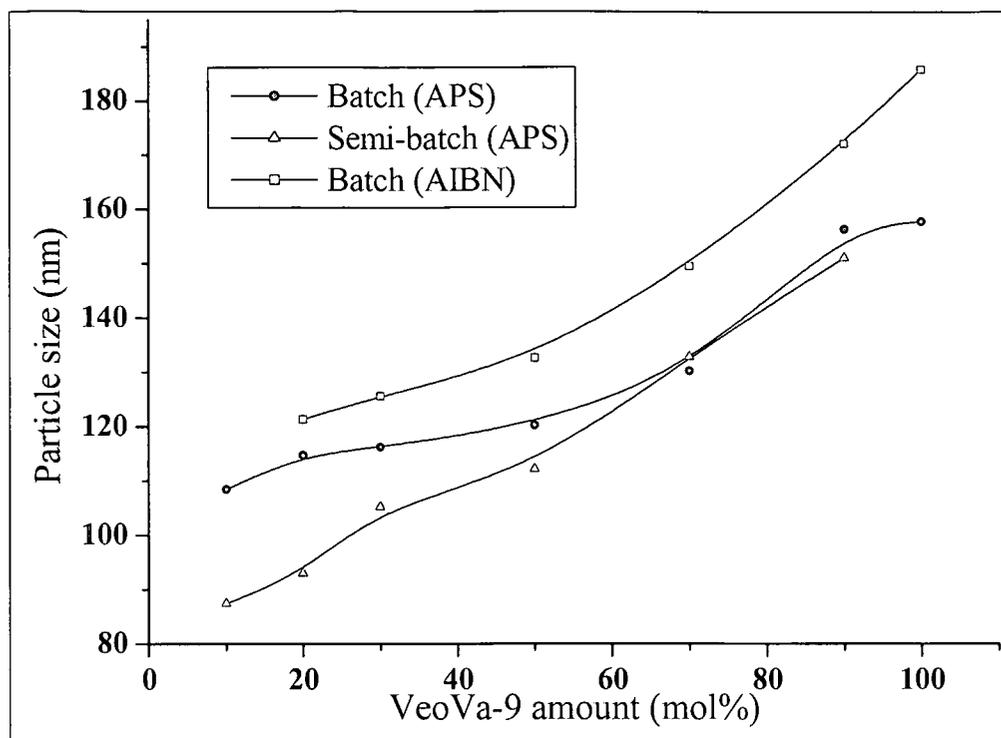


Figure 4.16: Particle size as a function of VeoVa-9 concentration in batch and semi-batch miniemulsion copolymerization of VeoVa-9/BA using APS and AIBN as initiators at 80°C.

As was discussed earlier, the slow propagation rate in both the aqueous phase and monomer droplets as the VeoVa-9 concentration increases might be reflected in the final particle size. If the monomer nucleation and entry rates are slow, then some monomer droplets are nucleated and form polymer particles, while others remain un-nucleated. The formed particles therefore may grow while the other droplets remain un-nucleated. If these particles consume a significant amount of monomer, a migration of monomer molecules (through the aqueous phase) from the un-nucleated droplets may occur. This may lead to a broad particle size distribution with some large particles, or may consume some of the small particles or droplets (due to monomer depletion and coagulation). Thus a large average particle size might result from slow nucleation. As shown in Figure 4.16, the particle size decreases as the VeoVa-9 fraction decreases in the feed; this could be due to the faster nucleation and entry as the BA fraction increases. These results are similar to those obtained by El-Aasser *et al.*⁴¹ for the miniemulsion copolymerization of vinyl acetate and vinyl 2-ethylhexanoate. They found that increasing the less water soluble monomer concentration resulted in an increase in the final particle size. These results also are similar to those obtained from the miniemulsion copolymerization of styrene (St) and butyl acrylate, in which the particle size increases with increasing St concentration in the miniemulsion³⁸.

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In the case of the oil soluble initiator, similar results were observed, except that the average particle diameter was larger in this case (see Figure 4.16). The particle diameter increased from 120 nm to 185 nm as the VeoVa-9 concentration increased from 20% to 100%. This increase in the particle diameter could, as stated earlier, be due to the slow propagation rate of the VeoVa-9. Furthermore, the larger particle diameter when using the oil-soluble initiator could be due to a lower addition efficiency of cyanoisopropyl radicals to the VeoVa-9 and a lower AIBN efficiency, resulting in a reduced polymerization rate, and hence particles grow larger.

In the case of a semi-batch process, not all of the starting materials were added at the beginning of the polymerization. For instance in the 90% VeoVa-9 (mol%) reaction, only the VeoVa-9 was emulsified (total surfactant concentration was used) and sonicated, while the 10% BA was fed as a neat monomer throughout the reaction. Due to this procedure, the initial solids content is not the same as at the end of the polymerization, which may affect the particle diameter¹⁷. Figure 4.16 (semi-batch miniemulsion) shows the change in the particle size as the VeoVa-9 concentration changes. Similar to the batch process a decrease in the particle size as the VeoVa-9 fraction decreases was observed, however in the semi-batch process the observed particle size is smaller than in that observed for the batch process.

These results could be explained by the change in both the VeoVa-9 concentration (and hence the overall water solubility of the monomers in the water^{38,41}), and the surfactant-to-monomer ratio (S) at the beginning of the polymerization. As discussed above, changing the VeoVa-9 concentration in the miniemulsion leads to an increase in the particle diameter. The other factor is that the surfactant-to-monomer ratios (S is the weight ratio of SDBS to VeoVa-9) may change at the start of each experiment, since only the VeoVa-9 was charged at this stage of the reaction. For instance, in the case of the 90% VeoVa-9 experiment, the initial S value is 0.011, while this value will increase with decreasing the VeoVa-9 fraction (the S value ranged from 0.011 to 0.072 as the VeoVa-9 concentration varied from 90% to 10%). The increase in the S value may lead to the presence of free surfactant molecules in the aqueous phase and even to the presence of free micelles at higher values of S, as shown by Landfester *et al.*²⁰ Surface coverage data indicates the presence of free micelles. As a result of this procedure, free surfactant molecules or even micelles might be present in the aqueous phase at the initial stage of the polymerization. Hence the nucleation mechanism might consist of a competition between droplet, homogeneous or/and micellar nucleation mechanisms.

