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THESE

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ELABORATION EN MILIEU DISPERSE DE MATERIAUX POLYURETHANE A STRUCTURE CŒUR-ECORCE

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- 2002 -

Dedicated to my parents…….

for your care, support & trust

& Rad……….
for your extraordinary patience, criticisms, encouragements and love

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Liste des abréviations

ABBREVIATIONS

ATRP	Atom Transfer Radical Polymerization
BPy	2,2'-bipyridine
CMC	Critical micellar concentration
DBTDL	Dibutyl tin dilaurate
DCC	1, 3-dicyclohexylcarbodiimide
DLS	Dynamic light scattering
DMF	Dimethylformamide
DMP	2,2–dimethoxy propane
DPM	1,1- iphenyl methane
DPMK	Diphenyl methyl potassium
DPTS	4-(dimethylamino) pyridinium 4- toluene sulphonate
DSC	Differential scanning calorimetry
EG	Ethylene glycol
f_n	Functionality
FTIR	Fourier transform infra-red spectroscopy
HD	Hexadecane
IPDI	Isophorone diisocyanate
$\overline{M}_n$	Number average molecular weight
$\overline{M}_w$	Weight average molecular weight
MBP	2-methyl bromopropionate
MMA	Methyl methacrylate
NAD	Non-aqueous dispersion
n-BuA	*n*-butyl acrylate
NMR	Nuclear magnetic resonance
NPG	Neo pentyl glycol
PAA	Polyacrylic acid
PDI	Polydispersity index
PEO	Polyethylene oxide
PMDETA	N,N,N',N'N''- Pentamethyl diethylene triamine
PMMA	Poly methyl methacrylate

PS	Polystyrene
PS-b-PEO	Poly (styrene)-b-poly (ethylene oxide)
PTSA	p-toluene sulphonic acid monohydrate
PUR	Polyurethane
PVP	Poly(vinyl pyrrolidone)
RI	Refractive index
SDS	Sodium dodecyl sulphate
SPS	Sodium persulphate
TCP	Tricresyl phosphate
TDI	Tolylene diisocyanate
TEA	Triethyl amine
TEM	Transmission electron microscopy
Tg	Glass transition temperature
THF	Tetrahydrofuran
TMP	Trimethylol propane
UF	Urea-formaldehyde
UV	Ultra violet

Introduction

Les techniques de polymérisation en milieu hétérogène telles l'émulsion, la suspension ou la dispersion sont particulièrement adaptées à l'élaboration de matériaux polymères sous la forme de particules. Les avantages économiques et pratiques qui caractérisent ces techniques – utilisation fréquente de l'eau comme phase dispersante, contrôle de l'exothermie de la polymérisation, quasi-absence d'accroissement de viscosité du milieu réactionnel ou encore facile mise en forme ultérieure des produits - suscitent des recherches toujours très soutenues dans les milieux industriels et académiques. De par leur technique d'élaboration, les matériaux ainsi préparés trouvent des applications dans de très nombreux domaines tels les revêtements, les adhésifs, les supports pour la chromatographie et la catalyse, l'encapsulation de médicaments, etc…

Il apparaît de façon assez évidente que les besoins que génère notre société dans les domaines cités, appellent à l'élaboration de nouveaux matériaux polymères de taille et de forme contrôlées et ayant une fonction bien définie en regard de l'application recherchée. Les études présentées dans ce manuscrit s'inscrivent dans ce thème avec l'objectif premier d'appliquer les techniques de polymérisation en milieu dispersé aux polymères issus d'un processus cinétique dit « par étapes » communément appelés « polycondensats ».

Si les données de la littérature sont très fournies s'agissant des polymérisations radicalaires en milieu hétérogène, peu d'études académiques traitent de la préparation en milieu dispersé de matériaux obtenus par polyaddition ou polycondensation. La première partie de la thèse à vocation bibliographique présente donc les différentes techniques d'obtention des matériaux polymères en milieu hétérogène en s'appuyant principalement sur les données de la polymérisation radicalaire. Un accent tout particulier est mis sur les différentes phases du processus d'obtention des particules ainsi que sur les critères de choix de l'agent tensio-actif qui va permettre la stabilisation colloïdale de la dispersion. Cette stabilisation peut être réalisée par simple adsorption physique de l'agent stabilisant à la surface de la particule en croissance ou par greffage chimique de ce dernier si celui-ci participe à la réaction de polymérisation. Enfin, les quelques exemples de polycondensats élaborés par ces différentes techniques dispersives sont rapportés dans cette première partie.

Le travail expérimental réalisé dans le cadre de cette thèse est ensuite discuté au cours des différents chapitres qui sont présentés sous la forme d'articles soumis à publication. Notre choix s'est porté sur la famille des polyuréthanes. L'éthylène glycol et le toluène diisocyanate ont été choisis comme monomères modèles et leur polymérisation a été étudiée en milieu dispersé dans le cyclohexane à 60°C en présence de dibutyl dilaurate d'étain (DBTL) comme catalyseur.

L'obtention de polyuréthane (PUR) sous la forme de particules requiert l'utilisation d'agents tensioactifs adaptés à la nature chimique du matériau préparé. Ainsi, dans le deuxième chapitre, l'emploi de copolymères à blocs de type polystyrène-b-poly(oxyde d'éthylène), PS-b-PEO et de polystyrène fonctionnalisé par une fonction hydroxyle en bout de chaîne, PS-OH, comme agents stabilisants de la dispersion, est comparé. Cette première étude montre très clairement que les PS-OH réactifs vis-à-vis des isocyanates sont des agents stabilisants de la dispersion efficaces en comparaison des copolymères à blocs (PS-PEO) qui ne peuvent induire une stabilisation des particules que par un phénomène d'adsorption. Cette première étude révèle également que les caractéristiques dimensionnelles des particules PUR formées sont très dépendantes de l'ordre et du mode d'addition de chaque réactif.

Ces premiers résultats nous ont alors conduit à tester d'autres agents stabilisants qui diffèrent par leur nature chimique et leur valence. Dans une première partie, le troisième chapitre discute l'aptitude de polybutadiène porteur d'une fonction hydroxyle, PBut-OH, à jouer le rôle d'agent stabilisant, au même titre que PS-OH, pour la préparation de PUR en milieu dispersé. Cette étude permet de relier les propriétés physico-chimiques et thermomécaniques (solubilité, température de transition vitreuse,…) des oligomères réactifs (PS-OH, PBut-OH) avec leur capacité à jouer le rôle d'agents stabilisants de dispersion. Ces agents stabilisants réactifs monovalents devant être considérés comme des "limitateurs" de chaîne en regard du processus de polymérisation par étapes, leurs homologues porteurs de deux fonctions hydroxyle en position géminée – au même bout de la chaîne - ont été synthétisés par polymérisations anionique vivante et radicalaire contrôlée puis testés pour la synthèse de polyuréthanes en milieu dispersé. L'influence de la valence des agents stabilisants sur la qualité des latex préparés est discutée dans la deuxième partie de ce chapitre.

C'est dans l'objectif de préparer des matériaux polyuréthane avec des propriétés adhésives que les poly(acrylate de butyle)s de type P*n*BuA-OH et P*n*BuA-$(OH)_2$ ont été élaborés puis testés comme agents stabilisants selon la même stratégie que précédemment. Ainsi, le quatrième chapitre discute dans un premier temps la préparation de ces agents stabilisants par polymérisation radicalaire contrôlée par transfert d'atome et les conditions requises pour obtenir ces oligomères de taille et de valence contrôlées. Dans un deuxième temps, la préparation des latex de PUR est décrite et discutée en fonction de divers paramètres liés à l'agent stabilisant (taille, valence, concentration,…) ou au mode d'addition de chaque réactif. La possibilité d'organiser les particules ayant un cœur PUR et une écorce polyacrylate dans des structures de type nids d'abeilles et l'évaluation des propriétés des films correspondants dans le domaine des adhésifs sont décrites dans une troisième partie de ce chapitre.

Le cinquième et dernier chapitre rassemble les méthodes et techniques de polymérisation qui ont été utilisées pour atteindre les objectifs visés. Les méthodes de caractérisation des particules synthétisées sont également rapportées.

CHAPTER 1:

BIBLIOGRAPHY

GLOSSARY

1 Introduction

Step-growth polymerization refers to an impressively broad spectrum of chemical processes whose reaction mechanism and catalysis are varied and complex. These reactions can generate an important category of polymeric materials, ranging from thermoplastic polymers to hard, high-softening thermosets, which for historical reasons are termed as "Condensation Polymers and resins".

The chain-growth mechanism proceeds via a step-by-step succession of elementary reactions between reactive sites. Reactive centers are in most cases functional groups or multifunctional groups, aromatic and hetero-aromatic rings, multiple bonds and related systems, ions, complexes and free radicals (generated by oxidation or thermal scission). We can define step-growth polymerization as a method in which the growth of the polymer chains proceeds by condensation or addition reactions between molecules of all degrees of polymerization.

Indeed, step-growth polymerization includes polyaddition and polycondensation. In addition polymerization there involves no elimination of byproducts, whereas in condensation reaction there occurs elimination of byproducts such as water, HCl, etc… In Table 1-1 is summarized some of the widely studied examples of these types of polymers obtained by step-growth polymerization.

In nature itself, a large number of polymers are synthesized by step-growth polymerization. Natural rubber (polyisoprene latex) was found to be produced via a series of enzyme catalyzed step-growth polymerization.[1] Another interesting naturally occurring polymer, synthesized by step-growth polymerization is poly(hydroxy butyrate), (PHB). This polymer has attracted considerable interest as a versatile biodegradable thermoplastic for the development of biomaterials[2] and for microencapsular drug delivery systems.

Synthetic polycondensates are conventionally produced by bulk, solution, melt or interfacial processes.

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[1] a) T. G. Fox, S. Gratch, *Ann. N. Y. Acad. Sci.*, 57, 367, **(1953)**; b) B. Jirgensens, *Natural Organic Macromolecules*, p161, Pergamon Press, New York **(1962)**.

[2] R. Arshady, *J. Controlled Release*, 17, 1, **(1991)**.

Bulk polymerization is carried out in the absence of solvent. This process concerns polyesterification of dicarboxylic acids or their alkyl esters with diols, polyamidation of dicarboxylic acids with diamines, poly-coordination of metal compounds with polydentate ligands and other reactions.[3] The advantages of this technique include the simplicity of the technological scheme, the possibility to synthesize polymer of high purity and the direct utilization of the polymer melt obtained for the final production of films and fibers. However, the high energy consumption, the long polymerization time to achieve complete conversion as well as the requirement for highly thermally stable initial monomers to avoid decomposition are the major drawbacks of this process.

Type	Reactants	Byproducts	Linkages	Polymers
Condensation	Dicarboxylic acids + diols	H_2O	$-CO_2-$	Polyesters
	Urea + formaldehyde	H_2O	$-HNCH_2$	Amino resins
	Bis(chloroformate)s + diamine	HCl	$-O_2CNH$	Polyurethanes
Addition	Diisocyanates + diols	-	-NHCOO-	Polyurethanes
	Diisocyanates + diamines	-	-NHCONH-	Polyureas
	Dinitriles + diols	-	-CONH-	Polyamides

Table 1-1 : Widely studied examples of polymers obtained by step-growth polymerization.

Infact, relatively milder conditions could be obtained by using a solvent. The monomer and the polymer are usually placed in a single-phase solution resulting in very high molar mass polymers. The usage of solvent eases the removal of low molar mass byproducts, at the same time assuring efficient heat transfer especially in case of exothermic reactions. The temperature of the polycondensation in solution is in the range of 20-250°C. However, the solvent itself and the impurities present in it (e.g. moisture) can give rise to undesirable side reactions such as exchange reactions, deactivation, blocking

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[3] V. V. Korshak, V. A. Vasnev, *Comprehensive Polymer Sci.*, Vol-5, Chp-9, 131, **(1989)**.

etc…. The use of solvent can also give rise to number of ecological problems. Solution polycondensation is used in the industry to produce aromatic polyamides, polyarylates, polycarbonates, polyurea etc.[4]

Most of the disadvantages faced in bulk and solution step-growth reactions can be overcome by performing the polymerization in dispersed medium. The growth of the macromolecules proceeds in a liquid or solid dispersed phase distributed in a liquid medium. In recent years, heterogeneous techniques such as emulsion, mini-emulsion, suspension, dispersion and precipitation have gained importance for the production of major polycondensates. These polycondensates include amino resins, phenolic resins, polyesters, polyamides, polycarbonates and polyurethanes.

A distinguishing feature of polycondensation in heterogeneous system is the high rate of the reaction, which is conducted as a rule at not very high temperature. This allows the use of thermally unstable monomers, preserves unsaturated bonds and other reactive groups in the macromolecules as well as avoids the thermal degradation of polymers. Moreover these techniques offer the possibility for manufacturing finished products such as films, membranes, fibers directly without any further processing.

Heterogeneous polycondensation often produces solvent free powders, beaded resins, or high solid (aqueous) dispersion. As a result, it provides ease of handling and processing and more important it reduces environmental pollution. These polymerization techniques have been developed for the preparation of microspheres. These polymer particles possessing uniform particle size and shape have gained considerable commercial importance as well as scientific interest due to the fact that they find varied applications as ion-exchange resins, surface coating for metal panels especially in automotive industries,[5,6] pharmaceutical reagents, biomaterials, parental drug delivery systems, toners for photocopying and printing, supports for solid phase synthesis and chromatographic media for separations,[7] etc…

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[4] P. M. Hergenrother, *Polym. J.,* 19, 73*,* **(1987)**.

[5] D. J. Walbridge; *Comprehensive Polymer Science*, Vol., 4, Ch. 15, 243, **(1989)**.

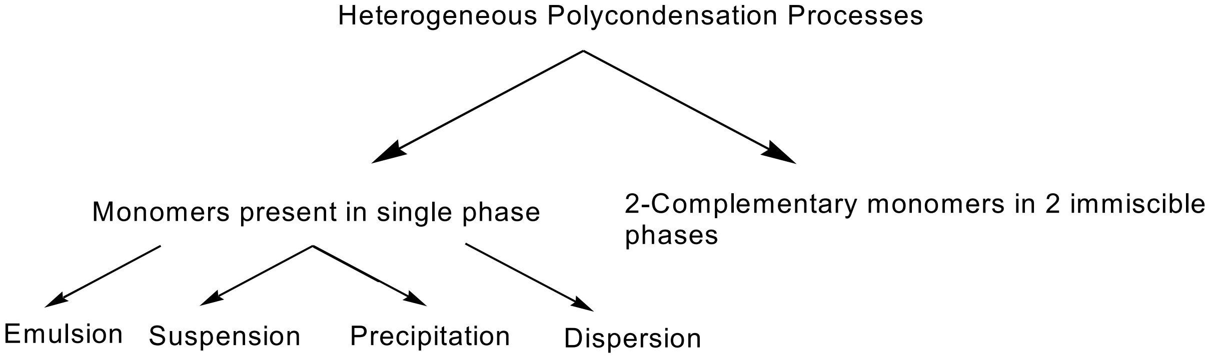
[6] N. Numa, *JP 02 228 320,* **(1989)**.

[7] K. Li, H. D. H. Stover, *J. Polym. Sci., Polym Chem*., 31, 2473, **(1993)**.

However, in comparison with those of vinyl monomers, details of step-growth polymerization in dispersed medium are less fully established and very few detailed studies of these above polymers are given in the literature.

2 Heterogeneous Polymerization Processes

On the basis of the initial state of polymerization as shown in Scheme 1-1, the heterogeneous methods employed for the production of polycondensates are classified into two main categories.



