STUDIES ON PARTICLE FORMING POLYCONDENSATION AND RING OPENING POLYMERIZATION PROCESSES

Thesis submitted to the

UNIVERSITY OF PUNE
for the degree of
DOCTOR OF PHILOSOPHY

in

CHEMISTRY

by

L S RAMANATHAN

Division of Polymer Chemistry
National Chemical Laboratory
PUNE : 411 008
INDIA

APRIL 2000

DECLARATION

Certified that the work incorporated in this thesis entitled **"Studies on particle forming polycondensation and ring opening polymerization processes"** submitted by **L S Ramanathan** was carried out under my supervision. Such material as obtained from other sources has been duly acknowledged in this thesis.

April 2000 **Dr. S. Sivaram**
Pune (Research Guide)

ACKNOWLEDGEMENTS

First and foremost I would like to record my deep sense of gratitude to my research supervisor Dr S Sivaram. He supported and guided me offering extremely valuable research inputs throughout the course of this work. He taught me the *mantra* "learning is a never-ending process and beyond anything hard work and dedication lead to success". I am forever indebted to him.

I would like to thank Council of Scientific and Industrial Research, New Delhi for the award of the research fellowship and Director, NCL for allowing me to carry out this investigation in this prestigious research laboratory

I thank Dr P G Shukla and Dr C Bhaskar for their valuable discussions and kind cooperation in the lab. I express my sincere thanks to Dr D Baskaran, who taught me to manipulate the very tough polymerization chemistry, the anionic polymerization method.

I would like to acknowledge the members of 'macroforum' for their constructive criticism and valuable suggestions whenever I presented my research work.

I take this opportunity to thank the members of Polymer Chemistry Division, NCL for their cooperation and friendship. A special appreciation to my friends in NCL with whom I interacted during the course of my research work. I thank the members of central NMR facility, elemental analysis, SIL, SMIS, RPBD, glass blowing, stores, workshop and administrative groups for their technical support.

I thank Dr. Pradip and Dr. Manjunath of TRDDC, Pune for helping me in particle size analysis.

I am forever grateful to my beloved parents, brothers and sisters for their love, support, and patience beyond limits. Without their endurance this thesis would have been a mere dream.

I must thank my fiancée, Jaiya for her constant encouragement through email. This gave me a great impetus to finish the thesis very quickly and successfully.

(L S Ramanathan)

Contents

Chapter 1: Introduction

Chapter 2: Scopes and objectives of the present work

Chapter 3: Synthesis and characterization of steric stabilizers

Chapter 4: Preparation of polyurethane particles by dispersion and suspension polymerization

Chapter 5: Ring opening dispersion polymerization of cyclic amides

Chapter 6: Applications of particle forming polymerization process

STUDIES ON PARTICLE FORMING POLYCONDENSATION AND RING OPENING POLYMERIZATION PROCESSES

Abstract

A thesis submitted by L S Ramanathan

The present thesis examines the many facets of particle forming polymerization techniques in non aqueous medium for the preparation of poly(urethane) and poly(amide) particles. The size of the particles obtained is in the range between 0.2 and 2 μ with narrow particle size distribution. The key to this successful particle forming polymerization is the use of a novel polymerizable steric stabilizer.

The particle forming polymerization of a diol and diisocyanate was carried out in the presence of a macrodiol stabilizer, namely, poly(alkyl methacrylate) having two primary hydroxyl groups at one end of the chain. The macrodiol takes part in the polymerization process and stabilizes the polymer particles effectively. The efficacy of these stabilizers are compared with an amphiphilic block copolymer stabilizer, namely, poly(1,4-isoprene-*b*-ethylene oxide).

The effective incorporation of the macrodiol stabilizer during particle formation relies on the reactivity of the functional group attached to it and as well as the mol ratio of the isocyanate/hydroxyl ratio. The molecular weight of the macrodiol stabilizer and its concentration are critical factors for controlling polyurethane particle size and its dispersity. An increase in molecular weight of the macrodiol stabilizer produces smaller particles with narrower particle size distribution. A similar behavior was observed with the block copolymer stabilizer.

The amount of macrodiol stabilizer grafted onto the polymer particles was estimated and found to be nearly quantitative. On the other hand, the block copolymer stabilizer stabilizes the polymer particles by physical adsorption. The mechanism of polyurethane particle formation and subsequent stabilization clearly proves the efficacy of the

macrodiol stabilizer for the dispersion polymerization of polyurethane. This is because the stabilizing component is covalently linked to the particles during particle formation. On the other hand, the block copolymer stabilizer stabilizes the particle after the formation of primary particles by adsorption mechanism. Furthermore, the inevitable desorption of block copolymer from the particle surface leads to certain degree of particle aggregation.

The polyurethane particle forming reaction carried out in various dispersion medium reveals that the nature of dispersion medium influences the particle size, its distribution and molecular weight of the polyurethane particles. The correct choice of polarity of the dispersion medium alone is not sufficient to produce monodisperse polyurethane particles. The polymerization also depends on the chain conformation of the stabilizer in the dispersion medium employed.

The kinetics of polyurethane particle formation by both dispersion and suspension polymerization was investigated and the results were compared with precipitation and solution polymerization. The rates of solution and dispersion polymerization were similar upto 70% conversion. Thereafter the rate of solution polymerization was higher. This observation is explained based on the mechanism of polyurethane particle formation. The kinetics of dispersion polymerization in various dispersion medium was studied and found to be diffusion controlled.

Dispersion and suspension polymerization of various diols and diisocyanates were carried out using polymerizable and polymeric steric stabilizers. When higher molecular weight diols were used (e.g PEG 1000, PPG 1000), the block copolymer stabilizes the polyurethane particles effectively when compared to the macrodiol stabilizer.

The particle forming polymerization was also extended to the ring opening polymerization of cyclic amides to produce poly(amide) particles. A polymerizable stabilizer with cyclic amide terminal group and an amphiphilic block copolymer were explored as a steric stabilizer. It was found that the stabilizer molecular weight and its concentration substantially affects the poly(amide) particle formation. The amphiphilic block copolymer stabilizes the polymer particles more effectively compared to the polymerizable stabilizer. In the case of amphiphilic block copolymer, the hydrophilic poly(ethylene oxide) segment efficiently anchors onto the polar poly(amide) particles. This prevents the aggregation of the primary particles and, therefore, produces smaller particles with narrow particle size distribution. Conversely, the polymerizable stabilizer, namely, is N-acyl lactam, can, in principle, activate the anionic polymerization of ε-caprolactam. In such case, each growing particle will have a stabilizer fragment and therefore the particles are stabilized effectively. However, this was not observed in the present study. Nylon 12 and copolymers of nylon 6/12 were also prepared in particulate form using the polymerizable steric stabilizer. In both the cases, the polyamide particles are stabilized by physical adsorption rather than by grafting.

The potential applications of polyurethane particle formation were also investigated. Dispersion polymerization of diol and diisocyanate in the presence of carbon black produces carbon black filled spherical polyurethane particles. The conductivities of carbon black filled polyurethane particles were much lower than the physical mixtures. Further, a highly dispersed polyurethane-clay nanocomposite was prepared using this technique. The clay layers were intercalated with a suitable quaternary ammonium salt. Dispersion polymerization was carried within the expanded gallery of the intercalated clay. Polymerization proceeds with the exfoliation of the clay. These polyurethane-clay nanocomposites exhibits good thermal properties compared to pristine polyurethane as well as macrocomposites.

GLOSSARY

AIBN	α,α'-azoisobutyronitrile
CL	ε-Caprolactam
Cs	Chain transfer constant
DABCO	Diamino bicyclo [2,2,2] octane
DBTDL	Dibutyl tin dilaurate
DCC	N,N'-dicyclohexylcarbodiimide
DMAP	4-dimethylaminopyridine
$\overline{D}_n$	Number average particle size
DSC	Differential scanning calorimetry
$\overline{D}_w$	Weight average particle size
EHG	2-ethyl-1,3-hexane diol
EO	Ethylene oxide
GPC	Gel permeation chromotography
HMDI	Hexamethylene diisocyanate
IPDI	Isophorone diisocyanate
LL	Lauryl lactam
LMA	Lauryl methacrylate
MAA	Mercapto acetic acid
MMA	methyl methacrylate
$\overline{M}_n$	Number average molecular weight
$\overline{M}_w$	Weight average molecular weight
NMR	Nuclear magnetic resonance
PEG	Poly(ethylene glycol)

PEO	Poly(ethylene oxide)
PI	Poly(isoprene)
PLMA	Poly(lauryl methacrylate)
PMMA	Poly(methyl methacrylate)
PPG	Poly(propylene glycol)
SEM	Scanning electron microscope
TDI	Toluene diisocyanate
T_g	Glass transition temperature
T_m	Melting temperature
TMP	Trimethylolpropane
VPO	Vapor pressure osmometry
XRD	x-ray difraction
δ	Solubility parameter
ρ	Resistivity
σ	Conductivity
$\bar{f}_n$	Average functionality
η_{inh}	Inherent viscosity

List of Tables

Table Page

List of Figures

Figure Page

Chapter 1 Introduction

1.1 Particle forming polymerization processes

Preparation of polymer particles/dispersions possessing uniform particle size and shape, has gained considerable commercial/scientific interest in recent years. This has been largely motivated by many versatile applications of these materials as ion-exchangers, calibration standards, surface coatings, pharmaceutical reagents, biomaterials, medical diagnostics, parenteral drug delivery systems, toners for photocopying and digital printing, supports for solid phase synthesis and chromatographic media for separations.

Particle forming polymerization process can be classified into dispersion, suspension and emulsion polymerization. They are clearly distinguished on the basis of initial state of polymerization medium, polymerization kinetics, mechanism of particle formation and the size of polymer particles formed.

1.1.1 Dispersion polymerization

In this process, the monomer, initiator and the stabilizer are soluble in the polymerization medium and the polymerization is initiated in homogeneous solution. Once the critical chain length is achieved the growing polymer precipitates and causes phase separation. This leads to the formation of primary particles. The stabilizer present in the medium is adsorbed on the particle and prevents their aggregation. The stabilized particles are significantly swollen by monomer and become the main loci of polymerization. However, the locus of polymerization is controlled by factors such as dispersion medium and ratio of monomer to dispersion medium. The size of the polymer particles obtained is usually with in the range of 0.2 to 2 μ. The underlying theoretical principles of the dispersion polymerization process as well as detailed description of this technique have been well documented[1].

1.1.2 Suspension polymerization

In this technique monomer is suspended in the continuous phase, usually, water as small droplets by using suitable stabilizers such as, poly(vinyl alcohol). In this process, the initiator is soluble in the monomer and the polymerization occurs in the monomer droplets[2]. These monomer droplets are directly converted to polymer particles with negligible change in the particle diameter. The uniformity of the monomer droplets and that of final polymer particles are largely governed by nature of stabilizers, agitation rate and monomer to continuous phase ratio. The particle diameter of the polymer particles ranges between 50 and 100 μ.

1.1.3 Emulsion polymerization

Here the monomer is insoluble in the polymerization medium but is emulsified using a surfactant. Unlike suspension polymerization, the initiators are soluble in the polymerization medium and insoluble in the monomer. The formation of polymer particle proceeds by the two simultaneous processes, namely, micellar nucleation and homogeneous nucleation[3]. The relative extents of these processes vary with the solubility of the monomer in the polymerization medium and surfactant concentration. The final particle diameter is in the range between 0.1 and 0.4 μ.

Among particle forming polymerization techniques, dispersion polymerization has been found to be the most efficient method for producing monodisperse polymer particles with sizes ranging from sub micron to several microns in diameter. The preparation of monodisperse polymer particles has been studied using other techniques such as seeded polymerization[4] and emulsifier free emulsion polymerization[5]. A methodological survey on dispersion, suspension and emulsion polymerization has also been reported[2].

1.2 Stabilization of polymer particles in non aqueous media

The need for polymer dispersions with controlled particle size in organic media has been largely motivated by the requirement of the surface coatings industry. The polymer dispersions prepared in a liquid medium need to be stabilized in order to avoid aggregation of the polymer particles. When the medium is water, the stabilization of the polymer particles is achieved by electrostatic stabilization. However, when colloidal dispersions are prepared in organic media, electrostatic stabilization no longer operates This will be further discussed in the following section.

1.2.1 Inadequacy of electrostatic stabilization in non aqueous media

In case of electrostatic stabilization, the polymer particles are stabilized by the generation of a repulsive force of sufficient magnitude to overcome the inherent attraction between the particles when they approach each other. This quantitative theory for the stabilization of charged polymer particles was developed by the independent efforts of Deryaguin and Landau as well as Vervey and Overbeek. However, this type of repulsive electrostatic forces generated in the aqueous medium are not generally available for stabilizing particles in organic media of low polarity such as aliphatic hydrocarbons. In such cases, the oligomeric/polymeric stabilizers present in the dispersion medium contribute to the stability of the colloidal particles. During particle formation, the dissolved polymeric chains of the stabilizer is attached to the growing particles, either, physically or chemically. When the particle approaches each other with a layer of stabilizer, repulsive forces are generated by the interaction of opposing dissolved polymer chains. This force keeps the polymer particles away from each other. This process is called polymeric stabilization.

1.2.2 Polymeric stabilization

The process of polymeric stabilization is further classified into two types. They are steric stabilization and depletion stabilization.

1.2.2.1 Steric stabilization

Steric stabilization of colloidal particles is imparted by macromolecules that are attached either by physical adsorption or by grafting to the surfaces of the particles. Whatever the mechanism of attachment, the nominally insoluble polymer servers to anchor the soluble moieties to the colloidal particles. Such polymer is accordingly referred as the anchor polymer. The role of soluble polymer is to impart steric stabilization and, for this reason, such chains are termed the stabilizing moieties. It is also possible to eliminate the need of anchor moiety if the stabilizing moieties can be covalently attached to the surface of the colloid. The mechanism of steric stabilization can be envisaged as follows. (Figure 1.1)

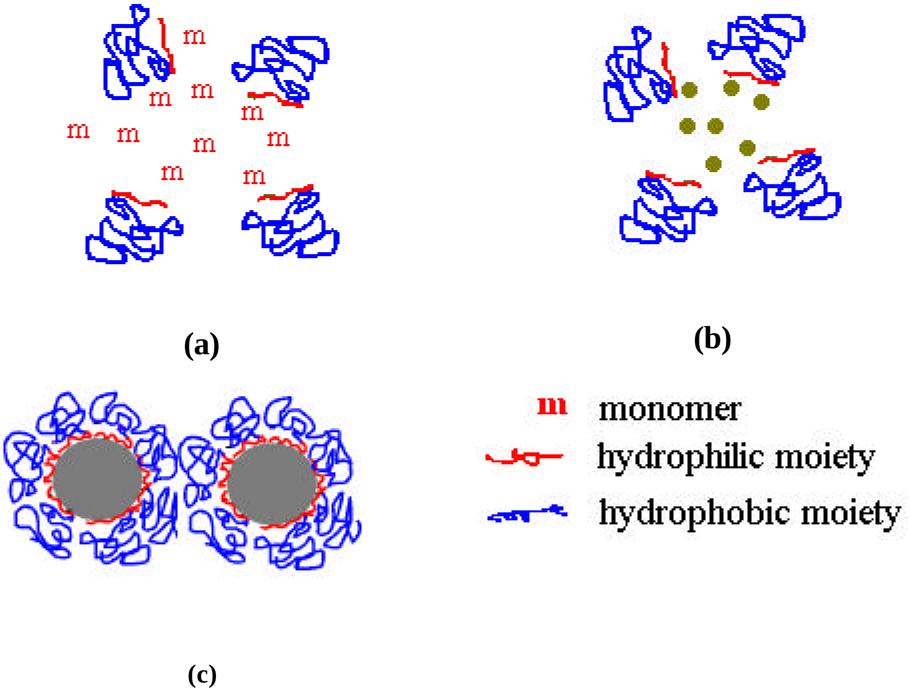


Figure 1.1. Mechanism of steric stabilization (a)Initially homogeneous polymerization medium; (b) Nucleation stage and (c) Stabilization of polymeric particles by the added stabilizer

When two particles which have stabilizer molecule attached to their surfaces approach one another the stabilizing moiety must be mutually repulsive if the polymer is to impart stability. In these circumstances, the Brownian collision stresses the stabilizing molecule, which endeavor to escape from the stress zone, either by desorption or by lateral movement over the particle surface. Effective anchoring prevents desorption of the stabilizing chains. Complete surface coverage of particles with the stabilizer prevents the lateral movement of the chains by repulsion from its neighbors. Amphiphilic block or graft copolymer with suitably disposed hydrophilic and hydrophobic moieties are found to be the most efficient steric stabilizers.

1.2.2.2 Depletion stabilization

This differs from steric stabilization in that stability is imparted not by attached polymer but rather by macromolecules that are free in solution. The effect of free polymer in colloidal stability has been studied and reviewed by Napper[6].

1.2.2.3 Combinations of stabilization methods

It is possible to have combinations of electrostatic and steric stabilization termed as electrosteric stabilization. The elecrostatic component may originate from a net charge on the particle surface and/or charges associated with the polymer attached to the surface. This phenomena is common in biological systems. In addition to electrosteric stabilization, it is possible to have combinations of depletion stabilization with both steric and/or electro steric stabilization. The combination depletion and steric stabilization is quite common at high concentrations of free polymer in the dispersion medium.

1.3 Overview of dispersion polymerization

Particle forming polymerization has been explored for variety of monomers via different modes of polymerization. Much of the available literature is devoted to radical dispersion polymerization. Little is known in the literature on ionic and condensation mode of dispersion polymerization. The available literature on dispersion polymerization is summarized in the following sections.

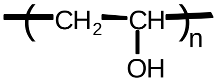
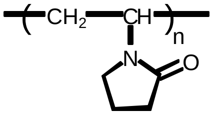
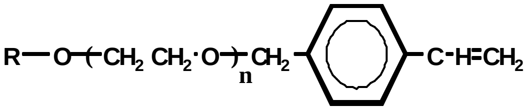
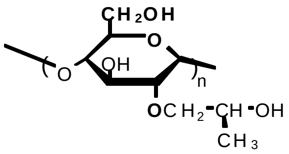
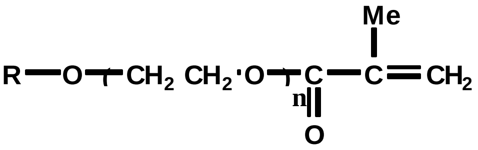
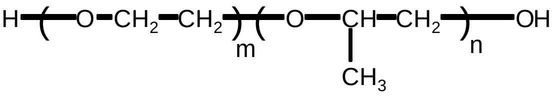
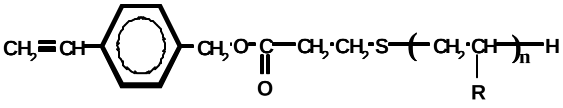
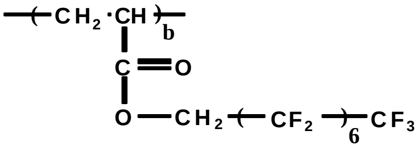
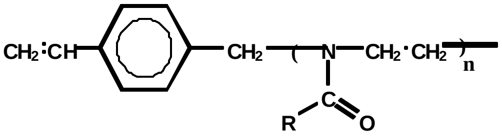
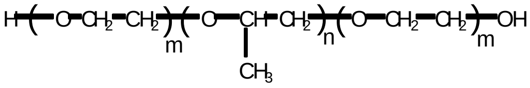
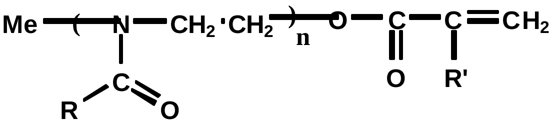
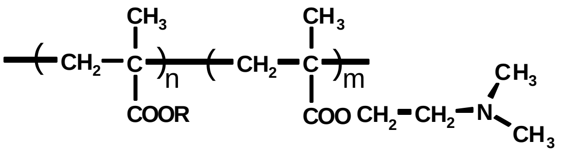
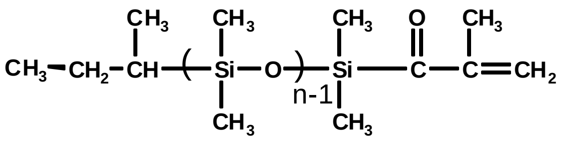
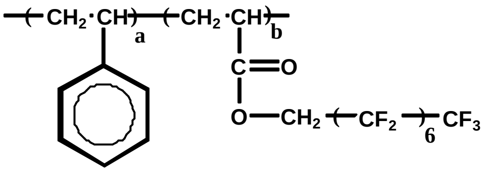
1.3.1 Radical dispersion polymerization.

Preparation of polymer particles with controlled size and shape has been extensively studied by radical dispersion polymerization in both aqueous and non aqueous media. Generally, the polymerization is carried out either by a single stage process or by two-stage feed process. The single stage process is, however, not suitable for accurate control of particle size. This is because the monomers are generally a good solvent for the polymer being formed. This increases the overall solvency of the polymerization medium and alters the conditions for precipitation. In addition, the effectiveness of the added stabilizer is reduced by the increased solubility of the anchoring component as result of increased solvency. These two factors lead to the formation of polydisperse particles. In the feed process, the monomer concentration can be maintained so that the overall solvency of the dispersion medium remains constant and the added stabilizer remains fully effective. The addition of feed monomer should be controlled. Otherwise, the solvency of the dispersion medium or the concentration of the added particle stabilizer alters the particle growth stage by further nucleation of new polymer particles.

1.3.2 Nature of steric stabilizers employed in radical dispersion polymerization.

Steric stabilizers can be classified into two major classes, namely, polymeric and polymerizable stabilizers. The most commonly used steric stabilizers in the radical dispersion polymerization are listed in Table 1.1

Table 1.1: Representative steric stabilizers used in radical dispersion polymerization

POLYMERIC TYPE	POLYMERIZABLE TYPE
 **(1)**  **(2)**	 **(9)**
 **(3)**	 **(10)**
 **(4)**	 **(11)**
 **(5)**	 **(12)**
 **(6)**	 **(13)**
 **(7)**	 **(14)**
 **(8)**	

1.3.2.1 Polymeric stabilizers

Homopolymers or random copolymers, amphiphilic block and graft copolymers are classified under polymeric steric stabilizers. They stabilize the polymer particles by physical adsorption. However, in some cases, grafting of polymeric stabilizers onto the growing particles have also been reported.

1.3.2.1.1 Homopolymers or random copolymers

Homopolymers, namely, poly(vinylpyrollidone), poly(vinylalcohol), and hydroxy propyl cellulose have been studied extensively in the dispersion polymerization of styrene in polar media. The use of additional surfactants along with steric stabilizer is reported in the literature[7-9]. Almong and Levy[7,8] reported the preparation of polystyrene particles using poly(vinyl alcohol) as steric stabilizer and sodium dodecyl sulfonate (SDS) as a cosurfactant. The effect of initiators and stabilizer concentration has been investigated. It has been shown that during dispersion polymerization of styrene, a considerable amount of emulsion polymerization also takes place which leads to submicron particles and high molecular weights. These particles have an adverse effect on the characteristics of the polymeric powder. To eliminate this problem, Almong and Levy[8] suggested the incorporation of electrostatic stabilizer, preferably, SDS. As an extension of this work Vanderhoff and coworkers[9] used an anionic, nonionic or comonomeric costabilizer along with poly(vinyl pyrollidone). They showed that the inclusion of costabilizer resulted in a stable dispersion with narrow particle size distribution. Further, it was demonstrated that a dispersion with a bimodal particle size distribution was obtained without a costabilizer. In apparent contradiction to this work, Paine and MacNulty[10] found that the costabilizers used by Vanderhoff and coworkers[9] namely, Aerosol OT(anionic surfactant) Triton N-57, cetyl alcohol have no effect on the particle size distribution and molecular weight of the particles formed. More recent work carried out on the dispersion polymerization of styrene in polar media also reveal that costabilizer has no effect on the particle size distribution.[11]

Pioneering work were carried out on the preparation of monodisperse polystyrene particles using hydroxy propyl cellulose[12,13] in polar media, without any additional surfactants. The relationship between molecular weight, particle size and size distribution has been investigated. It was suggested that particle size control is a function of several thermodynamic and kinetic factors. These include, monomer-polymer solubility, reactant composition, temperature and solvent medium. Temperature governs both thermodynamic factors (that is, solubility) as well as kinetics of initiator decomposition which in turn determines the rate of polymerization and particle nucleation. It was shown that the particle diameter increases with a decrease in the initial concentration of the monomer. In the dispersion polymerization of styrene using hydroxy propyl cellulose as stabilizer, it was proved that grafted hydroxy propyl cellulose-polystyrene acts as the true stabilizer[13]. Therefore, the molecular weight of hydroxy propyl cellulose has a definite influence on the polarity and the stabilizing ability of hydroxy propyl cellulose graft polystyrene. A simple mechanistic model was developed to predict the particle size of the microspheres[14]. It was shown that partially hydrolyzed poly(vinyl alcohol) (35 mol %) acts as an effective stabilizer in the dispersion polymerization of styrene in alcoholic media[15]. Also, copolymer dispersions of styrene and n-butyl methacrylate in aqueous alcohol medium with poly(vinyl alcohol) as the single steric stabilizer, has been reported[16,17]. Factors, such as, concentration of initiator and stabilizer, polarity of the medium on the size and mono dispersity of the polymeric particles were investigated. It was concluded that higher concentration of initiator produces larger particles with significant size distribution, whereas, the reverse is true for higher stabilizer concentration. Also, increase in polarity of the medium produces highly monodisperse polymer particles with smaller size. This is because the nucleation rate is much faster in polar media and if the added stabilizer is sufficient enough to stabilize the primary particles, then larger number of smaller particles are formed with narrow particle size distribution.

It has been shown recently[18] that the use of a mixture of steric stabilizers, namely, poly(acrylic acid) and hydroxy propyl cellulose in the dispersion polymerization of styrene and n-butyl methacrylate in aqueous methanol medium produces micrometer size monodisperse particles. It was suggested that the relative ratio of the steric stabilizer control the surface charge of the copolymer particles. Polystyrene derivatised microspheres were prepared[19,20] and the effect of various parameters viz, monomer and surfactant concentration, solvents etc., on the particle diameter and size distribution were elucidated. Possible ways to modify the surface of the poly(chloromethylstyrene) with amine, hydroxyl and carboxylate group have been discussed[20]. Microspheres of polymethyl a-(hydroxymethyl) acrylate have been synthesized in aqueous medium using poly(vinyl alcohol) as stabilizer[21]. It was observed that significantly broader size distribution was obtained when poly(vinyl alcohol) was replaced by sodium lauryl sulfate as surfactant. It has been shown from kinetic studies using ^{1}H NMR that the polymerization reaction is first order in monomer concentration.

1.3.2.1.2 Block copolymers

Block copolymers used in dispersion polymerization usually comprise of covalently bonded hydrophilic and hydrophobic segments or blocks. The effectiveness of these amphiphilic copolymers as steric stabilizers in dispersion polymerization, both in aqueous and non aqueous medium, has given a great impetus to the development of new classes of block copolymers. The precise control of these block copolymer structures in terms of molecular weight and balance between hydrophilic and hydrophobic segment is of paramount importance in dispersion polymerization. Amphiphilic copolymers with well-defined block characters are best synthesized using controlled and/or living polymerization methods. Various classes of block copolymers employed as steric stabilizers are listed in Table 1.2. The block copolymers, which are used for living radical dispersion polymerization and ionically initiated dispersion polymerization, are discussed separately.

Table 1.2: List of block copolymer steric stabilizer employed in radical dispersion polymerization

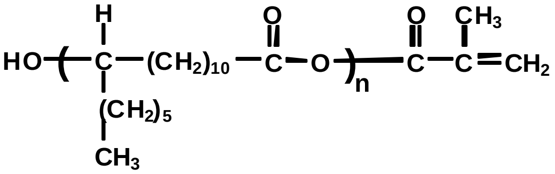
Block copolymer	Monomer	Dispersion medium	Notes	Reference #
Poly(styrene-b-dimethyl siloxane)	Styrene	n-heptane	Dispersions with narrower particle size distributions were prepared by seeded polymerization	22

Block copolymer	**Monomer**	**Dispersion medium**	**Notes**	**Reference #**
Poly(styrene-b-ethylene oxide)	Styrene	ethanol and methanol	The effect of solvent on the propagation rate coefficient for styrene and methyl methacrylate was examined using pulsed laser polymerization.	[23]
(7)	Styrene	alc. media MeOH to 1-octanol	Near-monodisperse micrometer-sized polystyrene particles were produced	[24]
Poly(styrene-b-ethylene oxide)	Styrene	MeOH	The effects of stabilizer mol. wt., stabilizer/anchor ratio, and stabilizer concentration on particle diameter and polydispersity were examined.	[25]
polystyrene-block-poly(ethylene-*co*-propylene)	MMA/ vinyl acetate	n-alkanes	Thickness of the stabilizing surface layer was calculated	[26]
Poly(styrene-*b*-dimethyl siloxane)	MMA	n- alkanes	Area coverage per poly(dimethylsiloxane) chain was estimated	[27]
Poly (styrene-*b*-FOA) **(8)**	Styrene	supercritical carbon dioxide	Discussed the importance of effective surfactants	[28]
siloxane-based block copolymer	Styrene	supercritical carbon dioxide	A kinetics of study of the polymerization showed that both the mol. wt. and the conversion increase as a function of time.	[29]
Poly(isoprene-*b*-styrene-*b*-isoprene)	MMA	heptane	The rate of dispersion polymerization increased with concentration. of the polymer dispersant.	[30]

Block copolymer	**Monomer**	**Dispersion medium**	**Notes**	**Reference #**
poly(styrene-b-MMA).	MMA	cyclohexane	The particles retained stability when the dispersion medium was a theta system for the polystyrene chains	[31]
Polystyrene-block-poly(ethylene-*co*-propylene)	MMA	decane	Light-scattering characterization of spherical particles	[32]
Polystyrene-block-poly(ethylene-*co*-propylene)	MMA	decane	The kinetics of polymerization seems to be only little affected by the colloidal character of the system	[33]
Poly(Ethylene-*co*-Propylene)	MMA	Decane and Diisopropyl ether	Characterized equilibrium and Non-equilibrium copolymer micelles	[34]
Polystyrene-block-poly(ethylene-*co*-propylene)	MMA	Non aqueous	Determination of sizes of spherical particles by analysis of the particle scattering.	[35]
Poly(styrene)-block-poly(ethene-*alt*-propene)	MMA	Non aqueous	Thermal and microwave-induced free-radical non aqueous dispersion polymerization. of MMA	[36]
Amphiphilic block and graft polyurethane acrylates	MMA	nonane	Adsorption of stabilizers on the PMMA surface from nonane was studied.	[37]
Fluorinated and siloxane-based stabilizers	Vinyl acetate (VA) and ethylene/VA	Super critical CO_2	The fluorinated stabilizers gave rise to smaller particles when compared to the siloxane-based stabilizers.	[38]

1.3.2.1.3 Graft copolymers

Macromonomers can be prereacted to form graft copolymers which are subsequently introduced in the dispersion polymerization reaction, or they can be allowed to react *insitu* to form graft copolymers.