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Due to these possible nucleation mechanisms and the contribution of a slow polymerization rate at higher VeoVa-9 concentration, the particle diameter decreased as the amount of VeoVa-9 decreased. The average particle diameter is smaller than in the case of batch polymerization. The contribution of the homogeneous and maybe micellar nucleation mechanisms could explain the significant decrease in the particle size at low VeoVa-9 concentrations (lower than 50% VeoVa-9). The presence of free surfactant molecules or/and micelles could also affect the copolymer composition, since the low water solubility of VeoVa-9 reduces the migration of this monomer from the monomer droplets to the new particles formed by homogeneous or micellar nucleation.

4.5. Copolymer study via 2-D chromatography

Two-dimensional chromatographic analysis of copolymers produced in miniemulsions was carried out. Liquid Chromatography at Critical Conditions (LC-CC) and Size Exclusion Chromatography (SEC) were used as the first and second dimensions respectively to characterize the produced copolymers. The critical point of adsorption approach enables a separation of polymer heterogeneity according to its chemical composition with high efficiency. The critical conditions in which the polymer molecules elute independently of molecular weight can be achieved by using a temperature profile⁴³ or using a solvent system at constant temperature⁴⁴.

In this study, the two-dimensional chromatography (2-D) approach was used to characterize VeoVa-9/BA copolymers that were prepared by miniemulsion polymerization. The analysis of these copolymers was based on separating the BA homopolymers in the copolymer using critical conditions for the PBA. The critical conditions of the PBA were achieved as found by Pasch *et al.*⁴⁴ using a solvent system which included a mixture of tetrahydrofuran (THF) and cyclohexane 15.5:84.5 (v/v%) respectively at 30°C. Under such conditions, the PBA homopolymers will elute at the same time, independent of molar mass. As shown in Figure 4.17, all of the PBA homopolymers of different molar masses eluted at the same time, indicating that at these conditions the PBA can be separated from the copolymers.

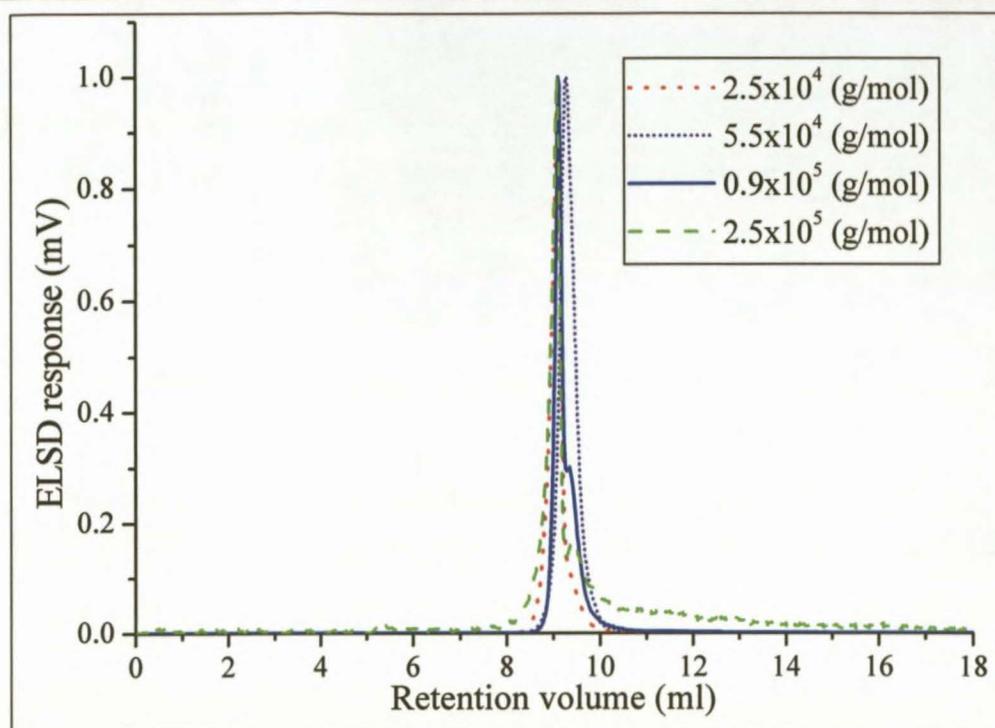


Figure 4.17: Chromatograms for PBA homopolymers with different molar mass in the LC-CC mode; eluent: THF/cyclohexane 15.5:84.5 (v/v%) at 30°C.

The PBA homopolymers were prepared via emulsion polymerization of BA using SDBS as surfactant and APS as an initiator at 80°C. The variation of the molar mass was achieved by using 1-dodecanethiol as a transfer agent. The molar masses of these polymers were 25 000, 45 000, 90 000, and 250 000 g/mol. This variation of the molar mass was used to ensure that PBA homopolymers elute at the same volume regardless of the polymer molar mass. Figure 4.17 shows that there was no strong molecular weight dependent column interaction for the PBA homopolymers with different molar masses. The peak maxima were observed between 9.1 and 9.2 mL.

These conditions (solvent combination at constant temperature, 30°C) were applied on a mixture of both PBA and PVeoVa-9 homopolymers, to examine the separation efficiency of the system. The result of this separation is shown in Figure 4.18, which also shows the elution order of each homopolymer in the first dimension (liquid chromatography at critical conditions). As it can be seen in Figure 4.18 the peaks of each homopolymer are well separated. From this result it was concluded that these conditions are capable of separating the PBA homopolymers from the copolymers.