Scheme 1-1 : Classification of heterogeneous polycondensation.

In one category, the monomers are present in a single phase, while in the other, two complementary monomers are formally present in two immiscible phases.

In the case where the monomers are dissolved in two immiscible liquids, there may occur some partition of the monomers in the two phases. The reaction proceeds at the interface of the solvent. This type of system is described as "Interfacial Polycondensation". This is one of the most common way to produce polycondensates. The rate of this polymerization is very high especially when it is gas-liquid interfacial polymerization as compared to liquid-liquid interfacial polymerization. However, the system demands an equal reactivity for both the monomers used, as otherwise it would become more complicated. Interfacial polycondensation is widely used for the synthesis of polyesters, poly(thio-ester)s, polyarylates[8,9] etc... The efficiency of the polymerization is increased by performing the reaction in the presence of interfacial transfer catalyst. Schnell[10] reported for the first time the use of interfacial transfer catalyst for the synthesis of polymers. In this report polycarbonates were synthesized using tertiary amines and quaternary ammonium salts as the phase transfer catalyst.

Interfacial polymerization will not be discussed further in this chapter, as we will only focus on the techniques which yield polymers in particle form.

The case in which polymers are obtained in particle form is widely studied. In this case, the monomers are present in a single phase. The reaction proceeds in the full volume of one of the phase. Using this technique, dispersed polymers can be produced through several processes including emulsion polymerization, inverse emulsion, dispersion polymerization, mini-emulsion polymerization, micro-emulsion polymerization and by emulsification of the preformed polymers.

The distinction of the polymerization techniques is made on the following four criteria.

1) Initial state of the polymerization mixture
2) Kinetics of the polymerization
3) Mechanism of particle formation
4) Shape and size of the final polymer particles

Emulsion polymerization is by far the most common process for the production of dispersed polymers, also called as latexes.[11,12] It is very difficult to discriminate between interfacial polycondensation in liquid-liquid system and emulsion polycondensation. The changeover from the interfacial (surface) to the emulsion (volume) polycondensation

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[8] P.W. Morgan, *'Condensation Polymers by Interfacial and Solution Methods'*, Interscience, New York, **(1965)**.

[9] P. W. Morgan, *J. Macromol. Sci.*, A15, 683, **(1981)**.

[10] H. Schnell, *'Chemistry and Physics of Polycarbonates',* New York, **(1962)**.

[11] J. M. Asua (Ed), *Polymeric Dispersions: Principles and Applications*, Kluwer Academic Publishers, Dordrecht, **(1997)**.

[12] R. M. Fitch, *Polymer Colloids: A Comprehensive Introduction*, Academic Press, London, **(1997)**.

process depends on the type of the solvent used, which influences the general course of the reaction.

The characteristics of these polymerization techniques are tabulated below (Table 1-2) and the details of these techniques in terms of classical free radical polymerization are discussed thereafter. Then the specificity of step-growth polymerization using the different techniques as well as the polycondensates synthesized by these techniques are presented and discussed.

Type of Polymerization	Continuous Phase	Characteristics	Products
Precipitation	Water, Organic liquids	Monomer and initiator soluble in continuous phase ; auto accelerated polymerization due to gel effect.	Agglomerated polymer or slurry
Emulsion	Water, Organic liquids	Low monomer solubility, initiator soluble in continuous phase ; ionic/non-ionic surfactants; high rates due to radical isolation	Stable latex (0.1-0.33µm)
Suspension	Water, Organic liquids	Low monomer solubility, initiator soluble in monomer ; low level of ionic surfactant; gel effect	Coarse (>5µm) suspension in water
Dispersion	Water	Low monomer solubility, initiator soluble in continuous phase, polymeric surfactants; gel effect	Coarse (0.5-1.0µm) but stable emulsion
	Organic	Monomer and initiator soluble in continuous phase, graft copolymer surfactants; gel effect	Stable latex (0.1-0.5µm) dispersion up to 5µm possible

Table 1-2 : Characteristic features of heterogeneous polymerizations.

2.1. Emulsion polymerization

Emulsion polymerization is a heterogeneous process that produces polymer particles in sub-micron size range. They find applications in coatings, adhesives and additives for other products. In some cases, the polymer is separated from the continuous phase to produce synthetic elastomers and thermoplastics. The monomer droplets are usually dispersed in emulsion polymerization with diameter ranging from a few microns to >10 µm. The final polymer particle size is usually lower than 0.5 µm.

2.1.1. Chemistry of emulsion polymerization

Emulsion polymerization involves the growth of relatively water-insoluble monomer in numerous sub-micron latex particles dispersed in an aqueous phase. These latex particles can be stabilized by adsorption of surfactant species also referred to as emulsifiers (e.g., sodium dodecyl sulfate (SDS)), on the particle surface and the polymerization is generally initiated by a water soluble initiator (e.g., sodium persulfate (SPS)), leading to a unique free radical segregation effect.[13]

2.1.2. Mechanism of particle formation

2.1.2.1. Nucleation

The continuous water phase contains the initiator, the monomer and the emulsifier dissolved as individual molecules, sometimes in the form of micelles. The monomer is in relatively large monomer droplets, some is solubilized in the micelles and some dissolved in water. Emulsion polymerization starts with the particle nucleation by capture of free radicals by monomer swollen micelles (Figure 1-1),[14] as shown in interval I. The emulsifier helps to stabilize the droplets. Three nucleation mechanisms have been proposed namely micelle penetration, homogeneous precipitation and monomer droplet penetration.

2.1.2.1.1. Micellar nucleation

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[13] C. S. Chern, S.Y. Lin, T.J. Hsu, *Polymer Journal*, 31 (6), 516, **(1999)**.

[14] G. W. Poehlein, in *'Emulsion Polymerization'*, Polymer material Encyclopedia, Vol, 3, CRC press, **(1996)**.

Surfactants can form micelles, and these in turn can play the role of nuclei. This theory was put forward by Harkins.[15] According to this theory, the initiator radicals generated in the aqueous phase can enter the monomer-swollen surfactant micelles, as a single radical or oligo-radicals and form monomer-swollen polymer particles which grow by propagation reactions.[16] This internal polymerization disturbs the monomer-partitioning equilibrium and addition monomer diffuses into the newly formed particle through the water phase of the droplet. This type of nucleation ends with the disappearance of the micelles after which the number of particles generated remains constant.

2.1.2.1.2. Homogeneous nucleation

Precipitation of growing free radicals in the aqueous phase is called as homogeneous nucleation.[17] In this process, the radicals formed in the aqueous phase, propagate by monomer addition to form oligomers which are initially water soluble. These oligomers precipitate out from the water when the propagating chain reach the critical chain length of solubility i.e. j_{cr}. Fitch and Tsai[18] proposed that the rate of appearance of primary particles would thus initially be equal to the rate of generation of free radicals. The precipitated oligomeric radicals form primary particles, which are stabilized by the surfactants. The growth of these primary particles further takes place by addition of monomers, allowing further propagation.

2.1.2.1.3. Droplet nucleation

In emulsion polymerization, the monomer is insoluble in the solvent. It results in the formation of droplets dispersed in the solvent. The radicals generated in the aqueous phase can enter these droplets as a single radical or as oligo radicals and propagate to form particles.[19,20] The colloidal stability is due to the adsorption of surfactant molecules on the surface of the monomer droplets and the growing polymer particles. In monomer droplet

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[15] W. D. Harkins, *J. Am. Chem. Soc.*, 69, 1428, **(1947)**.

[16] W. V. Smith, R. H. Ewarth, *J. Chem. Phys.* 16, 592, **(1948)**.

[17] B. Jacobi, *Angew. Chem.*, 64, 539, **(1952)**.

[18] R. M. Fitch, C. H. Tsai, in *Polymer Colloids*, R.M. Fitch (ed), Plenum, New York, p 73, **(1971)**.

[19] D. H. Napper, R.G. Gilbert, *Makromol. Chem., Macromol. Symp.*, 10/11, 503, **(1987)**.

[20] P. L. Kuo, N. J. Turro, C M. Tseng, M. S. El-Aasser, J. M. Vanderhoff, *Macromolecules*, 20, 1216, **(1987)**.

nucleation, very small amount of the surfactant is adsorbed on the droplet as compared with that in other locations, hence free radicals are more likely to enter the monomer droplets and polymerize them. However, monomer droplet nucleation is usually not considered significant in emulsion polymerization because the emulsifier adsorbed on the droplet surface is very small as compared to the other locations such as the micelles and the ones dissolved in the medium.

2.1.2.2. Particle growth

Particle nucleation ends when the surface area of the particles and monomer droplets formed is sufficient to adsorb all the emulsifier and accommodate the hydrophilic end groups of the initiator. A conversion up to 5% is reached at this stage. In Interval II, the growth of the latex particles by recruiting monomer and surfactant from the emulsified monomer droplets occurs. Most of the monomers are in the form of droplets. In the continuous phase are present these monomer droplets and the particles.

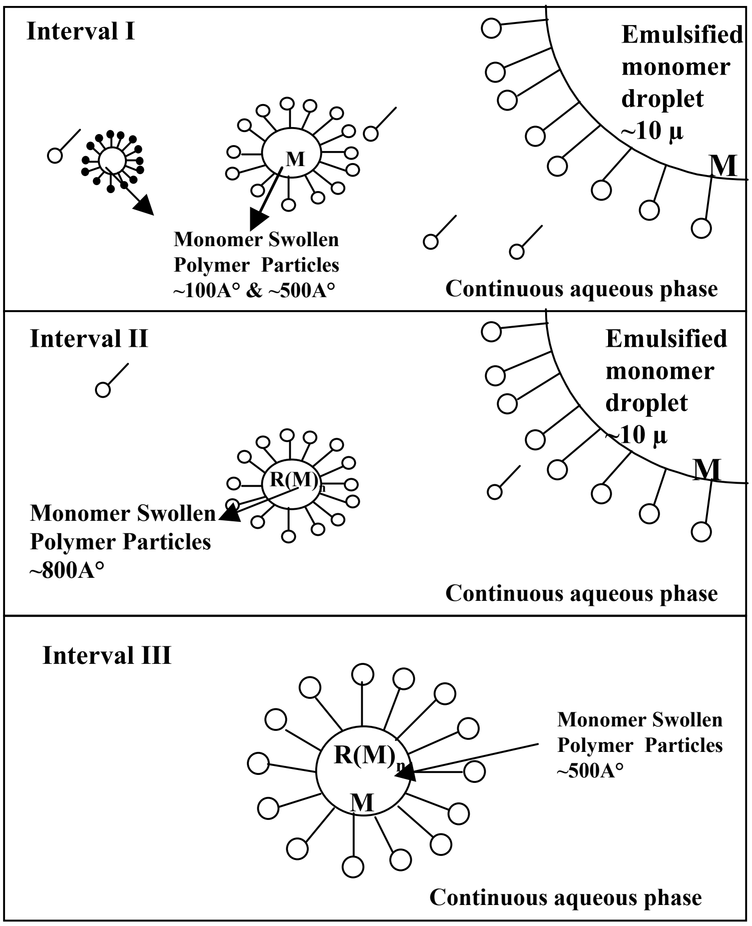

Figure 1-1 : Schematic diagram of the three intervals of emulsion polymerization.

Polymerization proceeds by diffusion of the monomer from the monomer droplets into the continuous phase. The diffusion process ends when the polymer concentration in the monomer approaches that in the polymer particles. The total interfacial area (particle + droplets) increases during Interval II. The monomer concentration in the particles is relatively constant during this period. The monomer concentration in the polymer particle decreases during Interval III. This results in a difference in the density between the monomer and the polymer. As a result, the volume fraction of the disperse phase decreases. The viscosity of the reaction medium decreases and the emulsifier surface coverage increases as the reaction proceeds.

The course of the reaction in emulsion polymerization could be well understood by taking into account the chemical reactions and the transport phenomena occurring in the system as shown in Figure 1-2. Figure 1-2 is a diagram of a monomer-swollen polymer particle in which the internal reactions and the transport of the different species are taking place.

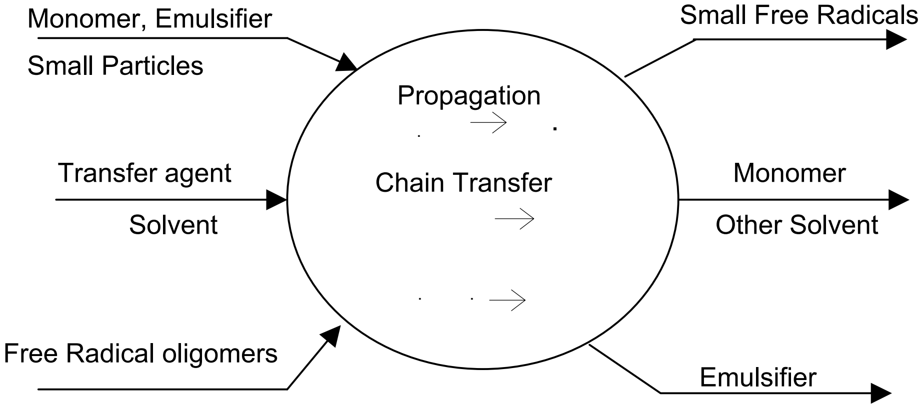

Figure 1-2 : Reactions and transport phenomena with a monomer-polymer particle.

2.1.3. Stabilizers used for emulsion polymerization

Stabilizers are also termed as emulsifiers in emulsion polymers. They are the most challenging part of emulsion polymerization technique. The emulsifiers need to permit the formation of a monomer emulsion and to stabilize the polymer particles formed without affecting the performance of the resulting polymers. Various ionic and polymeric stabilizers have been used to obtain stable emulsions. Ionic stabilizers are usually referred as emulsifiers or surfactants. However, when non-ionic polymers play the role of stabilizing the particles, they are referred as stabilizers.

2.1.3.1. Ionic emulsifiers

Ionic emulsifiers are of anionic and cationic type.

Anionic oil-in-water emulsifiers are the most widely used, commercially as well as for research. The negatively charged hydrophilic head group of the anionic surfactants may comprise sulfate, sulfonate, sulfosuccinate or phosphate groups attached to an hydrophobic backbone.[21] The nature of the hydrophilic group will influence:

a) the extent of electrostatic stabilization,

b) the behavior of surfactants as a function of pH,

c) the degree of hydrolysis and

d) the variation of latex stability with time and temperature conditions.

The nature of the hydrophobic backbone will influence:

a) the adsorption behavior of the surfactant/emulsifier onto the latex particle surfaces,

b) the Critical Micellar Concentration (CMC) values and

c) the interfacial tension which affects monomer emulsification and the extent of steric stabilization.

However, ionic surfactants have certain disadvantages such as electrolytic sensitivity, lack of freeze-thaw stability. Desorption from the particle also occurs on keeping it for long time. This reduces the shelf-lives of these polymers. Instability in post-reaction formulation processes on applying shear and stress takes place because the stability offered by these stabilizers are by electrostatic stabilization. This affects the application performance, such as reduced coating adhesion.[14] Sodium lauryl (dodecyl) sulphate is an example of widely used anionic surfactants in emulsion.

Cationic surfactants/emulsifiers are used infrequently in emulsion polymerization, mainly because they are not compatible with the negatively charged latex particles.

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[21] Witco Co., *Surfactants for Emulsion Polymerization*, Technical Bulletin, **(1988)**.