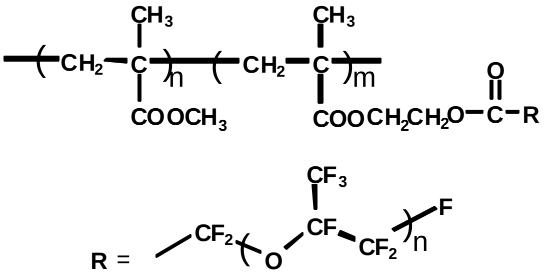


$$HO\left(\underset{\underset{CH_3}{|}}{\underset{(CH_2)_5}{\underset{|}{\overset{\overset{H}{|}}{C}}}}-(CH_2)_{10}-\overset{\overset{O}{\|}}{C}-O\right)_n-\overset{\overset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{C}=CH_2$$

(15)

A classical example is the use of a poly(12-hydroxy stearicacid) macromonomer **(15)** with a methacrylate end group[1]. This was polymerized with methyl methacrylate to produce a comb-graft copolymer. These graft copolymers effectively stabilize the polymer particles in non aqueous media. Amphiphilic graft copolymers have also been found to be effective stabilizers in aqueous dispersion polymerization. Micron size monodisperse PMMA have been prepared in methanol/water mixture using poly (2-ethyl-2-oxazoline) (PETOZO) and branched polyethylene imine (PEI)[39] as polymeric stabilizers. The particle size decreased when the concentration of the stabilizer was increased. The same phenomena have been observed in the dispersion polymerization of styrene in alcohol[40]. A narrow particle size distribution has been achieved at higher stabilizer concentration. It was observed that the diameter of the particles obtained by using the PEI stabilizer was smaller than that obtained by using the PETOZO stabilizer. This was explained as due to the combined steric and electrostatic stabilization of PEI. The later stabilization arises due to the partial ionization of amino groups of PEI in aqueous methanol solution.

A series of graft copolymers, poly(methyl methacrylate-*co*- hydroxyethyl methacrylate)-*g*-poly(perfluoropropylene oxide) **(16),** was synthesized for application as stabilizers in the dispersion polymerization of methyl methacrylate in supercritical carbon dioxide.



(16)

The backbone, poly(methyl methacrylate-*co*-hydroxyethyl methacrylate), is effectively insoluble in carbon dioxide and the grafted chains, poly(perfluoropropylene oxide), are completely miscible in carbon dioxide at moderate pressures. The effect of molecular architecture of the graft copolymer on polymerization rate and poly(methyl methacrylate) particle size was evaluated. A careful balance between anchor group size and the soluble component is necessary but not sufficient to achieve adequate stabilization. The distribution of the soluble component along the anchor group is also important. Furthermore, the backbone molecular weight was shown as the key factor for stabilization, provided that enough CO_2-philic component has been included to ensure solubility[41].

Many reports are available on the preparation of comb-shaped amphiphilic graft copolymers composed of hydrophobic backbones and hydrophilic side chains. Generally they are prepared by radical polymerization ofalkyl acrylates or styrene in the presence of poly (ethylene oxide) macromonomers **(9) (10)**[42-44]. These amphiphilic graft copolymers can in principle act as an effective steric stabilizer in the dispersion polymerization of acrylate and styrene monomers. However, dispersion polymerization has not been carried out so far using these amphiphilic graft copolymers.

1.3.2.2 Polymerizable Stabilizers.

Stabilization of polymer particles using polymerizable stabilizer is of relatively recent origin and offers a convenient route to prepare uniform polymer particles. These stabilizers have a functional group at their chain terminal and so they take part in the polymerization process. So they are often called as macromonomer or macromer.

Poly(ethylene oxide) macromonomer **(9)** **(10)** has been studied extensively in the dispersion polymerization of styrene, methyl methacrylate and other acrylate monomers in aqueous alcohol media[45-49]. The synthesis of 2-methyl-2-oxazoline macromonomer **(12)** which possess a polymerizable styryl group via ring opening polymerization, was reported by Saegusa *et al.*[50]. Dispersion copolymerization of styrene[40,51] using this macromonomer as stabilizer, in aqueous ethanol solution gives micron size polystyrene particles with narrow size distribution. Styryl type poly(2-alkyl-2-oxazoline) macromonomer **(12)** have been reported as an effective polymeric stabilizer for preparing monodisperse PMMA[52] and poly (N-vinylformamide)[53] particles in polar media. Siloxane- based macromonomer **(14)** is employed as a steric stabilizer in the dispersion polymerization of methyl methacrylate in supercritical CO_2[54]. The attachment of stabilizing component to the growing particles has also been accomplished using macro initiators[55] and polymeric chain transfer agents[56,57]. In all cases, the grafting of stabilizer moiety on the polymer particles have been demonstrated. The molecular architecture of the stabilizing moieties and the reactivity of the functional groups attached to them was found to influence the particle size and its distribution.

1.3.3 Living radical dispersion polymerization.

In recent years, several research groups have explored the possibility of using living radical polymerization technique for making monodisperse polymer particles. TEMPO mediated radical dispersion polymerization of styrene in n-decane[58] and aqueous alcohol media[59] using stabilizers poly(styrene-b-propylene-alt-ethylene) and poly(N-vinylpyrollidone) respectively have been reported. The polymer particles obtained by this method have spherical morphologies but their size distribution was very broad. More recently, dispersion polymerization of methyl methacrylate by Atom Transfer Radical Polymerization in super critical carbon dioxide using fluorinated surfactants has been demonstrated[60]. The authors were unable to isolate free flowing particles, although, the particles obtained were spherical. This was attributed to the inefficient stabilization of the low molecular weight stabilizers. The authors anticipate that higher molecular weight stabilizer would stabilize the growing particles effectively and produce free flowing polymer particles.

1.3.4 Dispersion polycondensation

Conventionally, condensation polymers are produced by solution, melt, or interfacial polymerization processes. The first recorded example of making condensation polymer particles was carried out by grinding solid resins in aliphatic hydrocarbons in the presence of dissolved rubber[61]. Much later, stable dispersions of condensation polymers are produced by the direct dispersion polymerization of soluble reactants in organic solvents in the presence of a polymeric stabilizer or stabilizer precursor[62,63]. In dispersion polycondensation process, generally, the polymer particles are obtained by two ways. In the first method the initially homogeneous reactants mixture in organic media is polymerized to completion in a single stage. The second, a feed process, utilizes initial seed stage, in which a polymer dispersion of low solids is formed by a single stage and then the polymerization is completed by the continuous addition of reactants to the seed particles. The process of dispersion polycondensation is analogous to radical dispersion process. Nevertheless, these methods are relatively less developed than vinyl polymerization techniques.

1.3.4.1 Poly(ester)s.

Most of the readily available monomers used for polyesterification reactions are insoluble in hydrocarbon solvents and, thus, limits the scope of particle forming dispersion polymerization technique. Generally, polyesters are obtained in particulate form by suspending the monomers in the dispersion medium using suitable stabilizers. This is, in principle, a suspension polymerization according to the classification of particle forming polymerization techniques. A few reports are available for the preparation of wholly aromatic polyester particles by dispersion polycondensation. Poly(4-oxybenzoate-co-2,6-oxynapthonate) was obtained in particulate form using a mixture of polymeric and hydrophobic inorganic particle stabilizer[64].

1.3.4-2 Poly(urethane)s.

Conventionally, polyurethane particles are prepared by cryogenic grinding of thermoplastic polyurethanes [65] or by suspension polymerization of isocyanate terminated prepolymers in aqueous or non-aqueous medium[66,67]. In none of these prior methods the control of particle size is possible. There is, however, only a solitary report on the particle forming polymerization of an isocyanate with a diol to produce polyurethane microspheres[68]. In this study, suspension polymerization of oligomeric glycols with diisocyanates or isocyanate terminated prepolymer was carried out in non aqueous medium. Poly(ethylene oxide-*b*-dimethylsiloxane) (2-10 wt%) was used as steric stabilizer. The particle size obtained was in the size ranges from 2 to 50 μ. The yield of free flowing polymer particle was around 65%.

1.3.4.3 Poly(siloxane)s

The controlled hydrolysis and condensation of alkyl trialkoxysilanes produces spherical silicone resin particles. It is interesting to note that spherical poly(siloxane) particles were prepared by both suspension and dispersion polymerization without the use of steric stabilizers[69]. However, the yield of the polymer was around 60 %. The authors used various types of anionic and non ionic surfactants and observed that there was no significant improvement in the yield. Furthermore, the particle size distribution was not narrow. A careful selection of steric stabilizer with suitable amphiphilic character might improve the efficiency of the particle forming process. Some of the commercial grades of such spherical particles and their applications have been described[70].

1.3.4.4 Phenolic Resins

Until early 90's, phenolic thermoset resin particles have been prepared by suspension polycondensation process using polysaccharide as particle stabilizers[71]. However, recently, the synthesis of polyphenol particles by dispersion polymerization has been demonstrated.[72,73] The polymerization of phenol was carried out enzymatically in a mixture of 1,4-dioxane and phosphate buffer. The polymeric particles formed are stabilized by the use of polymeric stabilizers such as poly(vinyl methyl ether) poly(ethylene glycol) and poly(vinyl alcohol). The control over particle size and its distribution using suitable steric stabilizer was demonstrated.

1.3.4.5 Conducting polymer particles

Conducting polymers are difficult to process because of their insolubility in common solvents. The preparation of colloidal dispersions of conducting polymer particles is one of the ways to obviate this problem. Colloidal forms of conducting polymers such as poly(acetylene), poly(aniline) and poly(pyrrole) have been reported to date. Colloidal poly(acetylene) particles has been synthesized in cyclohexane-THF mixture using poly(*tert*-butyl styrene-b-ethylene oxide) as steric stabilizer[74]. Dispersion polymerization of pyrrole has been carried out in aqueous as well as non aqueous medium using steric stabilizeres like poly(vinyl methyl ether)[75] ethylhydroxyethyl cellulose, poly(2-vinylpyridine-co-butyl methacrylate), poly(vinyl acetate)[76]. Similarly, poly(aniline) particles were prepared in aqueous and non aqueous media by oxidation of aniline using particle stabilizers such as poly(vinyl alcohol) and poly(vinyl pyrollidone)[77] and poly(vinyl pyridine)[78], poly(vinyl methyl ether)[79] and methyl cellulose[80]. In all the cases the particle size obtained was in the range from 300 nm to few microns. It is interesting to note that even though, the surface of these particles was covered by the stabilizer moieties, their conductivities were not affected.

1.3.5 Ionically initiated dispersion polymerization

Poly(ethylene) and poly(propylene) have been prepared as colloidal dispersion in aliphatic hydrocarbons using poly(ethylene-*alt-co*-propylene) and poly(1-octene) as steric stabilizers[81]. Although, the mode of stabilization was not studied in detail, it appears that the free polymer chains in the dispersion medium is responsible for stabilizing dispersed poly(alkene) particles. This mode of stabilization is referred as depletion stabilization[6]. Recently, copolymers of vinyl aromatic compounds and olefins have been synthesized by dispersion polymerization in the presence of metallocene catalyst systems[82]. The polymerization was carried out in pentane in the presence of styrene-diene di- or triblock polymer as particle stabilizer. In this case poly(styrene) segment is insoluble in pentane and effectively anchors the polymer particles at the on set of polymerization. The diene segment in the block copolymer stabilizer acts as stabilizing moiety and provides effective stabilization via steric stabilization mechanism.

Polymers in particulate form have been carried out by anionic initiation method. The method was first reported for styrenic monomers in hexane using n-butyl lithium as initiator[83]. Various types of rubbers namely, poly(butadiene), poly(butadiene-*co*-styrene) and poly(isoprene) were used to stabilize the polymer particles. Later, many research groups demonstrated the feasibility of particle forming anionic dispersion polymerization of styrenic monomers using various steric stabilizers. These include poly(vinyl alkyl ether)[84], poly(*tert*-butylstyrene-*b*-styrene), poly(styrene-*b*-dimethylsiloxane), poly(styrene-b-butadiene)[85] poly(*tert*-butyl styrene) as stabilizer precursor[86] and poly(styrene-*b*-4-trimethyl silyl styrene)[87].

The dispersion polymerization technique in organic media has also been demonstrated for a wide range of heterocyclic ring compounds using ionic modes of initiation. These include the polymerization of cyclic ethers, cyclic esters and cyclic amides. Ring opening polymerization of ε-caprolactone has been carried out in heptane with dibutyl zinc as catalyst in the presence of polymer dispersants such as poly(lauryl methacrylate) and poly(vinyl chloride -*co*- lauryl methacrylate) to produce spherical polymer particles[88]. A similar method was employed to prepare copolymer dispersions of ε-caprolatone with ethylene oxide and other cyclic ethers[89]. Recently, monodisperse spherical particle of poly(caprolactone) and poly(DL-lactides) were prepared by ring opening polymerization in heptane - dioxane solvent mixture in the presence of poly(dodecyl acrylate-*g*-caprolactone) as steric stabilizer[90]. Poly(amide)s have also been prepared in particulate form by ring opening dispersion polymerization of lactams using poly(olefin) as particle stabilizer[91]. Similarly many processes have been reported for preparing polyamide in particulate form using stabilizers such as alkali metal stearates[92], copolymer of N-methacryloyl caprolactam and methyl methacrylate[93] and silica.[94,95] Formation of highly uniform polyamide particles has been demonstrated by phase separation.[96] The phase separation is done by taking a 1 wt% solution in a theta solvent above the theta temperature and cooling it rapidly. The serious disadvantage of this method is the use of large amount of solvent. The formation of nylon 6 particles in spherical form by ring opening dispersion polymerization of caprolactam without any added particle stabilizer has been reported[97]. Here, ethyl benzene was used as dispersion medium. The authors, however, observed coalescence of the particles during solidification. This is clearly due to the absence of stabilizer and, therefore, it is essential to stabilize the polymer particles with added steric stabilizers.

1.3.6 Kinetics of dispersion polymerization

Dispersion polymerization is one of the heterogeneous polymerization processes. The rate and number of particles formed in heterogeneous polymerization depends on many polymerization variables. In both emulsion and dispersion polymerization the number of particles formed depends directly on the concentration of the stabilizer used. In emulsion polymerization the rate is usually strongly dependant on the number of polymer particles and is often, directly proportional it. However, in dispersion polymerization the rate is virtually independent on both particle size and number over a wide range. A comparison of polymerization rate for dispersion, precipitation and solution polymerizations of methyl methacrylate in aliphatic hydrocarbon at 80 °C have been reported[1]. The polymerization rate in dispersion polymerization was much faster than solution polymerization. However, the rate of precipitation polymerization was same as that of dispersion. The enhancement of rate in precipitation over solution polymerization has been attributed to the hindered termination of the growing polymer radicals. Many researchers have reported detailed kinetic investigations on the radical dispersion polymerization in non aqueous[98] and aqueous media[99-103]. Various reaction parameters that affect the kinetics of radical dispersion polymerization in non aqueous[104] and aqueous[105] media have been reviewed. Kinetic studies have also been carried out in supercritical carbon dioxide for the dispersion polymerization of methyl methacrylate[29], anionic dispersion polymerization[106] of styrene in various alkane solvents and ring opening dispersion polymerization of lactides and ε-caprolactone[107,108]. Very few reports are available on the kinetics of dispersion polycondensation. Kinetics and mechanisms for the synthesis of aromatic polyamides by dispersion polycondensation of acid chlorides and diamines are described[109]. It was reported that swelling of the particles as a result of high local concentration of the reactants in the dispersed phase affects the kinetics the polycondensation process.

1.3.7 Mechanism of particle formation in dispersion polymerization

The formation and growth of polymer particles during dispersion polymerization strongly depends on the solvency of the dispersion medium, the amount of stabilizer and its nature, the molecular weight as well as solubility of anchoring and stabilizing component in the dispersion medium. In all dispersion polymerizations reported so far, the common features are (i) the particle size decreases as the concentration and molecular weight of the stabilizer is increased. (ii) whether the growth of particles is in the continuous phase or in the particle phase is governed by the partition behavior of the monomer(s). Therefore, the molecular weight of the particles formed is strongly dependent in the solvency of the dispersion medium. (iii) when preformed stabilizer precursors are employed, the particle size and their distribution is controlled by the reactivity of the stabilizer precursors. (iv) when dispersion polymerization is carried out by continuous feed of monomers, the rate of monomer addition should be carefully controlled to avoid renucleation in order to obtain uniform particle size.

1.3.8 Stabilizer free dispersion polymerization

Stable dispersions of stabilizer free particles can be obtained if the chemical nature of the particles and the dispersion medium are similar. In such cases, the short-range interactions at contact distances due to permanent dipole effect is greatly reduced. Such systems do not exist in practice. Nevertheless, dispersions of this type can be prepared by crosslinking the polymer particles, which prevents their complete dissolution but allow some degree of swelling to takes place. Poly(urethane) microgels[110], poly(alkyl acrylate-co-divinylbenzene)[111] and poly(chloromethyl styrene-co-divinylbenzene)[112] are some examples of such polymerization processes. A term auto-steric stabilization[110] is used to describe the mechanism of particle stabilization. Here the polymerization is carried out in theta solvents and in the presence of crosslinkers. The polymerization initially proceeds in a homogeneous medium. When the polymer precipitates out, the outer surface of the polymer particle swells to the extent allowed by the degree of crosslinking. The solvent swollen surface layer thus stabilizes the polymer particles against aggregation[113].

1.3.9 Factors influencing dispersion polymerization

In the dispersion polymerization, the particle size and particle size distribution can be controlled by various factors such as temperature, concentration of initiator and stabilizer, monomer/dispersion medium ratio and the type and structure of steric stabilizers. However, the latter mainly dictates the course of dispersion polymerization.

1.3.9.1 Stabilizer molecular weight

It is evident from the detailed analysis of dispersion polymerization literature that the molecular weight of the steric stabilizer is the key factor in controlling the particle size and its distribution. The dispersion polymerization of styrene in polar solvents have been carried out and the influence of reaction parameters on particle size and molecular weight in poly(n-vinylpyrrolidone)-stabilized reactions are reported[114]. The molar mass of the stabilizer has a direct influence on particle size and size distribution. El-Aasser et al[115] reported that in the dispersion polymerization of methyl methacrylate using poly(vinyl pyrollidone) as stabilizer, the particle size decreased with increasing molecular weight of poly(vinyl pyrollidone). This is because an increase in poly(vinyl pyrollidone) molecular weight increases the viscosity of the continuous phase that results in a thicker adsorbed layer onto the precipitated polymer surface[116]. This phenomenon reduces the extent of nuclei aggregation and results in smaller particles. In the dispersion polymerization of methyl methacrylate in supercritical CO_2, using poly (FOA) **(5)**, it was observed that high molecular weight poly (FOA) resulted in larger poly(methyl methacrylate) particles when compared to low molecular weight poly (FOA)[117].

1.3.9.2 Block segment molecular weight

When amphiphilic block copolymer is used as steric stabilizer, the ratio of hydrophilic to hydrophobic block is very critical in controlling the polymer particle size and its distribution. The influence of anchor/stabilizer block length on particle size and particle size distribution for the dispersion polymerization of styrene in alcohol media using poly(styrene-b-ethylene oxide) as polymeric stabilizer have been examined[25]. The increase in block length results in an increase in number of smaller particles with broad size distribution. The authors claim that it is possible to produce large particles with uniform size using a low molecular weight poly(styrene-b-ethylene oxide) block copolymer. Poly(styrene-b-dimethylsiloxane) was used as steric stabilizer in the dispersion polymerization of styrene in organic media[22]. The effect of block lengths on the particle size and particle size distribution has been studied. It has been demonstrated that poly(styrene-b-FOA) **(8)** acts as an effective stabilizer when compared to poly (FOA) homopolymer **(5)** stabilizer, in the dispersion polymerization of styrene in supercritical CO_2[28]. The effectiveness of this block copolymeric stabilizer is due to the anchoring ability of the polystyrene block to a growing polystyrene particle and stabilizes through a steric stabilization mechanism. Recently a study carried out on the dispersion polymerization of styrene using poly(ethylene oxide) macromonomer **(9)** shows that the macromonomer stabilizers are efficient compared to homopolymers[46]. Similarly, Kobayashi et al[118] reported poly (2-alkyl-2-oxazoline) type polymerizable stabilizers **(12)** are more effective in the dispersion polymerization of methyl methacrylate when compared to poly (2-alkyl-2-oxazoline) homopolymer. This was attributed to the adsorption of the stabilizer on the particle surface when the homopolymer was employed as a stabilizer. It was envisaged that a small amount of stabilizer was adsorbed on the polymer surface and the remaining exists in solution. However, the situation was quite different when macromonomer was used as a stabilizer. The macromonomer gives polymer particles that are chemically adsorbed with the stabilizer chains and hence a low concentration was sufficient to stabilize the polymer particles.

The dependence of particle size and particle size distribution on the molecular weight of the macromonomer has also been examined. The effect of hydrophilicity of the macromonomer on the particle size has also been studied. It was observed that a macromonomer with higher hydrophilic segment stabilizes the polymer particle more effectively. A similar observation was reported in the seeded emulsion polymerization using a polymerizable stabilizer with poly(ethylene oxide) as hydrophilic segment[5].

The mode of stabilizer anchoring, including adsorption, absorption and grafting have been distinguished in dispersion polymerization by isolating the grafted and adsorbed stabilizer from the polymer particles[13,56]. However in some cases the inverse relationship of the stabilizer concentration and the particle size is plotted on a double logarithmic graph and from the slope, the mechanism of stabilization has been predicted. For simple physical adsorption mechanism the amount of surface area stabilized would be proportional to the stabilizer concentration[1], predicting a slope of -1. Values of such slope for dispersion polymerization using various steric stabilizers are listed in Table1.3.

Table 1.3: Prediction of mechanism of stabilization from double logarithmic plot

Stabilizer type	Slope[(a)]	Stabilizer remaining[(b)] on the particle surface (%)	Mechanism of stabilization[(c)]	Reference
Block copolymer	- 0.5 ± 0.05[(d)]	-	Adsorption	[119]
	- 0.78	-	Adsorption	[120]
	- 0.60[(d)]	Upto 17 %	Adsorption	[121]
	- 0.12	-	Adsorption	[24]
	- 0.77	-	Adsorption	[27]
	- 0.13[(d)]	Upto 30 %	Adsorption	[122]
	- 0.8 ± 0.1	Upto 30 %	Adsorption and ≤ 7 % grafting	Present study
Polymerizable	- 0.60	28.5%	Grafting	[45]
	- 1.71[(d)]	Upto 14%	Grafting	[56]
	- 0.26[(d)]	-	Grafting	[40]
	- 0.51	> 90 %	Grafting	Present study

(a) Obtained from the double logarithmic plot of particle size vs stabilizer concentration
(b) Physically adsorbed and/or grafted
(c) Suggested by the author's
(d) Slope values computed from the Tables given in the respective references

1.3.9.3 Dispersion medium

In dispersion polymerization, the stabilizer, monomer and catalyst employed should be soluble in the dispersion medium and also it should be a non solvent for the polymer formed. These criteria place some limitations on the type of solvents that are useful. Earlier work has focused on the dispersion polymerization in hydrocarbon media[1,22,27,123]. More recent studies have been devoted to the dispersion polymerization in polar media[12,52,101,115]. In many cases dispersion polymerization has been carried out in mixed polar solvents. It was noted that the polarity of the solvent has significant effect on the particle size and a correlation existed between particle volume and the solubility of the dispersion medium. There is a decrease in the particle size with the increased polarity of the reaction medium when non polar monomers are polymerized in polar solvents[16]. The nature of dispersion medium not only affects the particle size and particle size distribution, but also, the molecular weight of polyurethane particles. Studies on the radical dispersion polymerization by many researchers have shown that the molecular weight of the polymer particle increases with the increase in solvency of the dispersion medium. This was attributed to gel effect, as a result of monomer partitioning [53,124-126].

1.4 Conclusion

The key to the success of dispersion polymerization depends on the uniform size of the polymer particles produced. Evidently, the nature of polymeric stabilizer and its concentration have a major effect on the particle size control and their distribution. However, the dispersion medium and the concentration of monomer also play a vital role in producing monosize particles. Other reaction parameters such as temperature, agitator speed and N_2 purge have an indirect influence in determining the polymer particle size. It is evident that compared to conventional steric stabilizers viz., poly(vinyl alcohol), hydroxy propyl cellulose, and poly(vinyl pyrollidone), the amphiphilic copolymer, and polymerizable type steric stabilizers are more effective in the dispersion polymerization of styrene and other acrylic monomers in aqueous media. Furthermore, the amounts of polymerizable stabilizer used are low compared to conventional steric stabilizers. It is apparent from this brief overview that prospects are very bright for using dispersion polymerization in the synthesis of polymers with well-controlled particle size and distribution. The progress made in this field is a direct reflection of the detailed understanding of the structure property relationships among the steric stabilizers. Suitably designed amphiphilic copolymers and polymerizable type steric stabilizers are likely to see expanding applications in the future dispersion polymerization processes.

1.5 References

1. Barrett, K. E. J. *Dispersion polymerization in organic media*; Barrett, K. E. J., Ed.; Wiley: London, 1975.

2. Arshady, R.; George, M. H. *Polym. Eng. Sci* **1993**, *33*, 865-76.

3. *Emulsions and emulsion technology*; Lissaint, K. J., Ed.; Marcel Dekker: New York.

4. Ugelstad, J.; Berge, A.; Ellingsen, T.; Schmid, R.; Nilsen, T. N.; Mork, P. C.; Stenstad, P.; Hornes, E.; Olsvik, O. *Prog.Polym.Sci* **1992**, *17*, 87-161.

5. Palluell, A. L. L.; Westby, M. J.; Bromley, C. W. A.; Davis, S. P. *Macromol. Chem., Macromol. Symp* **1990**, *35/36*, 509.

6. Napper, D. H. *Polymeric stabilization of colloidal dispersions*; 1 ed.; Academic Press: London, 1983; Vol. 3.

7. Almog, Y.; Levy, M. *J.Polym.Sci., Part A: Polym.Chem.Ed.,* **1980**, *18*, 1-11.

8. Almog, Y.; Levy, M. *J.Polym.Sci., Part A: Polym.Chem.Ed.,* **1981**, *19*, 115.

9. Tseng, C. M.; Lu, Y. Y.; El Aasser, M. S.; Vanderhoff, J. W. *J.Polym.Sci., Part A: Polym.Chem.,* **1986**, *24*, 2995-3007.

10. Paine, A. J.; McNulty, J. *J.Polym.Sci., Part A: Polym.Chem.,* **1990**, *28*, 2569-74.

11. Saenz, J. M.; Asua, J. M. *J.Polym.Sci., Part A: Polym.Chem.,* **1995**, *33*, 1511-21.

12. Ober, C. K.; Lok, K. P.; Hair, M. L. *J.Polym.Sci., Part C: Polym.Lett.Ed* **1985**, *23*, 103-8.

13. Paine, A. J. *J.Colloid Interface Sci.,* **1990**, *138*, 157-69.

14. Paine, A. J. *Macromolecules,* **1990**, *23*, 3109-17.

15. Dawkins, J. V.; Neep, D. J.; Shaw, P. L. *Polymer* **1994**, *35*, 5366.

16. Ober, C. K.; Lok, K. P. *Macromolecules* **1987**, *20*, 268-73.

17. Tuncel, A.; Kahraman, R.; Piskin, E. *J.Appl.Polym.Sci* **1993**, *50*, 303-319.

18. Horak, D.; Svec, F.; Frechet, J. M. J. *J.Polym.Sci., Part A: Polym.Chem.,* **1995**, *33*, 2329-38.

19. Shahar, M.; Meshulam, H.; Margel, S. *J. Polym. Sci., Part A: Polym. Chem.* **1986**, *24*, 203-13.

20. Margel, S.; Nov, E.; Fisher, I. *J.Polym.Sci., Part A: Polym.Chem.Ed.*, **1991**, *29*, 347-355.

21. Margel, S.; Tennenbaum, M.; Gottlieb, H. E. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 1499-502.

22. Dawkins, J. V.; Taylor, G. *Eur.Polym.J.*, **1979**, *15*, 453-7.

23. Morrison, B. R.; Piton, M. C.; Winnik, M. A.; Gilbert, R. G.; Napper, D. H. *Macromolecules* **1993**, *26*, 4368-4372.

24. Baines, F. L.; Dionisio, S.; Billingham, N. C.; Armes, S. P. *Macromolecules* **1996**, *29*, 3096-102.

25. Winzor, C. L.; Mrazek, Z. W., Mitchell A; Croucher, M. D.; Riess, G. *Eur.Polym.J.*, **1994**, *30*, 121-8.

26. Dawkins, J. V.; Maghami, G. G.; Shakir, S. A.; Higgins, J. S. *Polym.Prepr.* **1985**, *26*, 234-5.

27. Dawkins, J. V.; Taylor, G. *Polymer* **1979**, *20*, 599-604.

28. Canelas, D. A.; Betts, D. E.; DeSimone, J. M. *Macromolecules*, **1996**, *29*, 2818-21.

29. Canelas, D. A.; DeSimone, J. M. *Polym.Prepr.* **1996**, *37*, 542-543.

30. Susoliak, O.; Barton, J. *Chem.Pap.*, **1985**, *39*, 379-90.

31. Dawkins, J. V.; Shakir, S. A.; Croucher, T. G. *Eur.Polym.J.*, **1987**, *23*, 173-5.

32. Stejskal, J.; Kratochvil, P.; Koubik, P.; Tuzar, Z.; Urban, J.; Helmstedt, M.; Jenkins, A. D. *Polymer*, **1990**, *31*, 1816-22.

33. Stejskal, J.; Kratochvil, P. *Makromol.Chem., Macromol.Symp* **1992**, *58*, 221-226.

34. Stejskal, J.; Hlavata, D.; Sikora, A.; Konak, C.; Plestil, J.; Kratochvil, P. *Polymer*, **1992**, *33*, 3675-3685.

35. Helmstedt, M.; Schaefer, H. *Polymer*, **1994**, *35, 3377-83 1994*, -83 1994.

36. Albert, P.; Hoelderle, M.; Mulhaupt, R.; Janda, R. *Acta Polym* **1996**, *47*, 74-8.

37. Emel'yanov, D. N.; Lisova, I. P.; Chernorukova, Z. G.; Novospasskaya, N.; Yu *Colloid J.*, **1999**, *61*, 35-38.

38. Canelas, D. A.; Betts, D. E.; DeSimone, J. M.; Yates, M. Z.; Johnston, K. P. *Macromolecules* **1998**, *31*, 6794-6805.

39. Kobayashi, S.; Uyama, H.; Yamamoto, I.; Matsumoto, Y. *Polym.J.* **1990**, *22*, 759-61.

40. Kobayashi, S.; Uyama, H.; Lee, S. W.; Matsumoto, Y. *J.Polym.Sci., Part A: Polym.Chem.*, **1993**, *31*, 3133-3139.

41. Lepilleur, C.; Beckman, E. J. *Macromolecules*, **1997**, *30*, 745-756.

42. Bo, G.; Wesslen, B.; Wesslen, K. B. *J.Polym.Sci., Part A: Polym.Chem.*, **1992**, *30*, 1799-1808.

43. Yamashita, Y.; Ito, K.; Mizuno, H.; Okada, K. *Polym.J.* **1982**, *14*, 255-60.

44. Arshady, R. *Trends in Polymer Science* **1993**, *1*, 86-91.

45. Liu, J.; Gan, L. M.; Chew, C. H.; Quek, C.; Gong, H. *J.Polym.Sci., Part A: Polym.Chem.*, **1997**, *35*, 3575-3583.

46. Lacroix Desmazes, P.; Guyott, A. *Polym.Bull* **1996**, *37*, 183-189.

47. Nugroho, M. B.; Kawaguchi, S.; Ito, K.; Winnik, M. A. *Macromol.Rep* **1995**, *A32 5&6*, 593-601.

48. Kawaguchi, S.; Winnik, M. A.; Ito, K. *Macromolecules* **1995**, *28*, 1159-66.

49. Capek, I.; Riza, M.; Akashi, M. *J.Polym.Sci., Part A: Polym.Chem.*, **1997**, *35*, 3131-3139.

50. Kobayashi, S.; Kak, M.; Sawada, S.; Saegusa, T. *Polym.Bull* **1985**, *13*, 447-51.

51. Uyama, H.; Kobayashi, S. *Polym.Int.*, **1994**, *34*, 339-44.

52. Kobayashi, S.; Uyama, H.; Choi, J. H.; Matsumoto, Y. *Polym.Int* **1993**, *30*, 265-270.

53. Uyama, H.; Kato, H.; Kobayashi, S. *Polym.J.* **1994**, *26*, 858-863.

54. O'Neill, M. L.; Yates, M. Z.; Johnston, K. P.; Smith, C. D.; Wilkinson, S. P. *Macromolecules* **1998**, *31*, 2838-2847.