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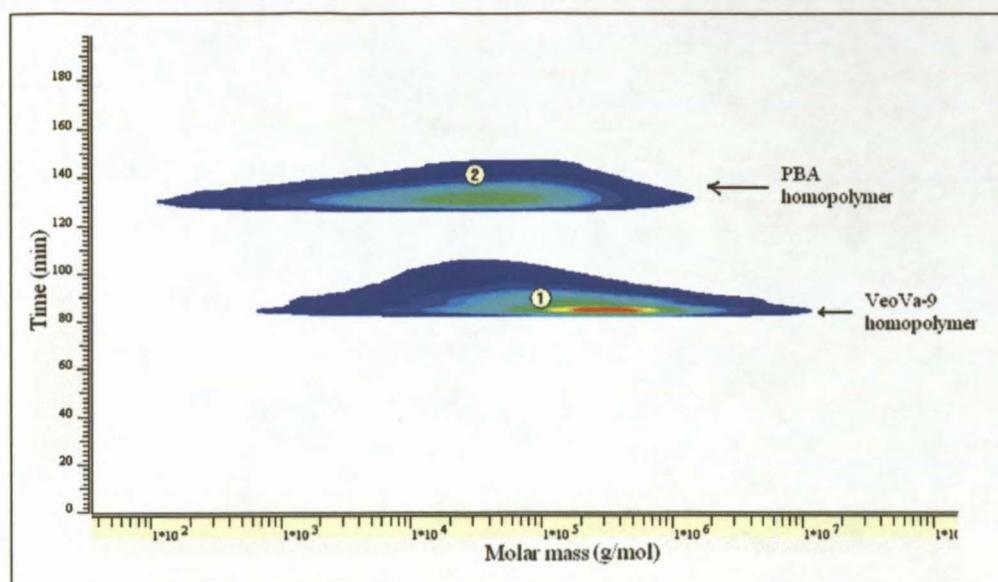


Figure 4.18: Contour plot of the 2D separation of the VeoVa-9 and PBA homopolymers mixture at the critical conditions of PBA; eluent: THF/cyclohexane 15.5:84.5 (v/v%) at 30°C.

The elution order of the polymers out of the column is usually determined by the interactions between these polymers and the column material (normal phase e.g. silica gel or reverse phase e.g. Si-C₁₈). These interactions are controlled by the polarity of the polymers and the type of materials used in the column⁴⁵. In this study, for instance, the PBA homopolymer shows a longer elution time in the silica gel column than the VeoVa-9, as depicted in Figure 4.18. This is due to the lower hydrophobicity of the PBA homopolymer with respect to that of VeoVa-9. The higher polarity of the PBA allows stronger interactions with the silica gel and hence it experiences longer retention time in the column.

4.5.1. Two-dimensional analysis of the copolymer

The combination of LC-CC with SEC is a very powerful technique that can provide information about the polymer heterogeneity, that is unlikely to be obtained by a single separation method⁴⁶. In this study, this technique was used to characterize VeoVa-9/BA copolymers that were prepared in miniemulsion using the batch and semi-batch procedures.

Figure 4.19 shows the 2-D contour plot of VeoVa-9/BA copolymer that was prepared using 50/50 mol% VeoVa-9/BA in batch miniemulsion copolymerization. Only one peak was observed, and there was no peak indicating the presence of PBA homopolymer. The colour simply indicates the signal intensity (e.g. the red colour gives the maximum intensity while the blue gives the minimum intensity).

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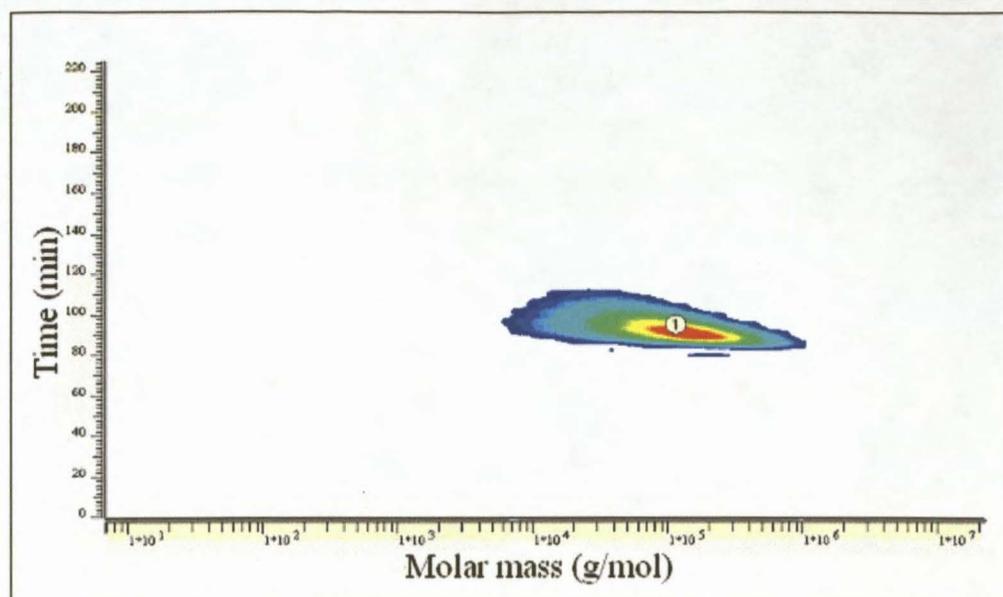


Figure 4.19: Contour plot of the 2-D separation of the VeoVa-9/BA (50/50 mol%) copolymer prepared via batch miniemulsion copolymerization, under the critical conditions of the PBA; eluent: THF/cyclohexane 15.5:84.5 (v/v%) at 30°C.

The absence of the PBA peak in Figure 4.19 indicates that the entire BA monomer was incorporated into the copolymer. Furthermore, the ^1H NMR analysis of the copolymer showed that the copolymer structure comprises about 51% BA units, which is comparable to the amount of the BA that was charged in the feed (50 mol% and >98% conversion).

In a comparison between the analysis of the copolymer and the mixture of the two homopolymers under these conditions (Figure 4.18 and Figure 4.19 respectively), the copolymer appears as a separate peak between both homopolymer peaks. The coupling of the LC-CC with SEC provides additional information about the molecular weight of the copolymer beside its chemical composition. In this case the number average molecular weight (based on linear polystyrene standards) of the copolymer was 2.3×10^5 g/mol.

For better control over the copolymer structure and a more even distribution of monomers along the copolymer structure, the semi-batch approach was used. In this case the overall monomer concentration in the miniemulsion was 20% relative to the aqueous phase. The procedure was as follows: the amount of VeoVa-9 (50 mol%) that was initially charged into the reactor was varied while the BA was fed into the reactor drop-wise during the time of polymerization. In this copolymerization, the addition of the BA started after 20 min of the initiator addition. The surfactant, costabilizer and initiator concentrations were 1 wt %, 3 wt% and 0.1 wt% respectively relative to the overall monomer concentration.

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The obtained copolymers were characterized by 2-D chromatography using the same conditions used to characterize the copolymers obtained from the batch miniemulsions. In Figure 4.20, the 2-D contour plot of the copolymer prepared in a semi-batch miniemulsion process is shown. The analysis of this copolymer gave three peaks, labelled 1, 2 and 3.