Examples of cationic surfactants are salts of long chain amines, quaternary ammonium salts (e.g. hexadecyl trimethyl ammonium bromide), poly(ethylene oxide) terminated with amino groups and their quarternized derivatives and amine oxides.[22]

2.1.3.2. Non-ionic emulsifiers

Non-ionic emulsifiers are the most commonly used to stabilize the particles in emulsion techniques. They are referred to as stabilizers. These are usually block copolymers or homopolymers that form a protective coating for the resultant colloids, imparting stability by steric stabilization mechanism, which is in contrast to the electrostatic stabilization provided by ionic stability. Non-ionic emulsifiers are characterized by much lower CMC as compared to the ionic emulsifiers because of the absence of electrostatic repulsion between the hydrophilic groups.

Some of the commonly used non-ionic surfactants are poly(ethylene oxide)-b-poly(styrene), poly(ethylene oxide)-b-poly(propylene oxide), poly(ethylene oxide) end-capped with a thiol group, long chain carboxylic acid esters, etc… A few of the surfactants are tabulated below in Table 1-3 with their structure.

Non-ionic surfactants	Structure
Poly(ethylene oxide)	PEO-OH
Poly(ethylene oxide) dodecyl ethers	$C_{12}H_{25}(OCH_2CH_2)_mOH$ m = 4, 14, 23, 30
Poly(ethylene oxide) nonyl phenyl ethers	$C_9H_{19}C_6H_4(OCH_2CH_2)_mOH$ m = 20, 30

Table 1-3 : Non-ionic surfactants used in emulsion polymerization.

It is notable that much larger particles are obtained when non-ionic emulsifiers are used alone ; these have lower diffusion coefficients than the ionic emulsifiers which would

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[22] M. J. Rosen, *Surfactants & Interfacial Phenomena*, 2nd edition, Wiley, New York, **(1989)**.

permit more extensive coalescence of the precursor particles.[23] It has been found that a mixture of ionic and non-ionic emulsifiers gives polymers with well controlled particle size and particle size distribution. This was attributed to the combined effect of steric hindrance and electrostatic repulsion in retarding radical entry or in preventing particle coalescence. For example, Piirma and Wang[24] used a mixture of sodium dodecyl sulfate and Emulphogene BC-840 (a tridecyloxy-poly(ethylene oxide)) in the ratio of 0.2 and they found that a very narrow size distribution of polystyrene latex was obtained.

2.1.3.3. Polymerizable stabilizers

Ionic or non-ionic emulsifiers stabilize the resultant particles by steric or electrostatic repulsions. Hence, these stabilizers can desorb from the latex with time or during processing of the latexes. One of the ways to reduce this negative effect is to use polymerizable or reactive stabilizers. The latter are able to react in the polymerization process either as initiators (inisurfs) or as transfer agents (transurfs) or most commonly as polymerizable surfactants (surfmers). Due to the fact that the surfactant possesses reactive end groups, they get covalently bounded to the particles. The resultant particles have better stability towards certain constraints such as shear stress and freeze-thawing processes.

It, at the same time, also ensures that no desorption from the polymer particle or migration in the polymer films takes place. A. Guyot *et al*. studied a variety of ionic and non-ionic surfactants[25] and a few of them are shown in Table 1-4.

Surfactants	Type

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[23] A. S. Dunn, *Polym. Int.,* 30, 547, **(1993)**.

[24] I. Piirma, P. C. Wang, Ch. 3, p 34, in *Emulsion Polymerization*, I. Piirma, J. L. Gardon (eds), ACS Symposium Series, Vol. 24, American Chemical Society, Washington, DC, **(1976)**.

[25] A. Guyot, K. Tauer, J. M. Asua, S. Van Es, C. Gautier, A.C. Hellgren, D. C. Sherrington, A. Motoya-Goni, M. Sjoberg, O. Sindt, F. Vidal, M. Unzue, H. Schoonbrood, E. Shipper, P. Lacroix-Desmazes, *Acta Polym.*, 50, 57, **(1999)**.

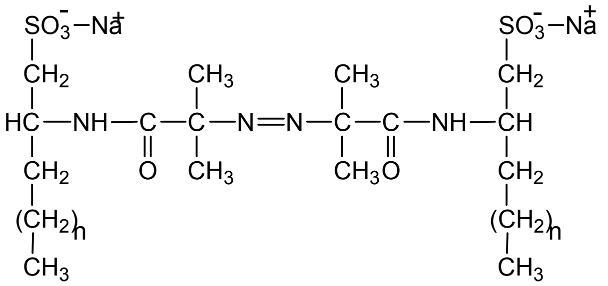
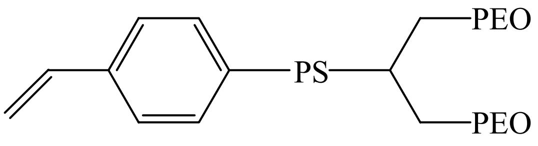
	Inisurfs
$C_nH_{2n+1}OCO\text{-}HC=CH\text{-}COONa$; n=8-18 Hemiester of maleic anhydride (Na salt)	Anionic Surfmers
$C_nH_{2n+1}OCO\text{-}HC=CH\text{-}COOCH_2CH_2N(CH_3)_3{}^+Br^-$; n=12 Alkyl maleate trimethylamino ethyl bromide	Surfmers
$Me\text{-}(\ CH_2CH_2O)_{45}\text{-}[(CH_2)_4)\text{-}O]_{10}H$ Hydroxy terminated poly(ethylene oxide)	Reactive precursor
$Me(CH_2CH_2O)_{45}-(CH_2CH(C_2H_5O))_{12}\text{-}OCOCH_2SH$ Thiol end-capped poly(ethylene oxide)-b-poly(butoxide)	Transurfs

Table 1-4 : Reactive surfactants used in emulsion polymerization.

Gibanel *et al.*[26] recently published the first report using non-ionic gemini type reactive stabilizers as shown in Scheme 1-2 in the emulsion polymerization of styrene. In this study the effect of the polymerization kinetics of the gemini type surfactant was compared with that of the linear homologue. Coagulum was obtained which was attributed both to the self association of the reactive surfactants in water as well as due to the high reactivity of the styrenyl entity.



Scheme 1-2: Gemini Type PS-b-PEO_2 macromonomer.[26]

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[26] S. Gibanel, J. Forcada, V. Heroguez, M. Schappacher, Y. Gnanou, *Macromolecules*, 34, 4451, **(2001)**.

2.1.4. Synthesis of polycondensates and the factors affecting emulsion technique

2.1.4.1. Factors affecting emulsion step-growth polymerization

2.1.4.1.1. Organic/aqueous phase ratio

Emulsion polymerization is usually performed in aqueous medium. However in step growth polymerization, the monomers used in most of the cases are solid and must be dissolved in organic solvent. The polymerization is then performed in aqueous medium. Hence, in emulsion polycondensation process, the system consists of 2-liquid phases, an organic solvent and water. One of the most important factor affecting the polymerization is the ratio between the two phases. An increase in the water content in the organic phase, results in an increase in the polarity of the medium. This speeds up the ability to undergo solvation, and in turn increases the chance of decomposition of the intermediate complexes. In the study involving polyamide synthesis from terephthaloyl dichloride with m-phenylenediamine, it was found that the rate constant increased from 1 to 3 to 25, while changing the solvent from anhydrous tetrahydrofuran to tetrahydrofuran containing 4.5 and 35% of water. Increase in the water content results in hydrolysis of the acyl chloride which future affects the polymerization rate. It is also noteworthy to mention that the volume ratio between the aqueous and organic phase is maintained between 1/1 – 1/3.[9,27]

2.1.4.1.2. Choice of organic solvent

As mentioned earlier, the changeover from interfacial polycondensation to emulsion polycondensation depends on the solvent used. The solvent influences the distribution coefficient of the monomer (K_D). Since in emulsion polycondensation processes, 2-liquid phases are present, polymerization usually proceeds in the bulk of the organic phase. Hence, the nature of the organic phase has considerable effect on the polymerization process. It has been found that the use of water miscible solvents like THF, acetone, 2,3-dimethyl tetramethylene sulfone etc… results in an increase in the coefficient of distribution, (K_D), for the monomers. In addition it increases the swelling behavior of the resultant polymer in the organic phase.[9,28] This results in high molar mass polymers. In polyarylate synthesis, the increase in the content of water-miscible solvent such as THF,

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[27] L. B. Sokolov, T. V. Kudim, *Vysokomom. Soedin.*, Ser. A, 7, 1899, **(1965)**.

[28] G. Reinisch, U. Gohlike, H. H. Ulrich, *Makromol. Chem., Suppl.*, 3, 177, **(1979)**.

resulted in a reduction of the molar masses. This was explained on the basis of the lower solubility of the first formed low molar mass oligomers.[28]

2.1.4.1.3. Effect of temperature

Temperature is another important factor affecting the polymerization rate and the polymers obtained thereafter. An increase in the reaction temperature lowers the molar mass of the formed polymer. The main reason for this is associated with an increased contribution of side reactions, such as the hydrolysis of acyl chloride which is one of the most commonly used monomer in condensation polymerization. At higher temperature the interaction between the chlorides and the solvent are also increased.[8] Emulsion polycondensation is usually performed at room temperature.

2.1.4.2. Synthesis of polycondensates by emulsion technique

With the help of emulsion polycondensation, various polycondensates have been synthesized. A couple of them have been detailed, while the others have been tabulated below.

2.1.4.2.1. Polyesters

Polyesters are conventionally prepared by condensing hydroxyl containing monomers with carboxylic acids containing monomers by continuously removing water formed as the by-product to increase the efficiency. Polyesters are a particularly preferred class of condensation polymers because their properties make them suitable for a variety of end-use applications including textile fibres, films, coatings and engineering plastics.

Saam[29] *et al.* reported the synthesis of polyesters under mild conditions by directly condensing hydroxycarboxylic acids or mixtures of monomeric or oligomeric poly functional alcohols and a monomeric or oligomeric polyfunctional carboxylic acids in a hydrophobic media using, a heterogeneous catalyst. Cationic, anionic or non-ionic surfactants have been used as the emulsion stabilizers. The stabilizer weight percentage was ranged from 0.1 wt. % to 20 wt. %. The resultant polyesters were found to be useful as plasticizers and as precursors for alkyl resins and other polymers.

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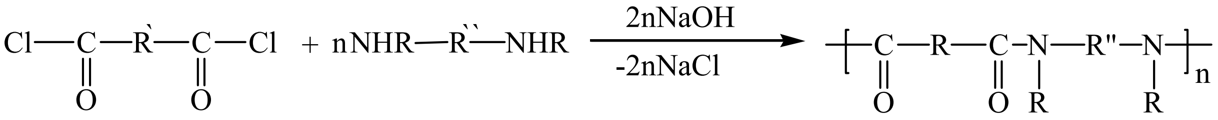
[29] J. C. Saam, Y. J. Chou, *US Patent*, 05,856 401, **(1982)**.

2.1.4.2.2. Polyamides

A variety of aromatic and aromatic-aliphatic polyamides (Scheme 1-3) have been successfully synthesized.



$$\mathrm{Cl{-}\underset{\underset{O}{\|}}{C}{-}R'{-}\underset{\underset{O}{\|}}{C}{-}Cl + nNHR{-}R''{-}NHR \xrightarrow[-2nNaCl]{2nNaOH} \left[\underset{\underset{O}{\|}}{C}{-}R{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{R}{|}}{N}{-}R''{-}\underset{\underset{R}{|}}{N}\right]_n}$$

R = H, Me

Scheme 1-3 : Polyamide synthesis by step-growth processes.

Aromatic copolyamides have been obtained in THF-water/Na_2CO_3 system. The monomers used for the studies comprised of ter- and iso-phthaloyl dichloride and m-phenylene diamine.[30] Using the similar system, statistical and block copolymers were synthesized by successive introduction of acyl dichloride and also by varying their concentration and ratio.

Another important class of polycondensates prepared by emulsion techniques is presented in Table 1-5. However, because of the numerous technological problems faced such as intensive stirring, solvent regeneration, clearing the polymer from the inorganic salts and formation of various byproducts, the studies concerning this class of polymers are rather limited.

Polymers	Monomers	Yield (%)	[η] (dl g^{-1})	ref
Polyamides	Terephthaloyl dichloride + trans-2, 5-dimethylpiperazine	94	3.4	9
Polyarylates	Terephthaloyl dichloride + Phenolphthalein	96	1.2	31
Polyurethanes	Bisphenol A + hexamethylenediisocyanate	98	0.91	32
Polyurea	p, p'-diaminodiphenylmethane bis (carbamyl chloride) + N, N'- dimethyl- p, p'-	80	0.14	17

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[30] V. V. Korshak, V. A. Vasnev, *Comprehensive Polymer Sci.*, Vol-5, Chp-11, 167, **(1989)**.

[31] T.V. Kudim, L. B. Sokolov, *Vysokomol. Soedin.*, Ser. A, 20, 1802, **(1978)**.

[32] S. Foti, P. Maravigna, G. Montaudo, *Chim. Ind.*, (Milan), 65, 337, **(1983)**.

	diaminodiphenylmethane			
Polyhydrazide	Isophthaloyl dichloride + Hydrazine hydrate	100	0.22	33

Table 1-5 : Polycondensates synthesized by emulsion technique.

2.2. Mini-emulsion polymerization

Mini-emulsion is a relatively stable, sub-micron dispersion of oil in water. It belongs to the class of emulsion polymerization. Ugelstad *et al*[34] were the first to report the polymerization of sub-micron styrene droplets using sodium lauryl (dodecyl) sulfate (SLS) and cetyl alcohol as the emulsifiers. Mini-emulsion processes have been applied to the encapsulation of different water-insoluble materials such as $CaCO_3$ and carbon black.[35]

2.2.1. Chemistry of mini-emulsion polymerization

Mini-emulsion is defined as the polymerization of all the monomer droplets present in the initial emulsion. The final particle size is reflected in the initial droplet size. It involves the dispersing of water insoluble monomers in sub-micron sizes.[36] The monomer droplet size ranges from 50-500 nm. These are obtained by shearing a system containing oil, water, surfactant and a co-stabilizer. As explained later, the role of the co-stabilizer is essential ; conventionally it is called the "hydrophobe".

The difference between emulsion polymerization and miniemulsion is unambiguous. In emulsion polymerization the final latex particle does not correspond to the primary droplet and the size is established by kinetic parameters such as temperature or amount of initiators which play a predominant role. These factors are independent in miniemulsion. The final latex is the copy of the original droplets, which is governed by the dispersion process and the droplet stability.

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[33] A. Ballisteri, D. Garozzo, G. Montaudo, A. Polliano, M. Giuffrida, *Polymer*, 28, 139, **(1987)**.

[34] J. Ugelstad, M. S. Al-Aasser, J. W. Vanderhoff, *J. Polym. Sci., Polym. Lett. Ed.,* 11, 503, **(1973)**.

[35] N. Bechthold, F. Tiarks, M. Willert, K. Landfester, M. Antonietti, *Macromol. Symp.,* 151, 549, **(2000)**.

[36] E. D. Sudol, M. S. El Aasser, in ‘*Emulsion Polymerization and Emulsion Polymers*; P. A. Lowell, M. S. El Aasser; Ed, Wiley, New York, 699, **(1997)**.

2.2.2. Mechanism of particle formation

2.2.2.1. Nucleation

Monomer droplets are the nuclei in miniemulsion polymerization. These droplets are achieved by homogenizing the oil-water mixture by subjecting the system to a very high shear field. This shear field is created by devices such as an ultrasonifier, a Manton Gaulin homogenizer or a microfluidizer. The resulting mechanical shear and/or cavitations results in the break up of the monomer present as the oil phase into sub-micron size droplets. These droplets are in turn stabilized by the use of ionic surfactants coupled with a low molar mass co-stabilizer. Appropriate surfactant/co-surfactant combinations are decisive in stabilizing these droplets.