55. Nakamura, K.; Fujimoto, K.; Kawaguchi, H. *Colloid Surface.A.* **1999**, *153*, 195-201.

56. Bourgeat Lami, E.; Guyot, A. *Colloid Polym.Sci.*, **1997**, *275*, 716-729.

57. Miyazaki, H.; Terada, K.; Sato, T.; Maruyama, H. ; Okaya, T. *J.Appl.Polym.Sci.*, **1996**, *60*, 2149-2157.

58. Hoelderle, M.; Baumert, M.; Muelhaupt, R. *Macromolecules* **1997**, *30*, 3420-3422.

59. Gabaston, L. I.; Jackson, R. A.; Armes, S. P. *Macromolecules*, **1998**, *31*, 2883-2888.

60. Xia, J.; Johnson, T.; Gaynor, S. G.; Matyjaszewski, K.; DeSimone, J. *Macromolecules* **1999**, *32*, 4802-4805.

61. Thompson, *British Patent* **1932**, *385,970*.

62. ICI, *British Patent* **1967**, *1,095,931*.

63. ICI, *British Patent* **1967**, *1,095,932*.

64. Bunn, A.; Griffin, B. P.; Macdonald, W. A.; Rance, D. G. *Polymer* **1992**, *33*, 3066-3072.

65. Mobay Chemical Co., *U S Patent 3214411* **1965**.

66. PPG Industries, *U K Patent 2157702* **1985**.

67. Armstrong Cork Co., *U S Patent 4083831* **1978**.

68. Nippon Paint Co.,*US Patent* **1997**, *5603986*.

69. Alder, K. I.; Sherrington, D. C. *Chem. Commun.* **1998**, *1*, 131-132.

70. Perry, R. J. *Chemtech*, **1999**, *29*, 39-44.

71. Brode, G. L.; Jones, T. R.; Chow, S. W. *Chemtech* **1983**, *13*, 676-81.

72. Uyama, H.; Kurioka, H.; Kobayashi, S. *Chem.Lett* **1995**, *9*, 795-6.

73. Kurioka, H.; Uyama, H.; Kobayashi, S. *Polym.J* **1998**, *30*, 526-529.

74. Edwards, J.; Fisher, R.; Vincent, B. *Makromol. Chem., Rapid Commun* **1983**, *4*, 393-7.

75. Digar, M. L.; Bhattacharyya, S. N.; Mandal, B. M. *Chem.Commun.* **1992**, 18-20.

76. Beaman, M.; Armes, S. P. *Colloid and Polym.Sci.*, **1993**, *271,* 70-75.

77. Stejskal, J.; Kratochvil, P.; Helmstedt, M. *Langmuir* **1996**, *12*, 3389-3392.

78. Armes, S. P.; Aldissi, M.; Agnew, S.; Gottesfeld, S. *Langmuir* **1990**, *6,* 1745-9.

79. Banerjee, P.; Bhattacharyya, S. N.; Mandal, B. M. *Langmuir* **1995.**, *11,* 2414-18.

80. Chattopadhyay, D.; Mandal, B. M. *Langmuir* **1996**, *12,* 1585-8.

81. Herculeus, *British Patent* **1969**, *1,165,840*.

82. BASF, *German Patent* **1997**, *19542356*.

83. Fire Stone Tyre and Rubber Co., *British Patent* **1965**, *1,007,476*.

84. Stampa, G. B. *J.Appl.Polym.Sci.* **1970**, *14*, 1227-1233.

85. Awan, M. A.; Dimonie, V. L.; El Aasser, M. S. *J.Polym.Sci., Part A: Polym.Chem.*, **1996**, *34*, 2633-2649.

86. Kim, J.; Jeong, S. Y.; Kim, K. U.; Ahn, Y. H.; Quirk, R. P. *J.Polym.Sci., Part A: Polym.Chem.*, **1996**, *34,* 3277-3288.

87. Schneider, M.; Muelhaupt, R. *Polym. Bull* **1994**, *32*, 545-50.

88. Union Carbide, *US Patent* **1972**, *3,632,669*.

89. Union Carbide, *US Patent* **1972**, *3,646,170*.

90. Sosnowski, S.; Gadzinowski, M.; Slomkowski, S.; Penczek, S. *J. Bioact. Compat. Polym* **1994**, *9,* 345-366.

91. Firestone Tyre and Rubber Co., *British Patent* **1962**, *1,008,001*.

92. ShintoToryo, *Japanese Patent* **1992**, *04072329*.

93. ICI, *British Patent* **1967**, *1,095,931*.

94. Atochem, *U S Patent 4,737,304* **1986**.

95. Autochem, *U S Patent 4,831,061* **1988**.

96. Hou, W. H.; Lloyd, T. B. *J.Appl.Polym.Sci* **1992**, *45,* 1783-1788.

97. Vasiliu-Oprea, C.; Dan, F. *J. Appl. Polym. Sci.* **1996**, *62*, 1517-1527.

98. Stejskal, J.; Kratochvil, P.; Konak, C. *Polymer* **1991**, *32*, 2435-2442.

99. Capek, I.; Riza, M.; Akashi, M. *Makromol.Chem.*, **1992**, *193*, 2843-2860.

100. Bourgeat Lami, E.; Guyot, A. *Polym.Bull.* **1995**, *35*, 691-6.

101. Kawaguchi, S.; Winnik, M. A.; Ito, K. *Macromolecules* **1995**, *28*, 1159-66.

102. Saenz, J. M.; Asua, J. M. *Macromolecules,* **1998**, *31*, 5215-5222.

103. Ahmed, S.; Farid; Poehlein, G. W. *Ind.Eng.Chem.Res.,* **1997**, *36*, 2605-2615.

104. Winnik, M. A.; Lukas, R.; Chen, W. F.; Furlong, P.; Croucher, M. D. *Makromol.Chem., Macromol.Symp.*, **1987**, *10-11*, 483-501.

105. Capek, I. *J.Disper.Sci.Tech.* **1999**, *20*, 945-992.

106. Schwab, F. C. *Polym.Prepr.* **1984**, *25*, 61-2.

107. Gadzinowski, M.; Sosnowski, S.; Slomkowski, S. *Macromolecules* **1996**, *29*, 6404-6407.

108. Slomkowski, S.; Sosnowski, S.; Gadzinowski, M. *Polym.Degrad.Stab.,* **1998**, *59*, 153-160.

109. Reinisch, G.; Gohlke, U.; Ulrich, H. H. *Makromol. Chem.*, **1979**, *Suppl 3*, 177-93.

110. Graham, N. B.; Mao, J. *Colloids Surf., A,* **1996**, *118*, 211-220.

111. Li, W. H.; Stover, H. D. H. *J.Polym.Sci., Part A: Polym.Chem* **1999**, *37*, 2899-2907.

112. Li, W. H.; Li, K.; Stover, H. D. H. *J.Polym.Sci., Part A: Polym.Chem.* **1999**, *37*, 2295-2303.

113. Downey, J. S.; Frank, R. S.; Li, W. H.; Stover, H. D. H. *Macromolecules* **1999**, *32*, 2838-2844.

114. Paine, A. J.; Luymes, W.; McNulty, J. *Macromolecules* **1990**, *23*, 3104-9.

115. Shen, S.; Sudol, E. D.; ElAasser, M. S. *J.Polym.Sci., Part A: Polym.Chem* **1993**, *31*, 1393-1402.

116. Shen, S.; Sudol, E. D.; El Aasser, M. S. *J.Polym.Sci., Part A: Polym.Chem.,* **1994**, *32*, 1087-100.

117. DeSimone, J. M. *Science* **1994**, *265*, 356.

118. Kobayashi, S.; Uyama, H.; Chio, J. H.; Matsumoto, Y. *Polym.Int.,* **1993**, *30*, 265-70.

119. Holderle, M.; Bar, G.; Mulhaupt, R. *J.Polym.Sci., Part A: Polym.Chem.,* **1997**, *35*, 2539-2548.

120. Ray, B.; Mandal, B. M. *Langmuir* **1997**, *13*, 2191-2196.

121. Armes, S. P.; Aldissi, M. *Polymer* **1990**, *31*, 569-574.

122. Hsiao, Y. L.; Maury, E. E.; DeSimone, J. M.; Mawson, S.; Johnston, K. P. *Macromolecules* **1995**, *28,* 8159-66.

123. Riess, G.; Desvalois, M. *J.Polym.Sci.,Part C: Polym.Lett* **1977**, *15*, 49-54.

124. Thomson, B.; Rudin, A.; Lajoie, G. *J.Polym.Sci., Part A: Polym.Chem.,* **1995**, *33,* 345-57.

125. Lu, Y. Y.; El Aasser, M. S.; Vanderhoff, J. W. *J.Polym.Sci., Part B: Polym.Phys.,* **1988**, *26*, 1187-203.

126. Paine, A. J. *J.Polym.Sci., Part A: Polym.Chem.,* **1990**, *28,* 2485-500.

Chapter 2: Scopes and objectives of the present work

2.1 Introduction

Particle forming polymerization processes have been generally performed, thus far, with vinyl monomers using chain growth polymerization chemistry[1-5]. Relatively less is known on particle forming polymerization as applied to step growth polymerization chemistry[6,7]. Therefore, the objective of the present work is to examine the feasibility of dispersion polymerization of diols with diisocyanates to produce polyurethane particles of uniform size and shape. Towards this goal, it is proposed to examine the utility of the following two steric stabilizers in the dispersion polymerization of diols with diisocyanates to form poly(urethane)s and ring opening polymerization of cyclic amides to form poly(amide)s.

1. Amphiphilic block copolymers with suitably disposed lipophilic and lipophobic groups.
2. Polymerizable steric stabilizers containing a reactive hydroxyl groups/cyclic amide moiety with a long hydrophobic acrylate ester moiety capable of being enchained during polymerization.

2.2 Synthesis of steric stabilizers

Steric stabilizers are polymeric surface-active agents. They provide a stability barrier to the dispersed polymer particles and prevent the aggregation of the particles. This phenomenon is called steric stabilization. The steric stabilizers generally used in radical dispersion polymerization are homopolymers or random copolymers or amphiphilic block or graft copolymers. In many cases these stabilizers have terminal polymerizable groups and therefore act as a comonomer. One of the most successful type of steric stabilizer devised for use in radical dispersion polymerization has been based on an amphiphilic block copolymer or a polymerizable stabilizer. *Accordingly, it is proposed to examine the efficacy of designed amphiphilic block copolymers and polymerizable steric stabilizers for the particle forming polymerization of poly(urethane)s and poly(amide)s. It is proposed to synthesize poly[1,4-isoprene-b-(ethylene oxide)] via living anionic polymerization techniques*[8] *This amphiphilic block copolymer is envisaged as an effective stabilizer because of the enhanced interaction of the hydrophilic ethylene oxide moiety with polar urethane and amide linkages and thus acts as an effective* *anchor block. Furthermore, the hydrophobic polydiene segment is freely soluble in wide range of organic solvents and makes the dispersion polymerization process more versatile. It is also proposed to synthesize a polymerizable steric stabilizer capable of taking part in the polymerization process. There are no reports available on polymerizable stabilizers capable of undergoing polycondensation or ring opening polymerization processes. Therefore, it is proposed to synthesize a polymerizable stabilizer namely poly(alkyl methacrylate) having two primary hydroxyl groups or a cyclic amide at one end of the chain. The former is capable of undergoing reaction with organic diisocyanates and the latter is capable of undergoing ring opening polymerization and forms a covalent linkage with the growing particles. In this way the soluble poly(alkylmethacrylate) chain is attached to the particle surface and provides steric stabilization.*

2.3 Preparation of polyurethane particles by dispersion and suspension polymerization

Solution polycondensation process is widely employed for making polyurethanes. However, in recent years the demand for powder coating products and environmentally benign polymers gave a great impetus to produce polyurethanes in particulate form. Conventionally, polyurethane particles are prepared by cryogenic grinding of thermoplastic polyurethanes[9] or by suspension polymerization of isocyanate terminated prepolymers in aqueous[10] or non-aqueous medium[11]. In none of these methods the control of particle size is possible. There is, however, a solitary patent on the dispersion polymerization of an isocyanate terminated prepolymer using amphiphilic block copolymer stabilizer in non aqueous medium[12]. *It is therefore, the objective of this work is to study the dispersion polymerization of diisocyanate and diol using a polymerizable and polymeric type steric stabilizers and to delineate many interesting features of this novel process. Some of these are (i) relationship between the stabilizer structure and its effectiveness in dispersion polymerization (ii) control of particle size and shape (iii) generality of the reaction to different types of isocyanates and diols. (iv) kinetics and mechanism of polyurethane particle formation with respect to molecular architecture of the steric stabilizer.*

2.4 Ring opening dispersion polymerization cyclic amides

Particle forming polymerization technique in organic media has been applied to a range of ring opening polymerization of hetero cyclic ring compounds using ionic modes of initiation. These include the polymerization of cyclic ethers, cyclic esters, cyclic amides, and cyclic acetals. Nevertheless, the ring opening polymerization of cyclic amides are less studied and much of the available information is in patent literature[13-15]. A few published articles are available in the open literature[16]. A fairly uniform spherical nylon particle has been synthesized by phase separation technique. The phase separation was achieved by dissolving the polymer in a theta solvent (1 wt %) above the theta temperature and cooling it rapidly. However, none of these methods employ a particle stabilizer. *Therefore, the present study will focus on ring opening polymerization of cyclic amides in the presence of a steric stabilizer, to prepare poly(amide)s in particulate form. The effect of steric stabilizer structure on the poly(amide) particle formation will be studied.*

2.5 Applications of dispersion polycondensation process

Dispersion polymerization produces uniform polymer particles under favorable conditions. These spherical polymer particles are used as ion-exchangers, calibration standards, surface coatings, pharmaceutical reagents, bio-materials, medical diagnostics, parenteral drug delivery systems, toners for photocopying and digital printing, supports for solid phase synthesis and chromatographic media for separations. Recently, in our laboratory, particle forming polyurethane polymerization has been utilized in encapsulating drugs and pesticides. This approach is further extended to encapsulate carbon black. Carbon black filled polymer particles is useful for coatings, inks, electrophotographic developers etc… Conventionally carbon black filled polymers have been obtained by melt blending or solution casting. Preparation of aqueous suspensions of polystyrene and polyurethane urea[17] filled with carbon black has been reported. However, aqueous suspensions of carbon black filled polymers are not suitable as carrier particles for electrophotographic developers and for such applications, carbon black dispersed in organic solvents containing the polymer is used. Stable dispersions of carbon black in organic media have also been achieved by grafting reaction on to carbon black surface[18]. This approach is limited because of poor grafting efficiency and number of monomers amenable for grafting onto carbon black surface is less. *Thus, it is proposed to study the encapsulation of carbon black in polyurethane matrix using a suitable steric stabilizer. A preliminary investigation was also undertaken towards preparing highly dispersed polymer-silicate nanocomposites using particle forming polymerization technique.* Research in the area of organic-inorganic composites is increasingly important because they offer potential applications. Preparation of polymer silicate nanocomposites by intercalation has been well documented[19-23]. However, significant amount of work has not been carried out to make well dispersed polymer silicate nanocomposites[24]. *Therefore, the present study attempts to make well dispersed clay polyurethane nanocomposites using particle forming polymerization technique. The synthetic strategy involves the intercalation of the clay layer using a dihydroxy onium salts. The hydroxyl group will be utilized for particle forming polymerization with diisocyanates.*

2.6 References

1. Ober, C. K.; Lok, K. P.; Hair, M. L. *J.Polym.Sci., Part C: Polym.Lett.Ed* **1985**, *23*, 103-8.
2. Kobayashi, S.; Uyama, H.; Yamamoto, I.; Matsumoto, Y. *Polym.J.* **1990**, *22*, 759-61.
3. Paine, A. J.; Luymes, W.; McNulty, J. *Macromolecules* **1990**, *23*, 3104-9.
4. Nugroho, M. B.; Kawaguchi, S.; Ito, K.; Winnik, M. A. *Macromol.Rep* **1995**, *A32 5&6*, 593-601.
5. Hsiao, Y. L.; Maury, E. E.; DeSimone, J. M.; Mawson, S.; Johnston, K. P. *Macromolecules* **1995**, *28*, 8159-66.
6. Sosnowski, S.; Gadzinowski, M.; Slomkowski, S.; Penczek, S. *J. Bioact. Compat. Polym* **1994**, *9*, 345-366.
7. Kurioka, H.; Uyama, H.; Kobayashi, S. *Polym.J* **1998**, *30*, 526-529.
8. Jurgen, A.; Andreas, P.; Lutz, W.; Dieter, R. *Macromolecules* **1997**, *30*, 1582-1586.
9. Mobay Chemical Co., *U S Patent 3214411* **1965**.
10. Armstrong Cork Co., *U S Patent 4083831* **1978**.
11. PPG Industries ,*U K Patent 2157702* **1985**.
12. Nippon Paint Co. Ltd., *US Patent* **1997**, *5603986*.
13. Atochem, *U S Patent 4,737,304* **1986**.
14. Autochem, *U S Patent 4,831,061* **1988**.
15. Ube Industries, *Eur.Pat.Appl 866088* **1998**.
16. Hou, W. H.; Lloyd, T. B. *J.Appl.Polym.Sci* **1992**, *45*, 1783-1788.

17. Dai Ichi Kogyo Seiyaku Co. *Jpn.Kokai 5222207* **1993**.

18. Tsubokawa, N.; Matsumoto, H.; Sone, Y. *J.Polym.Sci., Part A: Polym.Chem* **1982**, *20*, 1943-6.

19. Pinnavaia, T. J. *Science* **1983**, *220*, 365.

20. Wang, M. S.; Pinnavaia, T. J. *Chem. Mater* **1994**, *6*, 468-74.

21. Wang, Z.; Pinnavaia, T. J. *Chem. Mater* **1998**, *10*, 3769-3771.

22. Messersmith, P. B.; Giannelis, E. P. *Chem. Mater* **1994**, *6*, 1719-25.

23. Zilg, C.; Thomann, R.; Muelhaupt, R. *Adv. Mater* **1999**, *11*, 49-52.

24. Weimer, M. W.; Chen, H.; Giannelis, E. P.; Sogah, D. Y. *J.Am.Chem.Soc* **1999**, *121*, 1615-1616.

Chapter 3: Synthesis and characterization of steric stabilizers

3.1 Introduction

The function of steric stabilizers in stable colloidal dispersions is to provide a layer of material solvated by the dispersion medium on each particle surface. Each solvated moiety must be strongly attached or anchored to the surface of the particle in order to provide effective stabilization. The most successful type of steric stabilizer devised for use in dispersion polymerization has been based on amphiphilic block or graft copolymer. They consist of two essential polymeric components namely an insoluble and a soluble in the continuous phase. The insoluble component is referred as anchor block which adsorbs onto the polymer either physically or chemically. In this way, the soluble component is firmly attached at the surface and provides a surface coverage for the particles. Therefore, the main requirement for the anchor group is that it should not be soluble in the dispersion medium. It is not necessary for the adsorbed polymer to be identical in composition with the disperse phase polymer. However, its effectiveness may be greatly enhanced if it has some specific affinity for the dispersed polymer. On the other hand, the principal consideration in selecting the soluble component is that it should be freely soluble in the dispersion medium. The ratio of anchor to soluble component is also important in providing effective stabilization[1]. One can avoid the anchor part if polymerizable stabilizers are employed. Here, the soluble block is attached to the growing polymer by a covalent linkage. In such cases, the stabilization process greatly depends on the reactivity of the functional groups attached to the soluble component. Accordingly, we designed an amphiphilic block copolymer and a polymerizable steric stabilizer for the particle forming polymerization of poly(urethane)s and poly(amide)s.

Poly[1,4-isoprene-*b*-(ethylene oxide)] (PI-*b*-EO) was chosen as a steric stabilizer with the view that the hydrophilic ethylene oxide moiety will provide enhanced interaction with polar urethane and amide linkages and, thus, act as an effective anchor block. Furthermore, the hydrophobic polydiene segment is soluble in a wide range of organic solvents and makes the dispersion polymerization process more versatile. It is known that living anionic polymerization produces well-defined block copolymers with narrow molecular weight distribution. Poly(isoprene) with high degree of 1,4 micro structure can be obtained by using organo lithium initiators and hydrocarbon solvents[2]. However, alkali metal initiated polymerization of isoprene in polar solvents produces polymers with increased 3,4 microstructure. On the other hand, anionic ring opening polymerization of ethylene oxide takes place only in the presence of alkali metal initiators, preferably, potassium initiators and in polar solvents. Anionic ring opening polymerization of ethylene oxide by lithium initiators in non polar solvents effects only hydroxyethylation of the chain end without any propagation[3]. Nevertheless, addition of potassium salt or lithium complexing agent to lithium initiators effects the polymerization of ethylene oxide. The application of this technique in the preparation of poly(styrene-*b*-ethylene oxide) resulted in significant amount of poly(ethylene oxide) homopolymer and undesirable molecular weight distribution[4].

In this work, we have chosen a two step process for the preparation of PI-*b*-EO. In the first step, isoprene was polymerized anionically using *tert*-butyllithium in cyclohexane. The living poly(isoprene) was end capped with ethylene oxide to get hydroxyl functionalized poly(isoprene). In the second step, the hydroxyl group was deprotonated using trityl potassium. The resultant macroinitiator was used to initiate ethylene oxide in THF to produce PI-*b*-EO.

A polymerizable steric stabilizer capable of undergoing polymerization was also prepared. Polymerizable stabilizers have been well documented as an efficient stabilizer for radical dispersion polymerization in aqueous alcohol media[5-7]. However, there are no reports available on polymerizable stabilizers capable of promoting dispersion polymerization *via* polycondensation or ring opening polymerization processes. Although, macro monomers with antagonist functional groups are known for a long time, they can not be employed as steric stabilizer. Therefore, a polymerizable stabilizer poly(alkyl methacrylate) having two primary hydroxyl groups or a cyclic amide at one end of the chain was prepared. The former is capable of undergoing reaction with organic diisocyanates and the latter is capable of undergoing ring opening polymerization and forms a covalent linkage with the growing particles. In this way the soluble poly(alkyl methacrylate) chain is attached to the particle surface and provides steric stabilization. The polymerizable stabilizers were obtained by a two step process. In the first step, carboxyl group containing poly(alkyl methacrylate)s were obtained by polymerizing alkyl methacrylates in the presence of functional chain transfer agents using conventional free radical polymerization[8,9]. In the second step, the carboxyl group is converted to a glycol and a cyclic amide, respectively, by reacting with trimethylol propane and ε-caprolactam.

3.2 Experimental section

3.2.1 Materials and purification

3.2.1.1 Anionic polymerization method

Cyclohexane (Merck) was purified by sequential distillation from CaH_2 and from *n*-butyllithium. Tetrahydrofuran (THF) was purified by sequential distillation from sodium-potassium alloy and from the purple benzophenone-potassium adduct. Isoprene (Fluka) was purified by treatment with dibutylmagnesium for 12 h, then distilled onto *n*-butyllithium and allowed to stand 30 min at -20 °C immediately before use. Ethylene oxide (EO) (Pest Control India, Ltd, Mumbai) was passed through a column containing a molecular sieve and CaH_2 and condensed into an ampoule (Figure 3.1)

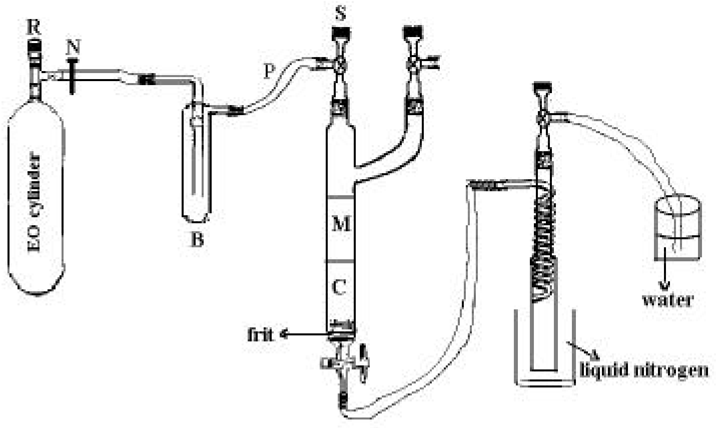


Figure 3.1. Assembly for condensing ethylene oxide. R-gas regulator, N-needle valve, B-gas bubbler, P-PVC tubing, S-septum adapter, M-molecular sieve, C-calcium hydride.

In a flame dried 50 mL glass ampoule, 500 milligrams of triphenyl methane was transferred and then 25 mL of THF was distilled directly into the ampoule. In a separate glass apparatus (Figure 3.2), 700 milligrams of potassium metal is charged in the bulb A and flamed the flask. The ampoule containing the triphenyl methane solution was attached to the bulb A and the solution was added to the potassium metal at room temperature. The appearance of bright right color indicates the formation of trityl anion. The solution was freeze dried and stirred at room temperature for 5 h. The contents were then transferred to bulb B and stored at 0 °C.

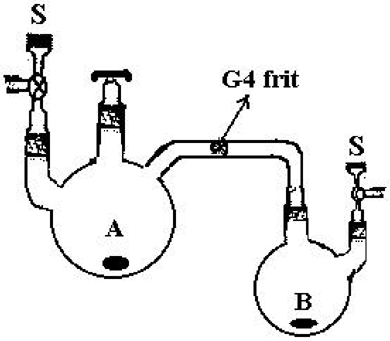


Figure 3.2: Apparatus for making trityl anion. S-septum adapter, A-bulb in which reaction is carried out, B-bulb in which trityl potassium is stored

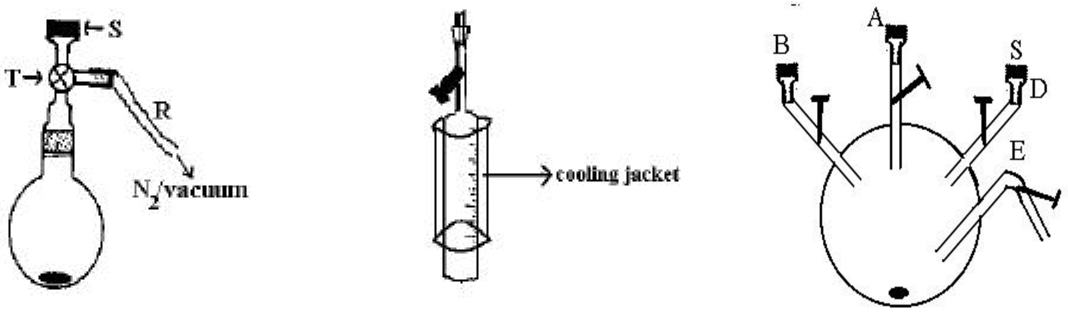
3.2.1.2 Radical polymerization method

Methyl Methacrylate (MMA) (Fluka) was stirred with CaH_2 and distilled under high vacuum. Lauryl methacrylate (LMA) (Aldrich) was stirred with CaH_2 (Aldrich) for 24 h and then passed through activated alumina. Mercaptoacetic acid (MAA) (Aldrich) was azeotropically distilled with benzene to remove traces of water followed by vacuum distillation. α,α'-Azoisobutyronitrile (AIBN) and trimethylolpropane (TMP) both procured from Aldrich were recrystallized from ethanol and acetone respectively. ε-Caprolactam (Gujarat Fertilizeres and Chemicals Ltd., Vadodara) was recrystallized from n-hexane/acetone mixture (90/10 v/v) Toluene, THF, n-hexane and cyclohexane were distilled over sodium wire. Dichloromethane and chloroform were dried over $CaCl_2$ and distilled. N,N'-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP) (Aldrich) and phenyl isocyanate (Fluka) were used as received.

3.2.2 Synthesis of steric stabilizers

3.2.2.1 Synthesis of poly(1,4-isoprene-*b*-ethylene oxide) by anionic polymerization (20c)

All manipulations were performed under high vacuum and using high purity nitrogen gas. To a flame dried 250 mL single necked round bottom flask (Figure 3.3-1) fitted with a septum adapter with N_2/vaccum inlet, 100 mL pure cyclohexane was transferred by stainless steel capillary tube under N_2.



(1) (2) (3)

Figure 3.3. Apparatus used for (1) preparing PI-OH (2) glass ampoules for storing ethylene oxide before reaction (3) preparing poly(isoprene-b-ethylene oxide)

The initiator *tert*-butyllithium was added drop-wise until a persistent pale yellow color of the initiator remained. Usually 0.2 - 0.4 mL of 0.09 M initiator was required to quench the impurities for 100 mL cyclohexane. Subsequently, the calculated amount of the initiator was added using a syringe. The temperature of the flask was maintained at 30 °C using an oil bath. Isoprene 3 mL was then added to the flask through stainless steel capillary tube within 10 s. The reaction was continued for 15 minutes followed by the addition of 10 fold excess of ethylene oxide over the initiator concentration. The mixture was stirred well for 6 h and terminated with acetic acid. The polymer was precipitated in cold methanol. The polymer obtained was dried under vacuum for 8 h. The protic impurities present was further removed by dissolving the polymer in dry toluene, the solvent removed under reduced pressure and stirred under vacuum for 8 h. This procedure was repeated thrice to ensure removal of all volatile protic impurities. To this purified prepolymer **(18c)**, 100 ml THF was added and transferred to the reaction flask (Figure 3.3-3) using a stainless steal capillary tube. The polymer solution was titrated with deeply rep colored trityl potassium. The titration was stopped after a slight orange color in the polymer solution persisted for 5 minutes followed by the addition of required amount of trityl potassium to form the macroinitiator **(19c)**. Then, 2 mL of purified 20% ethylene oxide in THF was transferred using a syringe into a glass ampoule (Figure 3.3-2). This ampoule was then attached to the reaction flask (Figure 3.3-3) and added the ethylene oxide solution. The reaction was continued for 32 h at 60 °C. The polymerization was terminated with acetic acid. The block copolymer thus obtained **(20c)** was precipitated in methanol and dried at room temperature under vacuum for 5 h.

Yield 92%; FTIR (neat, cm^{-1}): 1660 ($\nu_{C=C}$), 1110 ($\nu_{C\text{-}O\text{-}C}$)

^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ = 5.2(s, -C=C$\underline{\mathbf{H}}$ 1,4 units), 4.6-4.8(br, -CH=CH_2), 3.6(s, -CH_2-CH_2-O-)

3.2.2.2 Synthesis of poly(alkyl methacrylate) macrodiol (22a)

The macrodiols were synthesized in two steps. In the first step, a carboxyl terminated prepolymer with was prepared according to the procedure is given below.

In 3 neck 100 mL round bottomed flask fitted with a magnetic needle, thermowell, condenser and a nitrogen inlet tube added 2g LMA, 0.73 g MAA, 0.16 g AIBN and 35 mL toluene. The mixture was stirred well and nitrogen gas was purged well for about 1 h. The flask was then heated to 80 °C. The reaction was continued for 5 h. The polymer obtained was precipitated in 75/25(v/v) methanol/water mixture and washed thoroughly with the same mixture. The polymer was dissolved in chloroform and dried under sodium sulfite for 24 h. % Yield 88%. IR (neat cm^{-1}): ^{1}HNMR($CDCl_3$, ppm) δ = 11.2 (s;-COO$\underline{\mathbf{H}}$), 3.8-4.0 (br;-COOC$\underline{\mathbf{H}}_2$), 1.8-2.0 (br; -COOCH_2-C$\underline{\mathbf{H}}_2$-CH_2-), 1.6(s;-C$\underline{\mathbf{H}}_2$-); 1.1-1.5 (br-C$\underline{\mathbf{H}}_2$-); 0.75-0.8 (t;-CH_2-C$\underline{\mathbf{H}}_3$)

In the second step, the prepolymer (**21a**), 3 g (4.23×10^{-3} mol) was dissolved in dichloromethane in a round bottom flask, fitted with a magnetic needle. The mixture was cooled to 0 °C followed by addition of 0.8 g (5.88×10^{-3} mol) TMP, 1.3 g (6.3×10^{-3} mol) DCC and 0.025 g (2.05×10^{-4} mol) DMAP under an atmosphere of argon. The reaction was continued for 4 h. The urea formed was removed by filtration. The macrodiol (**22a**) thus obtained was washed three times with 50 mL portions of methanol/water (90/10) mixture, and dissolved in chloroform. It was dried over anhydrous sodium sulfate for 12 h and further purified by column chromatography on silica gel column (60-120 mesh size) using chloroform as an eluent. Yield: 85%, IR:(neat, cm^{-1}): 3560 (ν_{OH}), 2960 (ν_{C-H}) and 1740 ($\nu_{C=O}$).