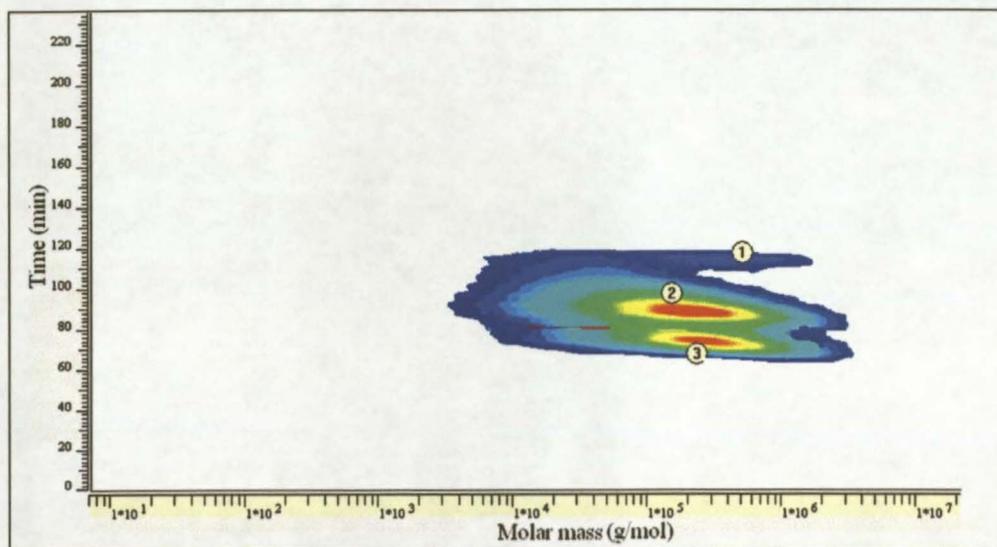


Figure 4.20: Two-dimensional contour plot of VeoVa-9/BA (50/50 mol%) copolymer prepared via semi-batch miniemulsion copolymerization.

According to the copolymerization process, in which the BA was added to the reaction as discussed earlier (Section 4.4.3.2), three possible components may be formed: P_{VeoVa-9} homopolymer, VeoVa-9/BA and BA-rich copolymer or PBA. Therefore these three peaks could be assigned as: (i) peak 3 corresponds to the VeoVa-9 homopolymer, (ii) peak 2 corresponds to the VeoVa-9/BA copolymer and (iii) peak 1 corresponds to BA-rich copolymer or homopolymers. This assignment was made according to the position of the peaks, which is determined by the hydrophobicity of these components. The hydrophobicity of these components is in the order PBA < VeoVa-9/BA copolymer < P_{VeoVa-9}, and the lower hydrophobicity corresponds to longer elution time. This means the higher the PBA concentration in the copolymer is, the stronger the interactions with the silica gel in the column will be, resulting in a longer elution time. As a result of these interactions the elution order of these components is P_{VeoVa-9}, VeoVa-9/BA copolymer, and lastly PBA.

Accordingly, the presence of these peaks could be explained as follows: peak 3 may indicate the presence of VeoVa-9 homopolymer that formed at early stages of the copolymerization reaction. Since the BA was first only added after 20 min from the start of the polymerization, about 30% of the VeoVa-9 monomer that was charged had already been consumed to make

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Veova-9 homopolymer (as shown in Figure 4.13). The peak intensity (area) of each fraction corresponds to its concentration with respect to the overall feed composition (total peaks intensity). Peak 3, which corresponds to the Veova-9 homopolymer in Figure 4.20, has an intensity of 35% of the total peaks intensity in the contour plot. This may correspond to amount of Veova-9 that was polymerized in the first 20 min, before the addition of the BA monomer. Peak 2 corresponds to the copolymer which started forming as soon as BA addition into the reaction started; this monomer was fed for about three more hours. In this time, most of Veova-9 monomer was consumed; its concentration was much less than the BA concentration, which might explain the presence of peak 1.

Peak 1 was assigned to be associated with the BA-rich copolymer units or homopolymers. Two factors could explain the presence of this fraction. The first possibility is that the copolymer was formed at a late stage of the copolymerization reaction. At this stage the concentration of BA was much higher than that of the Veova-9 in the reaction mixture, which resulted in a copolymer rich in BA units. The second possibility is that this copolymer was formed in particles formed by micellar and/or homogeneous nucleation. As was discussed earlier (Section 4.4.3.2), due to the possible existence of free surfactant molecules and/or micelles, some of the added BA might react to form polymer particles through homogeneous or/and micellar nucleation. The Veova-9 might have reached the locus of polymerization (particles that formed from homogeneous or micellar nucleation) by desorption and migration from the monomer droplets of the Veova-9 through the water phase to such particles. Due to its low water solubility, desorption of the Veova-9 monomer to the water phase is expected to be very slow and hence only a limited amount of it will reach any particles that might have formed by homogeneous or/and micellar nucleation.

The latter possibility (homogeneous/micellar nucleation) could explain the position of peak 1 in the molecular weight scale in Figure 4.20, which shows that this fraction of the copolymer has a higher apparent molar mass than the other fractions. The position of this peak in the retention time scale could be explained by a larger fraction of BA units in the copolymer than Veova-9 units. Since the concentration of the BA is higher than the Veova-9 in the copolymer, its peak will be shifted toward the critical position at which the PBA elutes, regardless of its molecular weight. Due to these results (copolymer composition) the addition mode of the BA to the reaction was changed to start with the addition of the initiator solution (see Section 3.4.2.2. This might eliminate the presence of peak 3 in the contour plot

(VoeVa-9 homopolymer), since the polymerization will start in the presence of both monomers and hence a better distribution could be obtained.

4.6. Characterization of VeoVa-9/BA copolymers

Polymer properties are of major interest and importance. Polymer properties are largely affected by a number of factors, including the chemical structure of the polymer, which is largely determined by the chemical structure of monomers used. For instance, the glass transition temperature and also the water resistance of a polymer are functions of the monomeric structure^{47,48}.