Unlike emulsion polymerization where 3-different nucleation mechanisms exist, as detailed in section 2.1.2.1, the monomer droplet itself is the dominant site for particle nucleation in miniemulsion.[37] However, micellar nucleation and homogeneous nucleation cannot be ruled out. In fact miniemulsion is performed with the intent of only particle nucleation and eliminating the other two types of nucleation. Micellar nucleation is eliminated by keeping the aqueous phase concentration of the surfactant below its CMC.

In case of free radical polymerization process, homogeneous nucleation is reduced by providing free radical sinks, i.e. droplets and particles. The small size monomer droplets which results due to the high shear provides relatively larger surface area for particle adsorption. This reduces the life time of an oligomeric radical in the aqueous phase below that required for it to grow beyond its limit of water solubility. This reduces the possibility of homogeneous nucleation. Hence, we can conclude that in miniemulsion the monomer droplets indeed becomes the dominant site for particle nucleation.

2.2.2.2. Growth of the particles

Each monomer droplet polymerizes independently of each other. The monomer droplets before the polymerization and the final polymer particles after the polymerization have the same size and are composed in a similar manner. This has been proven by a combination of Small Angle Neutron Scattering (SANS), surface tension measurements

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[37] P.L. Tang, E. D. Sudol, M. E. Adam, C. A. Silebi, M. S. Aasser, *In Polymer Latexes: Preparation, Characterization, and Application*; E. S. Daniel, E. D. Sudol, M. S. El Aasser, Eds; ACS Symposium Series, 492, ACS, Washington DC, 72, **(1992)**.

and conductometry.[38] For the dispersed droplet after miniemulsification, the changes in the particle size and the particle number can occur by two processes namely growth by Ostwald ripening (τ_1 processes) and growth by collision between the droplets (τ_2 processes).

2.2.2.2.1. Growth by Ostwald ripening

Oswald ripening is the case of monomer diffusion from the smaller droplets into the larger droplets. This results in a pressure increase higher than the Laplace pressure. The Laplace pressure results from the interfacial droplet tension. This Ostwald ripening can be suppressed by using hydrophobes (co-surfactant) having extremely low water solubility. The commonly used hydrophobes are hexadecane and cetyl alcohol.[39,40,41] Alkyl thiols[42] and blue dye[43] have also been reported to be used. The hydrophobes work by creating an osmotic pressure in each droplet and diminishes the Ostwald ripening.

2.2.2.2.2. Growth by collision

After miniemulsification, a point of "critical stability" is reached, whereby the system is osmotically stable but critically stabilized against particle collision. To reach a stable state, the growth of the system should occur by collision until the Laplace pressure and osmotic pressure are counter balanced. At this point, each droplet can be polymerized by a 1:1 coping process with respect to the initial monomer droplet size. The size of the final polymer droplet is the same as that of the initial monomer droplet. This is due to the fact that the growth of particles by collision is slow as compared with the actual polymerization time. In fact long term stability of this critical state can be achieved by addition of approximate amount of surfactant for post stabilization.

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[38] K. Landfester, N. Bechthold, S. Förster, M. Antonietti, Macromol *Rapid Commun*., 20, 81, **(1999)**.

[39] Y. T. Choi, M. S. El Aasser, E. D. Sudol, J. W. Vanderhoff, *J. Polym Sci., Poly. Chem. Ed*., 23, 2973, **(1985)**.

[40] J. Delgado, M. S. El Aasser, J. W. Vanderhoff, *J. Polym Sci., Polym. Chem. Ed*., 24, 861, **(1986)**.

[41] D. Mouran, J. Reimers, J. F. Schork, *J. Polym. Sci., Polym. Chem*, 34, 1073, **(1996)**.

[42] C. S. Chern, T. J. Chen, *Colloid Polym. Sci.,* 275, 546, **(1997)**.

[43] C. S. Chern, T. J. Chen, Y. C. Liou, *Polymer,* 39, 3767, **(1998)**.

2.2.3. Factors affecting miniemulsion polymerization

The two important factors affecting miniemulsion polymerization are the homogenization and the nature of the hydrophobe.

2.2.3.1. Effect of shear on homogenization

Homogenization is an important factor affecting the size and the size distribution of the resultant particles. Efficient homogenization results in small and homogeneously distributed droplets.[44] It can be achieved using different methods, such as simple stirring which is usually followed by ultrasonification for small quantities, whereas microfluidizer or high pressure homogenizers are used for emulsification of bigger quantities.

The process of homogenization begins with stirring the sample using mechanical stirrer in order to achieve droplets. This is followed by ultrasonification, which reduces the droplet size until an equilibrium is reached. In fact, in the beginning of homogenization, the size distribution of the droplet is still quite high, but by constant fusion and fission processes, distribution of the particle size decreases.

2.2.3.2. Effect of the hydrophobe

After homogenization, the unstable dispersions can undergo growth by Ostwald ripening or by collisions (coalescence). The suppression of both these mechanisms are necessary to achieve stable miniemulsions. Coalescence can be avoided by using an efficient surfactant, whereas Ostwald ripening is suppressed by using hydrophobic agents also called as co-surfactants. As already said, this agent can counteract the Laplace pressure of the droplet by remaining trapped in the droplet and creating an osmotic pressure.

A highly efficient hydrophobe is the one that has less water solubility and the more effective is as an osmotic pressure agent. Many different molecules (Table 1-6) can be used as hydrophobes such as, hexadecane or other molecules, which may act as a dye, a co-monomer, or other additives. Silanes, siloxanes, isocyanates, polyesters, fluorinated alkanes and many others have found to be efficient in suppressing ostwald ripening.

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[44] B. Abismail, J. P. Canseleir, A. M. Wilhelm, H. Delmas, C. Gourdon, *Ultrason. Sonochem.,* 6, 75, **(1999)**.

Polymers make an ideal hydrophobe[45] because it is able to fulfill the major requirements of any hydrophobe : water insoluble and monomer compatibility. In Table 1-6, is given a list of different hydrophobes used in miniemulsion. Since they are sparingly soluble in water, they form micellar aggregates, the size of which are also given.

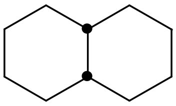
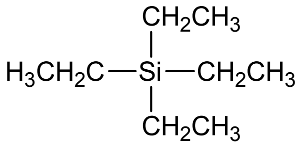
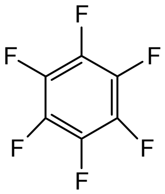
Hydrophobes	*Diameter, nm*	*Surface tension, mN m^{-1}*
$CH_3-(CH_2)_{14}-CH_3$	*102*	*67.2*
Oligostyrene; Mw =1000	*96*	*68.2*
	*78*	*68.4*
 $H_3CH_2C-\underset{CH_2CH_3}{\overset{CH_2CH_3}{Si}}-CH_2CH_3$	*99*	*68.2*
	*86*	*69.2*
Olive oil	*80*	*52.8*
Polyesters	*82*	*50.1*

Table 1-6 : Different Hydrophobes used in Miniemulsion.[46]

2.2.4. Synthesis of polycondensates by miniemulsion technique

Miniemulsion technique have been used for the synthesis of a wide variety of polycondensates.

2.2.4.1. Polyurethanes

Aqueous polyurethane is widely used for application such as adhesives and coatings. Their films show excellent elasticity and abrasion resistance and superior low

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[45] J. Ugelstad, P. C. Mork, K. H. Kaggerud, T. Ellingsen, A. Berge, *Adv. Colloid Interface Sci.*, 13, 101, **(1980)**.

[46] K. Landfester, *Macromol. Rapid Commun.*, 22, 896, **(2001)**.

temperature impact resistance. These are usually synthesized by a two-step process involving synthesis of the prepolymer in a bulk or in an inert solvent followed by emulsification, using high shear treatment. Polyurethane particles with average diameters of 200 nm were synthesized by Landfester *et. al* in a one step process using miniemulsion techniques.[47] The characteristics of the polyurethane dispersion are given in Table 1-7, (see page :27).

Mini-emulsions were generated by intense shearing of a system containing a hydrophobic monomer, water, a surfactant and a hydrophobe. The monomers used in the synthesis were isophorone di-isocyanate and 1,12-dodecanediol. Hexadecane was chosen as the hydrophobe. Sodium dodecylsulfate (SDS) was used as the stabilizer for this purpose. Bisphenol A, instead of 1,12-dodecanediol was also used as the reaction partner for IPDI and the dispersion characteristics were found to be the same.

2.2.4.2. Epoxy resins

Epoxy resins find application in a wide range of purposes since the standard recipes of gluing and coating formulations are based on epoxy chemistry. The synthesis of epoxy resins by miniemulsion represents a meaningful improvement for the synthesis of these epoxy resins.

Landfester[48] *et al.*, successfully performed the polyaddition by mini-emulsion technique using a series of ionic polymeric stabilizers. The surfactants used in this synthesis are given in Table 1-8. The addition polymerization involved different di-, tri-, and tetra epoxides with varying diamines, dithiols and bisphenols as shown in Table 1-9. Particles were obtained in the size range of 83 nm – 175 nm by varying the different stabilizers.

Stabilizer	Structure
SDS	$CH_3(CH_2)_{11}OSO_3Na$
CTMA-Cl	$CH_3(CH_2)_{15}N(CH_3)_3Cl$

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[47] F. Tiarks, K. Landfester, M. Antonietti, *J. Polym. Sci. Part A: Polym. Chem.*, 39, 2520, **(2001)**.

[48] K. Landfester, F. Tiarks, H-P, Hentze, M. Antonietti, *Macromol. Chem. Phys*. 201, 1, **(2000)**.

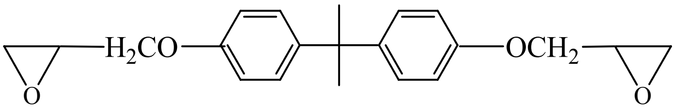
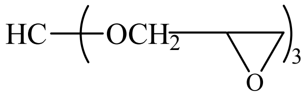
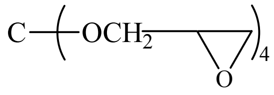
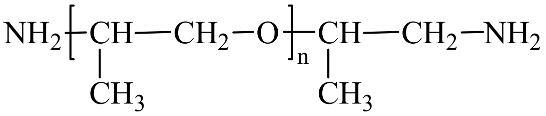
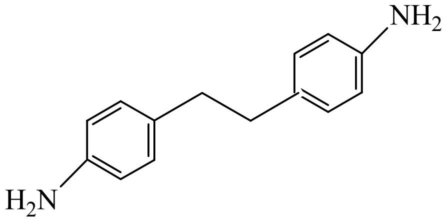
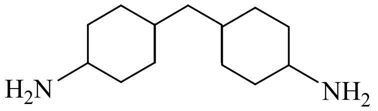
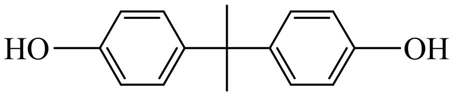
PS/PEO	$(Sty)_{10}$-block-$(EO)_{114}$; $(Sty)_{10}$-block-$(EO)_{68}$; $(Sty)_{30}$-block-$(EO)_{68}$
Lutensol AT 50	$(C_{16}H_{33})(EO)_{50}$

Table 1-8 : Types of surfactants used for mini-emulsion of epoxy polymers.[48]

No	Monomers, (g)		Surfactants[a], (g)	H_2O, (g)	Hydrophobe[b], (g)	Coagulum, (%)	Particle size, (nm)	Standard deviation	Surface tension, (mN/m)
1	IPDI	3.5	0.25	30.1	0.15	<5	202	0.43	41.8
	1,12-Dodecanediol	3.0							
2	IPDI	3.4	0.1	30.2	0.15	<5	208	0.34	50.9
	1,12-Dodecanediol	3.0							
3	IPDI	3.4	0.05	30.6	0.15	15	232	0.38	55.4
	1,12-Dodecanediol	3.0							
4	IPDI	3.4	0.025	30.6	0.15	43	229	0.35	57.6
	1,12-Dodecanediol	3.0							
5	IPDI	3.3	0.1	20.2	0.25	<5	228	0.33	46.1
	Bisphenol A	3.4							
6	IPDI	3.4	0.25	20.2	0.25	-	167	0.38	35.6
	1,12-Dodecanediol	2.0							
	NPG	0.5							
7	IPDI	3.3	0.25	20.0	0.25	-	232	0.30	36.6
	Bisphenol A	2.3							
	NPG	0.5							

[a] Surfactant: SDS
[b] Hydrophobe: Hexadecane

Table 1-7 : Characteristics of PUR latexes.[47]

Substances	Structures	$\overline{M_W}$ or WPE[a], g/mol
Epoxides	 Epikote E828	$\overline{M_W}$ = 312
	 Denacol Ex-314	WPE = 227
	 Denacol Ex-411	WPE = 144
Amines	 $NH_2[CH(CH_3)—CH_2—O]_n—CH(CH_3)—CH_2—NH_2$ Jeffamin D2000	$\overline{M_W}$ = 2032
	 4,4'-diaminobibenzyl	$\overline{M_W}$ = 212
	$NH_2—(CH_2)_{12}—NH_2$ 1,12-diaminododecane	$\overline{M_W}$ = 200
	 4,4'-diaminodicyclohexylmethane	$\overline{M_W}$ = 210
Dithiol	$SH—(CH_2)_6—SH$ 1,6-Hexanedithiol	$\overline{M_W}$ = 150
Bisphenol	 Bisphenol A	$\overline{M_W}$ = 228

[a] WPE : Weight per epoxide unit

Table 1-9 : Monomers used for poly-addition in miniemulsion.[48]

Depending on the chemical nature of the monomers, the amount of the surfactants and the pH of the reaction mixture, latex particles with diameter between 30 nm and 600 nm and narrow size distribution were obtained.

2.3. Suspension polymerization

Suspension polymerization is a widely used heterogeneous process for producing commercial polymers and various ion-exchange resins.[49] It is also known as bead or pearl polymerization because smooth, spherical particles are produced suspended in aqueous phase. In this technique, the monomer is suspended in the continuous phase, usually water, as very small droplets, by using suitable stabilizers such as poly(vinyl alcohol). The initiator is soluble in the monomer and the polymerization process occurs in the monomer droplets.[50] The nucleation predominantly occurs in the droplets. The monomer droplets are directly converted to polymer particles with negligible change in the particle diameter. The uniformity of the monomer droplets and that of the final polymer particles are governed by the nature of the stabilizers, the monomer to continuous phase ratio and the agitation rate. The particle diameter ranges from 50-100 µm.

2.3.1. Chemistry of suspension polymerization

In suspension polymerization each droplet acts as a small bulk polymerization reactor. The suspension medium itself acts as an efficient heat transfer agent. As a result, high rates of polymerization can be maintained to achieve complete conversion during relatively short periods of time.

2.3.2. Mechanism and kinetics of particles formation

The reaction takes place in the monomer droplets and each droplet acts as a small bulk polymerization reactor. The kinetic mechanism of free radical polymerization in suspension is similar to that of bulk polymerization. The reaction rates are not influenced to a great extent by bead size.[51]

Suspension polymerization consists of three stages. The polymerization starts with the monomer being suspended as droplets in an aqueous phase with continuous agitation. To prevent coalescence, suspending agents also called as stabilizers are added. At this stage, the viscosity of the organic phase is low, the droplet size is small and the particle size distribution is relatively narrow, depending on the agitation and the nature of the

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[49] A. Dawkins, In *Comprehensive Polymer Science*; G. C. Eastwood, et al., Eds.; Pergamon New York, 4, 231, **(1989)**.