3.2.2.2.1 Synthesis of bis(urethane)s

250 milligram (3.52×10^{-4} mol) of thoroughly dried (**22a**) was dissolved in 10 mL dry THF in a 25 mL three neck round bottomed flask fitted with a magnetic needle, condenser, thermowell and nitrogen inlet tube. The mixture was heated to 70 °C and 80 milligram (7.14×10^{-4} mol) of phenyl isocyanate was added. The reaction was continued for 5 h. The bis(urethane) formed was washed several times with hexane and dried under vacuum at 40 °C for 2 h. Yield: 94%, IR (neat, cm^{-1}): 3350 (ν_{NH}), 1750 ($\nu_{C=O}$) ester, 1710 ($\nu_{C=O}$) urethane. ^{1}H NMR (acetone D_6): δ = 7.0-7.5 (m; -aromatic); 3.8-4.0 (br; -$COOC\underline{H}_2$); 1.8-2.0 (br; -$COOCH_2$-$C\underline{H}_2$-CH_2-); 1.6(s;-$C\underline{H}_2$) 1.1-1.2 (br;-$C\underline{H}_2$) 0.75-0.8 (t; -CH_2-$C\underline{H}_3$)

3.2.2.3 Synthesis of caprolactam terminated poly(alkyl methacrylate) (23a)

Prepolymer **(21a)**, 3 g (4.23×10^{-3} mol) was dissolved in dichloro methane in a round bottom flask, fitted with a magnetic needle. The mixture was cooled to 0 °C followed by addition of 0.8 g (5.88×10^{-3} mol) ε-caprolactam, 1.3 g (6.3×10^{-3} mol) DCC and 0.025 g (2.05×10^{-4} mol) DMAP under an atmosphere of argon. The reaction was continued for 4 h. The urea formed was removed by filtration. The cyclic amide containing macromonomer **(23a)** thus obtained was washed three times with 50 mL portions of methanol/water (90/10) mixture, and dissolved in chloroform. It was dried over anhydrous sodium sulfate for 12 h and further purified by column chromatography on silica gel column (60-120 mesh size) using chloroform as an eluent. Yield: 85%, IR:(neat, cm^{-1}): 3560 (ν_{OH}), 2960 (ν_{C-H}) and 1740 ($\nu_{C=O}$).

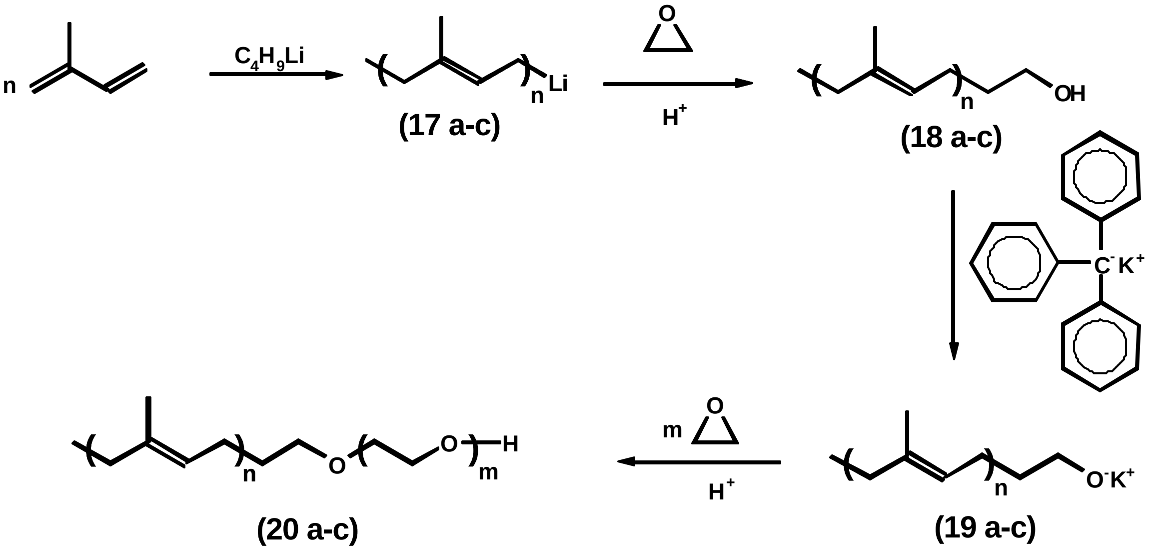
3.2.3 Analysis

Size exclusion chromatography (SEC) experiments were carried out at 30 °C using Waters 150 C instrument. μ-Styragel columns with a porosity range 10^5 to 100Å and one ultra-Styragel column of continuous porosity were used together with a differential refractometer. The eluent was THF with a flow rate 1 mL/min. Poly(styrene) standards were used for calibration. The number average molecular weight for the poly(isoprene) prepolymers and polymerizable stabilizers were determined by KNAUER vapour pressure osmometer in chloroform at 35 °C. Acid value was detrmined according to ASTM method D 1980-87. A known amount of sample was dissolved in 50 mL of toluene/isopropanol (1:1 v/v) mixture. The solution was titrated against standardized alcoholic KOH using Metler D 25 automatic titrator fixed with glass electrode DG 112. Acid value (mg of KOH/ g sample) was calculated from the formula (BR*N*56.1)/W Where, BR = volume of KOH consumed, N = normality of alcoholic KOH and W = weight of sample. The hydroxyl value was determined according to ASTM method E 1899-97. A known amount of thoroughly dried sample was taken in 250 mL Iodimetric flask. 10 mL of pyridine/acetic anhydride (10:1 v/v) mixture was added. The contents were refluxed for about 6 h and cooled. 10 mL of distilled water was then added and again refluxed for about 30 minutes. The flask was then cooled using ice water mixture and titrated against 0.5 N HCl using Metler D25 automatic titrator. Similarly a blank run was carried out with out sample. The hydroxyl value was calculated using the formula (B-S*N*56.1)/W Where, B = volume of HCl consumed for blank S = volume of HCl consumed for sample, N = normality of alcoholic HCl and W = weight of sampleIR spectra were recorded on a PE 16PC FT-IR spectrophotometer. ^{1}H NMR spectra were recorded on a 200 MHz Bruker AC 200 NMR spectrometer.

3.3 Results and discussion

3.3.1 Synthesis of amphiphilic block copolymer

Poly(isoprene-*b*-ethylene oxide) was synthesized according to the earlier reported procedure[2] (Scheme 3.1). The first step involves the synthesis of hydroxyl terminated poly(isoprene), (PI-OH). Functionalization was achieved by reacting the living PI with an excess of ethylene oxide. It was demonstrated under these conditions exclusively one unit of ethylene oxide was added to the poly(isoprene) chain end.[3] The microstructure of PI-OH was analyzed by comparing the ^{1}H NMR (Figure 3.4) signal intensities of the olefinic proton at 5.1 ppm associated with 1,4 structure and at 4.7 ppm for 3,4 structure. It was found that the polymers contain 90 - 95% 1,4 units and 5-10% 3,4 units. The molecular weight data of the PI-OH is shown in Table 3.1. The molecular weight obtained by SEC and the end group analysis are similar and corresponding well to that of the calculated molecular weight. The molecular weight distribution obtained by SEC is also narrow. This is as expected for the polymers obtained by anionic polymerization technique.



Scheme 3.1. Synthesis of poly(1,4-isoprene-b-ethylene oxide)

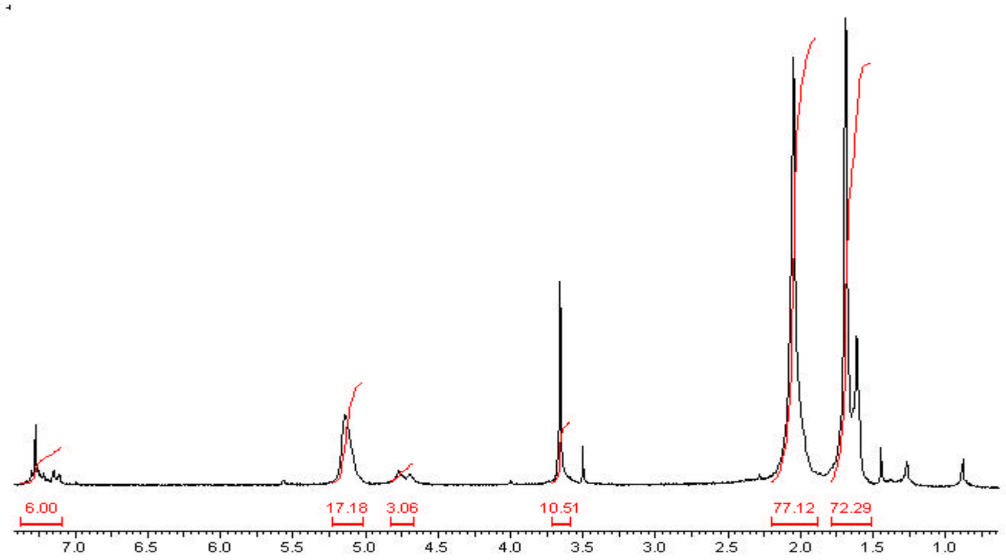


Figure3.4 ^{1}HNMR spectra of poly(isoprene-b-ethylene oxide) (**20c)**

Table 3.1: Molecular weight characterization of poly(isoprene) prepolymers.

Sample	$[M_1]$ $\times 10^2$	$[I_1]$ $\times 10^5$	$\overline{M}_n$ SEC	$\overline{M}_w / \overline{M}_n$	Hydroxyl value (mg KOH g^{-1})	$\overline{M}_n$ (end group analysis)
18a	7.34	2.45	2466	1.14	24.0	2336
18b	7.34	1.22	5657	1.14	9.4	5993
18c	7.34	0.66	10,000	1.14	5.5	10,200

In the second step, the poly(isoprene) prepolymer **(18b)** was deprotonated by titrating with trityl potassium and converted into macroinitiators **(19b)**. In case of under titration, the fast proton exchange between the protonated and deprotonated chain ends compared to the slow propagation reaction ensures homogeneous growth of all chains.[2] The addition of ethylene oxide to the macroinitiators produces poly(isoprene-*b*-ethylene oxide) **(20b)**. The properties of the block copolymers are listed in Table 3.2. The molecular weight distribution and SEC eluogram of the prepolymer **(18b)** and block copolymer **(20b)** is shown in Figure 3.5. It is evident from the results that the amphiphilic copolymers have well defined block lengths without any homopolymer contamination.

Table 3.2: Molecular weight characterization of the block copolymers

Sample	$\overline{M}_n$ PEO block			SEC_{total}		$\overline{M}_w / \overline{M}_n$
	Calcd	NMR	SEC	$\overline{M}_n$	$\overline{M}_w$	
20a	5000	4000	4134	6600	8500	1.20
20b	11000	9800	10343	16000	18000	1.16
20c	2500	2420	2700	12700	15230	1.19

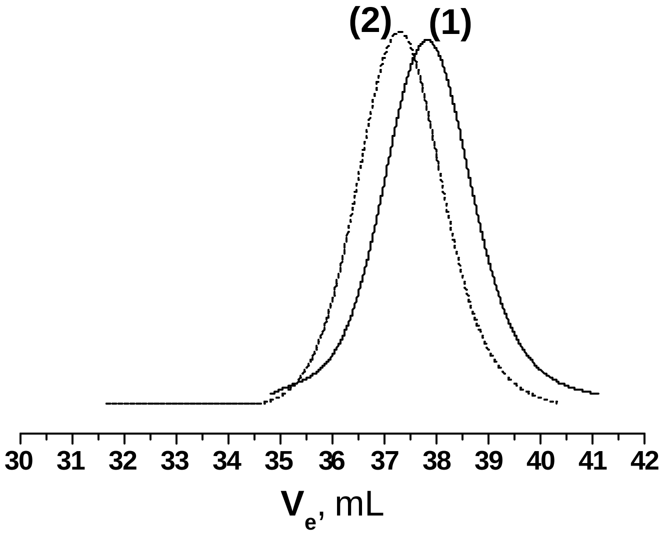


Figure 3.5. GPC eluogram of (1) poly(isoprene) prepolymer **18b** and (2) Poly(isoprene-*b*-ethylene oxide) **20b**

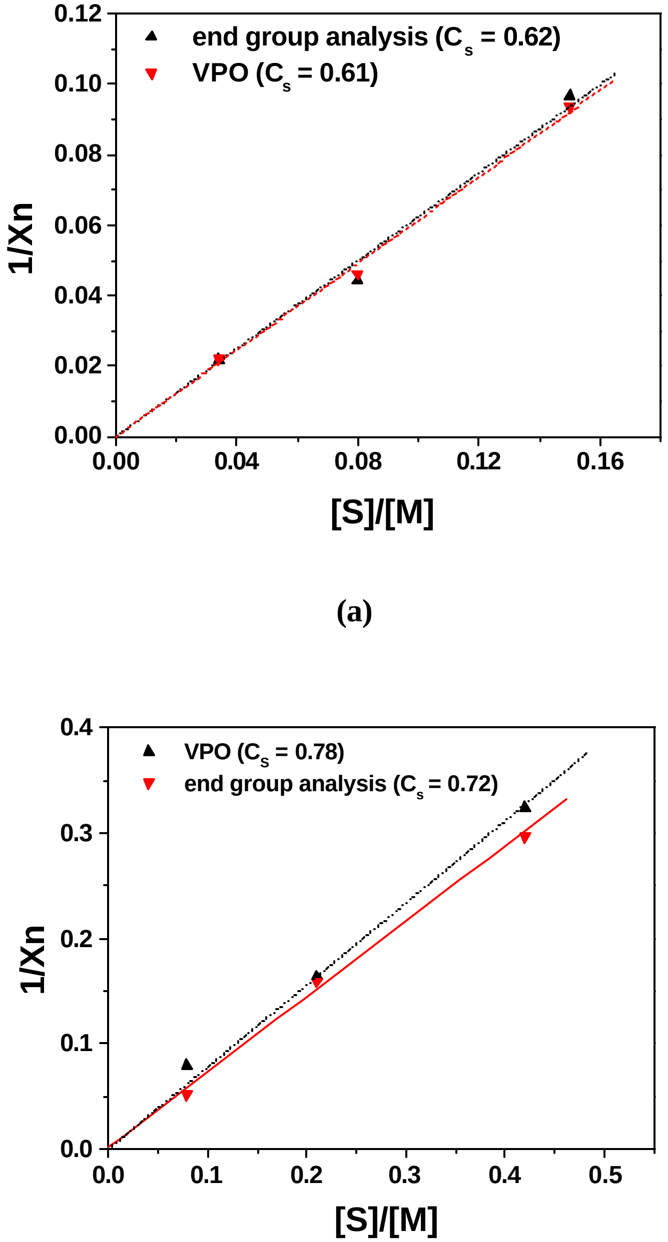
3.3.2 Synthesis of polymerizable steric stabilizers

The macrodiols were synthesized in two steps. In the first step, the carboxyl terminated prepolymer with different molecular weights were prepared according to reported procedures. [8,9] The results obtained are tabulated in Table 3.3. From the molecular weight data determined by VPO and end group analysis, the average functionality $\overline{f}_n$ was calculated. The values of f_n are close to 1.0 which indicates the degree of polymerization is close to the feed ratio.

Table:3.3 Properties of carboxyl terminated poly(alkyl methacrylate) prepolymers

Sample	[S]/[M]	$\overline{M}_n$ theory[(a)]	Acid value (mg KOH/g)	$\overline{M}_n$		$\overline{f}_n$
				End group	VPO	
21a	0.150	1050	54.2	1030	1060	0.97
21b	0.080	2000	24.8	2260	2170	1.01
21c	0.034	4700	12.3	4560	4520	1.01
21d	0.420	950	71.8	780	850	0.91
21e	0.210	1900	36.2	1550	1600	0.97
21f	0.079	5100	11.3	4960	4920	1.01

(a) Calculated by Mayo's equation



(a)

(b)

Figure 3.6. Plot of 1/Xn vs [S]/[M] for (a) MMA polymerization and (b) LMA polymerization in the presence of mecrcapto acetic acid

The relation between $1/X_n$ and [S]/[M] of the acid functionalized PMMA and PLMA is given in Figure 3.6. The slope gives the value of chain transfer constant Cs. The Cs values of MMA prepolymers determined by end group analysis and VPO are 0.62 and 0.61 respectively. These values are in agreement with that of reported values. For PLMA prepolymers, the Cs values are respectively 0.72 and 0.78 as determined by end group and VPO analysis respectively.

The polymerizable steric stabilizer poly(alkyl methacrylate)s with two primary hydroxyl groups and cyclic amide groups were prepared by the reaction of carboxyl terminated prepolymer (**21**) with TMP and caprolactam respectively (Scheme 3.2). The properties of the macrodiols and PLMA-CL are listed in Table 3.4 and Table 3.5 respectively. The hydroxyl values and the obtained functionalities of the macrodiol indicate that the terminal carboxyl group reacts quantitatively with TMP. To further confirm the presence of glycol group in the polymer chain, the macrodiols were reacted with phenyl isocyanate in THF at 70 °C to form the corresponding bis(urethane)s. A typical ^{1}H NMR of a bis(urethane) is shown in Figure 3.7. The signal intensity ratio of methyl protons (0.75-0.8 ppm) to phenyl protons (7.4-8.0 ppm) of the bis(urethane)s conclusively establishes the presence of two hydroxyl groups per chain. In the case of PLMA-CL macromonomers, the incorporation of caprolactam into the PLMA COOH was confirmed by determining acid value for the final polymer. The products **23a-f** did not show significant free acid groups. This indicates that the terminal carboxyl group reacts quantitatively with CL. The introduction of CL into the polymer chain was further established by ^{1}H NMR spectra (Figure 3.8) for samples **23d-f**. The ratio of signal intensities at 3.2 ppm corresponding to $-CH_2-(C\underline{\mathbf{H}}_2)_3-CH_2-$ of ε-caprolactam moiety to $-C\underline{\mathbf{H}}_2-CH_3$ protons of PLMA at 0.9–1.0 ppm conclusively indicates the quantitative incorporation of CL.

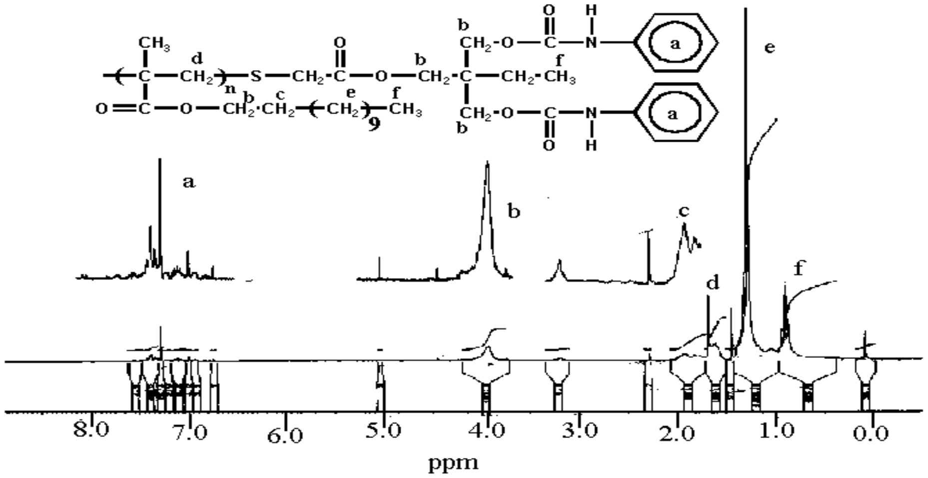


Figure 3.7. ^{1}H NMR of bis (urethane)s derivative obtained from macrodiol (**22f**)

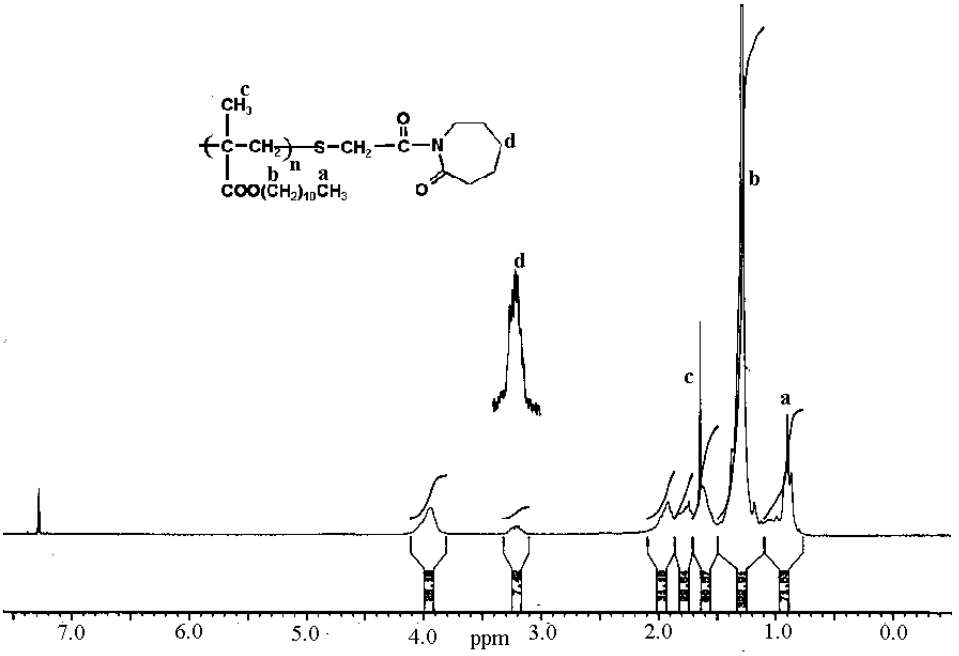
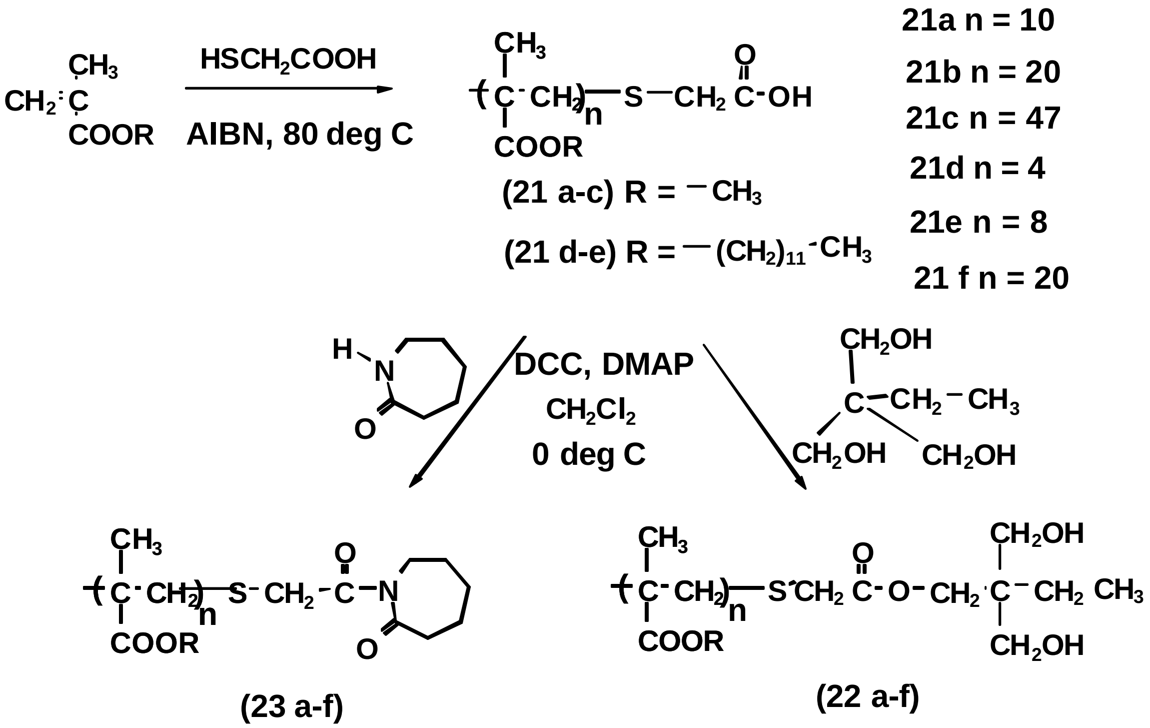


Figure 3.8. ^{1}H NMR of polymerizable stabilizer **(23e)**



Scheme 3.2. Synthesis of polymerizable stabilizers

Table 3.4: Properties of macrodiol stabilizer.

Macrodiol	Hydroxyl value mg KOH/g	$\overline{M}_n$		$\overline{f}_n$	
		End group	VPO	End group	^{1}H NMR$^{(a)}$
22a	124	905	960	1.9	-
22b	57	1960	1970	2.0	-
22c	29	3870	4340	1.8	-
22d	157	710	760	1.9	1.9
22e	76	1490	1670	1.8	1.9
22f	26	4300	4720	1.8	1.8

(a) from ^{1}H NMR of bis(urethane) derivatives.

Table 3.5: Properties of caprolactam terminated poly(alkyl methacrylate).

Sample	$\overline{M}_n$ (VPO)	% conversion[(a)]	$\overline{f}_n$ [(b)]
23a	-	100	-
23b	-	98	-
23c	-	99	-
23d	720	100	0.93
23e	1700	97	0.97
23f	4400	100	0.89
N-stearyl caprolactam[(c)(d)]	-	94	0.83

(a) Determined by acid value analysis
(b) Obtained by ^{1}H NMR
(c) Prepared by reacting stearic acid with CL in presence of DCC and DMAP
(d) Elemental analysis: Found/(cal); C: 76.5/ (76), N: 6.7/ (3.7), H: 12.2/ (11.9)

3.4 Conclusion

The synthesis of well defined amphiphilic copolymer by anionic polymerization method is demonstrated. These block polymers have narrow molecular weight distribution and did not contain any homopolymers. The calculated molecular weights are in good agreement with the results obtained by VPO, end group analysis and NMR. Acid functionalized poly(alkyl methacrylate)s were prepared by radical chain transfer polymerization and the carboxyl group was successfully converted into hydroxyl and lactams. The introduction of the functional groups was quantitative. These functional groups are capable of participating in particle forming polymerization and thus the hydrophobic poly(alkyl methacrylate) gets attached to the polymer surface. According to theories of steric stabilization, these macromonomers would provide better stability for the growing particles in the non-aqueous media.

3.5 References

1. *Dispersion polymerization in organic media*; Barrett, K. E. J., Ed.; Wiley: London, 1975.

2. Jurgen, A.; Andreas, P.; Lutz, W.; Dieter, R. *Macromolecules* **1997**, *30*, 1582-1586.

3. Quirk, R. P.; Ma, J. *J.Polym.Sci., Polym.Chem.Ed* **1988**, *24*, 2031.

4. Quirk, R. P.; Kim, J.; Kausch, C.; Chun, M. *Polymer.Int* **1996**, *39*, 3.

5. Kobayashi, S.; Uyama, H.; Choi, J. H.; Matsumoto, Y. *Polym.Int* **1993**, *30*, 265-270.

6. Liu, J.; Chew, C. H.; Wong, S. Y.; Gan, L. M.; Lin, J.; Tan, K. L. *Polymer* **1997**, *39*, 283-289.

7. Lascelles, S. F.; Malet, F.; Mayada, R.; Billingham, N. C.; Armes, S. P. *Macromolecules* **1999**, *32*, 2462-2471.

8. Corner, T. *Adv. Polym. Sci* **1984**, *62*, 95-142.

9. Rempp, P. F.; Franta, E. *Adv. Polym. Sci* **1984**, *58*, 1-53.

Chapter 4: Preparation of polyurethane particles by dispersion and suspension polymerization

4.1 Introduction

Polyurethanes are generally prepared by the reaction of diisocyanates with diols in organic solvents. Much of the polyurethanes produced are used for coatings and adhesive applications where they are used as solution in organic solvents. However, for special applications, there is an interest in preparing polyurethanes in particulate form. Polymers in particulate form can be prepared using heterogeneous polymerization techniques namely dispersion, emulsion and suspension. Of these, dispersion polymerization is a well known technique for producing polymer particles with controlled particle size and shape. Radical dispersion polymerization is, generally, method of choice for preparing polymer particles. Preparation of polymer particles via polycondensation is scarcely reported in the literature. Particularly, the synthesis of polyurethane particles by dispersion polymerization in non aqueous medium has not been reported thus far.

Conventionally, polyurethane particles are prepared by cryogenic grinding of thermoplastic polyurethanes [1] or by suspension polymerization of isocyanate terminated prepolymers in aqueous [2] or non-aqueous medium[3]. In none of these methods the control of particle size is possible. There is, however, only a solitary report on the particle forming polymerization of an isocyanate with a diol to produce polyurethane microspheres using amphiphilic block copolymer as steric stabilizer[4].

We, therefore, undertook an exploration of the dispersion polymerization of diisocyanate and diol with a view to delineate many interesting features of this novel process. Specifically, these are (i) relationship between the stabilizer structure and its effectiveness in dispersion polymerization (ii) control of particle size and shape (iii) kinetics and mechanism of polyurethane particle formation with respect to molecular architecture of the steric stabilizer (iv) generality of the reaction to different types of isocyanates and diols.

4.2 Experimental section

4.2.1 Materials

Lauryl methacrylate (LMA) (Aldrich) was stirred with CaH_2 (Aldrich) for 24 h and then passed through activated alumina. Mercaptoacetic acid (MAA) (Aldrich) was azeotropically distilled with benzene to remove traces of water followed by vacuum distillation. α,α'-Azoisobutyronitrile (AIBN) and trimethylolpropane (TMP) both procured from Aldrich were recrystallized from ethanol and acetone respectively. DABCO (diamino bicyclo [2,2,2] octane, E-Merck) was purified by sublimation at 80 °C Toluene, THF, n-hexane and cyclohexane were distilled over sodium wire. Dichloromethane and chloroform were dried over $CaCl_2$ and distilled. N,N'-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP) (Aldrich), 2-ethyl 1,3-hexanediol, (EHG) (Fluka), toluene diisocyanate (TDI), dibutyltin dilaurate (DBTDL) (E Merck), and paraffin oil heavy, (s.d.fine, India) were used as received.

4.2.2 General procedure for preparing polyurethane particles

Both dispersion and suspension polymerization technique were employed to synthesize polyurethane particles. A typical experimental procedure is given below.