Polymer properties are important in determining the polymer's final use (e.g. coatings or other applications). From an industrial point of view, a polymer must exhibit a number of characteristics for a particular application. Important polymer characteristics include the following: (a) molecular relaxation (thermal properties), (b) barrier properties, (c) mechanical properties, (d) surface and adhesion properties, (e) electrical properties and (f) optical properties. All of these properties can be modified and improved by changing the monomer or combining different type of monomers with different structures⁴⁷.

Due to the importance of acrylate and vinyl ester polymers, especially in the coatings applications^{2,3}, the surface properties and thermal properties of VeoVa-9/BA copolymers were investigated; these properties are critical for the copolymer applications.

4.6.1. Thermal properties

One of the most important properties of a polymer is the glass transition temperature (T_g) at which the long range cooperative chain movement becomes possible. This is important in determining the final use of the polymer as well as determining the polymer performance (e.g. its surface properties)⁴⁹. In this study the T_g of VeoVa-9/BA copolymers that were produced in the miniemulsion (both batch and semi-batch) were evaluated using dynamic mechanical analysis (DMA), and the T_g was determined from the storage modulus and the tan delta curves.

Figure 4.21 shows the T_g of the copolymers as a function of the VeoVa-9 content for the batch and semi-batch copolymers. The error bars show the difference between the T_g

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determined from the storage modulus and from the tan delta. Figure 4.21 shows that in both cases (batch and semi-batch), there was an increase in the copolymer's T_g as the VeoVa-9 concentration increased, and that the T_g values ranged between the T_g values of the two homopolymers T_g (the T_g values of PVeoVa-9 and PBA are +70 and -45°C respectively).

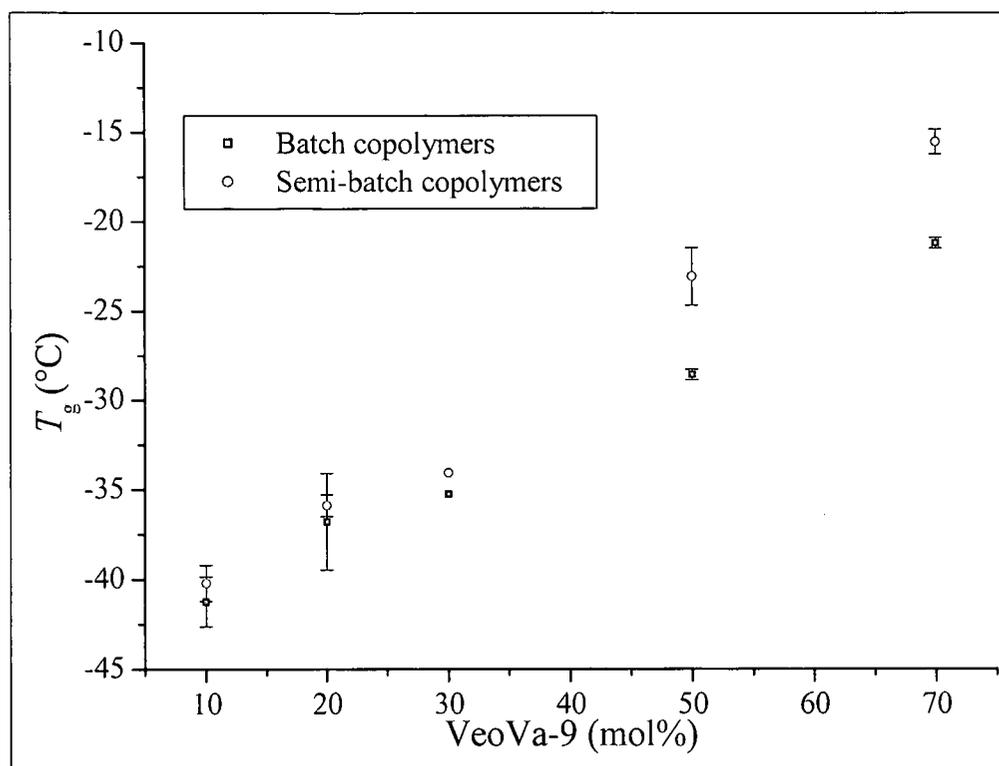


Figure 4.21: T_g values of the VeoVa-9/BA copolymers prepared via the miniemulsion technique as a function of the VeoVa-9 concentration (mol%).

In both cases (batch and semi-batch copolymers) and at most of the VeoVa-9 concentrations, only one T_g was observed. This could indicate that there is no homopolymer present in the samples (or that it is low molar mass). However at the high VeoVa-9 concentration (70%) two T_g values were detected, at -21 and 62°C , indicating that there is a fraction of VeoVa-9 homopolymer or a VeoVa-9-rich copolymer phase present in the sample prepared via batch process. This result was however not observed for any of the semi-batch copolymers. Observation of one T_g value in the case of all the semi-batch polymers could be due to a gradual change in structure from rich in one monomer to rich in the other, with not sufficient phase separation to be differentiated by DMA. Molecularly the 2-D chromatography indicates some division of species, as this is not dependent on phase separation of the scale needed to differentiate in the DMA.

4.6.2. Contact angle analysis

The contact angle (θ) of a liquid on a solid is the angle that forms between the boundary of the three phases: liquid, solid and air (see experimental Section 3.5.4). Determination of the contact angle is a very simple technique, which provides powerful information about the surface properties and the wetting ability of a polymer surface⁵⁰. It can be stated that the wetting of a surface can be determined from the contact angle values, for instance, a low θ value means that the liquid wets the polymer surface, while a high θ value indicates poor wetting⁵¹. A liquid that is in contact with a solid will exhibit a contact angle, and this angle depends on whether the liquid is at rest or in motion on the solid surface. When the liquid is at rest the so called “static contact angle” is obtained, and when the liquid is in motion the so called “dynamic contact angle” is obtained⁵⁰. The angle formed by an advancing liquid front on the solid surface is known as the advancing contact angle (θ_a), while the angle that is formed by a receding liquid front on the solid surface is known as the receding contact angle (θ_r). The difference between advancing and receding contact angles (θ_a and θ_r) is referred to as contact angle hysteresis⁵². In this study the surface properties of a series of VeoVa-9/BA copolymers with different compositions were investigated in terms of the effect of the VeoVa-9 content on the wetting ability, by determining the contact angle of water.

Figure 4.22 shows the static contact angles of the copolymers that were obtained from both batch and semi-batch miniemulsion as a function of the VeoVa-9 concentrations. As was described in the experimental chapter (Section 3.5.4), the films of these copolymers were made by spin casting of the VeoVa-9/BA copolymers/THF solutions.