[50] R. Arshady, M.H. George, *Polym. Eng. Sci.,* 33, 865, **(1993)**.

[51] M. Munzer, E. Trommsdorff, In *Polymerization Processes*, C. H. Schildknecht, I. Skeist, Eds, Wiley Interscience, New York, 106, **(1977)**.

suspending agent. The suspension is stable as the droplet population dynamics is fast and the assumption of the quasi steady state is valid.

The second stage starts at about 20-30 % conversion when the droplets become highly viscous and visco-elastic, and when the breakage and coalescence rates decrease. However, the breakage rate decreases faster than the polymerization so the average droplet size increases. Moreover if the coalescence rate dominates or if this stage lasts too long, a broadening of particle size distribution or even agglomeration will occur. The suspending agent are very crucial at this stage when the droplets become sticky and are easily agglomerated. At even higher conversions, the mobility of the polymer chains within the droplets diminishes due to entanglements which results in reduction of the termination rate, this effect is called the "Trommsdorff or gel effect".[52] This effect also results in a overall increase in the rate of the reaction. The "Trommsdorff or gel effect" is a function of temperature, conversion, polymer size, etc.[53]

At high conversion, the third stage begins whereby the particles are solid. The monomer molecules start to have diffusional problems and the propagation rate decreases. This results in reduced rate of reactivity and sometimes the polymerization is not 100% complete.

2.3.3. Stabilizers used for suspension polymerization

Suspending agents or stabilizers play an important role in preventing coalescence during the second stage when the particles become more sticky and show a tendency to coagulate. These are usually water-soluble polymers also called as protective colloids or finely divided inorganic salts

2.3.3.1. Inorganic salts

Finely divided, inorganic salts such as talc, calcium and magnesium carbonates, silicates and phosphates, together with small amount of surfactants can act as suspending agents.[51] The actual mechanism of stabilization by these agents are not well understood, but it is postulated that surface adsorption and formation of a protective layer is a

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[52] E. Trommsdorff, H. Kohle, P. Lagally, *Makromol. Chem.*, 1, 169, **(1948)**.

[53] G. Odian, *Principles of Polymerization*; John Wiley & Sons: New York, **(1981)**.

dominating factor.[54] Wetting characteristics of these dispersing agents at the surface of the droplet are also reported to be an important factor.[54]

2.3.3.2. Protective colloids

Water soluble polymers used as suspending agents or stabilizers are also referred to as protective colloids. These include biopolymers as well as synthetic polymers. Biopolymers used are gelatine, proteins, cellulose derivatives and polysaccharides. Synthetic polymers include poly(vinyl alcohol), poly(vinyl pyrrolidone), and other hydrophobic-hydrophilic block copolymers.[52] A good steric protective colloid is a diblock copolymer (A_mB_n) with one block compatible with the surface of the particle (A) and the other block compatible with the continuous phase (B).

The mechanism of stabilization by protective colloids occurs in two ways. First, they decrease the interfacial tension between the monomer droplets and the aqueous phase which results in the formation of smaller droplets dispersed in the medium. Second, they are adsorbed at the surface of the monomer droplet to produce a thin layer that prevents coalescence when the collision occurs. The protective mechanism is thus due to the repulsive force that the two polymer-covered surfaces feel when the segments begin to overlap. Poly(vinyl alcohol) is the most widely used protective colloid.

2.3.4. Factors affecting suspension polymerization

The average size of the monomer droplet and in turn the resulting particle size can be readily controlled by varying the stirring speed, volume ratio of the monomer to suspension medium and the viscosities of both phases according to the Equation (1) reported by a number of workers.[55]

$$\bar{d} = k \frac{D_v \; R \; \nu_d \; \varepsilon}{D_s \; N \; \nu_m C_s} \qquad \text{...Eq. (1)}$$

where $\bar{d}$ = average particle size; k = parameters such as apparatus design, type of stirrer, self established, etc., D_v = diameter of vessel; D_s= diameter of stirrer; R = Volume ratio of the droplet phase to suspension medium; N= Stirring speed (or power of mixing); ν_d = viscosity of the droplet phase; ν_m = viscosity of the

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[54] J.E. Puig, E. Mendizàbal, *Polymeric Material Encyclopedia*, CRC press Vol 10, 8215, **(1996)**.

[55] R. Arshady, *Colloid and Polymer Science*, 270, 717, **(1992)**.

suspension medium; ε = interfacial tension between the two immiscible phases and Cs = Concentration of the stabilizer.

2.3.4.1. Stirring speed

Among the parameters indicated in Eq (1), stirring speed is by far the most convenient means of controlling particle size. It is usually found that with increasing stirring speed, one obtains smaller particle size. A typical example of the dependence of particle size on stirrer speed is given in the Figure 1-3 for the suspension polymerization of styrene using hydrophobically modified poly(ethylene oxide) as the stabilizer.[56] However, this pattern of particle size control by stirrer speed is generally observed for well-established suspension systems although the slope of the curve may vary, depending on the magnitude of other parameters in the above Eq (1).

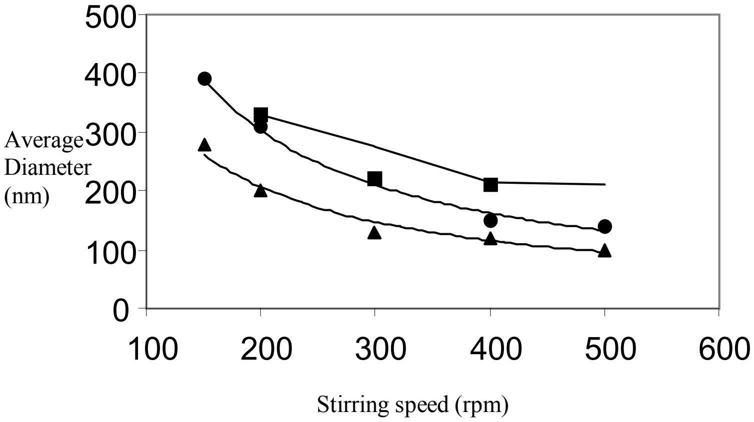

Figure 1-3 : Effect of stirrer speed on particle size in suspension polymerization of styrene in the presence of 0.2% (■), 0.3% (•), or 0.4% (▲) of a hydrophobically modified poly (ethylene oxide) stabilizer.[56]

2.3.4.2. Solvent

The surface and the bulk morphology are important aspects of the polymer obtained by suspension polymerization. The particle morphology is in turn strongly influenced by the use of a suitable monomer diluent (except water) in suspension polymerization. This is related to the degree by which the polymer dissolves, swells or precipitates in the monomer phase. The monomer diluent, i.e. the solvent, plays its own important role. When the polymer is soluble in the monomer mixture, the resulting particles have smooth surface and a non-porous texture. In the reverse case, the final particles have a rough surface and a

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[56] S. M. Ahmed, *Disp Sci. Technol.*, 5 (3 & 4), 421, **(1984)**.

porous surface. In the same manner, highly porous polymer is obtained when a very good non-solvent for the monomer as well as the final polymer is selected. As an example, a highly non-porous polymer was obtained in the suspension copolymerization involving styrene, 2,4,5-trichlorophenyl acrylate and divinyl benzene, in chlorobenzene-octane mixture which is a poor solvent for both the monomers as well as the polymer. However a porous polymer was obtained when chlorobenzene alone was used as the solvent since it is a good solvent for the monomers. Porous 3D polymers are of particular interest in the production of cross-linked ion exchange resins and polymer supports.

2.3.4.3. Concentration of the stabilizer and monomer

The final particle size decreases when the concentration of the stabilizer increases. This can be explained on the basis of high stabilizer concentration which would be able to stabilize a large surface area leading to a large number of small particles.

At the same time, as the amount of the solvent increases, the particle size increases. When the amount of solvent is increased beyond a certain limit, coagulation occurs due to the lack of effective stabilizer concentration available for stabilization. Another factor that contributes is the increase polymerization rate due to dilution. Due to faster rates of polymerization, more nuclei are formed. These nuclei remain rather large in size, as the effective surface area covered is less in presence of reduced amount of stabilizer.

2.3.5. Synthesis of polycondensates by suspension technique

Suspension polymerization can be employed to produce particles from a size range of 100 nm to about 1-2 mm or even larger. However, in the case of chain polymerization of vinylic monomer, polymer particles within the range of 20 μm - 2 mm have been found to be efficiently formed. Preparation of particles smaller than 20 μm by suspension polymerization becomes more complicated.[57]

Polycondensation in suspension medium may be carried out in aqueous or in an organic medium. Depending on the medium, different types of condensation suspension polymerization are present. They can be classified as oil in water (o/w), oil in oil (o/o) or water in oil (w/o) suspension polymerization. Polyesters, polyurethanes and phenolic resins are the widely studied polymers in suspension.

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[57] Y. Almog, M. Levy, *J. Polym Sci.*, Part-A-19, Polym. Chem.,115, **(1981)**.

2.3.5.1. Polyesters

Oil in oil (o/o) suspension polymerization technique is usually used for polyester synthesis. One of the earliest examples of polyester synthesis was reported[58] in 1975. Poly(ethylene terephthalate) dispersion was obtained from a solution of bis (hydroxyl ethyl) terephthalate in high boiling petrol, by azeotropic distillation of ethylene glycol. A graft copolymer consisting of poly (methyl methacrylate) backbone with pendant poly (12-hydroxy stearic acid) soluble side chains was used as the dispersant. The resulting polyester was obtained in the form of spherical particles with a relatively broad particle size distribution.

2.3.5.2. Polyurethanes

Polyurethanes were prepared by suspension polymerization of isocyanate-terminated pre-polymer with diols in aqueous or non-aqueous medium. Researchers in Bayer developed the technology of aqueous suspension polycondensation for polyurethane. Their work has been well reviewed by Dietrich.[59] Since the chemistry involving the synthesis of polyurethane is very versatile, a number of process modifications has been performed. One of the most interesting way of modification involves the use of prepolymer ionomers.[60] The latter produces self-stabilized droplets upon dispersion in water and do not require the use of any droplet stabilizer.

Another way to produce polyurethane involves dispersing amide ended prepolymer at a temperature above the glass transition temperature of the polymer, resulting in the formation of droplet. Subsequently, formaldehyde is added as chain extenders and the polymerization is continued to a desired degree to obtain final polyurethane suspension. Usually, particle size in the range of 0.1 –10 µm are obtained.

The development of non-aqueous dispersion, i.e. (o/o) suspension polycondensation has been reported in a Japanese Patent.[61] According to the authors, a mixture of a polyester polyol (prepolymer) and hexanediisocyanate is stirred in paraffin oil, in the presence of a

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[58] K. E. J. Barret, *Dispersion polymerization in Organic Media*, Wiley-Interscience, New York, **(1975)**.

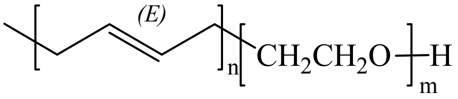
[59] D. Dieterich, *Chem Unserer Zeit.*, 24 (3), 135, **(1990)**.

[60] D. Dieterich, *Angew. Makromol Chem.*, 98, 133, **(1981)**.

[61] K. Kanetani, Kokai Koho *JP 0,206,519;* CA 113/79237r **(1990)**.

multi-component stabilizer system. Dibutyl tin dilaurate was used as the catalyst and the suspension polycondensation was carried out at 60°C.

Recently, Sivaram *et al.* reported polyurethane synthesis in suspension medium using a diblock copolymer as the steric stabilizers.[62] The structures of the stabilizers used are shown in Scheme 1-4. They suspended the two condensation monomers, ethylene glycol and tolylene diisocyanate in paraffin oil and carried out the polymerization at 60°C using dibutyl tin dilaurate as the catalyst. The characteristics of the polyurethane particles are shown in Table 1-10.



1a: n =57; m 19
1b: n =92; m = 50
1c: n = 463; m = 79

Scheme 1-4 : Amphiphilic block copolymer used as a steric stabilizer for PUR synthesis.

Block copolymers	Particle size, µ	D_w/D_n
1a	13	1.68
1b	22	1.7
1c	50	-

Table 1-10 : Characteristics of the polyurethane particles obtained in the presence of amphiphilic block copolymer used as stabilizer.

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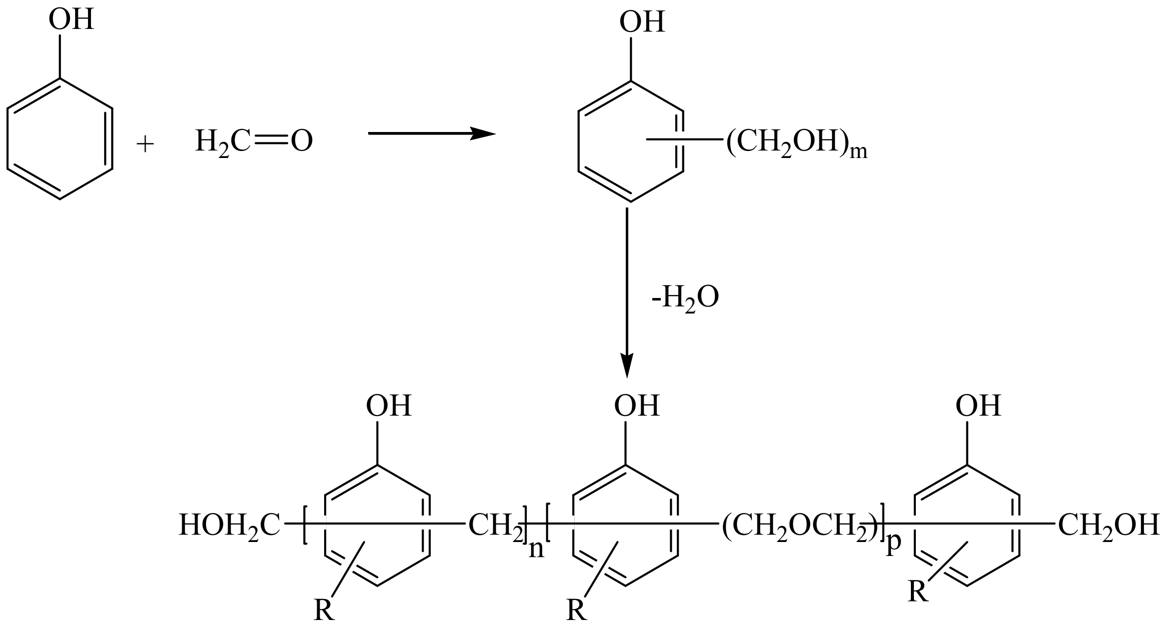
[62] L. S. Ramanathan, P. G. Shukla, S. Sivaram, *Pure and Appl. Chem.*, 70-6, 1295, **(1998)**.