4.2.2.1 Dispersion polymerization

4.2.2.1.1 Using poly(alkyl methacrylate) macrodiol stabilizer (22e)

Dispersion polymerization was carried out in a four-neck 250 mL round bottom flask fitted with a propeller stirrer, condenser, nitrogen inlet and a thermowell. Two types of stirrers [5] were used for this study namely a paddle stirrer with pitched blades (propeller stirrer) and a turbine stirrer (Rushton turbine, six blades on a disk). The macrodiol **(22e),** 0.75 g (5.03×10^{-4} mol) was dissolved in 25 g of paraffin oil and reacted with 0.11 g TDI (6.32×10^{-4} mol) in the presence of DBTDL (0.05 mol % wrt TDI and EHG) at 60 °C under an atmosphere of nitrogen. EHG 3.0 g (2.05×10^{-2} mol) and TDI 4.5 g (2.58×10^{-2} mol) were then slowly added to the isocyanate terminated prepolymer with a stirring speed 300 rpm. The reaction was continued till the complete disappearance of isocyanate groups. The polyurethane particle thus obtained was washed with hexane and dried under vacuum at room temperature for 4 h. Yield: 90 %, IR (KBr): 3350 (ν_{NH}), 1750 ($\nu_{C=O}$) ester, 1710 ($\nu_{C=O}$) urethane. ^{1}H NMR (acetone D_6): δ = 7.1-8.0 (m; -aromatic); 4.1-4.3(br; -COOCH$_2$); 1.1-1.5 (br; C$\underline{H}_2$) ; 0.75-0.8 (t; -CH$_2$-C$\underline{H}_3$)

4.2.2.1.2 Using poly(isoprene-b-ethylene oxide) (20c)

Into a four-neck 250 mL round bottom flask fitted with a turbine stirrer (Rushton turbine, six blades on a disk), condenser, nitrogen inlet and a thermowell, were added block copolymer **(20c)**, 0.75 g, DBTDL (0.05 mol % wrt TDI and EHG) and 25 g of paraffin oil. The reaction was stirred at 300 rpm at 60 °C under an atmosphere of nitrogen. EHG 3.0 g (2.05×10^{-2} mol) and TDI 4.5 g (2.58×10^{-2} mol) were then slowly added over a period of 30 minutes. The reaction was continued till the complete disappearance of isocyanate groups. The polyurethane particle thus obtained was washed with hexane and dried under vacuum at room temperature for 4 h. Yield: 90 %, IR (KBr): 3350 (ν_{NH}), 1750 ($\nu_{C=O}$) ester, 1710 ($\nu_{C=O}$) urethane. ^{1}H NMR (acetone D_6): δ = 7.1-8.0 (m; -aromatic); 4.1-4.3(br; -COOCH$_2$); 1.1-1.5 (br; C$\underline{H}_2$) ; 0.75-0.8 (t; -CH$_2$-C$\underline{H}_3$)

4.2.2.2 Suspension polymerization

4.2.2.2.1 Using poly(alkyl methacrylate) macrodiol stabilizer (22e)

Suspension polymerization was carried out in a conventional 100 mL emulsion kettle fitted with a turbine stirrer (Rushton turbine, six blades on a disk), condenser, nitrogen inlet and a thermowell. The macrodiol **(22e)**, 0.45 g (2.3×10^{-4} mol) was dissolved in 25 g of paraffin oil and reacted with 0.05 g TDI (2.9×10^{-4} mol) in the presence of DBTDL (0.05 mol % wrt TDI and EHG) at 60 °C under an atmosphere of nitrogen. Ethylene glycol 1.0 g (1.6×10^{-2} mol) and TDI 3.3 g (1.9×10^{-2} mol) were then slowly added to the isocyanate terminated prepolymer with a stirring speed 800 rpm. The reaction was continued till the complete disappearance of isocyanate groups. The polyurethane particles thus obtained were washed with hexane and dried under vacuum at room temperature for 4 h. Yield: 83 %.

4.2.2.2.1 Using poly(isoprene-b-ethylene oxide) 20c

Suspension polymerization was carried out in a conventional 100 mL emulsion kettle fitted with a turbine stirrer (Rushton turbine, six blades on a disk), condenser, nitrogen inlet and a thermowell. The block copolymer stabilizer **(20c)**, 0.45 g was dissolved in 25 g of paraffin oil and added DBTDL (0.05 mol % wrt TDI and EG). Ethylene glycol 1.0 g (1.6×10^{-2} mol) and TDI 3.3 g (1.9×10^{-2} mol) were then slowly added to the isocyanate terminated prepolymer with a stirring speed 800 rpm. The reaction was continued till the complete disappearance of isocyanate groups. The polyurethane particles thus obtained were washed with hexane and dried under vacuum at room temperature for 4 h.
Yield: 79 %

4.2.3 Analysis

Hydroxyl values of the macrodiols and isocyanate content of the prepolymer and polyurethane were determined according to ASTM methods D 1957-86 (1995) and D 2572-97 respectively. Detailed experimental procedure for determining hydroxyl value have been mentioned in Chapter 3, section 3.3.4 The isocyanate content was determined as follows. A known amount of sample was taken in 100 mL stoppered conical flask. 10 mL of dibutyl amine/toluene (1:10 v/v) was added and kept for 30 minutes. 50 mL of isopropanol was then added and titrated with standardized 0.5 N HCl. The isocyanate content (%) was calculated from the formula: $(BR\times N\times 4.2)/W$. Where, BR = burette reading, N = normality of HCl and W = weight of sample. All titrations were carried out using Metler DL 25 automatic titrator fixed with a glass electrode DG 111(for aqueous titration) and DG 112 (for non aqueous titration). Molecular weight of the macrodiol was determined by KNAUER vapour pressure osmometer in chloroform at 35 °C. IR spectra were recorded on a PE 16PC FT-IR spectrophotometer. ^{1}H NMR spectra were recorded on a 200 MHz Bruker AC 200 NMR spectrometer. Particle size and their distributions were measured using a Horiba LA-910 particle size analyzer. The polyurethane particles were dispersed in water containing 0.2 wt % Noigen X 100 (Dai-Ichi Krakaria Ltd., Pune, India), an alkyl phenol poly(ethoxy ether) surfactant having an HLB around 13-14. Particle size of polyurethane particles was also measured using Malvern photon correlation spectrometer, model 4700, with a vertically polarized 25mw He-Ne laser as light source. Scanning electron microscopy images was obtained using Leica (Stereoscan 440) scanning electron microscope (Cambridge, UK) at an accelerating voltage of 20 kV. Polyurethane particles dispersed in hexane was dried on aluminum stub and then coated with gold.

4.3 Results and discussion

Dispersion polymerization of EHG and TDI was initially carried out using 2-10 wt % commercially available dispersing agents. These include AOT (RO_2CCH_2 CH (SO_3 Na)--CO_2R; R=2-ethylhexyl), Emerest 2622 (PEG 200 dilaurate), silvet 222 poly(alkylene oxide) modified poly(dimethylsiloxane)s, Pluronic L 70 poly(ethylene oxide-b-propylene oxide) and di-n-hexadecyl phosphate. All polymerizations were unsuccessful as the whole mass was coagulated. These dispersents have a disadvantage of having either poor solubility of the stabilizing component or fewer number of anchoring component. As a result, they were unable to provide an adequate steric barrier to prevent agglomeration. Therefore, it is essential to use well defined steric stabilizers to prepare polyurethane in particulate form. The process of polyurethane particle formation is new and therefore it requires optimization of reaction conditions that generally affects the particle forming polymerization process.

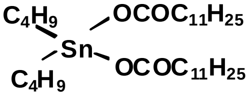
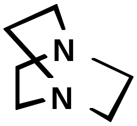
4.3.1 Standardization of reaction conditions

Generally the reaction between any diisocyanate and diol, the rate of reaction is controlled by the choice of catalyst and the polymerization temperature. In particle forming polymerization, the ratio of monomer/dispersion phase ratio influences the particle growth. Also, when dispersion polymerization carried out using a polymerizable stabilizer, the reactivity of the functional group attached to the stabilizing component is very important to get adequate stabilization. These parameters were optimized and the results are discussed in the following sections.

4.3.1.1 Catalyst type and polymerization temperature

The reaction between TDI and EHG were carried out in paraffin oil using 5 wt % macrodiol steric stabilizer **(22e)**. Two types of catalysts DBTDL and DABCO were chosen and the polymerization was carried out at three different temperatures. The isocyanate content was determined for both the polymer particles and the dispersion medium at various conversion levels and the values after 4 h are listed in Table 4.1. The results clearly indicate that the tin catalyst (DBTDL) is more efficient for the isocyanate-hydroxyl reaction.

Table 4.1: Effect of catalyst type on polyurethane particle formation

Catalyst		Isocyanate content(a)(%) at			Yield (%)
		35 °C	50 °C	60 °C	
 **DBTDL**	Particle	2.4	2.0	0.9	92
	Filtrate	0.65	0.51	0.12	
	Particle size(b) range (μ)	7-50	7-38	2-22	
 **DABCO**	Particle	3.3	3.1	2.5	61
	Filtrate	2.2	2.6	2.4	

(a) after 4 h
(b) observed by optical microscope for 50 particles

Earlier studies on the catalytic activity for isocyanate-hydroxyl reaction reveals that tin compounds are 10 times more powerful as catalyst than tertiary amines in the absence of added water[6]. The tertiary amine catalyzed isocyanate-hydroxyl reaction involves the formation of activated ionic complex[7]. The formation of such complex is not possible in organic medium of low dielectric constant. Furthermore, solubility of DABCO in paraffin oil is poor compared to DBTDL. The solubility of DABCO in paraffin oil was determined as follows[8]. A known quantity of DABCO was added to 25 g paraffin oil and the contents were stirred well using a magnetic stirrer at 60 °C, for about 8 h. The contents were filtered using G3 sintered glass crucible. A weighed quantity of the filtrate was then titrated against standardized HClO$_4$ solution. The solubility of DABCO in paraffin oil was found to be 0.4 wt%. Similarly, the solubility of DABCO in EHG was also determined and found to be 4.1 wt %. On the other hand, DBTDL was freely soluble in both paraffin oil and EHG. Therefore, it is evident that the catalyst DABCO was not available in the dispersion medium at the onset of primary particle formation. This reduces the number of particles formed and therefore, the yield of free flowing polyurethane particles were low

The analysis of the filtrate by IR, shows the presence of isocyanate groups (2260 cm^{-1}) and did not show any urethane group (1690-1720 cm^{-1}). This undoubtedly shows the unreacted isocyanates in the filtrate is from the free monomer (TDI) and not from the urethane oligomer. The amount of free TDI in DABCO catalyst polymerization is significantly higher and, therefore, reduces the yield of polyurethane particles. Besides catalytic activity, this study unequivocally demonstrates the polymerization takes place inside the particles once the primary particles are formed.

After complete conversion, the particles obtained at different temperatures using DBTDL catalyst was analyzed for particle size and its distribution. The particle size (in microns) was 72 (2.9) 49 (2.1) and 8 (1.24) at 35 °C, 50 °C and 60 °C respectively. The value in parenthesis indicates particle size distribution. It is clear that the control of particle size ant its distribution is possible at high temperature. At low temperatures, the particle formation takes place rather slowly and, therefore, the particle size distribution is broad. Also, aggregation of primary polymer particles formed at low temperature is inevitable because of high free monomer concentration.

4.3.1.2 Monomer/dispersion medium (M/D) phase ratio

In this set of experiments, dispersion and suspension polymerizations were carried out in three different ratios of M/D phase. The results obtained are tabulated in Table 4.2.

Table 4.2: Effect of monomer/dispersion phase ratio on polyurethane particle formation(a)

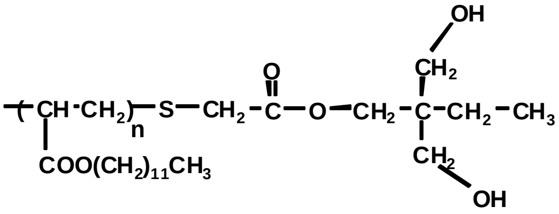
M/D ratio	Macrodiol stabilizer(b)				Block copolymer stabilizer(c)			
	Dispersion(d)		Suspension(e)		Dispersion(d)		Suspension(e)	
	Mean particle size (μ)	$\overline{D}_w / \overline{D}_n$	Mean particle size (μ)	$\overline{D}_w / \overline{D}_n$	Mean particle size (μ)	$\overline{D}_w / \overline{D}_n$	Mean particle size (μ)	$\overline{D}_w / \overline{D}_n$
1:3	13	1.37	23	1.8	32	1.4	78	2.2
1:6	22	1.35	37	1.72	58	1.6	102	(f)
1:12	72	(f)	96	(f)	(g)	-	(g)	-

(a) Polymerization was carried out using 5 wt% stabilizer concentration in paraffin oil
(b) Macrodiol stabilizer **(22e)**
(c) Poly(butadiene-b-ethylene oxide) M_n of poly(butadiene) component = 3500 and M_n of poly(ethylene oxide) component = 850. The samples were obtained from Prof. G Reiss, Mulhouse, France
(d) Carried out using EHG
(e) Carried out using EG
(f) Bimodal distribution
(g) lump formation

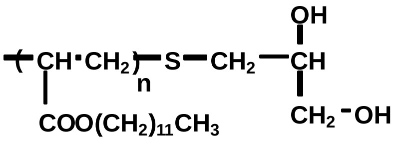
As the amount of dispersion medium increases, the particle size increases. At high levels of dispersion medium the particle formation is impaired severely. This is due to the fact that the increase in dispersion phase decreases the effective stabilizer concentration available for stabilization. In the case of macrodiol stabilizer, the effective grafting of the stabilizing component on the growing polyurethane particle decreases as the amount of dispersion phase is increased. On the other hand the rate of adsorption of block copolymer is low at high levels of dispersion medium. This is because the monomer concentration is very less. This phenomenon extends the particle formation stage and, therefore, increases the particle size. A similar observation was reported in the dispersion polymerization of MMA in aqueous alcohol media using PVP as steric stabilizer[9].

4.3.1.3 Functional groups reactivity

The effective incorporation of the stabilizing moiety to the growing particles relies on the reactivity of the functional group attached to it. To establish the role of reactivity of the functional groups on polyurethane particle formation, dispersion polymerization of TDI and EHG was carried out using macrodiol **(22e)** and macrodiol **(24)**. The synthesis of macrodiol **(22e)** is given in Chapter 3, Section 3.2.2.2. Macrodiol **(24)** was synthesized by polymerizing LMA (10.0 g, 3.9×10^{-2} mol) in the presence of thioglycerol (1.0 g, 9.2×10^{-3} mol) as chain transfer agent in 50 mL toluene at 70 °C. The macrodiol obtained had an average molecular weight 1850 (VPO). When macrodiol **(22e)** was employed as steric stabilizer spherical polyurethane particles with narrow particle size distribution were obtained. But, when macrodiol **(24)** was employed as stabilizer, the particles formed are not spherical and majority of the reaction mass was coagulated. This shows that macrodiol **(24)** was not effectively incorporated into the polymer backbone presumably due to the poor reactivity of the secondary hydroxyl group with isocyanates.



(22e)



(24)

Considering the influence of reactivity of the functional groups on polyurethane particle formation, dispersion polymerization was carried out in two steps. In the first step the macrodiol stabilizer **(22e)** was reacted with TDI to form an isocyanate terminated prepolymer which was subsequently reacted with an additional quantity of TDI and EHG. When all reagents were added to the macrodiol **(22e)** in a single step, the yields were low. This observation is ascribed to the fact that the chemical reactivity of the macrodiol towards TDI is lower when compared to EHG. Thus, the efficient inclusion of the macrodiol into the polyurethane backbone is essential for the formation of stable dispersions. The ratio of TDI/(**22**) is also an important factor in determining the final particle size of the polyurethane particles. For illustration, macrodiol **(22e)** was reacted with TDI in two different ratios. The properties of the polyurethane particles obtained from two different TDI/**(22e)** ratios are listed in Table 4.3.

Table 4.3: Dependence of particle size on TDI/(22e) ratio$^{(a)}$

Isocyanate/ **(22e)** ratio	Yield (%)	Mean particle size (μ)	$\overline{D}_w / \overline{D}_n$ (b)
Without stabilizer precursor	33	Irregular	
1.2	89	1.5	1.29
8.9	90	75	Bimodal

(a) Dispersion polymerization was carried out at using 10 wt% (**22e**)

(b) $D_w = \Sigma N_i D_i^4 / \Sigma N_i D_i^3$ and $D_n = \Sigma N_i D_i / \Sigma N_i$; where N_i and D_i are the frequency and the mean diameter of the polyurethane particles respectively.

The dependence of polyurethane particle size on TDI/**(22)** ratio can be understood as follows. At TDI/**(22e)** ratio = 8.9, both isocyanate terminated prepolymer and free TDI coexist in the reaction mixture. On account of reactivity reasons, TDI reacts faster with EHG. This phenomenon decreases the amount of macrodiol incorporation into polyurethane structure, leading to higher particle size. On the other hand, the amount of free TDI is negligible when TDI/(**22**) ratio = 1.2, and, therefore, the prepolymer reacts efficiently with the added glycol resulting in higher macrodiol incorporation in polyurethane structure producing smaller polyurethane particles. It is also observed that at higher TDI/(**22**) ratio (8.9) the prepolymer formed precipitates out since it is not soluble in the dispersion medium. This could be due to the fact that in presence of excess free TDI in the reaction mixture allophanate networks are formed[10]. As a consequence the prepolymer is not available for reaction.

4.3.2 Factors influencing polyurethane particle formation

A successful dispersion polymerization is accomplished by suitable choice of steric stabilizer and dispersion medium. The effect of these factors in polyurethane particle formation has been studied in detail and is discussed below.

4.3.2.1 Nature of steric stabilizer

The effect of molecular weight and concentration of the macrodiol stabilizer on polyurethane particle formation were studied at TDI/(**22**) ratio = 1.2 using both Rushton turbine stirrer and propeller stirrer at different agitation speed. The results are shown in Table 4.4. As the concentration of the macrodiol is increased, the particle size decreases and produces more uniform particles. This is expected because a higher stabilizer concentration stabilizes a larger total surface area and, therefore, produces a larger number of smaller particles. In addition, higher stabilizer concentration prevents coagulation of the initially formed nuclei and reduces the particle size and its distribution. The coagulation or aggregation of particles can be further controlled by increasing the agitator speed or by the choice of suitable agitator. This illustrates the observed fact that at a given concentration the particle size decreases with increasing agitator speed or its type. It is also observed that an increase in molecular weight of the macrodiol stabilizer decreases the particle diameter for a given stabilizer concentration and the particle size distribution becomes narrow at higher stabilizer concentration. We believe that upon increasing in the size of the stabilizing moiety results in better coverage of the particles. This provides effective stabilization at the onset of nucleation resulting in smaller particles. This observation is in accordance with the principles of steric stabilization[11].A similar observation has been reported for particle forming radical dispersion polymerization using reactive stabilizers[12].

Dispersion polymerization was carried out using various concentrations of amphiphilic block copolymer with different ratios of hydrophilic and hydrophobic components and the results are presented in Table 4.4.

Table 4.4: Effect of Molecular weight and concentration of steric stabilizer on polyurethane properties.

Polymerizable				Polymeric			
Stabilizer	Conc.[(a)] (wt %)	Mean particle size (μ)	$\overline{D}_w / \overline{D}_n$	Stabilizer	Conc.[(a)] (wt %)	Mean particle size (μ)	$\overline{D}_w / \overline{D}_n$
Nil	aggregated			Nil	aggregated		
(22d)	2	62	(b)	**2a** **(n_A=0.63)**	2	145	(b)
	5	35	(b)		3	124	(b)
	10	14	2.9		4	109	(b)
	15	17	1.52		5	87	(b)
(22e)	2	51	1.55		10	46	1.60
	5	13	1.37	**20b** **($n_{A=}$0.65)**	2	76	(b)
	10	1.5	1.29		3	61	(b)
	15	1.9	1.31		4	47	(b)
	15[(c)]	1.4	1.30		5	32	1.41
(22f)	0.5	132	(b)		10	24	1.45
	1	35	(b)	**(20c)** **($n_{A=}$0.21)**	2	8.6	1.40
	2	3.9	1.41		3	6.1	1.36
	5	2.3	1.34		4	2.8	1.28
	10	1.1	1.20		5	1.2	1.19
	10[(c)]	0.8	1.20		10	0.8	1.21
	10[(d)]	0.22	1.16	$\nu_A=N_A/(N_A+N_B)$ where N_A and N_B are the number of segments in the anchor and soluble block respectively			
	15	1.5	1.22				
	15[(c)]	1.2	1.21				
	15[(d)]	0.18	1.24				

(a) Based on urethane forming reactants.
(b) Bimodal particle size distribution
(c) Paddle stirrer speed 1000 rpm
(d) Rushton stirrer speed 1000 rpm

As expected the particle size decreases with increase in stabilizer concentration. It is also observed that the segment length of the block copolymer greatly affects the polyurethane particle formation. Here, stabilization occurs through physical adsorption of the anchor segment of the block copolymer to the growing polyurethane particles. The nature of adsorption depends strongly on the anchor fraction, $\nu_{A.}$ According to theoretical predictions, adsorption increases with the increase in segment length of the anchor block. If the size of the anchor segments is increased beyond an optimal value, the adsorbed amount decreases, since the long anchor block lie flat on the surface, leaving less place for other chains to adsorb[13]. Furthermore, one should also consider the formation of micelles with the increase in segment length of the anchor block. It is believed that the dissociation rate of micelles to free polymer chain in organic solvent is extremely low. Therefore, the stabilizer may not be available to stabilize the particles

4.3.2.1.1 Estimation of steric stabilizer in the polyurethane particles

During polyurethane particle formation the amount of stabilizer adsorbed or chemically linked to the particles has been estimated quantitatively for both macrodiol and block copolymer stabilizer.

The IR spectrum of the polyurethane particle obtained by using a macrodiol stabilizer shows both an ester (1750 cm^{-1}) and an urethane (1710 cm^{-1}) groups which provide support to the hypothesis that the macrodiol stabilizer participates in the urethane forming reaction. In addition, a control experiment in the absence of macrodiol stabilizer resulted in immediate coagulation leading to lump formation. These two factors unequivocally show that the macrodiol takes part in the polymerization. To quantify the amount of macrodiol stabilizer grafted to the polyurethane particles during particle formation, a controlled acid hydrolysis procedure was followed[14]. Under specified conditions, hydrolysis of polyurethanes with ester groups leads to complete and selective hydrolysis of the ester groups leaving the urethane linkages largely unaffected. In the present study also, we observed the hydrolysis is specific as the ^{13}C NMR of the hydrolyzed product shows both urethane carbonyl (153 ppm) and carboxylic acid carbonyl (178 ppm). (Figure 4.1)

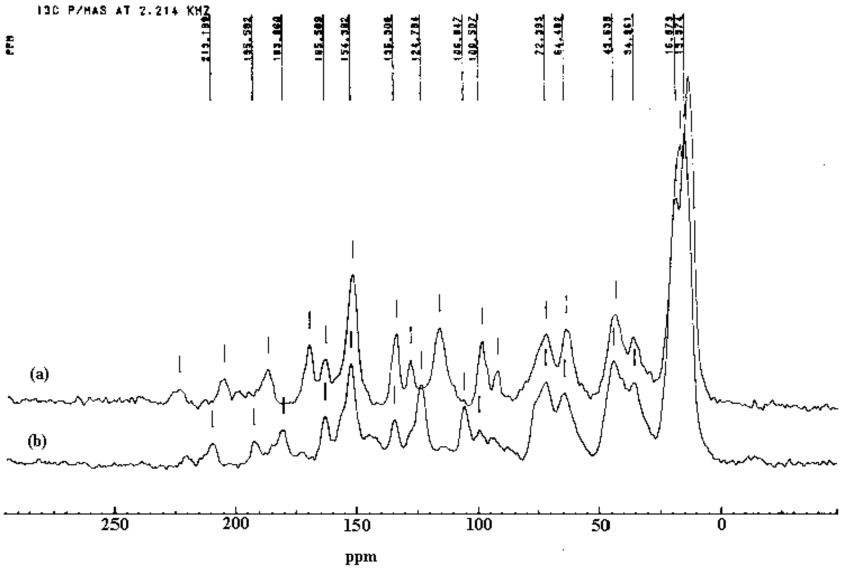


Figure 4.1. ^{13}C NMR of polyurethane particles (a) neat (b) after acid hydrolysis

However, we were unable to isolate the carboxyl group terminated poly(lauryl methacrylate) which is the product of hydrolysis of the stabilizer fragment. Therefore, we decided to establish the amount of macrodiol reacted during the prepolymer formation by analyzing the free isocyanate content. It was found that macrodiols (**22d-22f**) react completely with TDI (Figure 4.2). Also, the isocyanate terminated stabilizer precursor was isolated and characterized by ^{1}H NMR. The ratio of signal intensities of aromatic protons(7.4 - 8.0 ppm) to the methyl protons of poly(lauryl methacrylate) segment (0.75-0.8 ppm) suggest that the macrodiols have reacted completely with the added TDI. Hence, it is reasonable to assume that the macrodiol is incorporated into the polymer during polyurethane particle formation. In addition, after particle formation, the filtrate was examined by IR. The absence of hydroxyl and ester functionality further implies the complete incorporation macrodiol into the polyurethane particles.

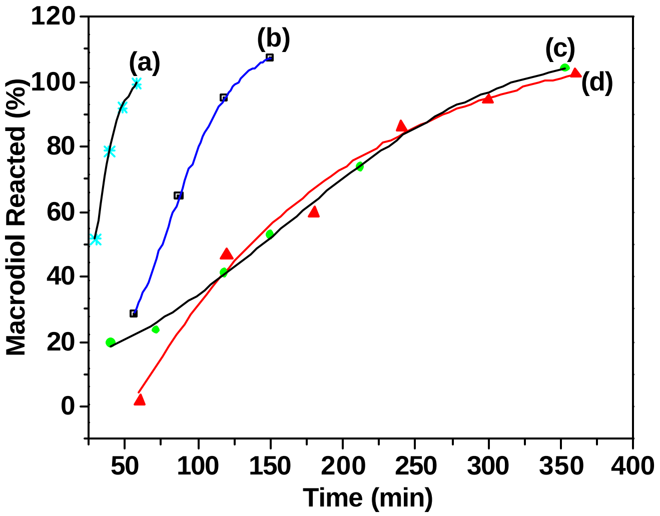
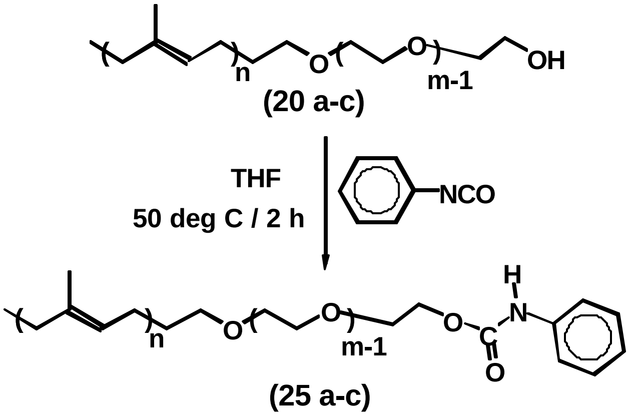


Figure 4.2. Reactivity of macrodiol with TDI (a) macrodiol (**22e**) (TDI/(**22e**) ratio = 8.9); (b) macrodiol (**22d**); (c) macrodiol (**22e**); (d) macrodiol (**22f**). Curves (b),(c),(d) represents the reactivity of respective macrodiols at TDI/macrodiol ratio = 1.2



Scheme 4.1: Preparation of protected block copolymer from stabilizer

In case of steric stabilization by block copolymers, several modes of stabilizer anchoring are possible. These include adsorption, absorption and grafting[15]. It is difficult to distinguish the modes of anchoring experimentally. However, there are reports which describe attempts to elucidate the different modes of anchoring[16,17]. When amphiphilic block copolymer stabilizers are used to stabilize polyurethane particles, besides physical adsorption grafting is also possible through the reaction between the free hydroxyl group of the stabilizer and the isocyanate groups of the growing particles. The amount of grafting was calculated indirectly by using a protected stabilizer that was obtained when the stabilizer was reacted with phenyl isocyanate. (Scheme 4.1) It was found that the protected block copolymer also stabilizes the polyurethane particles. Nevertheless, the amount stabilizer remaining on the particle surface was lower. (Table 4.5). This could be due to chemical reaction between the free hydroxyl group of the stabilizer **(20c)** with the isocyanate group.

Table 4.5: Amount of steric stabilizer remaining on polyurethane particles(a)

Stabilizer		Mean particle Size (μ)	Stabilizer amount (wt %) in dispersion medium(b)	Stabilizer remaining on particles (wt%)
Type	Feed (wt %)			
2c	5	0.9	3.6	1.0
2c	10	0.3	7.4	1.9
2c Protected	10	0.5	8.1	1.5

(a) Dispersion polymerization was carried out in cyclohexane

(b) Determined gravimetrically. The residue was examined by IR and confirmed the presence of stabilizer moiety and absence of unreacted monomers.

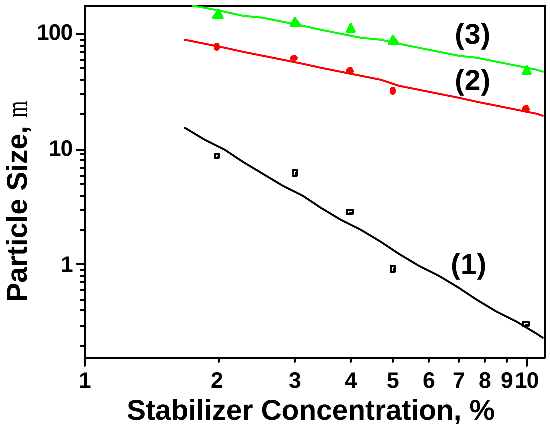


Figure 4.3: Double logarithmic plot of particle size vs stabilizer concentration (1) stabilizer **(20c)** slope = -0.92; (2) stabilizer **(20b)** slope = -0.81; (3) stabilizer **(20a)** slope = -0.72.

The physical adsorption of the block copolymer stabilizers is further evident from the double logarithmic plot of particle size vs stabilizer concentration. (Figure 4.3) The slope obtained for these block copolymers suggests that the particle formation followed an adsorption mechanism[18]. On the other hand, the values of such slope obtained for macrodiol stabilizer **(22f)** is found to be -0.51 (computed form the values given in Table 4.4). For macrodiols **(22d)** and **(22e)** the slope values are -0.73 and -1.82 respectively. Although, these values suggest that the macrodiols **(22d)** and **(22e)** did not take part in the grafting reaction, we could not isolate any physically adsorbed stabilizer. The reason could be that the macrodiols **(22d)** and **(22e)** have short stabilizing component compared to macrodiol **(22f)**. This allows aggregation of primary particles although the macrodiols are grafted. We believe, for this reason, the slope values did not reflect the grafting mechanism. It is worth pointing out here that dispersion polymerization carried out using a polymerizable stabilizer, where the mechanism of stabilization is completely by grafting, gave a slope value of -1.71 (computed from Table 2 of ref [12]). Furthermore, dispersion polymerization carried out using a block copolymer stabilizer, where the mechanism of particle formation is predominantly physical adsorption, a slope value of -0.12 (computed from Table 1 of ref [19]) has been reported. Therefore, predicting the mechanism of stabilization through the slope values obtained by the double logarithmic plot must be regarded to some extent ambiguous.

4.3.2.2 Dispersion medium

In dispersion polymerization, the stabilizer, monomer and catalyst employed should be soluble in the dispersion medium and it should be a non solvent for the polymer formed. Accordingly, dispersion polymerization of EHG and TDI was carried out in various dispersion medium using both macrodiol and block copolymer stabilizers. The results are presented in Table 4.6. The result shows that there is a significant variation in particle size and particle size distribution as the solvency of the dispersion medium is altered. Since isooctane is a non- solvent for polyurethanes, the nucleation occurs very early. This results in larger number of smaller particles with narrow particle size distribution. Further increase in solvency increases the particle size to certain extent and particle formation is impaired when the dispersion medium becomes a good solvent for the polyurethane particles.