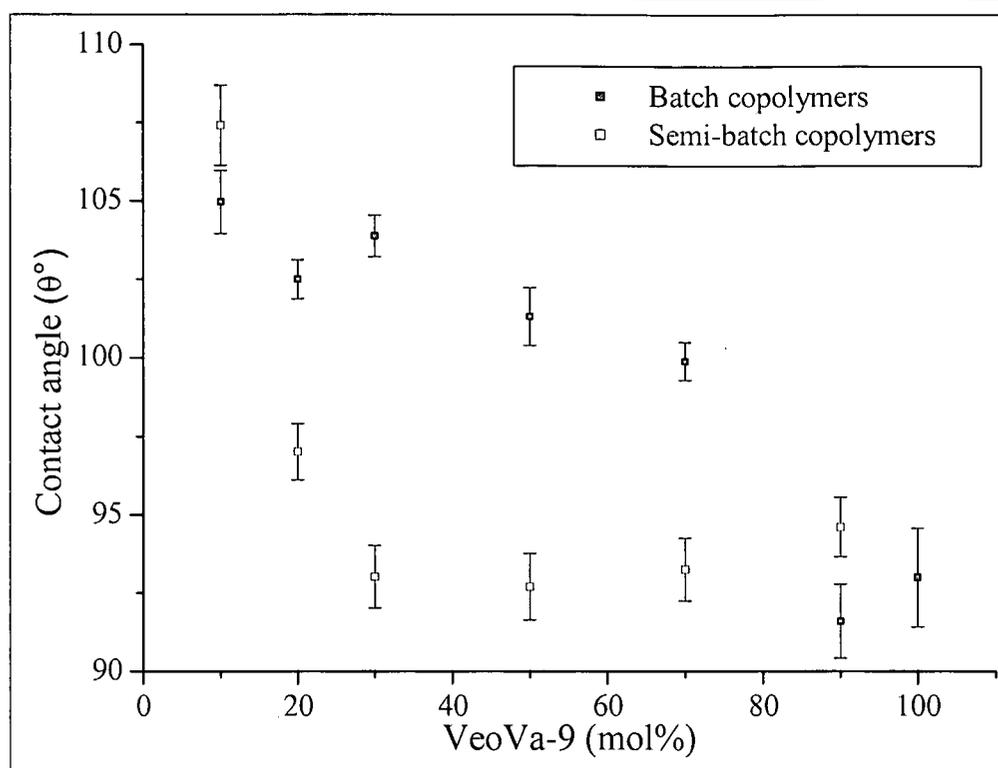


Figure 4.22: Static contact angle to water on VeoVa-9/BA films at 20°C and about 55% humidity as a function of VeoVa-9 concentration. Note that the films are surfactant free (refer to Section 3.5).

In Figure 4.22, the contact angle of all of the copolymers is greater than 90°, indicating poor wetting of the surfaces by water due to the nature of the copolymers^{48,49}. The water resistance or hydrophobicity of a polymer is a function of the nature of the monomeric units and their oxygen content⁴⁸. In this case, both the hydrophilicity and the oxygen content of VeoVa-9 are lower than they are for the BA. Hence the contact angle of these copolymers (which indicates a surface hydrophobicity) should increase with an increase in VeoVa-9 content. This was not observed however; results showed an increase in the contact angle with a decrease in the VeoVa-9 content.

The observed results could be attributed to the flexibility of the copolymers which increases as the VeoVa-9 concentration decreases⁵³. In other words, as the T_g of the copolymers decreases with decreasing VeoVa-9 concentration, the surface tension of the copolymers decreases due to the higher mobility of the copolymer chains⁵⁴. As a result, the difference between the surface tensions of the copolymers and the water increases, leading to a reduction in the wetting ability of the copolymer surfaces. This could also be explained by Equations 4.10 and 4.11, which give both the contact angle ($\cos\theta$) and spreading coefficient ($S_{L/S}$) as a function of surface tensions of solid/liquid (γ_{sl}), solid/vapour (γ_{sv}) and

liquid/vapour (γ_{lv}).

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad (4.10)$$

$$S_{L/S} = \gamma_{sv} - (\gamma_{lv} + \gamma_{sl}) \quad (4.11)$$

From both equations, a decrease in the surface tension of the solid leads to an increase in the contact angle, and hence a decrease in the wetting ability of the solid as the spreading coefficient (S) decreases. Another possibility that can affect the value of contact angle is phase separation of the copolymers.

Figure 4.22 shows that the difference between the observed contact angles was in the range of 5 degrees for the copolymers that contain less than 70% VeoVa-9 in the case of the batch process. This could be due to the T_g value of the copolymers, which is much lower than the temperature at which the analyses were performed (20°C) (see Figure 4.21). In the case of the semi-batch polymers, the increase in the contact angle is only notable at low VeoVa-9 content (<20%); this could be due to a better distribution of both monomers along the copolymer chains than in the case of the batch process. Furthermore, these results could also be due to phase separation of the copolymer, with PBA migrating towards the surface of the copolymer.

The static contact angle could give misleading information about the polymer hydrophobicity and interface stability, since the polymer segments could undergo orientation when they are in contact with water⁵⁵ to minimize the interfacial free energy⁵⁶.

An alternative method by which to test polymer hydrophobicity is the hysteresis contact angle (H). Contact angle hysteresis is defined as (i) the difference between advancing (θ_a) and receding contact angles (θ_r), (ii) the difference between the cosines of the receding and advancing angles or (iii) as the ratio of the difference between the advancing and receding contact angle to the advancing contact angle (Equation 4.12)⁵². In this study the latter definition of contact angle hysteresis was used. Figure 4.23 shows the hysteresis contact angle of the VeoVa-9/BA copolymers as a function of the VeoVa-9 content.