2.3.5.3. Phenolic resins

Phenol-formaldehyde resins, also referred to as phenolic thermospheres, are one of the most well developed suspension polycondensation processes.[63,64]

Step: 1



Resole Intermediate: R = H or CH_2OH

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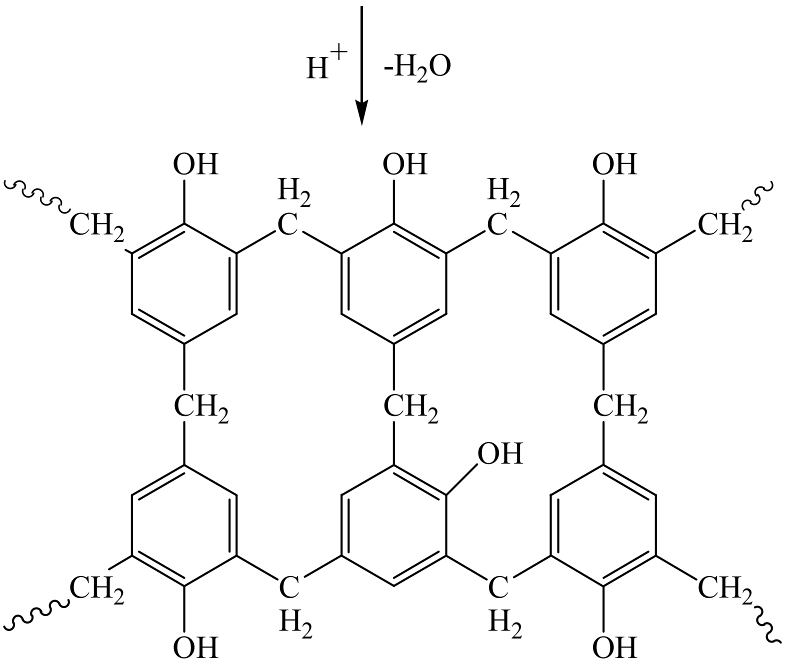
[63] T. R. Jones, S. W. Chow, G. L. Brode, *Chemtech*, 678, **(1983)**.

[64] G. L. Brode, *J. Macromol Sci.*, *Reviews*, 22, (5-7), 895, **(1985)**.

Step: 2

Resole Intermediate



Tridimensional resin product

Scheme 1-5 : "Resole" and resin formation in polycondensation of phenol with formaldehyde.

The process involves two steps, (Scheme 1-5) whereby in the first step, phenol is condensed with formaldehyde in a concentrated aqueous solution in the presence of barium hydroxide (pH = 8). This results in water soluble oligomers also referred to as "Resole".

In the second step, the mixture is acidified with sulphuric acid, resulting in the formation of droplet suspension of "resole" in water. Two polysaccharides, gum arabic and gum agar were used as steric stabilizers. The average size of the "resole" droplets and that of the resulting microspheres were controlled by the concentration of the stabilizers, pH and rate of stirring. A detailed study in this respect[65,63] have been carried out by the authors and the results have been reported in Table 1-11. It was found that pH played an important role as it determines the proportion of phenolate groups on the surface of the resole as well as it influences the solubility of the stabilizers, which in turn controls the particle size.

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[65] T. R. Jones, S. W. Chow, G. L. Brode, *Chemtech*, 678; **(1983)**.

Stabilizer effect		pH effect	
Stabilizer[a] (%)	Particle size (µm)	pH	Particle size (µm)
0.5	58±20	2.8	75±35[b]
1.0	27±5	3.2	38±20
2.0	13±4	4.1	20±7
		6.7	10±4

a= based on phenol weight
b= Unstable suspension

Table 1-11 : Effect of stabilizer and pH on the particle size of phenolic resins.

2.3.5.4. Urea-formaldehyde resins

Ebdon[66] and his colleagues have reported the synthesis of beaded UF resin, in w/o suspension. An aqueous solution of formaldehyde and urea was stirred in paraffin and allowed to react at a pH of 7.5 in the presence of Span 85 as the droplet stabilizer. The resulting droplet suspension was maintained at 82°C for 2h with constant stirring, followed by acidification and further stirring for 16h at the same temperature. The resulting beads were then made free of low molar mass materials and cured by cross-linking using ammonium chloride at 105°C. Beaded melamine-formaldehyde resins have also been produced similarly.

2.3.5.5. Polyimine ion-exchange resins

Poly(ethylene imine-epichlorohydrin) was successfully produced by w/o suspension polymerization by Seko *et al.*[67] In this process an aqueous solution of poly(ethylenimine) was suspended in heptane containing sorbitan trioleate as the stabilizer. Epichlorhydrin

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[66] J. R. Ebdon, B. J. Hunt, M. Al-Kinany, in A. H. Fawcet ed., *High Value Polymers*, 109, RSC, London **(1991)**.

[67] M. Seko, T. Myaka, K. Takeda, K. Imammura, *JP Kokai, 7,673,087*; CA 85: P79254X, **(1976)**.

was then added to the mixture and the stirring was continued at 40°C for 1h. This was followed by further heating at 90°C for 4-6h to obtain beaded resin product.

2.4. Dispersion polymerization

Dispersion polymerization was first developed in the 1950's to meet industrial need for non-aqueous dispersion coating technologies suitable for automotive paints. The successful development has since led to many other applications including reprographics, adhesives, encapsulants, colored polymer particles and coatings.[68]

Dispersion polymerization usually starts as a homogeneous solution of the monomer, the initiator or the catalyst and a steric stabilizer in organic solvents. This type of polymerizations are thus often called as non-aqueous dispersion (NAD) for historical reasons, though water is also sometimes used as the co-solvent. The resultant polymer is insoluble and precipitates out to form colloidal dispersion, with the polymeric stabilizer added to prevent flocculation. The stabilizer may become adsorbed, or more commonly grafted on the particle surface. One of the most important factors in dispersion polymerization, concerns the role and function of this steric stabilizer. Its interaction with the polymer and the solvent, which in turn determines the particle size, size distribution and polymer molar mass, will be discussed in the following sections.

2.4.1. Chemistry of dispersion polymerization

Dispersion polymerization depends on the homogenous nucleation of particles from the reaction medium in a manner similar to the particle formation process in emulsion polymerization.[69] Therefore when nucleation occurs in a short period of time at the start of the reaction, little or no coalescence occurs, narrow distribution of particle size is expected. This process differs from emulsion polymerization in several important elements that include the difference in the use of a polymeric steric stabilizer instead of the commonly used ionic surfactant as stabilizer. The presence of a single phase at the beginning of the polymerization in contrast to the multiple phases present during an emulsion polymerization is another important distinguishing factor. Once polymerization has begun,

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[68] H. D. H. Stover, *Polymeric Material Encyclopedia*, CRC press Vol 3, 1900, **(1996)**.

[69] C. K. Ober, K. P. Lok, *Macromolecules*, 20, 268, **(1987)**.

the polymer formed precipitates out of the solvent. The precipitated polymers in the form of particles are stabilized by a soluble polymer added to the mixture.

2.4.2. Mechanism and kinetics of particle formation

In dispersion polymerization, the reaction begins with all the component in the homogeneous solution. The initial locus of the polymerization is the continuous phase itself, though it may later shift to the interior of the polymer particles, depending on the solvency. The actual process of dispersion is complex.

2.4.2.1. Nucleation

The period over which nucleation occurs is known to be short. Several nucleation theories have been proposed, including micellar entry,[70] homogeneous nucleation,[71] aggregative nucleation,[72] and the latest comprehensive model reported by Paine,[73] which suggested the growth mechanism by both homo and hetero-coagulation. In Figure 1-4 is shown the proposed stages of dispersion polymerization. During nucleation and in specific case of free radical polymerization, the polymerization begins with the formation of oligomeric radicals. Due to the poor solvency of the medium, the oligomeric radicals contracts and form colloidally unstable precursor particles. These particles may further coagulate, until they have adsorbed enough stabilizer from the medium onto the surface to become sterically stabilized. At this point a conversion of only 1% is reached. The total number of the particles become fixed and nucleation ceases when the stabilizer coverage becomes sufficient to prevent further homocoagulation. Nuclei have been detected in the MMA: methanol system by dynamic light scattering and have diameters in the range of 25 nm, which corresponds to approximately 200 oligomer chains.[74]

However, a very different particle nucleation occurs in step growth polymerization as compared to vinylic monomers chain growth polymerization. Indeed, the oligomers are built up gradually through out the reaction rather than by individual chains being initiated

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[70] J. W. Goodwin *Br. Polym. J.*, 5, 347, **(1973)**.

[71] J. W. Goodwin, *Colloid. Polym. Sci.*, 252, 646, **(1974)**.

[72] P. J. Feeney, D. H. Napper, R. G. Gilbert, *Macromolecules*, 20, 2922, **(1987)**.

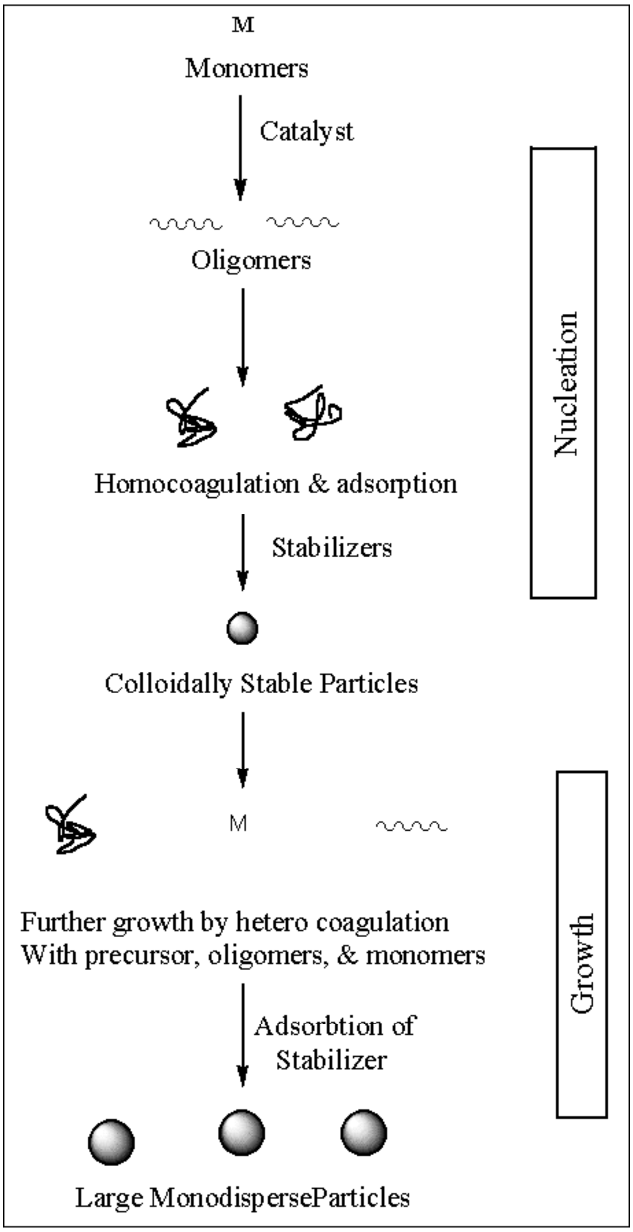
[73] A. J. Paine, *Macromolecules*, 23, 3109, **(1990)**.

[74] S. Shen, E. D. Sudol, M. S. El Aasser, *J. Polym. Sci., Polym. Chem.*, 32, 1087, **(1994)**.

and rapidly growing in the presence of the monomer.[75] Indeed, in step growth polymerization the average degree of polymerization, j is just 10 at 90% conversion, 100 at 99% conversion etc.... Thus critical chain length for self-nucleation, j_{cr} may be reached at very high conversion.

2.4.2.2. Particle growth

After nucleation, the oligomers are captured by the existing particles (heterocoagulation) before they can adsorb enough stabilizer to create a second generation of stable particles. This process leads to the formation of polymer microspheres in the size range from 0.1 µm-20 µm with very narrow size distribution. This process of particle nucleation applies for all stabilizers, including functional homopolymers and macromonomers which stabilize by *in situ* formation of graft or block copolymers.



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[75] R. M. Fitch, *Polymer Colloids: A Comprehensive Introduction*, Academic Press, Chp 4, 63, **(1997)**.

Figure 1-4 : Particle formation and growth in dispersion polymerization.

2.4.3. Particle stabilization

Particles produced by dispersion polymerization in the absence of stabilizer are not sufficiently stable and may coagulate during their formation. Adding a small percentage of a suitable stabilizer to the polymerization mixture produces stable particle dispersion. Particle stabilization in dispersion polymerization is usually referred to as "steric stabilization".

2.4.3.1. Principle of steric stabilization

Polymer dispersions prepared in the absence of stabilizer are unstable and coagulate as soon as they precipitate out leading to precipitation polymerization. Hence, it is always necessary to have a small percentage of stabilizer to produce stable particle dispersion. Some of the more common stabilizers used in dispersion polymerization of styrene or methyl methacrylate in polar solvents are hydroxypropylcellulose (HPC), poly(vinylpyrrolidone) (PVP), poly(acrylic acid) (PA).[76,77,78]

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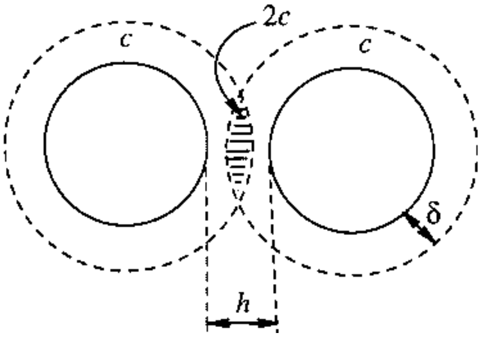
[76] A. J. Paine, *J. Colloid. Interface Sci.,* 138, 157, **(1990)**.

[77] A. J. Paine, W. Luymes, J.Mc Nulty, *Macromolecules,* 23, 3104, **(1990)**.

[78] C. K. Ober, K. P. Lok, M. L. Hair, *Polym. Sci. Polym. Lett. Ed.*, 23, 103, **(1985)**.



c= Concentration of stabilizer chain, h=distance between particle surfaces; δ=thickness of the stabilizer layer in solution.

Figure 1-5 : Schematic representation of the close approach of sterically stabilized particles.

These homopolymers react with the monomers to form graft copolymers which serve as steric stabilizers. The non polar graft anchors this copolymer onto the particle surfaces while the polar stabilizer backbone forms a protective brush layer that prevents coagulation of the particles. This type of stabilization is called as steric stabilization.[79] It is believed that the colloidal stabilization density results from the interpenetration or compression of the polymer sheets (c) when two particles approach one another (Figure 1-5).[80] The osmotic diffusion of solvent into this region of increased stabilizer concentration (2c) generates a repulsive force, causing the particles to separate.

2.4.3.2. Stabilizers used for dispersion polymerization

Three types of polymeric stabilizers have been used in case of dispersion polymerization.

2.4.3.2.1. Homopolymers

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[79] D. W. J. Osmond, F. A. Waite, In *Dispersion Polymerization in Organic Medium*; Barrette, K. E. J.; Ed.; Wiley London, ‘Preparation of Polymer Particles by Dispersion Polymerization’, **(1975)**.

[80] R. H. Ottewill, T. Walker, *Kolloid-Z.Z. Polymere*, 227, 108, **(1968)**.

Homopolymers can act as stabilizers by formation of *in situ* graft copolymer. It involves chain transfer of the monomers with a stabilizer precursors[81] resulting in the formation of an amphipathic copolymer. Poly(vinylpyrrolidone), poly(vinyl alcohol) and hydroxy propyl cellulose, are the polymers which have been studied under this class of polymers as stabilizers in the dispersion polymerization of styrene in polar medium.[82,83] Bourgeat-Lami *et al* have reported thiol end-capped poly(ethylene oxide) as the reactive stabilizer for styrene dispersion polymerization.[84] The length of the homopolymers and its concentration are important parameters in determining the stability of the polymer particles. The efficiency of the reactive stabilizer is due to the high reactivity of the stabilizer itself and it was found that thiol end-capped PEO stabilized the dispersion of styrene more efficiently than a hydroxy terminated PEO.