Table 4.6: Effect of solvency on PU particle formation(a)

Solvent		Solubility Parameter(b) $(Mpa)^{1/2}$	Macrodiol stabilizer			Block copolymer stabilizer		
			η_{inh}(c)	Mean particle size (μ)	$\overline{D}_w / \overline{D}_n$	η_{inh}(c)	Mean particle size (μ)	$\overline{D}_w / \overline{D}_n$
Isoocatane		13.5	1.1	1.7	1.23	1.0	0.4	1.19
n-hexane		14.9	1.3	2.0	1.20	-	-	-
Cyclohexane		16.8	1.7	1.9	1.18	1.5	0.9	1.18
CCl_4		17.6	(d)	nd	nd	-	-	-
Toluene		18.2	0.8	(e)	-	nd	(e)	-
Acetone		20.3	1.0	(e)	-	-	-	-
Hexane / Toluene mixture(f) (wt/wt)	20/80	17.59	(d)	14.7	Broad	-	-	-
	40/60	16.95	(d)	nd	nd	-	-	-
	50/50	16.6	3.1	5.4	Broad	-	-	-
	70/30	15.96	2.3	2.0	1.60	-	-	-

(a) Dispersion polymerization was carried out at using 5 wt% stabilizer
(b) Ref[21]
(c) Inherent viscosity were obtained for 0.5 wt % sample in DMF at 30 °C
(d) Some of the particles were not spherical and were not soluble in DMF
(e) No particle formation (solution polycondensation)
(f) Solubility parameter of liquid mixtures was calculated according to ref[20]
nd denotes not determined

Two phenomena occur concurrently when the solvency is altered. (1) the nucleation stage is protracted because, the oligo urethanes are soluble in the dispersion medium and tend to aggregate sooner it becomes a primary particle with other nuclei or existing particle and (2) the stabilizer chain conformation is greatly affected. The stabilizer would not have the same extended configuration in toluene and acetone when compared to aliphatic hydrocarbons. When hexane is mixed with toluene spherical particles were obtained. This further supports the role of chain conformation in stabilizing the incipient primary particles. Furthermore, cyclohexane and hexane/toluene (1:1) mixture have the same solubility parameter but the particle size and particle size distribution obtained from the both the cases varies significantly. This is again due to the chain conformation of the stabilizer in both the cases. A similar observation was reported by Ober and Lok who concluded that the correct polarity alone is not sufficient to produce monodisperse particles and the polymerization must also depend on the interaction of the solvent and the stabilizer [20].

The nature of dispersion medium not only affects the particle size and particle size distribution, but also, the molecular weight of polyurethane particles. Studies on the radical dispersion polymerization by many researchers have shown that the molecular weight of the polymer particle increases with the increase in solvency of the dispersion medium. This was attributed to gel effect, as a result of monomer partitioning[22-25]. In the present study also, as the solvency of the dispersion medium is increased, the primary particles formed, which are presumably oligourethanes, swells in the dispersion medium.

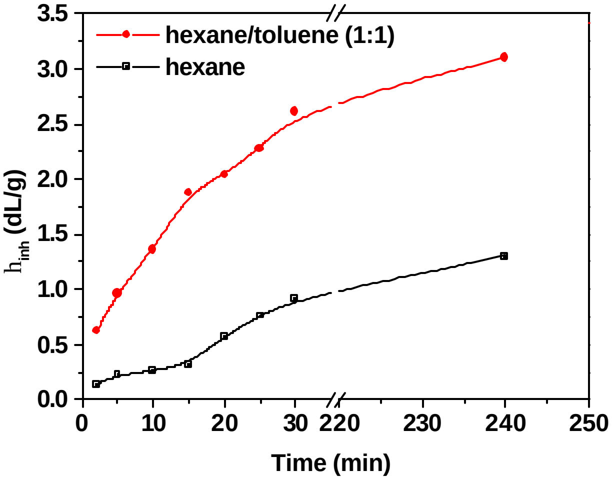


Figure4.4: Dependence of η_{inh} on the nature dispersion medium

This allows the monomers to partition from the dispersed phase to the particle phase. In short, there is a gel effect when the solvency is increased. This leads to the formation of polyurethane particles with higher molecular weight. One can argue at this juncture, the occurrence of gel effect in aliphatic hydrocarbon medium which is more favorable for the partitioning of monomers. However, the nucleation and subsequent primary particle formation stage is very early in aliphatic hydrocarbon media and does not allow the monomer to partition between the particles and dispersion medium. In such a case, all particles are formed in the continuous phase and there is no growth inside the polymer particles. An indirect evidence of swelling can be seen from the particle size of polyurethane particles dispersed in neat hexane and toluene and also in the presence of EHG. (Table 4.7). It can be further seen from the viscosity vs time plot (Figure 4.4) of the dispersion polymerization of EHG and TDI in hexane and hexane / toluene mixture that the molecular weight is higher when the solvency of the dispersion medium is increased.

Table 4.7. Particle size distribution$^{(a)}$ (volume %) of polyurethanes$^{(b)}$ in hexane and toluene.

Solvent	Particle counts in microns by volume %					
	0-1	1-2	2-5	5-8	8-15	>15
Hexane	(c)	11.2	87.6$^{(d)}$	1.2	(c)	(c)
Hexane+EHG	(c)	4.6	74.8	20.6	(c)	(c)
Toluene	18.9	38.1	32.4	8.8	3.7	(c)
Tolene+EHG	38.3	12.1	10.4	6.4	17.6	15.2

(a) Obtained by using Malvern Photon Correlation Photometer, model 4700 with a vertically polarized 25 mw He-Ne laser as light source
(b) Polyurethane particles as mentioned in Table 4, n-hexane experiment
(c) No polymer particles in the specified range
(d) Majority of the particles between 2-3 microns

4.3.2.3 Mode of monomer addition.

The influence of initial monomer concentration on particle size and its distribution is shown in Table 4.8. The results show that the initial monomer concentration significantly affects the polyurethane particle formation. The increase in particle size as a result of increased monomer concentration is attributed to the solvency effects of dispersion medium as discussed earlier. Accordingly, one would expect the particle size of polyurethane obtained from experiment C to be more than experiment B. Nevertheless, the particle size obtained from experiment C is much less than experiment B. Furthermore, the particle size distribution is quite narrow in case of Experiment C. This indicates that the mode of monomer addition also plays a significant role in controlling the particle size and their distribution. In case of B, the presence of EHG at the onset of polymerization produces hydroxyl terminated stabilizer precursor. When TDI is added to the dispersion medium, the effective incorporation of stabilizer on the growing particles is less as compared to the isocyanate terminated stabilizer precursor. This leads to the poor stabilization of the primary particles and forms higher particle size. In case of C, the experiment is carried out at 30 °C initially in the presence of isocyanate terminated stabilizer precursor, EHG and TDI. The presence of TDI at the early stages of polymerization makes the stabilizer precursor isocyanate terminated and obviously the stabilizer incorporation on to the particles is better than experiment B.

Table 4.8. Effect of initial monomer concentration on polyurethane particle formation[(a)].

Experimental conditions	Solubility parameter (Mpa)^{½}	Mean particle size (μ)	$\overline{D}_w / \overline{D}_n$
A	14.9	2	1.20
B[(b)]	15.4	118	Broad
C[(c)]	16.8	14	1.24

(a) Dispersion polymerization was carried out in hexane using 5 wt% stabilizer (**22C**).

(b) After the formation of isocyanate terminated prepolymer, EHG was added at once and then TDI was added dropwise for a period of 30 min.

(c) After the formation of isocyanate terminated prepolymer, the temperature was reduced to 30 °C and then added EHG and TDI together. The reaction was continued at 30 °C for 1 h then for 3 h at 60 °C

4.3.3 Kinetics and mechanism of polyurethane particle formation

The kinetics of polyurethane particle formation by both dispersion and suspension polymerization was investigated and the results are compared with precipitation and solution polymerization. Earlier reported studies on the rates of catalyzed isocyanate-hydroxyl reaction in organic solvents follows a second order kinetics and the rate constant is given by the equation[26]:

$$k_2 t = \frac{2.3.03}{a^2}\log\frac{x}{a-x} + \frac{1}{a(a-x)} + k$$

a = initial concentration isocyanate

x= concentration at time t

This simplified treatment is only useful for comparison of rates of heterogeneous polymerization with solution polymerization and does not reflect the complexity of particle forming polymerization. For this study dispersion and suspension polymerizations were carried out in parffin oil using both macrodiol **(22f)** and block copolymer (**(20c)**) stabilizers. Precipitation polymerization (polymerization without any stabilizer) was carried out in paraffin oil and solution polymerization was carried out in N-methyl-2-pyrrollidone (NMP). The rate of all polymerization was followed by the conversion of isocyante with time (Figure 4.5) and the rate constant was determined by the plot of $[NCO]_0/[NCO]$ vs time. The slope of the line divided by the initial concentration of isocyanate gives the rate constant, k_2 (Table 4.9)

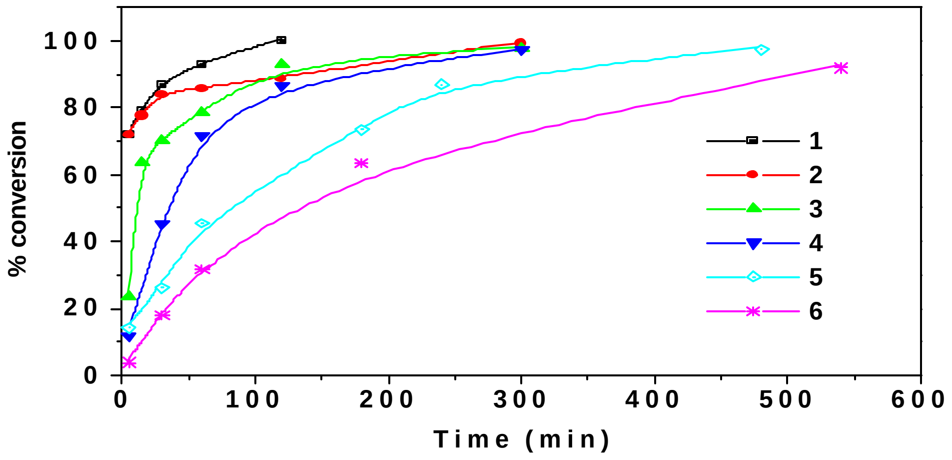


Figure 4.5: Isocyanate conversion (%) with time(1) Solution polymerization; (2)dispersion polymerization using macrodiol (**22f**); (3) suspension polymerization using macrodiol (**22f**); (4) Precipitation polymerization; (5)dispersion polymerization using block copolymer (**20C**);(6) suspension polymerization using block copolymer (**20C**)

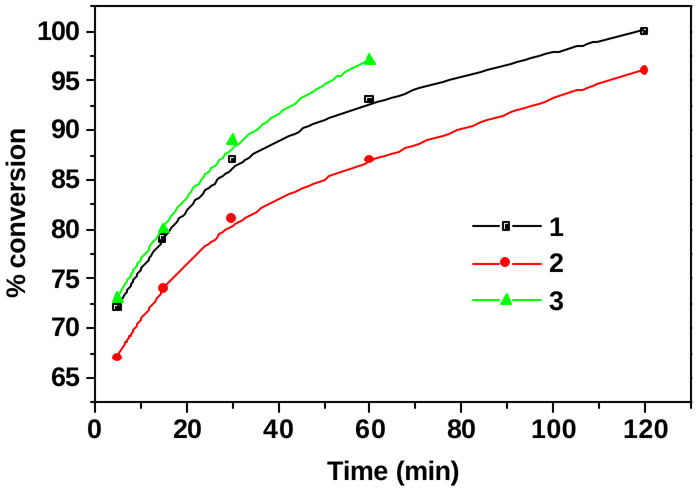


Fig 4.6: Isocyanate conversion (%) with time in different dispersion medium (1)cyclohexane/toluene/NMP (60/35/5); (2)paraffin oil (3)isooctane

Table 4.9: Rate constants for polyurethane formation$^{(a)}$ **by various polymerization techniques**

Polymerization	Stabilizer	k_2 mol^{-1} min^{-1}
Dispersion	Macrodiol	1.76
	Macrodiol$^{(b)}$	1.92
	Macrodiol$^{(c)}$	4.10
	Block$^{(d)}$	1.01
Suspension	Macrodiol	0.68
	Block	0.71
Precipitation	-	1.23
Solution$^{(e)}$	-	3.80

(a) Dispersion polymerization carried out in paraffin oil using 5 Wt % stabilizer **(22f)**

(b) Dispersion medium - isooctane

(c) Dispersion medium - cyclohexane/toluene/NMP (60/35/5)

(d) Stabilizer (2c)

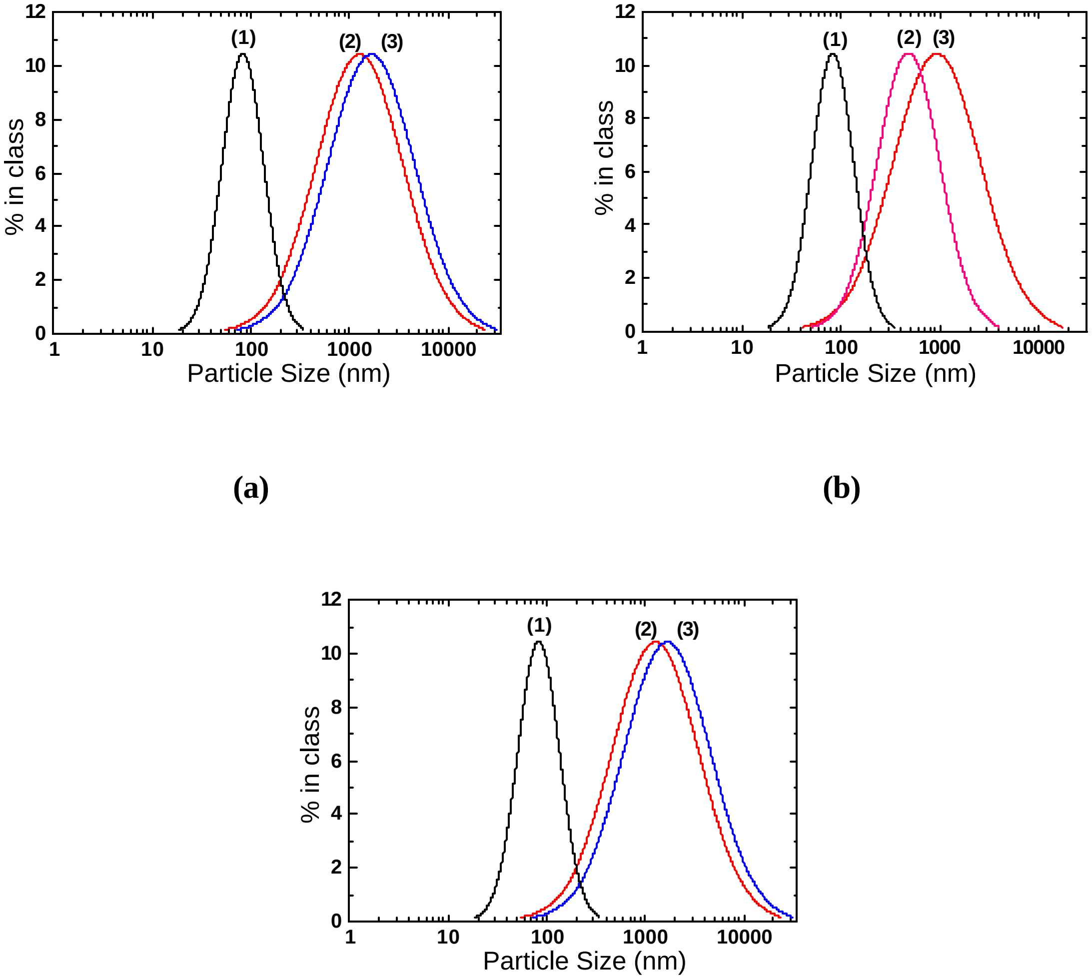
(e) Carried out in NMP

Many studies on the kinetics of dispersion polymerization reveals that the rate constants for dispersion polymerization are much higher than the solution polymerization[27-32]. Nevertheless, in the present study, upto 70 % conversion the rates of solution and dispersion polymerization are similar. Thereafter, the rate of solution polymerization is higher. This observation is unusual in dispersion polymerization kinetics. In the kinetic investigation reported earlier for radical and ionic dispersion polymerization, the particle formation has been shown to take place both in dispersion medium and in the particle phase. However in the present study the particle formation is exclusively in the particle phase as described in section 4.3.1.1. This clearly shows that after the formation of primary particles, the rate of polymerization is dictated by the diffusion of monomer in the particle phase. For this reason, the rate of dispersion polymerization is equal to solution polymerization until particle formation stage. The initial nucleation stage was observed at 20 % conversion (at this stage the reaction mass turns turbid) and the particles were found to grow till 70% conversion. A detailed particle growth mechanism will be discussed later. In order to demonstrate the diffusion controlled kinetics of dispersion polymerization, the isocyanate-hydroxyl reaction was carried out using macrodiol stabilizer in two different dispersion medium namely isooctane and mixture of cyclohexane/toluene/NMP (60/35/5) (Figure 4.6). The rate constants for this polymerization are respectively 1.92 and 4.10. When dispersion polymerization was carried out in isooctane the particle formation is only in the continuous phase as isooctane is poor solvent for polyurethane. Conversely, when dispersion polymerization was carried out in the solvent mixture, the swelling of primary particles enables the diffusion of monomer more towards particle phase, causing the rate to increase.

The mode of particle stabilization also affects the kinetics of dispersion polymerization. The rate of dispersion polymerization is higher when macrodiol was used as stabilizer. The change in rate of dispersion polymerization with the type of steric stabilizer is more to be regarded as a result of change in size of the polymer particles rather than the nature of stabilizer. The rate of precipitation polymerization is almost similar to dispersion polymerization. This is obvious as dispersion polymerization is similar to precipitation polymerization except for the presence of added steric stabilizer. Such observation was reported in the radical dispersion polymerization of MMA in non aqueous medium.

The mechanism of polyurethane particle formation and subsequent stabilization has also been studied using both polymerizable and polymeric steric stabilizers. Three experiments were conducted in cyclohexane to establish the role of stabilizer concentration during particle formation. In the first and second experiments, a stabilizer concentration of 5 wt% and 10 wt% respectively, were added initially and dispersion polymerization was carried out. In the third case, dispersion polymerization was carried out using 5 wt% stabilizer initially. Once the primary particles are formed, further 5 wt% stabilizer was added in five installments. In case of macrodiol the isocyanate terminated stabilizer precursor was added. In all cases we observed the primary particles are formed within 2 min (< 20 % conversion). The growth of particles and their size distribution at various conversion levels for macrodiol stabilizer and block copolymer stabilizer are shown in Figure 4.7 and Figure 4.8 respectively. A typical scanning electron micrograph of the polyurethane particles obtained using both the stabilizers after complete conversion is shown in Figure 4.9.

This study clearly reveals that (a) the primary particles formed are stable initially and are stabilized well by the stabilizer. However, after 20 % conversion, the particle size distribution becomes broad and remains unchanged even after complete conversion (b) even excess amount of stabilizer added initially could not prevent the particle aggregation at later stages and (c) when preformed stabilizer is added gradually after the formation of primary particles, the particle size distribution is quite narrow upto 70% conversion. However, this phenomenon is not observed in the case of particle stabilization by block copolymers.



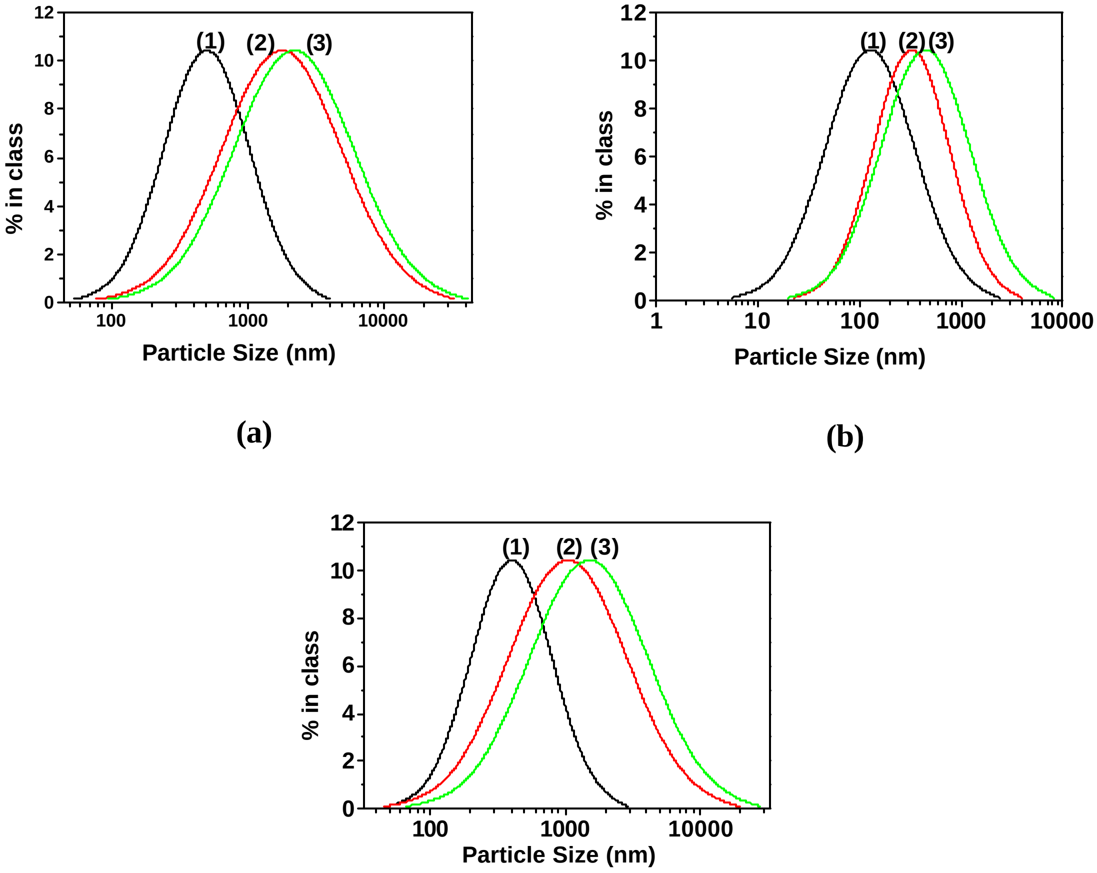
(a)

(b)

(c)

Figure 4.7: Particle size histograms of polyurethane particles

(a) 5 wt% stabilizer **(22f)**; (b)10 wt% stabilizer **(22f)** and (c)10 wt% stabilizer **(22f)** in batch. Curves (1) (2) and (3) represents particle size distribution obtained at 20%, 70% and 100% conversions respectively.



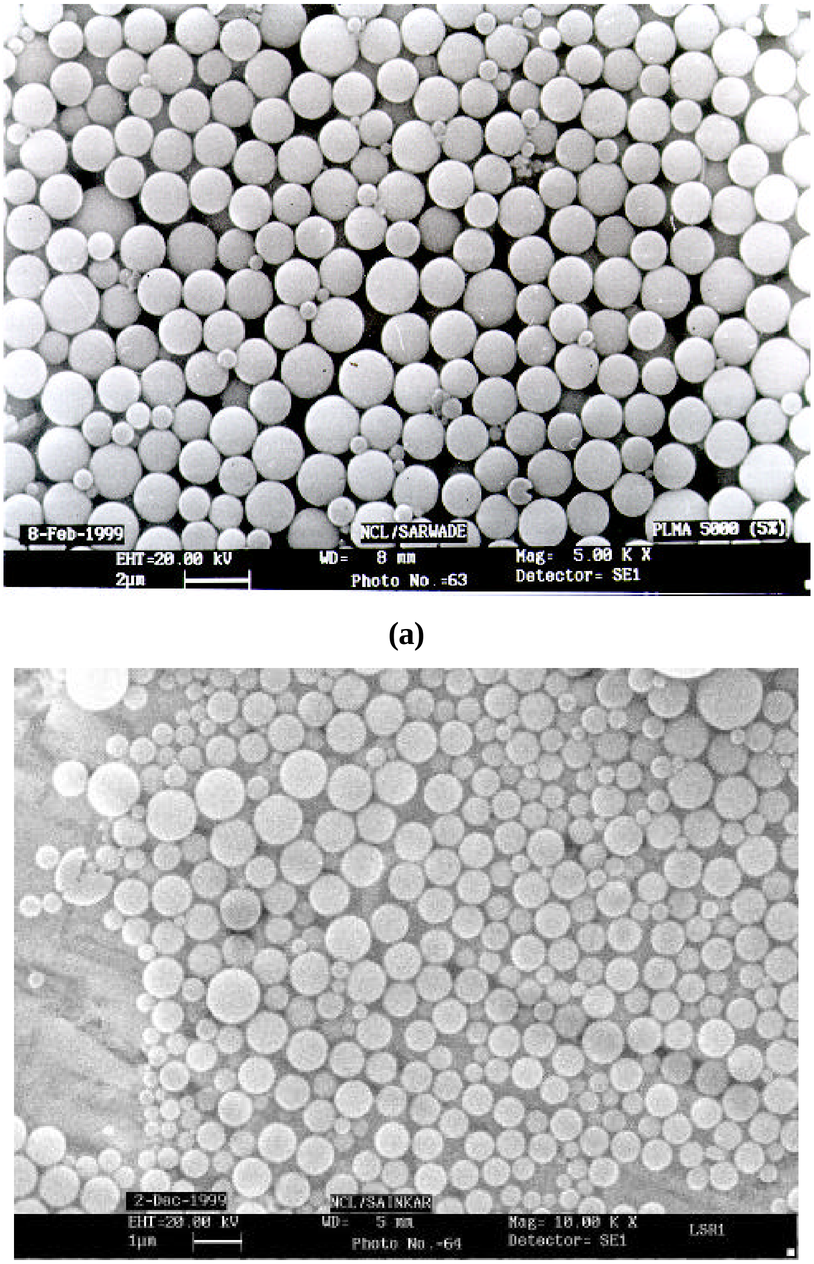
(a) (b)

(c)

Figure 4.8: Particle size histograms of polyurethane particles

(a)5 wt% stabilizer **(20c)**; (b)10 wt% stabilizer **(20c)** and (c)10 wt% stabilizer **(20c)** in batch. Curves (1) (2) and (3) represents particle size distribution obtained at 20%, 70% and 100% conversions respectively.

This mechanistic study clearly indicates the macrodiol stabilizer stabilizes the polyurethane effectively. This is because the stabilizing component is covalently linked to the particles during particle formation. Whereas, the block copolymer stabilizer, stabilizes the particle after the formation of primary particles by adsorption mechanism. Furthermore, the inevitable desorption of block copolymer from the particle surface leads to certain degree of particle aggregation.



(a)

(b)

Figure 4.9: SEM of polyurethane particles obtained using (a) stabilizer **(22f)** 10 wt % and (b) stabilizer **(20c)** 10 wt %

4.3.4 Polyurethane particles: Structure property relationship

To check the generality of polyurethane particle formation, various diisocyanates and diols were employed in dispersion and suspension polymerization using macrodiol and block copolymeric steric stabilizers.

4.3.4.1 Dispersion polymerization

One of the essential criteria for carrying out dispersion polymerization is the solubility of monomers in the dispersion medium. The solubility of various monomers generally used polyurethane synthesis is checked in aliphatic or aromatic hydrocarbons or their mixtures. (Table 4.10) Except EHG none of the diols are soluble in aliphatic or aromatic hydrocarbon solvents. Nevertheless, most of the diols when mixed with EHG are soluble in the dispersion medium. Dispersion polymerization was carried out using various monomer combinations and the results are presented in Table 4.11.

Table 4.10: Solubility of monomers in various dispersion medium

Monomer	Solubility[(a)]		
	Cyclohexane	Toluene	CH/TOL/ EHG[(b)]
Ethylene glycol	I(insoluble)	I	I
1,4-butane diol	I	I	I
1,6-hexane diol	I	I	S(soluble)
1,8-octane diol	I	I	S
1,4-cyclohexane diol	I	I	S
Cyclohexane dimethanol	I	I	I
PPG 650	I	S	S
PPG 1000	I	S	S
Polyester[(c)]	I	S	S
TDI[(d)]	I	S	S
IPDI	S	S	S
HMDI	S	S	S

(a) Solubility (1g in 10 mL) was checked both in room temp and at 65degC in the presence of stabilizer (5 wt. based on diol)

(b) Mixture of cyclohexane, toluene and EHG in the weight ratio (1:1:0.2)

(c) Polyester is based on neopentyl glycol, adipic acid and isophthalic acid (Mn=850).

(d) TDI is soluble in cyclohexane in the presence of EHG (1:1 mol ratio)

Table 4.11: Properties of polyurethane particles obtained by using different diols and diisocyanates

Monomer		Yield (%)	Mean particle size μ	$\overline{D}_w / \overline{D}_n$
Diol	Diiso cyanate			
EHG	TDI	93	2.0	1.18
	IPDI	91	1.2	1.20
	HMDI[(a)]	aggregated		
	HMDI[(b)]	86	20-92[(c)]	nd
EHG +1,8 OD (80/20)	TDI	92	2-8[(c)]	nd
EHG + PTMG 650 (80/20)	TDI	86	6-20[(c)]	nd

(a) Stabilizer precursor with HMDI end groups

(b) Stabilizer precursor with TDI end groups

(c) Particle size range was determined by counting the sizes of 50 individual particles in optical microscope

The results show that both aliphatic and aromatic isocyanates can be employed in dispersion polymerization. However, dispersion polymerization of HMDI and EHG did not produce spherical particles. This could be due to the poor incorporation of the stabilizing component to the growing polyurethane particles. The stabilizer precursor with HMDI groups at the chain ends will considerably be less reactive than the TDI or IPDI terminated stabilizer precursor. When dispersion polymerization of HMDI and EHG was carried out using TDI terminated stabilizer precursor, spherical polyurethane particles are obtained. This again demonstrates the importance of the reactivity of stabilizer precursor (section 4.3.1-3) in the dispersion polymerization when macrodiols are used as steric stabilizers.

4.3.4-2 Suspension polymerization

Polymerizations of various diols and diisocyanates was carried out in paraffin oil using both macrodiol and block copolymer stabilizers. The results are tabulated in Table 4.12

Table 4.12: Suspension polymerization of various diols with TDI

Diol used	Macrodiol stabilizer[(a)]			Block copolymer stabilizer[(b)]	
	Mean Particle size (μ)	$\overline{D}_w / \overline{D}_n$	T_g °C	Mean Particle size (μ)	$\overline{D}_w / \overline{D}_n$
Ethylene glycol	23	1.8	89	78	2.4
1,4-butane diol	28	1.9	62	48	2.5
1,6-hexane diol	22	1.7	28	47	2.6
1,8-octane diol	30	1.5	5	41	1.9
Cyclohexane dimethanol	6-32[(c)]	nd			
PPG 650	(d)		nd	8-52[(c)]	nd
PPG 1000	(d)		nd	8-52[(c)(d)]	nd

(a) Macrodiol stabilizer **(22f)**

(b) Block copolymer stabilizer **(20c)**

(c) Particle size range was determined by counting the sizes of 50 individual particles in optical microscope

(d) aggregates

Other than PPG 650 and PPG 1000 all diols produced spherical polyurethane particles in considerable yield. When poly(alkylene glycol)s are used in polyurethane particle formation, the time at which the threshold molecular weight is reached for precipitation, there will be a sudden formation of high molecular material in high concentration. Under such conditions the macrodiol incorporation to the growing particle is poor and leads to aggregation. Crosslinking of polyurethane particles produces stable dispersions in theta solvents (toluene). The stability of such dispersions may be due to auto-steric stabilization as described earlier[33]. However, free flowing spherical particles could not be obtained from such dispersions. Interestingly, suspension polymerization of PPG 650 and

TDI using of amphiphilic block copolymer stabilizer produces polyurethane particles with mean particle size 30μ with particle size distribution 1.6.