$$H = \frac{(\theta_a - \theta_r)}{\theta_a} \quad (4.12)$$

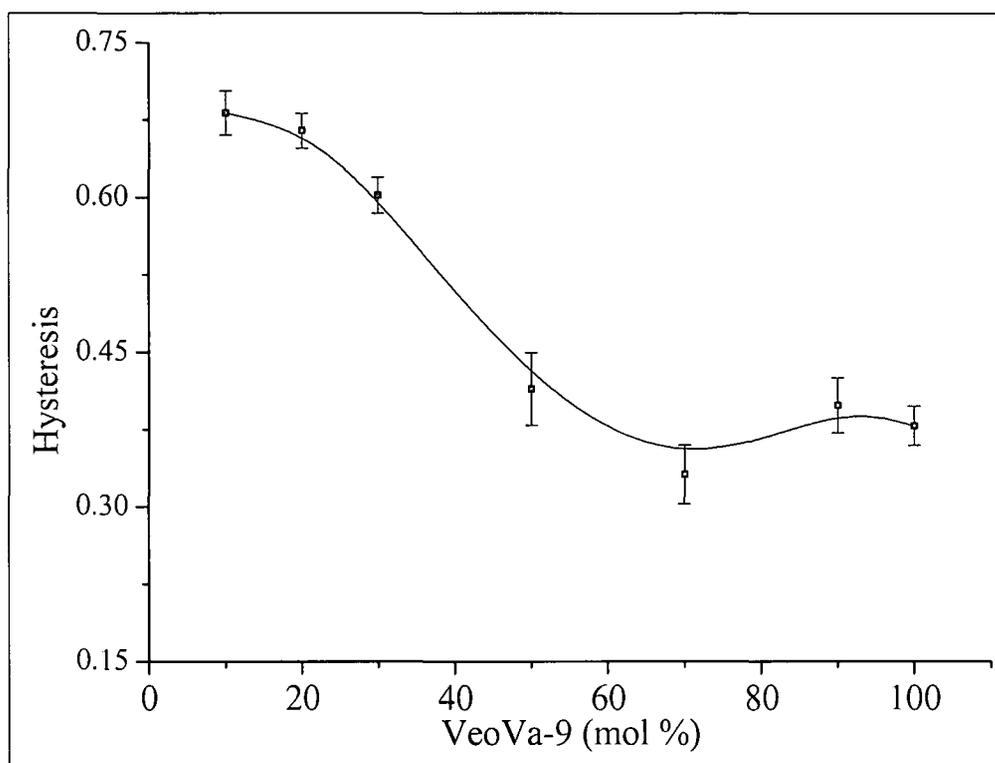


Figure 4.23: Variation of the contact angle hysteresis on VeoVa-9/BA copolymers films as a function of the VeoVa-9 concentration (mol%).

As was expected, the hysteresis contact angle increased as the VeoVa-9 concentration decreased in the copolymer. This normally points to the surface restructuring by the orientation of the more non-polar side groups towards the surface in air. While in water the side groups of the BA which are much smaller than those of the VeoVa-9, and the favourably low T_g of the copolymers, allows the orientation of the BA side group more easily than that of the VeoVa-9 side group leading to a decrease in the receding contact angle and hence an increasing hysteresis. The contact angle hysteresis results of the VeoVa-9/BA copolymers showed that the interface stability of these copolymers increases as the VeoVa-9 content increases.

The effect of surfactant concentration on the contact angle of the copolymers was also investigated. The films of VeoVa-9/BA (50/50 mol%) copolymers were prepared by (i) casting the latexes directly on microscope glass slides and (ii) casting copolymer/THF solutions (12.5 mg/mL) at 2250 rpm for 2 minutes. The difference between these films is the presence of surfactant when the films were made from latexes. The solvent films are surfactant free, as the surfactant was removed (see Section 3.5). Figure 4.24 shows the observed static contact angle of both cases as a function of surfactant concentration.

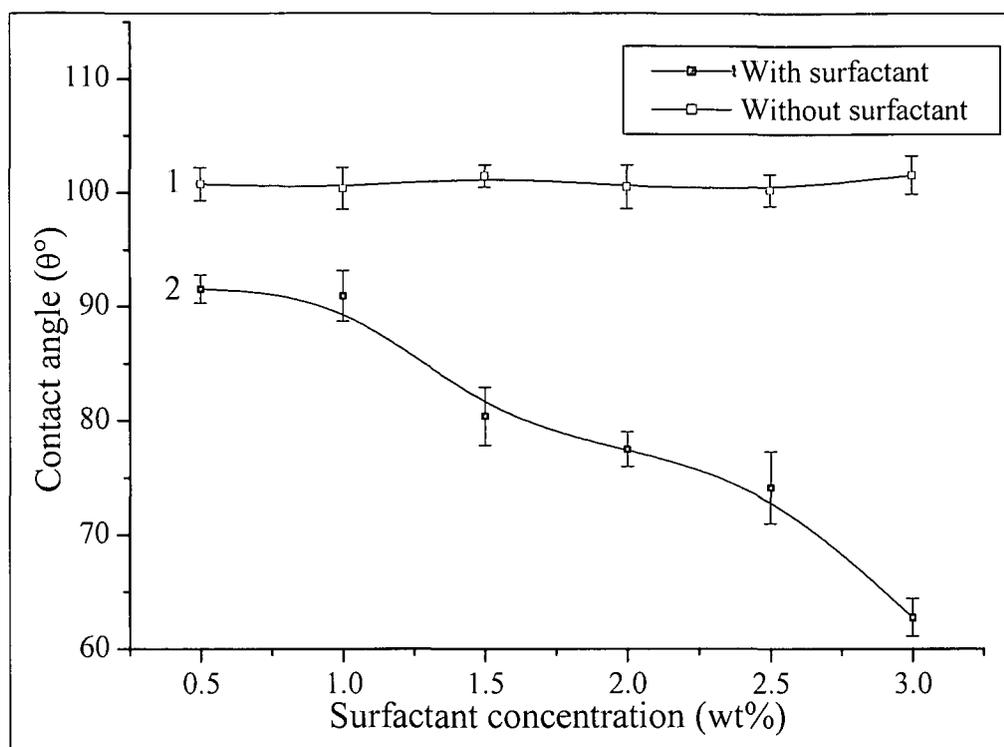


Figure 4.24: Static contact angle to water of VeoVa-9/BA (50/50 mol%) films at 20°C and about 55% humidity as a function of surfactant concentration (wt%).