2.4.3.2.2. Block copolymers

The most successful type of stabilizers for non-aqueous dispersion polymerization are block copolymers. Block copolymers contain one block which is the soluble stabilizing moiety and another block which is the anchor component insoluble in the continuous phase which is adsorbed on the particles thereby stabilizing the resultant polymer particles. A careful balance must be struck between the anchor and soluble component of the stabilizer to avoid formation of micelles as the rate of dissociation of micellar aggregates into a single molecule is very slow in organic solvent as compared to aqueous medium. Block copolymers of the type AB and ABA are used as stabilizers.

Block copolymers such as poly(styrene)-b-poly(ethylene-co-propylene)[85] and poly (styrene)-b-poly(ethylene oxide)[86] are being increasingly used as steric stabilizers. In analogy to the graft copolymer described above, block copolymers adsorb selectively.

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[81] J. M. Sàenz, J. M. Asua, *J. Polym. Sci., Polym. Chem.*, 34, 1977, **(1996)**.

[82] Y. Cheng, H. W. Yang, *J. Polym Sci., Polym Chem.*, 30, 2765, **(1992)**.

[83] K. Cao, B-F Li, Y; Huang, B-G Li, Z-R, Pan, *Macromol. Symp*. 150, 187, **(2000)**.

[84] E. Bourgeat-Lami, A. Guyot, *Colloid Polym Sci.*, 275, 716, **(1997)**.

[85] J. Stejskal, P. Kratochvil, C. Konak, *Polymer*, 32 (13), 2435, **(1991)**.

[86] C. L. Winzor, *et al.*, *Eur. Polym. J.*, 30(1), 121, **(1994)**.

However, the adsorption of these compounds onto the polymers is weak leading to poor stabilization of the polymer particles.[87]

2.4.3.2.3. Macromonomers

Another class of steric stabilizer that is receiving increasing attention is the class of macromonomers. The use of macromonomers in dispersion polymerization was pioneered by ICI.[58] These are low molar mass polymers with high affinity for the polymerization medium that bear a polymerizable end-group. These macromonomers behave as the co-monomer and the stabilizer simultaneously. They are therefore covalently bonded to the polymer material so their desorption from the polymer particles or migration in the polymer films are impeded. Macromonomers can be used for a wide variety of monomers and reaction media.

2.4.4. Factors affecting dispersion polymerization

2.4.4.1. Concentration of the stabilizer

As already explained, the concentration of the stabilizer is an important factor affecting the size and the size distribution of the resultant particles. It is found that as the concentration of the stabilizer increases, the particle size decreases and more uniform particles are obtained. This can be explained on the basis of the higher stabilizer concentration that is available to stabilize a larger total surface area, resulting in 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. Tuncel *et al*[88] studied the dispersion polymerization of styrene in different alcohol/water media, using poly (acrylic acid) (PAA) and found that an increase in the stabilizer concentration resulted in a decrease in the average size and the size distribution of the particles.

An exception to the general rule of particle size decreasing with increased stabilizer concentration is the polymerization of styrene in aqueous ethanol,[89] stabilized by PAA, where the particle size passed through a distinct maximum at 4 wt. % PAA.

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[87] C. L. Winzor, Z. Mrazek, M. A. Winnik, M. D. Croucher, G. Reiss, *Eur. Polym. J.* 30, 173, **(1994)**.

[88] A. Tuncel, R. Kahraman, E. Piskin, *J. Appl. Polym. Sci.*, 50, 303, **(1993)**.

[89] T. Corner, *Coll. Surf.*, 3, 119, **(1981)**.

In case of macromonomer systems, most of the stabilizer will be irreversibly bonded. Hence, macromonomers of quite low molar mass (1000-2000 g mol^{-1}) are effective stabilizers and can produce stable particles at concentration as low as 0.2 wt. % (relative to monomers) compared to at least 5 wt. % of the homopolymer bearing the same repeating units.[90,91]

2.4.4.2. Concentration of the monomer

The concentration of the monomer is decisive on the amount of the diluent used. Hence, as the diluent increases it reduces the concentration of the monomer as well as the stabilizer concentration. This leads to an increase in particle size. When the amount of solvent is increased beyond a certain limit, it results in coagulation. Shen *et al*[92] reported a similar observation in case of dispersion polymerization of MMA in aqueous alcohol using PVP as the steric stabilizer

2.4.4.3. Effect of temperature

A rise in the polymerization temperature results in fast reactions and hence low molar mass polymers. The nucleation step is prolonged as a result of which the particle size increases and sometimes it even leads to coagulation or to particles with broader particle size distribution.[93] A gradual increase in the temperature could be a right solution for this problem. Li *et al.* have reported a stepwise increase in reaction temperature.[7] This should also help to avoid the dangerous effect of the exothermic effects which could be encountered during scale up of the polymerization.

2.4.4.4. Effect of reactor geometry

Dispersion polymerization begins as a homogenous solution of the monomers with the stabilizer and the catalyst. The initially formed nuclei are soluble in the medium until they reach the critical length of insolubility. After attaining this critical length, the stabilizer and its concentration is detrimental in affecting the size and the size distribution

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[90] S. Kobayashi, H. Uyama, S. Lee, Y. Matsumoto, *J. Polym. Sci., Polym. Chem.*, 31, 3133, **(1993)**.

[91] S. Kobayashi, H. Uyama, J. Y. Choi, Y. Matsumoto, *Polym. Int.*, 30, 265, **(1993)**.

[92] S. Shen, E. D. Sudol, M. S. ElAasser, *J. Polym. Sci., Part A: Polym. Chem*, 31, 1393, **(1993)**.

[93] Y. Chen, H. Yang, *J. Polym. Sci., Polym. Chem.*, 30, 2765, **(1992)**.

of the resultant particles. The ultimate particle size is a product of a solubility controlled nucleation and growth process. Dispersion polymerization unlike emulsion and suspension polymerizations, is generally found not affected by the stirring rate and the reactor geometry. Stirred and unstirred reaction can give the similar particle sizes under identical experimental condition[94] which seems rather unusual.

2.4.5. Synthesis of polycondensates by dispersion technique

The first example of dispersion polycondensates in organic media involved mechanically grinding solid resins polymers in aliphatic hydrocarbons in the presence of dissolved rubber.[95] Much later in 1969, Rohm and Haas have got a patent dealing with the reactants being dispersed in aliphatic hydrocarbon in the presence of swelling agents such as tetra methylene sulfone.[96] However, these methods generally provide only relatively crude and ill-defined polymer particles of poor dispersion stability. Stable dispersion could be obtained by direct dispersion polymerization of soluble reactants in organic solvents in the presence of polymeric dispersants or its precursors.

2.4.5.1. Polyesters

Polyesters synthesis involving the condensation between diacid chlorides and diols in the presence of an amine as an acid acceptor are the most widely studied polycondensates in dispersion.

Duelle and Thomas have described the preparation of aromatic polyesters by poly-condensation of various diols and diacid chlorides in ethyl acetate in the presence of suitable stabilizers.[97] A wide range of specially designed amphiphilic, ionic and/or reactive stabilizers, as shown in the Scheme 1-6, were used.

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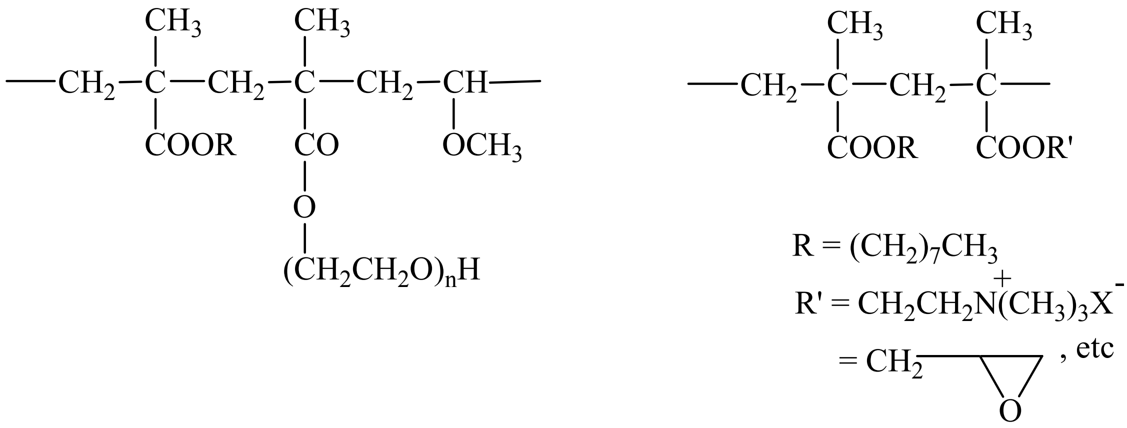
[94] J. L. Cawse, in '*Emulsion Polymerization and Emulsion Polymers*; P. A. Lowell, M. S. El Aasser; Ed, Wiley, New York, 754, **(1997)**.

[95] British Thomson-Houston, *British Patent, 385,970*, **(1932)**.

[96] Rohm and Haas, *British Patent, 1,151,518*, **(1969)**.

[97] E. G. Duelle, H.R. Thomas, *British Patents*, 1,095,931, & 1,095,932, **(1967)**.



$$-CH_2-C(CH_3)(COOR)-CH_2-C(CH_3)(CO-O-(CH_2CH_2O)_nH)-CH_2-CH(OCH_3)-$$

$$-CH_2-C(CH_3)(COOR)-CH_2-C(CH_3)(COOR')-$$

$R = (CH_2)_7CH_3$

$R' = CH_2CH_2\overset{+}{N}(CH_3)_3X^-$

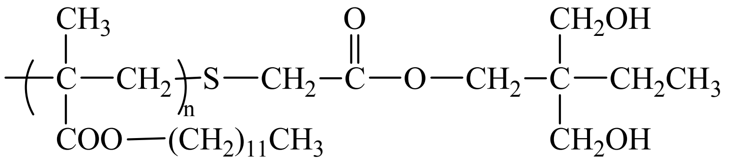
$= CH_2$, etc

Scheme 1-6 : Chemical structures of typical amphiphilic, ionic and reactive stabilizers used for polyester dispersion in organic solvents.

2.4.5.2. Polyurethanes

Conventionally polyurethane particles are prepared by cryogenic grinding of thermoplastic polyurethane.[98] Synthesis of polyurethane by dispersion polymerization was reported by Hoeschele,[99] whereby thermoplastic polyurethane, directly in the form of powder was prepared by reacting polyether or polyester glycol and low molar mass diols with diisocyanates. The stabilizers used in this case contained reactive glycidyl groups which became covalently bonded to the particles, by reacting with the polymer particles.

More recently, Sivaram *et al.* reported the dispersion polymerization of polyurethane, in paraffin oil as the solvent. The polyurethane particles were synthesized using polycondensable macromonomer based on dihydroxy-terminated polydodecylmethacrylate.[62] The structure of the stabilizer is shown in Scheme 1-7. Particles in the size range of 2-10 μm were obtained. Characteristics of the polyurethane particles synthesized using this stabilizer is shown in Table 1-12.



$$-(C(CH_3)(COO-(CH_2)_{11}CH_3)-CH_2)_n-S-CH_2-C(=O)-O-CH_2-C(CH_2OH)_2-CH_2CH_3$$

2a: n = 3.0
2b:n= 6.6
2c: n = 18.6

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[98] Mobay Chemicals Co., *US Patent* 3214411, **(1965)**.

[99] G. K. Hoeschele, *German Patent* 2,556,945 **(1974)**; *US Patent* 3,933,759; CA 84: P107271a.

Scheme 1-7 : Macromonomer used for PUR synthesis.[62]

Macromonomer	Conc, wt%	Particle size, nm	D_w/D_n	% Yield
2a	15	Coagulation		
2b	5	Partially agglomerated		
	10	-	-	88
	15	1400	1.3	93
2c	5	-	-	93
	10	220	1.16	95
	15	180	1.24	95

Table 1-12 : Characteristics of the polyurethane synthesized using dihydroxy-terminated polydodecylmethacrylate macromonomer as the stabilizer.[62]

2.4.5.3. Polysiloxanes

Synthesis of polysiloxanes involves the condensation of the hydrolyzed alkyl trialkoxy silane. These particles have been synthesized by dispersion polymerization in the presence as well as in the absence of stabilizer.[100] Surprisingly no coagulation was obtained when the polymerization was carried out even in the absence of a stabilizer. Microspheres were obtained in both cases. Various types of anionic and cationic surfactants were used as stabilizers. However, the efficiency of the stabilizers was less resulting in broad particle size distribution. The yield of the polymer was almost the same when the dispersion was carried out in the absence of a steric stabilizer.

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[100] K. I. Alder, D.C. Sherrington, J. Chem. Soc., *Chem. Commun.*,1, 131, **(1998)**.

2.4.5.4. Phenolic resins

The synthesis of phenolic thermoset resins have been reported by dispersion polymerization.[101,102] The polymerization of phenol was carried out enzymatically in a mixture of 1,4-dioxane and phosphate buffer. Polymeric stabilizers such as poly(vinyl methyl ether), poly(ethylene oxide) and poly(vinyl alcohol) were used as the steric stabilizer.

2.4.5.5. Urea-formaldehyde resins

Salyer and Osmani reported in 1979 the formation of porous urea formaldehyde network by dispersion polymerization.[103] According to their study, particle formation was accomplished by polycondensation of a non-etherified urea-formaldehyde pre-polymer under acidic conditions, in the presence of a polyether stabilizer (Pluronic F-68). The non-etherified pre-polymer is assumed to be a branched Urea-Formaldehyde pre-polymer with free methylol groups (CH_2OH). Addition of phosphoric acid to the aqueous pre-polymer solution leads to rapid polycondensation/crosslinking, and hence the formation of aggregated microspheres.

2.5. Precipitation polymerization

Precipitation polymerization has been defined as the polymerization process leading to the formation of macroscopically apparent polymer precipitates by Arshady.[50] The basic process of precipitation polymerization is distinct from the closely related dispersion polymerization process in that no steric or electrostatic stabilizers are present. Therefore, this process produces polymers uncontaminated by any residual stabilizer or surfactant.

2.5.1. Chemistry of precipitation polymerization

Precipitation polymerization starts as homogeneous solution of monomers and initiator in a solvent. Since the resultant polymer is insoluble in the medium, it tends to aggregate and once it exceeds a critical solubility chain length, precipitation begins. The

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[101] H. Uyama, H. Kurika, S. Kobayashi*, Chem. Lett.*, 9, 795, **(1995)**.

[102] H. Kurika, H. Uyama, S. Kobayashi, *Polym. J.*, 30, 526, **(1998)**.

[103] I. O. Salyer, A. M. Osmani, *J. Appl. Polym. Sci.*, 23, 381, **(1979)**.

absence of stabilizers in precipitation technique usually leads to the formation of polydisperse and irregular polymer particles.

In case of free radical polymerization, a large number of free radicals can be immobilized inside the particles and hence can lead to enhancement of polymerization rate. This phenomenon could also be attributed to the hindered termination within the precipitated polymer. It has also been reported that under certain conditions, the living radicals remain trapped inside the particles and can initiate further polymerization.[104]

2.5.2. Synthesis of polycondensates by precipitation technique

2.5.2.1. Polyamides

An interesting example of polyamide synthesis by precipitation polymerization relates to the development phase of the aramide Kevlar, a Dupont product.[105] Poly (phenyleneterephthalamide) was obtained in the presence of hexamethylphosphoramide (HMPA), or N-methylpyrrolidone – calcium chloride (NMP/ $CaCl_2$) as the polymerization medium. The low molar mass fraction of the polymer formed in NMP/$CaCl_2$ results from premature nucleation and precipitation of the polymer.