4.4 Conclusion

A novel polycondensable macrodiol with a long hydrophobic acrylate ester moiety and an amphiphilic block copolymer were successfully used in the particle forming polymerization of diisocyanate and diol. The performance of the macrodiol and the block copolymer as steric stabilizers depends both on their molecular weight and concentration. The rate of primary particle aggregation is successfully controlled by gradual feeding of stabilizer precursor to the growing polyurethane particles. The solvency of the dispersion medium significantly affects the particle size, its distribution and the molecular weight of the polyurethane particles. Although, initial monomer concentration affects the particle formation, it is the mode of monomer addition, which controls the size of particles and their distribution. Physical parameters, namely, agitator types and rate of agitation controls the coagulation or aggregation of the particles and thus influences the final particle size and particle size distribution of polyurethane particles. The macrodiol stabilizer participates in the urethane forming reaction. On the other hand, the amphiphilic block copolymers are adsorbed on the polyurethane particles. Thus, the polyurethane particles are stabilized by a steric stabilization mechanism.

References

1. Mobay Chemical Co., *U S Patent 3214411* 1965.
2. Armstrong Cork Co., *U S Patent 4083831* 1978.
3. PPG Industries, *U K Patent 2157702* 1985.
4. Nippon Paint Co. Ltd., *US Patent* 1997, *5603986*.
5. Zlokarnik, M.; Judat, H. *Ullmann's Encyclopedia of Industrial Chemistry*; 5 ed.; Zlokarnik, M.; Judat, H., Ed.; VCH: Germany, 1988; Vol. B2, pp 25-1.
6. Woods, G. *Flexible polyurethane foam chemistry and technology*; App.Sci.Pub.:, 1982; Vol. Chapter 2.
7. Thiele, L. *Advances in urethane science and technology* 1993, *12*, 59.

8. Snell, F. D.; Hilton, C. L. *Encyclopedia of Industrial Chemical Analysis*; Snell, F. D.; Hilton, C. L., Ed.; Inter Science Publishers: New York, 1967; Vol. 5, pp 272.

9. Shen, S.; Sudol, E. D.; ElAasser, M. S. *J.Polym.Sci., Part A: Polym.Chem* 1993, *31*, 1393-1402.

10. Yokoyama, T.; Furukawa, M. *International Progress in Urethane*; Technomic: USA, 1980; Vol. 2.

11. *Dispersion polymerization in organic media*; Barrett, K. E. J., Ed.; Wiley: London, 1975.

12. Bourgeat Lami, E.; Guyot, A. *Colloid Polym.Sci.*, 1997, *275*, 716-729.

13. Evers, O. A.; Scheutjens, J. M. H. M.; Fleer, G. J. *J.Chem.Soc., Faraday Trans.* 1990, *86*, 1333-1340.

14. Barreiro, M. F.; Dias, R. C. S.; Costa, M. R. N. *Macromolecules* 1994, *27*, 7650-3.

15. Napper, D. H. *Polymeric stabilization of colloidal dispersions*; 1 ed.; Academic Press: London, 1983; Vol. 3.

16. Stejskal, J.; Kratochvil, P.; Konak, C. *Polymer* 1991, *32*, 2435-2442.

17. Paine, A. J. *J.Colloid Interface Sci.*, 1990, *138*, 157-69.

18. Paine, A. J.; Luymes, W.; McNulty, J. *Macromolecules* 1990, *23*, 3104-9.

19. Hsiao, Y. L.; Maury, E. E.; DeSimone, J. M.; Mawson, S.; Johnston, K. P. *Macromolecules* 1995, *28*, 8159-66.

20. Ober, C. K.; Lok, K. P. *Macromolecules* 1987, *20*, 268-73.

21. Bandrup, J.; Immurgut, E., H *Polymer Handbook*; 3 ed.; Bandrup, J.; Immurgut, E., H, Ed.; Wiley: New York, 1989.

22. Thomson, B.; Rudin, A.; Lajoie, G. *J.Polym.Sci., Part A: Polym.Chem.*, 1995, *33*, 345-57.

23. Lu, Y. Y.; El Aasser, M. S.; Vanderhoff, J. W. *J.Polym.Sci., Part B: Polym.Phys.*, 1988, *26*, 1187-203.

24. Paine, A. J. *J.Polym.Sci., Part A: Polym.Chem.*, 1990, *28*, 2485-500.

25. Uyama, H.; Kato, H.; Kobayashi, S. *Polym.J.* 1994, *26*, 858-863.

26. Oberth, A. E.; Bruener, R. S. *J.Phy.Chem* 1968, *72*, 845.

27. Winnik, M. A.; Lukas, R.; Chen, W. F.; Furlong, P.; Croucher, M. D. *Makromol.Chem., Macromol.Symp.*, 1987, *10-11*, 483-501.

28. Ahmed, S.; Farid; Poehlein, G. W. *Ind.Eng.Chem.Res.*, 1997, *36*, 2605-2615.

29. Liu, J.; Chew, C. H.; Wong, S. Y.; Gan, L. M.; Lin, J.; Tan, K. L. *Polymer* 1997, *39*, 283-289.

30. Capek, I.; Riza, M.; Akashi, M. *Makromol.Chem.*, 1992, *193*, 2843-2860.

31. Slomkowski, S.; Sosnowski, S.; Gadzinowski, M. *Polym.Degrad.Stab.*, 1998, *59*, 153-160.

32. Gadzinowski, M.; Sosnowski, S.; Slomkowski, S. *Macromolecules* 1996, *29*, 6404-6407.

33. Graham, N. B.; Mao, J. *Colloids Surf., A*, 1996, *118*, 211-220.

Chapter 5: Ring opening dispersion polymerization of cyclic amides

5.1 Introduction

Poly (amide)s are synthesized by three principal means, namely, hydrolytic, anionic and cationic polymerization of cyclic amides, depending on the mode of monomer activation. Of these, anionic route is found to be an efficient method of polymerizing lactams[1]. However, these conventional methods do not produce spherical poly(amide) particles with uniform size and shape. Particle forming polymerization has been carried out to produce poly(amide) particles, and, the prior literature in this area has been described in Chapter1, Sec.1.3.5. Much of the steric stabilizers used for particle forming polymerization of poly(amide)s are homopolymers or inorganic dispersants. They stabilize the polymer particles by depletion stabilization mechanism[2]. In such cases the amount of stabilizer required for stabilization is quite high. Little attention has been paid towards the use of polymeric or polymerizable type steric stabilizers for the preparation of poly(amide) particles. Therefore, the present study was undertaken to prepare spherical poly(amide) particles using two steric stabilizers, namely, an amphiphilic block copolymer and a polymerizable stabilizer capable of undergoing ring opening polymerization.

5.2 Experimental section

5.2.1 Materials and purification

Caprolactam (GSFC, Vadodara) is recrystalized from acetone / petroleum ether (20/80 v/v) mixture and dried at 60°C under vacuum for 5 h. Lauryl lactam (Elf Atochem, France), sodium hydride (Aldrich), NaH, 80% dispersion in mineral oil phenylisocyanate (Fluka), PhNCO, paraffin oil (S.D` fine), and decahydronaphthalene (Aldrich) were used as received.

5.2.2 Preparation of nylon 6 in particulate form

All manipulations were carried out under a blanket of nitrogen. In a three neck 100 ml cylindrical reactor, fitted with a overhead stirrer, and nitrogen inlet, were charged 0.2 g of the stabilizer (**23f**), 28 g paraffin oil and 4 g (0.0354 mol) ε-caprolactam. The contents were mixed well using a stirring speed of 800-1000 rpm and heated to 80 °C. 31 milligram (2.9 mol %) of NaH was added and the temperature was maintained 1 h. 30 μL (1.55 mol%) phenyl isocyanate was added using a syringe and the temperature was quickly raised to 160 ^{o}C. The reaction was continued for 5 h. The nylon 6 particles thus obtained was washed with pet ether to remove paraffin oil followed by acetone to remove any unreacted ε-caprolactam. The sample was dried in vacuum oven at 80 ^{o}C for 5 h before characterization. The filtrate obtained was collected and washed with acetone to isolate unreacted caprolactam.

5.2.3 Preparation of nylon 6/12 copolymers in particulate form

In a three neck 100 ml cylindrical reactor, fitted with a overhead stirrer, and nitrogen inlet, were charged 0.1 g stabilizer (**23f**) 14 g paraffin oil, 0.6 g (5.3×10^{-3} mol) ε-caprolactam and 1.4 g (7.1×10^{-3} mol) lauryl lactam. The contents were mixed well using a stirring speed of 800-1000 rpm and heated to 80 °C. 14 milligram (3.6 mol %)of NaH was added and the temperature was maintained for one hour. 25 μL (1.85 mol%) phenyl isocyanate was added using a syringe and the temperature was quickly raised to 180 ^{o}C. The reaction was continued for 5 h. The copolyamide particles thus obtained was washed with pet ether to remove paraffin oil followed by acetone to remove any unreacted lactam monomer. The sample was dried in vacuum oven at 80 ^{o}C for 5 h before characterization. The filtrate obtained was collected and washed with acetone to isolate unreacted lactam monomer.

5.2.4 Analysis

The inherent viscosity of nylons (0.5 wt % in m-cresol) was determined using an Ubbelohde viscometer attached to Schott Gerate AVS 440 instrument at 25°C. Thermal analysis was carried out using Perkin Elmer DSC-7 thermal analyzer at a heating rate of 10 °C / min in nitrogen environment. Mean particle size was obtained by counting the size of 100 individual particles using 360P Olympus BX 50 (Japan) optical microscopy. ^{1}H NMR spectra were recorded on a 300 MHz Bruker AC 300 NMR spectrometer. Scanning electron microscopy images was obtained using Leica (Stereoscan 440) scanning electron microscope (Cambridge, UK) at an accelerating voltage of 20 kV.

Poly(amide) particles dispersed in hexane was dried on aluminum stub and then coated with gold. The X-ray diffraction experiments were performed using Rigaku Dmax 25000 diffractometer. The equipment consists of a rotating anode generator and wide angle powder goniometer and a slit collimated small angle goniometer. The generator was operated at 40 KV and 150 mA. The samples were scanned between 2θ = 10 and 35° at a speed of 1 deg/min. Crystallinity was calculated from the ratio of the area of crystalline peaks to total area.

5.3 Results and discussion

Anioinc ring opening polymerization of lactams are generally carried out using alkali or alkaline earth metals as initiators in the presence of additional activators at high temperatures (130 °C-220 °C). A similar experimental condition was employed to prepare poly(amide) particles by ring opening dispersion polymerization of ε-caprolactam. Many reaction variables such as type of initiator, activator, and their concentration were studied and optimized[3]. It was observed that there was no polymerization below 140 °C. However, upon increasing the amount of initiator and activator, polymer was obtained in reasonable yield. The nature and amount of activator also affects the polymer properties. For instance, when TDI was used as an activator in place of PhNCO, molecular weight of the polymer obtained was high and contains upto 15 % of m-cresol insoluble component.

5.3.1 Ring opening dispersion polymerization of ε-caprolactam

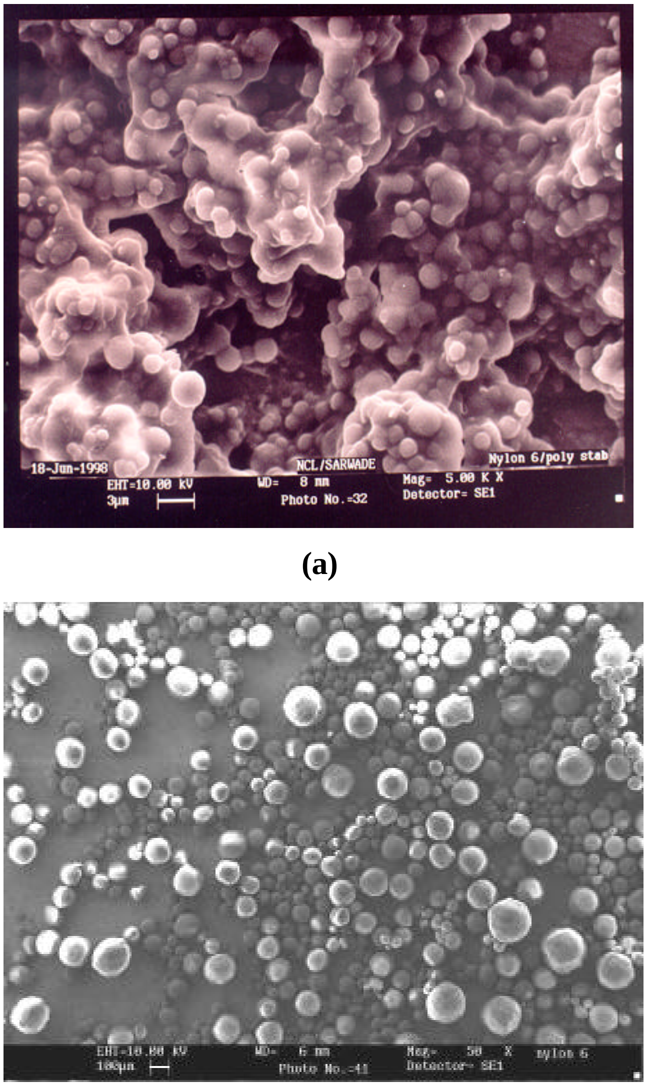
Poly(isoprene-b-ethylene oxide) (**20c**)and N-poly(alkyl acrylate) caprolactam (**23d-f**)were employed as steric stabilizers for the ring opening dispersion polymerization of ε-caprolactam. The results are presented in Table 5.1.

Table 5.1: Preparation of nylon 6 particles[(a)]

Stabilizer	Concentration[(b)] (wt %)	Yield (%)	η_{inh} (dL/g)	T_g (°C)	T_m (°C)	Mean particle size (μ)
(23f)	1	86	0.85	52	217	41
	3	68	0.65	51	215	23
	5	77	0.50	48	214	29
	5[(c)]	76	0.60	50	212	26
(23e)	1	32	0.29	52	212	15
	3	66	0.54	55	217	20
	5	88	0.76	54	217	22.
(23d)	1	nd	nd	nd	nd	d
	3	8	0.17	nd	nd	d
	5	76	0.64	49	217	d
N-Stearyl caprolactam	1	49	0.41	46	212	d
	3	72	0.45	45	214	d
	5	82	0.44	46	215	d
Polyisoprene[(e)]	1	35	0.33	nd	nd	d
	3	49	0.46	nd	nd	d
	5	24	0.218	nd	nd	d
(20c)	1	87	nd	nd	nd	1.3
	2	85	0.81	51	212	0.9 (1.12)[(f)]
	5	88	nd	nd	nd	1.1
(21f)	5		No particle formation			
Stearic acid	5		No particle formation			

(a) The polymerization is carried out with 2.9 mol % of NaH, 1.55 mol % of PhNCO and 8 wt % paraffin oil, based on monomer.
(b) based on monomer weight %
(c) Dispersion medium is decalin
(d) Particles are agglomerated
(e) Prepared via anionic polymerization technique. Mn = 10,000
(f) Values in parantheses indicate particle size distribution determined by Malvern LALLS instrument
(g) nd denotes not determined

The results indicate that the stabilizer molecular weight and its concentration greatly influence the nylon 6-particle formation. When the molecular weight of the stabilizer and its concentration is increased the particle size is decreased. This is generally true in dispersion polymerization for reasons previously explained (Chapter 4, Section 4.3.2.1). When the $\overline{M}_n$ of the hydrophobic segment is reduced to 1000, the particles are aggregated and do not yield free flowing nylon 6 particles. This shows that the length of stabilizing component is not sufficient to prevent aggregation of the particles. The same observation is found when N-stearyl caprolactam is used as the stabilizer. In the case of poly(isoprene), though the molecular weight of stabilizing component is sufficient enough to prevent aggregation, it does not have any anchoring component to build a steric barrier. According to theories of steric stabilization such homopolymers stabilizes the polymer particles by depletion stabilization mechanism. In the present case also, poly(isoprene) does stabilize the growing particles. However, the particles are aggregated severely. No free flowing particles could be obtained. On the contrary, dispersion polymerization carried out using an amphiphilic block copolymer, gave spherical polyamide particles. This illustrates the necessity of an anchoring group in the dispersion polymerization. The block copolymer used here stabilizes the particle by steric stabilization mechanism. A similar observation has been noted in the ionically initiated dispersion polymerization of ε-caprolactone[4]. The SEM micrograph of poly(amide) particles obtained using different stabilizer is given in Figure. 5.1



(a)

(b)

Figure 5.1: SEM images of polyamide particles **(a)** obtained using block copolymer stabilizer (**20c**) and **(b)** obtained using polymerizable stabilizer (**23e**)

They show that when compared to polymerizable stabilizer, the amphiphilic block copolymer efficiently stabilizes the polymer particles even at very low concentration. The SEM image of the poly(amide) particle obtained from block copolymer stabilizer appears aggregated in the SEM. However, the particles are readily dispersible in high boiling aliphatic hydrocarbons like paraffin oil and octadecane. A typical particle size distribution of nylon 6 particle dispersed in octadecane is shown in Figure 5.2.

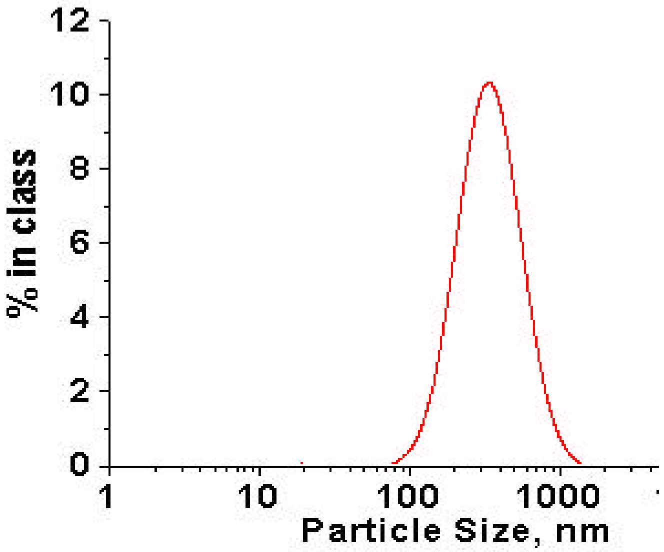


Figure 5.2: Particle size distribution of nylon 6 particles stabilized by block copolymer stabilizer **(20c)**

Two important factors which govern the process of stabilization are (a) molecular weight of the stabilizer and (b) the mechanism of stabilization. In the present case, the molecular weight of the stabilizing component in polymerizable stabilizer is lower when compared to the block copolymer. It is expected in dispersion polymerization the particle size increases with the decrease in molecular size of the stabilizing component. However, if the stabilizing component is anchored to the growing particles during polymerization, then a $\overline{M}_n$ of 5000 is sufficient to provide maximum steric barrier. This shows that the polymerizable stabilizers (**23d-23f**) are not efficiently attached to the poly(amide) particles. This fact will be further clarified when we consider the mechanism of particle formation and stabilization.

In the case of amphiphilic block copolymer, the hydrophilic PEO segment efficiently anchors onto the polar poly(amide) particles. This prevents the aggregation of the primary particles and, therefore, produces smaller particles with narrow particle size distribution. Conversely, the polymerizable stabilizer is N-acyl lactam, can, in principle, activate the anionic polymerization of ε-caprolactam. In such case, each growing particle will have a stabilizer fragment and therefore the particles are expected to be stabilized effectively. However, this was not observed in the present study. The stabilizer alone did not activate the polymerization and it requires an additional activator, namely, phenyl isocyanate. The ineffectiveness of this macromonomer as an activator may be due to the presence of long acrylic ester moiety, which reduces the reactivity of N-acyl derivative of the lactam. A similar inference has been reported on the activator structure on the anionic polymerization of ε-caprolactam.[5]

The other possibilities of stabilizing the poly(amide) particles are (i) the physical adsorption of caprolactam moiety attached to the stabilizing component to the growing particle. (ii) the *insitu* formation of poly(lauryl methacrylate -b- capromamide), which then stabilizes the growing poly(amide) by physical adsorption. In case (i), stabilization via physical adsorption can be ruled out, as the anchor segment length is too low compared to the stabilizing segment. In case (ii), if the stabilization had occurred via block copolymer formation, then carboxyl terminated poly(lauryl methacrylate) would also have produced spherical polyamide particles. Such block copolymer formation has been reported for the polymerization of lactams initiated with carboxylic acids[6]. Furthermore, after particle formation the IR analysis of the acetone extract from the dispersion phase (paraffin oil), showed the presence of stabilizer ($\nu_{C=O}$ 1740 cm^{-1}). However, the amount of stabilizer could not be quantified gravimetrically, as the acetone phase contains unreacted ε-caprolactam also.

5.3.2 Synthesis of copolyamide particles

For this study, various ratios of ε- caprolactam and lauryl lactam were polymerized using NaH and PhNCO in presence of **(23e)** (5 wt % on monomer concentration), as particle stabilizer. All polymerizations were carried out at 170 °C and in paraffin oil as the dispersion medium. The properties of the nylon 6/12 copolymers are listed in Table 5.2. It is clear from the table that there is no significant change in particle size as the concentration of lauryl lactam is increased in the feed. However, the particle size is much less when lauryl lactam is polymerized alone. This could be due to the solubility of lauryl lactam in the dispersion medium, which results in better dispersion polymerization. ε-caprolactam is insoluble in the paraffin oil, hence, when polymerized follows suspension polymerization route and results in bigger particles compared to nylon 12 particles. This phenomenon is in accordance with the mechanism of particle forming reaction[7].

Table 5.2: Properties of nylon 6/12 particles

Run	Composition(a)				T_g (°C)	T_m (°C)	Crstallinity (%)	Particle size (μ)
	Feed		^{1}H NMR					
	CL	LL	CL	LL				
1	100	0	nd	nd	54	217	58	22
2	90	10	nd	nd	43	208	55	25
3	70	30	nd	nd	36	200	51	21
4	50	50	48	52	30	160	47	30
5	30	70	nd	nd	25	128	15	21
6	20	80	24	76	26	153	41	28
7	10	90	nd	nd	33	165	42	28
8	0	100	nd	nd	49	180	52	13

(a) ε-Caprolactam(CL) and Lauryl lactam(LL) in mole ratio are added at once.

For 100 / 0 to 50 /50 CL / LL feed composition, 3.5 mol % of NaH, 1.8 mol % of PhNCO were used and for 30 / 70 to 0 / 100 CL / LL monomer ratio, 6 mol% of NaH and 4 mol % of PhNCO were used because there is no polymer formation at low mol % of initiator and activator. All manipulations were carried out at 170 °C and 800 rpm using **(23e)** (5wt% on monomer) as steric stabilizer.

The copolymer composition was calculated from ^{1}H NMR using the following equation[8]: $S_{(a+b)} = 8x+20y$ and $S_c = 2x+2y$. Where $S_{(a+b)}$ and S_c are the corresponding signal intensities; x and y are the number of protons in caprolactam and lauryl lactam respectively. A typical ^{1}H NMR spectrum of the nylon6/nylon12 (20/80) copolymer is shown in Figure 5.3.

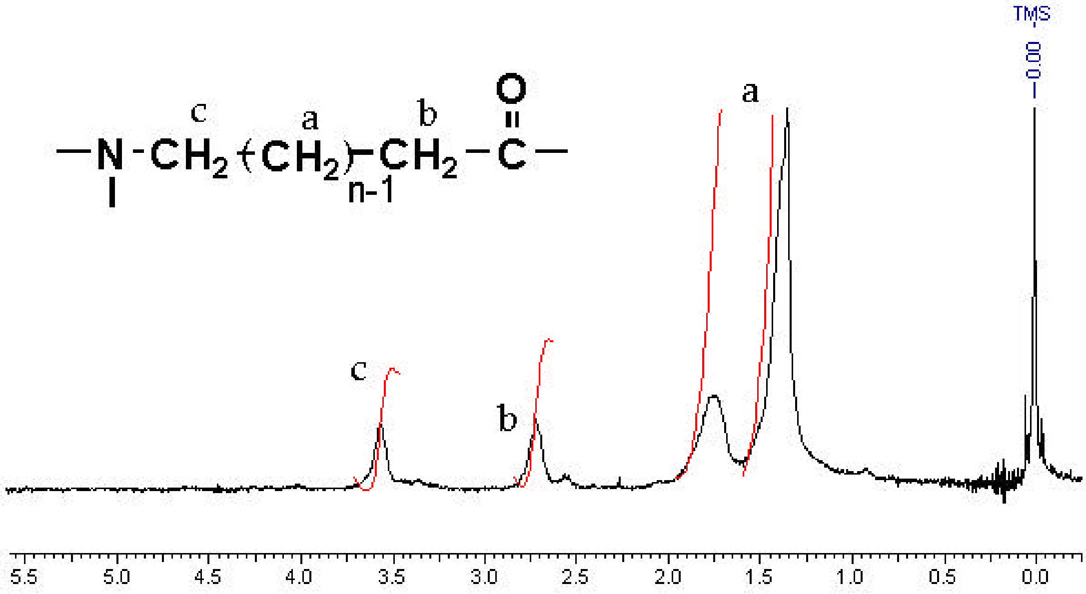


Figure 5.3 ^{1}H NNR spectrum of nylon 6/12 (20/80) copolymer

The thermal properties of nylon 6, nylon 12 and nylon 6/12 copolymer of various compositions are shown in Table 5.2. The results show that the T_g of nylon 6/12 copolymers fall progressively from the values of respective homopolymers and reaches a minimum at about 30/70 (CL/LL) mole ratio (Figure 5.4) A similar observation was reported for nylon 6/12 copolymers synthesized by anionic copolymerization in the melt[9,10]. The occurrence of a minimum Tg with composition is an unusual phenomenon as these values deviate from Fox-Flory equation. Goodman and Kehayogloue[9] explained this anomalous behavior in relation to the different co-unit composition of the crystalline and amorphous phases. The authors assumed that each copolymer is composed of discrete crystalline and amorphous phases and calculated the amount of monomer units present in the amorphous phase. They plotted the weight fraction of the monomer units in the amorphous phase against the weight fraction of the monomer units in the whole copolymer. It was shown that in the region of change over of the crystalline type, there is an abrupt change of composition in the amorphous phase.

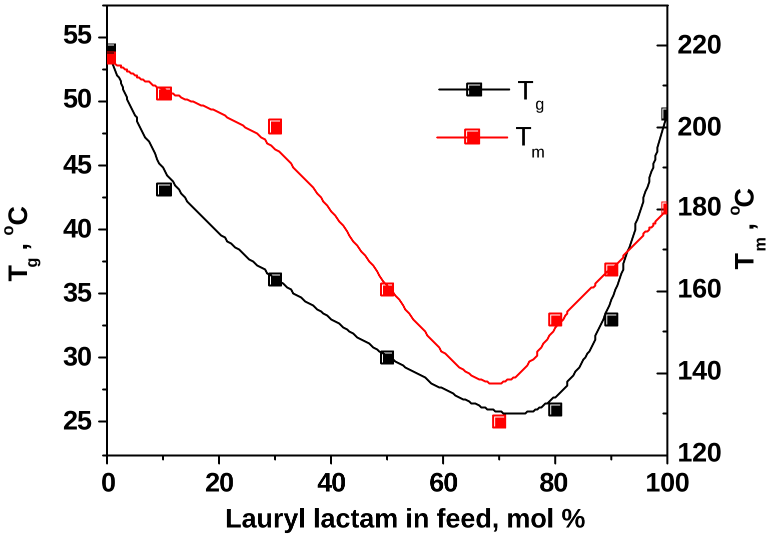


Figure 5.4 Plot of Tg and Tm of nylon 6/12 copolymers as a function of feed composition

The DSC thermogram and the XRD pattern of the copolymers are shown in Figures 5.5 and 5.6 respectively. The copolymer had melting characteristics similar to nylon 6 when caprolactam was excess in the feed. However, when lauryl lactam was in excess, the thermal behavior was similar to nylon 12. The T_m vs feed composition and crystallinity vs feed composition for these copolyamides clearly shows an eutectic behavior for 30/70 (CL/LL) copolymer. Such eutectic behavior was also reported for nylon 6/12 copolymers synthesized in melt using anioinc ring opening polymerization. Frunz et al[8] attributed this eutectic behavior due to the variation of sequence distribution of the monomer units for various copolymer compositions.

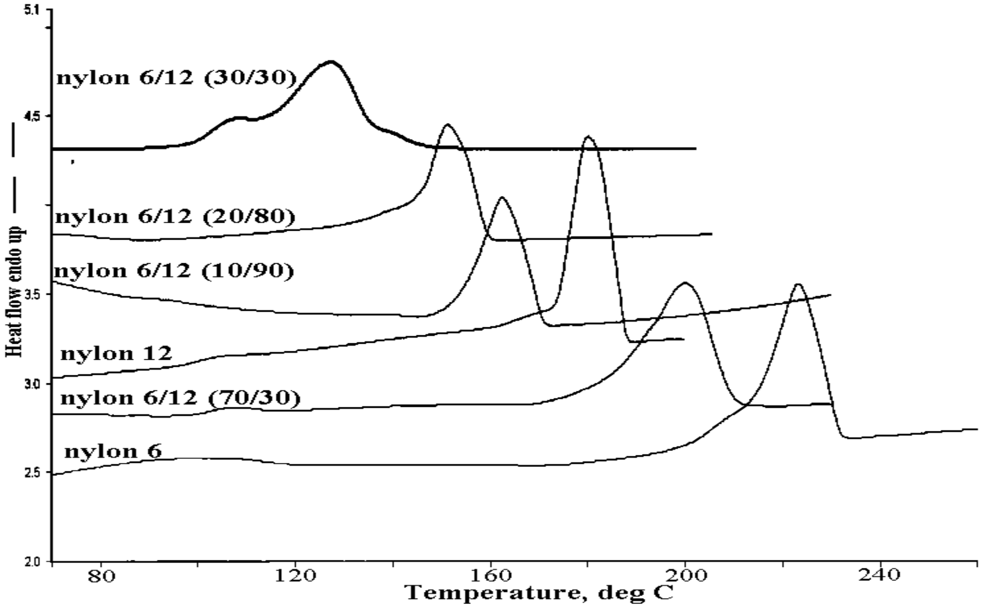


Figure 5.5: DSC thermograms of nylon 6, nylon 12 and nylon 6/12 copolymers

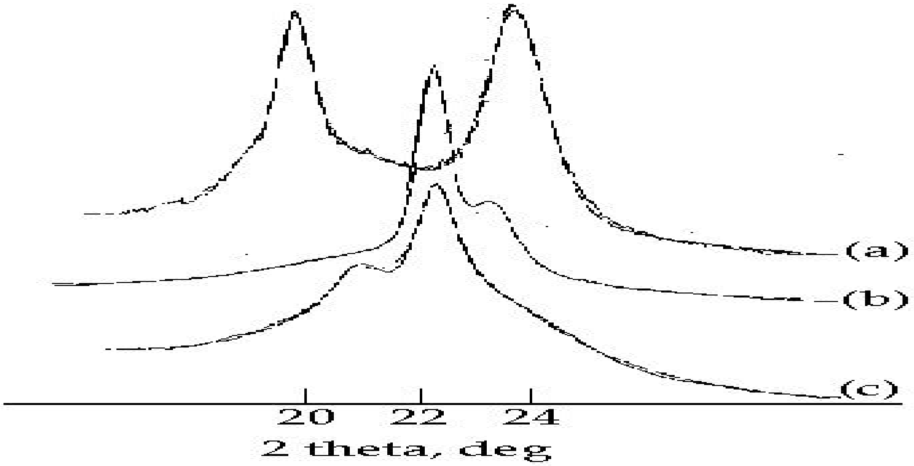


Figure 5.6: XRD patterns of (a) nylon 6, (b) nylon 12 and (c) nylon 6/12 copolymer (30/70)

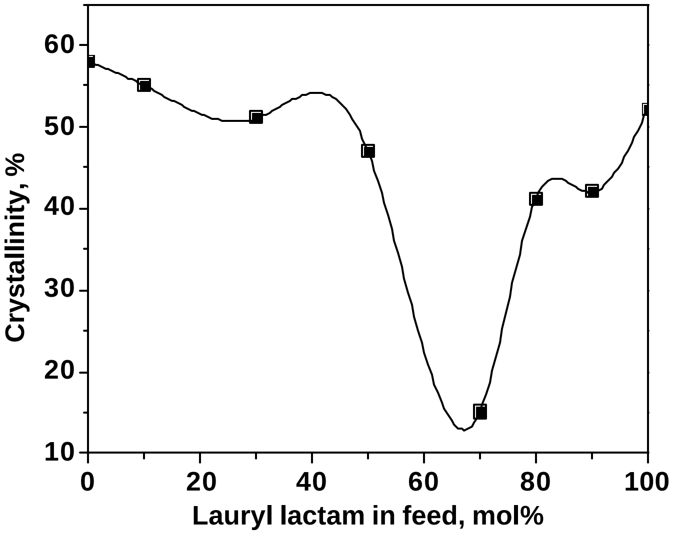


Figure 5.7: % crystallinity of nylon 6/12 copolymers as a function of feed composition.