Figure 4.24 shows the effect of both the presence of surfactant and its concentration on the static contact angle. In the case of the films that were surfactant free (curve 1) the value of the static contact angle remained constant at about $101 \pm 1^\circ$, while in the other case (curve 2) the presence of surfactant molecules in the films reduced the contact angle to about 90° when only 0.5 wt% of surfactant was used. The decrease in the static contact angle values with an increase in the surfactant concentration could be explained by the fact that the surfactant molecules prefer being at the solid/air interface, with their hydrophobic tails pointing towards the air and their polar heads towards the bulk⁵⁷. When the surface is in contact with water the surfactant molecules will orientate such that their hydrophobic tails orientate inside the films and the polar groups towards the film surface (polymer/water interface). Furthermore it was also found that the surfactant molecules migrate from the polymer films to the water phase⁵⁸. This migration and orientation of the polar group at the water/surface interfaces increases the surface tension of the surface and hence decreases the static contact angle.

In conclusion, the DMA analysis shows that only one T_g was detected, indicating to the resolution accuracy of the method the absence of homopolymers in the copolymer samples. However, only at higher VeoVa-9 concentrations (>70 mol%), the copolymer sample was found to consist of two fractions since the copolymer showed two transitions at -21 and

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+60°C. From the contact angle hysteresis results, the copolymer hydrophobicity increased as the VeoVa-9 concentration increases, and the presence of surfactant in the copolymer films enhance the wetting ability of the films.

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Chapter 5

Conclusions and recommendations

5.1. Conclusions

In this study the free-radical and miniemulsion copolymerization of VeoVa-9 with BA was investigated. The Mortimer and Tidwell approach provides a nonlinear least square method that was used in this study to determine the reactivity ratios for the VeoVa-9 and BA in the free-radical copolymerization. The 95% confidence limit was used to give accurate values for the reactivity ratios of each monomer. The reactivity ratios were estimated to be 6.95 (-0.53/+0.65) and 0.042 (± 0.014) for the BA and VeoVa-9 respectively. The rate of the copolymerization reaction in benzene at 80°C increases with an increase in BA concentration in the feed. The kinetics of the copolymerization of VeoVa-9/BA was investigated by measuring the decrease in monomer concentrations using the *in-situ* NMR approach. Results showed that about one VeoVa-9 unit was inserted every three BA units at 80°C and 50/50 mol% monomers concentration.

The miniemulsion copolymerization of VeoVa-9/BA was investigated in terms of the effect of surfactant and VeoVa-9 concentrations on the rate of polymerization and particle size. In terms of surfactant concentration, the copolymerization rate of the miniemulsion reaction increased as the surfactant concentration increased, while the particle size decreased as the surfactant concentration increased. The copolymerization rate also increased as the VeoVa-9 concentration decreased when oil- and water-soluble initiators were used. The decrease in the rate of the miniemulsion polymerization also affected the particle size; it increased as the VeoVa-9 concentration increased, in both cases (water- and oil-soluble initiators). Results showed that the amount of the hydrophobic VeoVa-9 affected the nucleation time of the polymerization when the water soluble initiator was used.

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The product copolymers from the miniemulsion reactions were characterized in terms of their chemical composition by using 2-D chromatography. A combination of liquid chromatography at the critical point of adsorption and size exclusion chromatography was used. Using the critical conditions of PBA for the copolymer prepared using batch miniemulsion, this analysis shows that the copolymer composition depended on the process by which the copolymers were prepared (batch or semi-batch). In the case of batch miniemulsion, 2-D chromatography showed that all of the BA monomer was incorporated into the copolymer, since there was no PBA homopolymer present in the copolymer. However, in the case of semi-batch miniemulsion polymerization, the copolymer composition depended on the addition mode of the BA. When the BA monomer was added about 20 minutes after the initiator, three peaks were observed in the contour plot. These peaks were assigned, according to hydrophobicity, to the VeoVa-9 homopolymer, VeoVa-9/BA copolymer and BA-rich copolymer. The presence of these fractions is due to the addition mode of the BA to the reaction mixture. The VeoVa-9 homopolymer was formed in the absence of BA in the first 20 minutes, as the BA was added to the reaction after the copolymer started to form. The presence of the BA-rich copolymer fraction was due to either the consumption of the VeoVa-9 prior to the reaction end, or due to micellar or/and homogeneous nucleation mechanisms, which are more feasible. Due to these results, and in attempting to obtain a better monomer distribution along the polymer chains, the addition of BA was started as soon as the initiator solution was added for all future systems.

The copolymers were also characterized in terms of their thermal properties and surface properties using DMA and contact angle measurements respectively. DMA results showed that the T_g of the copolymers increased as the VeoVa-9 concentration increased in both cases (batch and semi-batch), and only one T_g was observed for most copolymers. However, only at higher VeoVa-9 concentration (>70 mol%) in the batch process, two T_g values were observed. One of the obtained T_g values was far higher than the PBA's T_g , which indicates the formation of copolymer. The other T_g was close to that of the VeoVa-9 homopolymer which indicates the presence of VeoVa-9-rich copolymer or even VeoVa-9 homopolymer. The contact angle measurements showed that the contact angle values were $>90^\circ$, indicating poor wetting ability at all of the VeoVa-9 concentrations (10 to 100 mol%). The wetting ability of the copolymers was also investigated using the contact angle hysteresis; the wetting ability

Chapter 5: Conclusion and recommendations

decreased as the VeoVa-9 concentration increased. Contact angle measurements also showed the effects of the surfactant on the wetting ability of the copolymer; it increased as the surfactant concentration increased.

Generally highly hydrophobic copolymers were successfully synthesized using a miniemulsion system. This study showed that the hydrophobicity of the monomer can play an important role regarding the rate of the polymerization and latex particle size. The polymer hydrophobicity was also improved by introducing highly hydrophobic monomers.

5.2. Recommendations and future work

Due to the little information about the VeoVa type of monomers available in the literature, the copolymerization of the other type of VeoVa (VeoVa-10 and VeoVa-11) with other monomer such as acrylates, methacrylates and styrene could be investigated.

Investigate the presence of free surfactant molecules or/and micelles when the semi-batch miniemulsion is used.

Investigate the miniemulsion kinetics using different initiators with different water solubility.

Investigate the effect the VeoVa based copolymers on the permeation behaviour of liquids and vapours through these copolymers' films.

Due to the increasing interest in polymer-clay nanocomposites, the introduction of clay into the miniemulsion could be investigated, which could provide polymer-clay latexes.

Investigate the possibility of the grafting cellulose/VeoVa/BA copolymers using reversible addition fragmentation transfer (RAFT) technology