5.4 Conclusion

Nylon-6 particles were prepared successfully by particle forming ring opening polymerization technique. The type of stabilizer, its molecular weight and concentration greatly influence the nylon-6 particle formation. Although, spherical polyamide partilcles are obtained using polymerizable stabilizers, they do not effectively take part in the ring opening polymerization. Nylon 12 and copolymers of nylon 6/12 are also prepared in particulate form using polymerizable stabilizer. In both the cases, the polyamide particles are stabilized by physical adsorption of the stabilizer rather than grafting.

5.5 References

1. *n-nylons*; Aharoni, S. M., Ed.; Wiley: London, 1997.
2. Napper, D. H. *Polymeric stabilization of colloidal dispersions*; 1 ed.; Academic Press: London, 1983; Vol. 3.
3. Veerabadriah, S. *MSc Dissertation*, S K University, Anantapur.**1999**.
4. Slomkowski, S.; Sosnowski, S.; Gadzinowski, M. *Colloid Surface.A.* **1999**, *153*, 111-118.
5. Scetia, R. P.; Schonfeld, S. L.; Donaruma, L. G., , 1964 *J. Appl. Polym. Sci* **1964**, *8*, 1363.
6. Ozgun, H. B.; Kubanek, V.; Kralicek, J.; Veruovic, B. *Eur.Polym.J* **1986**, *22*, 1009-1014.
7. Barrett, K. E. J. *Dispersion polymerization in organic media*; Barrett, K. E. J., Ed.; Wiley: London, 1975.
8. Frunze, T. M.; Kurashev, V. V.; Ivanova, S. L.; Komarova, L. I.; Korshak, V. V. *Polym. Sci. USSR* **1976**, *18*, 348-353.
9. Goodman, I.; Kehayoglou, A. H. *Eur.Polym.J.*, **1983**, *19*, 321-5.
10. Garner, D. P.; Fasulo, P. D. *J.Appl.Polym.Sci.*, **1988**, *36*, 495-509.

Chapter 6: Applications of particle forming polymerization process

6.1 Introduction

Preparation of polymer particles/dispersions possessing uniform particle size and shape, has gained considerable commercial/scientific interest in recent years. This has been largely motivated by many versatile applications of these materials as ion-exchangers, calibration standards, surface coatings, pharmaceutical reagents, biomaterials, medical diagnostics, parenteral drug delivery systems, toners for photocopying and digital printing, supports for solid phase synthesis and chromatographic media for separations.

In the peptide synthesis the use of crosslinked monodisperse polystyrene particles as a support considerably reduces the duration of synthetic cycle[1]. Hydrophilically modified uniform, rigid and porous poly(styrene-divinylbenzene) finds application in protein recovery[2]. The properties and application of monosize magnetic polymer particles have been reported[3]. These magnetic particles find application in cell separation[4] that includes trophoplast cells, eosinophils, langerham cells, endothelial cells and antegen-specific B cells. They are also useful in the separation of nulecic acids, viruses and subcellular compartments. Aminated derivatives of monodisperse poly(glycidylmethacrylate) copolymers have been shown to bind antigens and antibodies efficiently and finds application in immunological examination. The effect of particle size distribution of spherical crosslinked polystyrene gel particles on the SEC column performance has been studied[5]. The results suggest that in column packed with particles of well defined size distribution, the broadening of chromatogram due to mobile phase dispersion is reduced. Uniform porous beads based on polystyrene are reported as an effective polymeric suspension media for high performance liquid chromatography. The effect of porosity and specific surface area on the chromatographic properties of the stationary phase is well documented. PMMA colloidal dispersions in organic media are significantly more sensitive as electron resists than its solution counterpart[6].

The potential applications of non aqueous dispersions as coating materials has been highlighted by Barrett[7]. Acrylic copolymers have been prepared by radical dispersion polymerization in a mixture of aliphatic and aromatic dispersion medium using acrylic type dispersants and their utility in high solids coatings have been described[8]. Preparation of colored copolymer particles by dispersion polymerization of styrene, n-butyl methacrylate and a polymerizable anthraquinone dye, in aqueous ethanol using polyacrylic acid as a steric stabilizer has been reported[9]. The authors showed that the use of polymeric dyes in the dispersion polymerization offers a straightforward route to synthesize colored polymer particles with functionalised surfaces. Interestingly, Frechet and co-workers[10] reported the preparation of monodisperse polymer particles by dispersion copolymerization of styrene, n-butyl methacrylate and non-polymerizable dyes. Experimental conditions have been investigated that enable the preparation of colored polymer particles with narrow size distribution. Polymeric stabilizers have also been employed to stabilize inorganic dispersions.

Recently, in our laboratory, particle forming polyurethane polymerization has been utilized in encapsulating drugs and pesticides[11]. In the present study, we examine the feasibility of encapsulating carbon black in polyurethane matrix. Carbon black filled polymer particles is useful for coatings, inks, electrophotographic developers etc… Conventionally carbon black filled polymers are obtained by melt blending or solution casting. Preparation of aqueous suspensions of polystyrene and polyurethane urea filled with carbon black has also been reported[12]. However, aqueous suspensions of carbon black filled polymers are not suitable as carrier particles for electrophotographic developers and for such applications, carbon black dispersed in organic solvents containing the polymer is used. In this case the dispersibility of carbon black in organic medium is poor and results in flocculation. Grafting the carbon black surface with a polymer can partially solve this problem[13]. However, because of lack of sufficient surface functionality on carbon black it is difficult to prepare good graft polymers

The particle forming polyurethane process was also utilized to make a dispersed polyurethane -clay nanocomposites. Polymer-clay nanocomposites continue to generate much interest, principally because of the potential they offer for application in tough and high temperature compatible, particle reinforced polymers, coatings, electronics and catalysts. Two types of nanocomposites have emerged (Figure 6.1). Intercalated or layered nanocomposites consists of well ordered stacked polymer multilayers within the host[14]. Polymerization of ε-caprolactam in the interlayer gallery region of clay[15], thermoset epoxy nanocomposites[16], nanolayer reinforcement of elastomeric polyurethanes[17] are examples of this kind. In delaminated nanocomposites the host is well dispersed in the polymer matrix. Very recently, delaminated polystyrene-clay nanocomposites has been demonstrated using living radical polymerization of styrene in the silicate layers[18]. However, unlike intercalated nanocomposites, for which excellent methodologies exist, there is no corresponding general method for the preparation of dispersed nanocomposites.

In the present study we have explored the feasibility of particle forming polymerization process inside the galleries of clay. We believe that, as the particle growth proceeds inside the galleries of clay, the layers will be gradually pushed apart and eventually exfoliate, leading to a well dispersed nanacomposites.

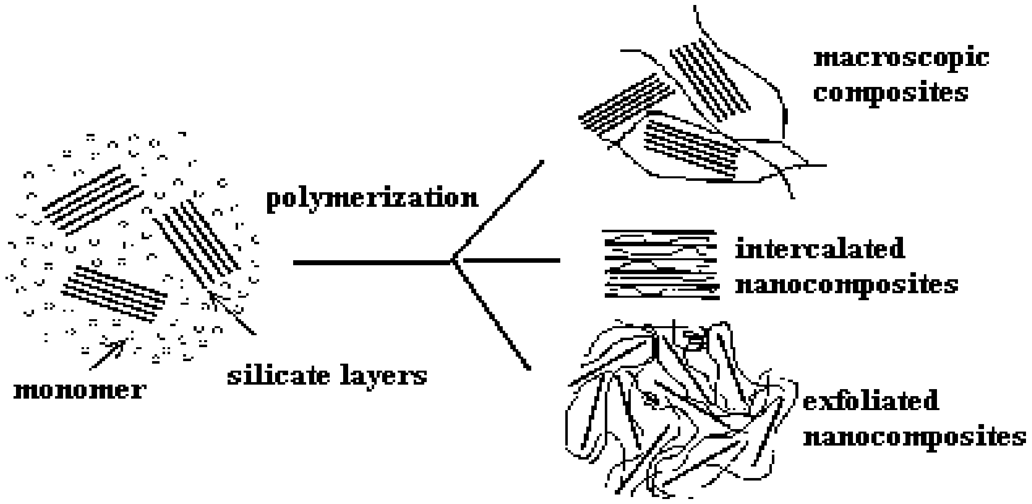
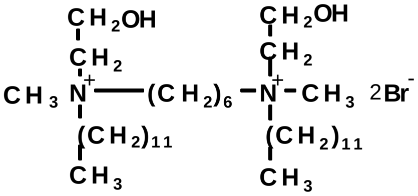


Figure 6.1: Types of nanocomposites

6.2 Experimental section

6.2.1 Materials

Carbon black (Vulcan XC 72, Average particle size 300 nm, Cabot Corporation, USA) and clay (Na^+-montmorilonite, Nanoncore, USA.) were dried at 120 °C for 8 h under vacuum before use. A bismethylol quarternary ammonium salt **(26)** was kindly supplied by Prof. (Ms) Surekha Devi, M S University, Vadodra. Cetyl trimethyl ammonium bromide (CTAB, s d fine) was used as received.



$$\begin{array}{ccccc} & CH_2OH & & CH_2OH & \\ & | & & | & \\ & CH_2 & & CH_2 & \\ & | & & | & \\ CH_3 & \overset{+}{N} & -(CH_2)_6- & \overset{+}{N} & -CH_3 \quad 2Br^- \\ & | & & | & \\ & (CH_2)_{11} & & (CH_2)_{11} & \\ & | & & | & \\ & CH_3 & & CH_3 & \end{array}$$

(26)

6.2.2 Preparation of carbon black filled polyurethane particles

In a four-neck 250 mL round bottomed flask fitted with a propeller stirrer, condenser, nitrogen inlet and a thermowell, were charged 1 g carbon black, 30 mL hexane, 0.5 g of 1% DBTDL solution in hexane, 0.75 g **(22d)**. The contents were sirred well at 800 rpm and the temperature was increased to 60 °C. TDI 50 μL was then added and the reaction was continued for 4 h. EHG 3.0 g (2.05×10^{-2} mol) and TDI 4.5 g (2.58×10^{-2} mol) were then slowly added. The reaction was continued till the complete disappearance of isocyanate groups. The carbon black filled polyurethane particles thus obtained were washed with hexane and dried under vacuum at room temperature for 4 h. Yield: 94 %.

6.2.3 Preparation of polyurethane-clay nanocomposites

In a four-neck 250 mL round bottomed flask fitted with a propeller stirrer, condenser, nitrogen inlet and a thermowell, was charged 0.3 g clay, 25 g paraffin oil, 0.5 g of 1% DBTDL solution in paraffin oil, 0.75 g macrodiol stabilizer (**22e**) and 0.1g hydroxyl onium salt **(26)**. The contents were stirred well at 800 rpm and the temperature was increased to 60 °C and kept at that temperature for 8 h to allow intercalation. TDI 50 μL was then added and the reaction was continued for 4 h. EHG 3.0 g (2.05×10^{-2} mol) and TDI 4.5 g (2.58×10^{-2} mol) were then slowly added. The reaction was continued till the complete disappearance of isocyanate groups. The polyurethane-clay nanocomposite particles thus obtained were washed with hexane and dried under vacuum at room temperature for 4 h. Yield: 92 %.

6.2.4 Analysis

Volume resistivity of the carbon black filled polyurethanes and physical mixtures were determined by using two probe Keithlay electrometer (Model 614). The samples (pellets) were placed in the sample holder which was closed in electromagnetic shield cell. A fixed voltage was applied across the sample and the change in current were noted and the resistivity, ρ was calculated from the formula $\rho = RA/l$ where R is the resistivity in ohms, A is the cross sectional area (cm^2) of the electrode and l = inter electrode spacing (cm). The conductivity, σ is calculated using the formula $\sigma = 1/\rho$ ($S\ cm^{-1}$). Elemental analysis was carried out using carlo Erba CHN-S EA 1108 elemental analyzer. Thermo gravimetric analysis was carried out using Perkin Elmer TGA-7 thermal analyzer. The X-ray diffraction experiments were performed using Rigaku Dmax 25000 diffractometer. The equipment consists of a rotating anode generator and wide angle powder goniometer and a slit collimated small angle goniometer. The generator was operated at 40 KV and 150 mA. The samples were scanned between 2θ = 2 and 35° at a speed of 1 deg/min. Crystallinity was calculated from the ratio of the area of crystalline peaks to total area. Scanning electron microscopy images was obtained using Leica (Stereoscan 440) scanning electron microscope (Cambridge, UK) at an accelerating voltage of 20 kV. Polyurethane particles dispersed in hexane was dried on aluminum stub and then coated with gold.

6.3 Results and discussion

6.3.1 Preparation of carbon black filled polyurethane particles

Different amounts of carbon black have been encapsulated in polyurethane particles and the results are presented in Table 6.1. For this study, macrodiol (**22d**) was used to stabilize the encapsulated particles. It was observed that at 5 wt % stabilizer concentration, satisfactory encapsulation could not be obtained as the whole mass agglomerated. However, when the stabilizer concentration was increased to 10 %, free flowing carbon black encapsulated polyurethane particles could be obtained. This is due to the fact that some amount of stabilizer is adsorbed on the carbon black surface. As a result, larger amounts of stabilizer is necessary to stabilize the growing particles. The amount of stabilizer adsorption on the carbon black surface is greatly dependent on the size of anchoring group. We believe that the adsorption of macrodiol on the carbon black surface will be considerably lower than that of amphiphilic copolymers. This is because the macrodiol possesses poor anchoring sites. For this reason we chose the macrodiol stabilizer. The encapsulated carbon black particles are spherical and did not contain any free carbon black or aggregated carbon black on the encapsulated particle surface. (Figure 6.2)

Table 6.1 Properties of carbon black filled polyurethane particles

Sample	Carbon black loading (wt %)	Particle size range[(a)] (μ)	Carbon black encapsulated (wt %)	
			Elemental analysis [(b)]	TGA[(c)]
1	1	6-20	98.2	96
2	3[(d)]	(e)		
3	3	4-20	98.6	97
4	3[(f)]	(e)	nd	nd
5	6	6-25	98.0	97
6	12	2-40	99.5	98
7	12[(g)]	2-40	99.2	-
8	25	2-40	99.4	98

(a) Calculated for 50 individual particles from SEM

(b) Determined from the increase % Carbon wrt neat polyurethane particles

(c) Weight fraction remained after 700 °C

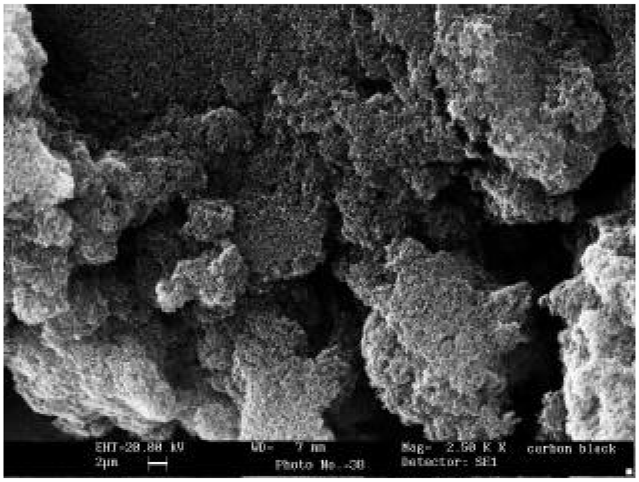
(d) Stabilizer (4d) 5 wt %

(e) Agglomerated

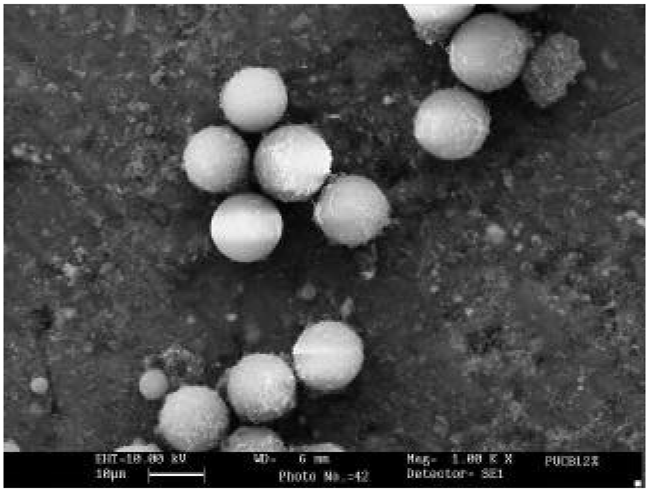
(f) Polymerization carried out in paraffin oil using stabilizer (4d) 10 %

(g) 20 wt % TMP on EHG was used as a crosslinker

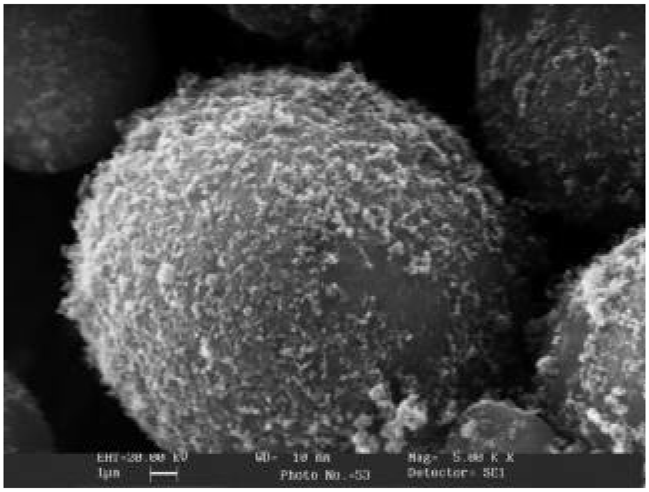
It is evident for the elemental analysis and TGA that the amount of carbon black encapsulated is essentially quantitative. In addition, the volume resistivity of encapsulated carbon black is higher than the physical mixture of the same composition (Figure 6.3). This indicates that the highly conductive carbon black particles are well encapsulated by the more insulating polyurethane sheath during particle formation.



(a)



(b)



(c)

Figure 6.2 SEM of carbon black and carbon black filled polyurethane particles **(a)** Carbon black neat **(b)** 12 % carbon black encapsulated and **(c)** single particle from Fig **(b)**

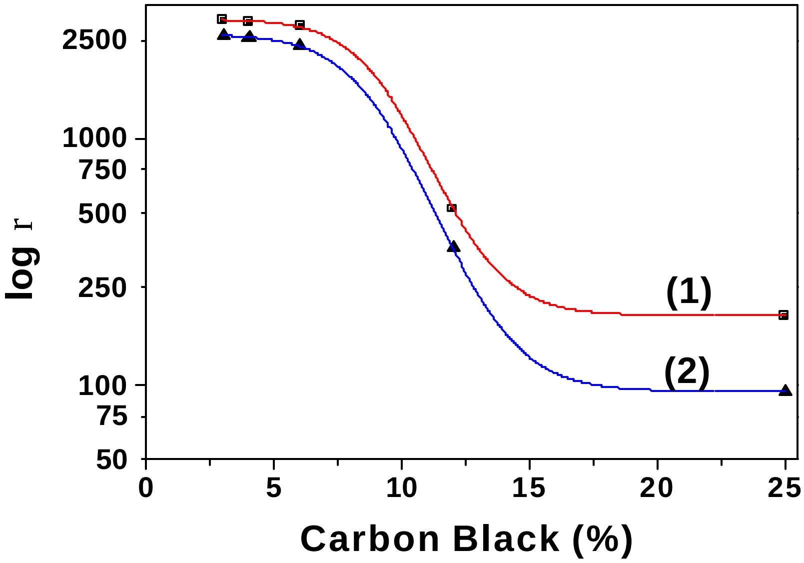


Fig 6.3: Volume resistivity of carbon black filled polyurethane particles **(1)** micro encapsulated particles **(2)** physical mixture.

6.3.2 Preparation of polyurethane clay nanocomposites

Na^+-montmorilonite was intercalated with a dimethylol quaternary ammonium salt **(26)** and CTAB. Particle forming polymerization was carried out in the presence of intercalated clay using 5 wt % polymerizable stabilizer **(22e)**. The polymer clay nanocomposites thus obtained was characterized by XRD (Figure 6.4). It was observed that when CTAB was used as an intercalating agent, the gallery size was increased from 9Å to 11Å (Fig. 6.4 b). However, when the clay was intercalated with dimethylol quaternary ammonium salt, there was an exfoliation as evident from the absence of peak in XRD around 2θ = 2-6 (Fig 6.4 c). Therefore, we presume when the clay was intercalated with **(26)**, the hydroxyl group present in the onium salt take part in the urethane forming reactions. As the polymerization proceeds, the particle will grow inside the galleries. When the threshold particle size is reached, the clay layer will exfoliate resulting in a well dispersed polyurethane -clay nanocomposites. The thermal degradation of the exfoliated polyurethane nanocomposites was found to be higher than the intercalated and pristine polyurethanes. (Figure 6.5)

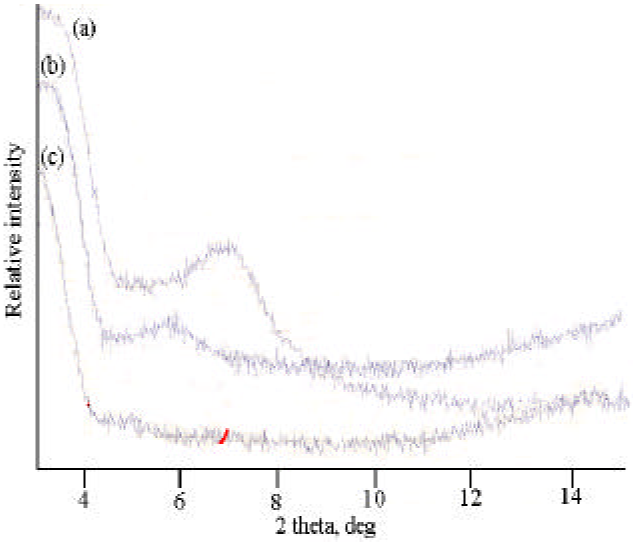


Figure 6.4 XRD Pattern (a) Clay; (b)Polyurethane-clay (intercalated with CTAB) and (c) Polyurethane-clay intercalated with **(26)**

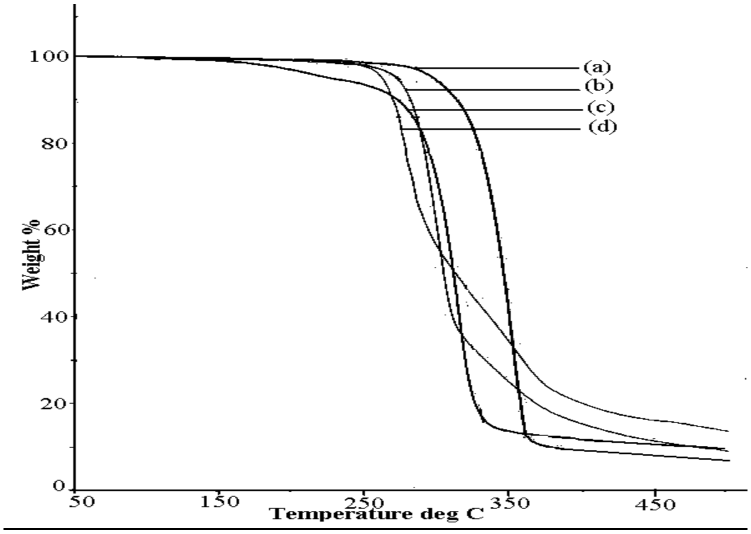


Figure 6.5 TGA curve of PU clay nanocomposites (a) clay intercalated with hydroxyl onium cation (b) clay intercalated with CTAB (c) clay without intercalation (macrocomposites) (d) pristine polyurethane

6.4 Conclusions

Dispersion polymerization of diisocyanate and diol in the presence of carbon black leads to carbon filled polyurethane spherical particles. The encapsulation of carbon black was quantitative. The specific conductivity of the encapsulated carbon black particles was much less than the physical mixtures. This indicates that the carbon black particles are covered by the insulating polyurethane sheath. These encapsulated particles are readily dispersible in aliphatic hydrocarbons. Preliminary studies on the reaction of diisocyanates with dimethylol quaternary ammonium salt exchanged clay show that polyurethane particle formation occurrs inside the galleries of clay. The polyurethane clay nanocomposites exhibit good thermal properties compared to neat polyurethane as well as macrocomposites.

References

1. Bayer, E. *Angew. Chem* **1991**, *103*, 117-33.
2. Ellingsen, T.; Aune, O.; Ugelstad, J.; Hagen, S. *J. Chromatogr* **1990**, *535*, 147-61.
3. Ugelstad, J.; Berge, A.; Ellingsen, T.; Schmid, R.; Nilsen, T. N.; Mork, P. C.; Stenstad, P.; Hornes, E.; Olsvik, O. *Prog.Polym.Sci* **1992**, *17*, 87-161.
4. Ugelstad, J.; Berge, A.; Ellingsen, T.; Aune, O.; Kilaas, L.; Nilsen, T. N.; Schmid, R.; Stenstad, P.; Funderud, S.; et al. *Makromol. Chem., Macromol. Symp.*, **1988**, *17*, 177-211.
5. Wang, Q. C.; Hosoya, K.; Svec, F.; Frechet, J. M. J. *Anal. Chem* **1992**, *64*, 1232-8.
6. Cowley, D. R.; Price, C.; Hardy, C. J. *Polymer* **1980**, *21*, 1356-7.
7. *Dispersion polymerization in organic media*; Barrett, K. E. J., Ed.; Wiley: London, 1975.
8. Yabuta, M.; Nakao, Y.; Tominaga, A. *High Solids Coatings in The Polymeric Materials Encyclopedia*; CRC Press, Inc:, 1996; Vol. CD ROM.
9. Winnik, F. M.; Ober, C. K. *Eur.Polym.J.*, **1987**, *23*, 617-22.
10. Horak, D.; Svec, F.; Frechet, J. M. J. *J.Polym.Sci., Part A: Polym.Chem* **1995**, *33*, 2961-8.
11. Shukla, P. G.; Sivaram, S. *J.Microencapsulation* **1999**, *16*, 517-521.
12. Dai Ichi Kogyo Seiyaku Co., *Jpn.Kokai 5222207* **1993**.
13. Tsubokawa, N.; Matsumoto, H.; Sone, Y. *J.Polym.Sci., Part A: Polym.Chem* **1982**, *20*, 1943-6.
14. Giannelis, E. P. *Adv. Mater.* **1996**, *8*, 29-35.
15. Wang, M. S.; Pinnavaia, T. J. *Chem. Mater* **1994**, *6*, 468-74.
16. Messersmith, P. B.; Giannelis, E. P. *Chem. Mater* **1994**, *6*, 1719-25.
17. Wang, Z.; Pinnavaia, T. J. *Chem. Mater* **1998**, *10*, 3769-3771.
18. Weimer, M. W.; Chen, H.; Giannelis, E. P.; Sogah, D. Y. *J.Am.Chem.Soc* **1999**, *121*, 1615-1616.

Chapter 7: Summary and conclusions

A summary of important findings and the salient conclusion from this study are listed below.

Uniform polyurethane particles were synthesized (in the particle size range 0.5 to 2 μ) by non aqueous dispersion polymerization using polymerizable and polymeric steric stabilizers. The molecular weight of the steric stabilizer and the nature of dispersion medium were the critical factors controlling the polyurethane particle size and its distribution. The macrodiol stabilizer takes part in the particle forming polymerization through chemical bond formation and covers the particle surface completely. On the other hand, the block copolymer stabilizer is adsorbed on the polyurethane particle surface. The macrodiol stabilizer stabilizes the polyurethane particles more effectively when compared to block copolymer at the onset of particle formation. However, efficient incorporation of the macrodiol stabilizers during dispersion polymerization is dependent on the relative reactivity of the stabilizer and the diol. It was observed that the incorporation of macrodiol stabilizer is poor when high molecular weight diols (e.g poly(ethylene glycol) with $\overline{M}_n$ 1000 to 2000) were used for polyurethane synthesis. It is, thus, very difficult to prepare an elastomeric polyurethane spherical particles using a macrodiol stabilizer. However, this can be achieved using an amphiphilic block copolymer as steric stabilizer.

The particle formation technique was successfully extended to poly(amide)s. Spherical particles of nylon 6 and copolymers of nylon 6/12 were synthesized using ring opening dispersion polymerization. The polymerizable stabilizer could not be enchained effectively during the polymerization Therefore, polymerizable and polymeric stabilizers stabilize the poly(amide) particles predominantly through physical adsorption.

The dispersion polymerization technique was successfully utilized to encapsulate carbon black particles. The dispersions of encapsulated particles were stable in aliphatic hydrocarbons. Also, highly dispersed polyurethane-clay nanocomposites were synthesized. It was demonstrated that the particle forming polymerization had taken place inside the galleries of clay. These dispersed nanocomposites exhibits superior thermal properties compared to intercalated polyurethane-clay nanocomposites and neat polyurethanes.

In conclusion, a novel macrodiol stabilizer was synthesized and successfully employed as a steric stabilizer in the particle forming polymerization of a diisocyanate and a diol. The macrodiol stabilizer participates in the urethane forming reaction and thus stabilizes the polymer particles effectively when compared to block copolymer stabilizer. Spherical poly(amide) particles were synthesized using a block copolymer and a polymerizable stabilizer. The latter did not take part in the ring opening polymerization process. The potential application of polyurethane particle forming polymerization was successfully demonstrated for the preparation of carbon black filled polyurethane particles as well as for a well dispersed polyurethane-clay nanocomposite.

Future perspectives

As the key to the successful dispersion polymerization lies on the choice of steric stabilizer, it is expected that, the synthesis of new steric stabilizer will continue to be a challenge. Very little is still known in the literature on dispersion polymerization of 2-hydroxyethyl methacrylate, vinyl acetate, N-vinylformamide and alkyl tralkoxysilane monomers. Well defined polymerizable steric stabilizers are essential to make monodisperse polymer particles of the polymers derived from monomers based above in good yield. Identification and synthesis of suitable polymerizable stabilizer for ring opening dispersion polymerization of cyclic monomers continues to be a challenge. The polymerizable stabilizer employed in the present study, for stabilizing poly(amide) particles, did not graft onto the poly(amide) particles. This is due to the decreased reactivity of the N-acyl lacatm. To overcome this limitation a cyclic amide with a reasonable hydrophobic moiety attached to the carbon atom (not to the nitrogen atom) should be tried

The polymer particles obtained from non aqueous dispersion polymerization using a polymerizable steric stabilizer can be used as a compatibilizer for making polymer blends. The fact that the polymer particles obtained *via* dispersion polymerization possess uniform particle size and shape, makes them attractive as powder coating materials. Furthermore, a variety of functional groups can be incorporated on the particle surface, thereby, altering the surface characteristic of the particle. Synthesis of nanoparticles of a wider range of polymers with narrow particle size distribution is also a continuing challenge to synthetic polymer chemist.