Another early report of synthesis of poly(terephthaloyl-2, 5-dimethyl piperazine) was reported by Morgan.[106] In this work a solution of dimethylpiperazine and trimethylamine in benzene was stirred at room temperature, followed by drop-wise addition of a solution of terephthaloyl chloride in the same solvent. The precipitated polymer powder which is formed instantaneously, was diluted with benzene and recovered by filtration.

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[104] Y. Minoura, Y. Ogata, *J. Polym. Sci*, Part A-1, Polym. Chem., 7, 2547, **(1969)**.

[105] A. P. Fitzgerald, R. S. Irwin, in A. H. Faweet, ed., *High Value Polymers*, 392, RSC, London, **(1991)**.

[106] P. W. Morgan, *J. Polym. Sci. Polym. Symp*., 4, 1075, **(1963)**.

3 Conclusion

The preparation of uniform polymer particles with control of their size and shape have gained considerable commercial as well as academic interests due to the versatile applications these materials find in various fields such as support in HPLC columns as ion exchange ligands, biomedical applications etc…. Various techniques namely emulsion, suspension, dispersion, and precipitation polymerizations have been reported in literature to produce beaded resins, dry powders and aqueous dispersions. The mild reaction conditions, the quantitative yields and the high molar masses of the resultant polymers are the major advantages of these above described process.

In these techniques, factors such as temperature, agitator speed, types of solvent, and stabilizer as well as monomer concentration etc.., influence the nature of the final particle size. Among these, the nature and the concentration of the stabilizer are decisive in achieving well-controlled monodisperse particles. From literature it is also evident that compared to conventional steric stabilizers such as block copolymers, functional homo, and copolymers are more effective as stabilizers, since the latter remain attached to the final particles and allow a better colloidal stability of the latex.

Recently these techniques have gained importance for the production of various "polycondensates" like, amino resins, phenolic resins, polyesters, polyamides, polycarbonates and polyurethanes.

Polyurethanes, an important class of environmentally benign polymers, have been gaining importance in the recent years. Indeed the synthesis in particulate form has been carried out by miniemulsion, suspension as well as by dispersion polymerization techniques. The studies have been performed using various ionic or polymeric stabilizers, in aqueous as well as in organic medium. Stabilizers based on reactive homopolymers or macromonomers of controlled structure and valence have never been looked into details. The use of such stabilizers would result in the formation of particles having a core-shell structure with specific properties. The nature of the particle shell can be changed by varying the reactive stabilizer to suit the purpose of the applications.

Hence it is apparent form this overview that the use of these reactive stabilizers for polyurethane synthesis would be a promising achievement towards particles with specific properties.

L'analyse bibliographique a notamment révélé toutes les potentialités des polymérisations réalisées dans des conditions hétérogènes. Quelle que soit la technique employée (émulsion, suspension, dispersion, etc…), l'obtention de polymères sous la forme de particules de taille contrôlée permet d'envisager de très nombreuses applications telles celles des "latex" pour les revêtements ou les peintures, par exemple. Parmi les polymères synthétisés en milieu hétérogène, les « polycondensats » connaissent actuellement un regain d'intérêt en raison des avantages qu'apportent les conditions de synthèse et également des propriétés mécaniques de ces matériaux.

De nombreux paramètres techniques et physico-chimiques sont à maîtriser pour préparer des polymères sous la forme de particules sphériques de taille contrôlée. A cet égard, l'agent de stabilisation de ces latex joue un rôle déterminant. Outre l'utilisation de copolymères à blocs "classiques" de type polystyrène-b-poly(oxyde d'éthylène) (PS-b-POE), les polymères réactifs utilisés comme agents de stabilisation connaissent un attrait tout particulier car ces derniers permettent l'accès à des particules de type "cœur-écorce" qui restent stables dans le temps.

La technique de polymérisation en milieu dispersé nous a semblé la plus intéressante pour préparer des particules dans un domaine de taille allant de 200 nm à environ 10 µm. Par ailleurs, le constat d'un assez faible nombre de travaux concernant la synthèse de polycondensats en milieu dispersé en présence d'agents de stabilisation réactifs spécifiques, nous a incité à nous investir dans ce domaine. Pour cela, nous avons choisi de nous intéresser à la synthèse de polyuréthanes issus de la réaction entre le tolylène-2,4-diisocyanate (TDI) et l'éthylène glycol (EG), en dispersion dans des diluants organiques. Les copolymères à blocs (PS-b-POE) et des polystyrènes réactifs, PS-OH, ont été testés et comparés comme agents de stabilisation de la dispersion. Les résultats expérimentaux sont présentés et discutés dans le chapitre 2.

CHAPTER 2:

PS-b-PEO & ω-HYDROXY POLYSTYRENE AS STABILIZERS FOR POLYURETHANE SYNTHESIS

GLOSSARY

1 Introduction

Due to growing industrial needs that require materials easy to process, the synthesis of polymer particles in the micron size range has been the subject of an intense research. Typically these materials find applications in many domains such as surface coatings, adhesives, encapsulants, etc.[1] Polymeric materials with spherical shapes are usually prepared from emulsion, suspension and dispersion polymerization techniques.[2] The polymerization in non-aqueous dispersion was found to be an effective alternative route for the preparation of uniform polymeric particles in a 1-10 µm size range.[3]

Typically, polymerization in a dispersed medium starts with the monomers dispersed in the organic phase and results in the formation of an insoluble polymer in the form of stable colloidal dispersion. Polymer microspheres with very narrow size distribution may be prepared in appropriate conditions. The role of the steric stabilizer is crucial in this procedure as it not only provides stability to the resultant particles but also affects the final particle size and size distribution as well as the polymer molar mass. Usually, amphipathic polymers -block or graft copolymers- are effective stabilizers[4] ; they strongly adsorb onto the forming particle surface by virtue of the insolubility of one of their block (also called the anchor part). Nevertheless, their desorption from the final material causing irreversible damages such as the loss of the stabilization of the particles may occur. One possibility to avoid this major drawback is to use reactive stabilizers or macro-monomers. These reactive stabilizers get covalently linked to the final particle.[5]

Even though this polymerization technique has gained industrial importance for the production of major polycondensates, such as polyesters,[6,7] polyamides,[8] polycarbonates and polyurethanes,[9,10] very few detailed studies of these above polymers in dispersed medium have been published.

Polyurethanes in particle form find applications in coating and adhesive industries. These have also been used in encapsulating drugs and pesticides.[11]

The technology of aqueous suspension polycondensation for polyurethane was developed by researchers in Bayer company. Their work has been reviewed by Dieterich.[9]

Recently, Landfester[12] *et al.* have reported the preparation of polyurethane particles with diameters of about 200 nm by miniemulsion in aqueous medium.

Particles forming suspension polymerization in non-aqueous medium resulting in the polyurethane microspheres have also been reported by Nippon.[13] According to this work, polyurethane particles in the size range of 5-50 μm were obtained by condensing oligomeric glycols with diisocyanates or isocyanate terminated pre-polymer in an organic medium. They used a block copolymer poly(ethylene oxide)-b-poly(dimethylsiloxane) as the steric stabilizer in 2-20 wt.% range.

Hoeschele[10] reported the preparation of thermoplastic polyurethane, directly in the form of powder, by reacting hydroxy telechelic polyether or polyester and low molar mass diols with diisocyanates in an organic solvent. The stabilizers used in this case contain reactive glycidyl groups which become covalently bonded to the particles.

Sivaram *et al.*[14,15] reported the use of a polycondensable macromonomer based on dihydroxy-terminated poly(dodecylmethacrylate) for the synthesis of polyurethane microspheres by dispersion as well as by suspension polymerization in aliphatic solvents.

The need to prepare novel materials, based on polycondensates, with specific properties (for instance as adhesives or reinforced materials) as well as the lack of really known researches in this field led us to investigate the step-growth polymerization in dispersed medium. Herein, we report our first data dealing with the preparation of polyurethane materials. A series of steric stabilizers based on polystyrene and poly(ethylene oxide) moieties have been synthesized and tested for that purpose. The parameters (time of addition of the reactants, nature and concentration of the stabilizer, etc…) that affect the particle size and the particle size distribution of the resultant polyurethane materials are discussed.

2 Polyurethane synthesis using PS-b-PEO block copolymer as the stabilizer

For the present study, the monomers ethylene glycol (EG) and tolylene-2,4-diisocyanate (TDI) have been selected. Dibutyl tin dilaurate (DBTDL) was chosen as the polymerization catalyst. The polyaddition was performed at 60°C in cyclohexane so as to comply with the requirements of insolubility of the resultant polymer formed. It is worth noting that EG is not soluble in cyclohexane unlike TDI. On the basis of literature data,[13] PS-b-PEO block copolymers were first tested as stabilizers for the synthesis of polyurethane in dispersed medium ; the polystyrene block providing the solvated moiety while the poly(ethylene oxide) block which is insoluble in cyclohexane, the anchoring moiety to the growing dispersed polyurethane.

Since the size and the stability of the resultant polymer particles depend both on the nature and concentration of the stabilizer, we synthesized a series of block copolymers by varying each of the length of the blocks. The characteristics of PS-b-PEO block copolymers are given in Table 2-1.

Stabilizer	$\overline{DP_n}$ [a]		$I_p=\frac{\overline{M_w}}{\overline{M_n}}$ [a]
	PS-Block	PEO-Block	
S1	115	455	1.06
S2	120	245	1.03
S3	120	115	1.04
S4	25	5	1.02

[a] determined by SEC

Table 2-1 : Characteristics of PS-b-PEO block copolymers.

As generally realized for polymerization using steric stabilizers in dispersed medium, all the reactants were added together, at the start of the reaction. For the study, we used 0.01 moles of EG and 0.012 moles of TDI in 20 g of cyclohexane. The amount of added stabilizer was varied from 1 to 20 wt.% with respect to the total amount of monomers. The monomer / solvent ratio (m/s) was varied from 1/12 to 1/3. Kinetic studies revealed that the polymerization goes to completion in 6 hours time ; data are given and discussed in the third part of the chapter. Results of the dispersion in terms of the polyurethane particles formation in the presence of PS-b-PEO block copolymers as stabilizers are first discussed and reported in Table 2-2.

Stabilizer	Stabilizer, wt. %	m/s[a] ratio	Particle size[b], $d_{(0.5)}$, µm	Span[c], $\frac{d(0.9)-d(0.1)}{d(0.5)}$	Observations
S0	-	1/6	-	-	Coagulation
S1	5,10,15,20	1/6	-	-	Coagulation
S2	5,10,15,20	1/6	-	-	Coagulation
S3	5,10,15	1/6	-	-	Coagulation
	20	1/6	2.75	14.1	Broad distribution
S4	1,2,	1/6	-	-	Coagulation
	5	1/6	63.60	3.4	Broad distribution
S4	10	1/3	29.00	3.9	Broad distribution
	10	1/6	50.70	2.0	Broad distribution
	10	1/12	57.90	1.9	Broad distribution

[a] m/s is the monomer over solvent ratio

[b] particle size obtained by performing light scattering measurements on a Malvern Master sizer 2000 (Hydro 2000S) apparatus

[c] particle size distribution or "span" = $\frac{d(0.9)-d(0.1)}{d(0.5)}$

where: $d_{(0.9)}$ =90% particles have size lower than the given value,
$d_{(0.5)}$ =50% particles have size lower than the given value,
$d_{(0.1)}$ =10% particles have size lower than the given value.

Table 2-2 : Results of PUR synthesized in cyclohexane using PS-b-PEO as the steric stabilizer at 60°C.

2.1. Influence of the PS-b-PEO length

As may be seen in Table 2-2, coagulation occurs in the absence of stabilizer (S0). Due to a quite long block of the PEO moiety, S1 does not exhibit any solubility in the reaction medium at the experimental conditions; its use as a stabilizer logically results in coagulation similar to the test carried out in the absence of any stabilizer (S0).

In addition while S2 is soluble in cyclohexane at 60°C, it does not participate in the stabilization process and coagulation occurs whatever its concentration used. Indeed, it has been shown by Walbridge that the growth of the particles without the continued provision of stabilizer from the medium resulted in coagulation.[16]

The balance between PS and PEO blocks was further reduced to 1:1 ratio (S3). It was found that large amount of stabilizer (20 wt.%) is needed to avoid coagulation but the particle size distribution remains broad. These observations led us to diminish further the length of the PEO moiety and stabilizer S4 was prepared accordingly (PS/PEO : 5/1). S4 does effectively stabilize the resultant particles but a broad distribution of particle size is again obtained indicating a rather bad control of the nucleation step.

The poor stabilization ability of these block copolymers was speculated to come from the formation of stable micelles in cyclohexane. Indeed, it has been noted that the dissociation rates of such micelles to free polymer may be very low in organic solvents. Formation of micelles could result in non-availability of these copolymers for stabilization. Therefore the ability of S4 to form micelles in cyclohexane have been examined by light scattering measurements at 25°C. The hydrodynamic radius R_H (nm) vs. concentration (mmoles/L) of the micelle formed was plotted in Figure 2-1. A critical micellar concentration (CMC) value was estimated at around 3 mmoles/L with a R_H value of around 3.5 nm. When S4 is used as the stabilizer at a 10 wt% concentration with respect to the monomers, its concentration in the reactor is close to 6.25 mmoles/L, value twice the one of the CMC. This clearly indicates that micelles are present in our experimental conditions. The micelle formation would be enhanced with increasing the length of the block copolymers. This could also have contributed to the poor stabilization in the case of S3 used as a stabilizer.

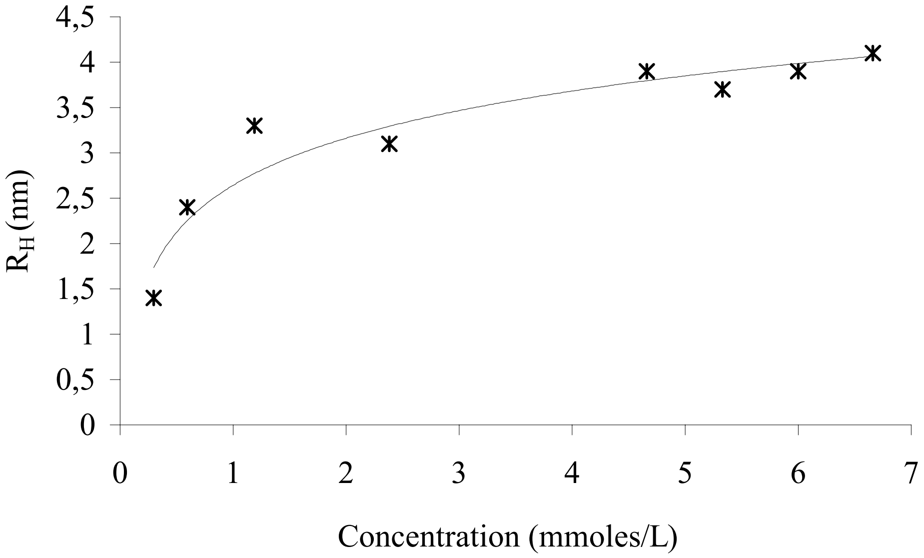


Figure 2-1 : Plot of R_H (nm) vs. concentration (mmoles/L) for PS-b-PEO block copolymer ($\overline{DP_n}$ (PS block) = 25; $\overline{DP_n}$ (PEO block) = 5) in cyclohexane at 25°C.

We carried out further studies to check the influence of the monomer/solvent (m/s) ratio and effect of the stabilizer concentration using S4 as the stabilizer.

2.2. *Influence of the monomer/solvent ratio (m/s)*

Another important factor that may govern the size and stability of the particles is the m/s ratio. In order to check the effect of this parameter onto the final particles, PUR particle synthesis was carried out in the presence of S4 (10 wt.%) and the m/s ratio was varied from 1/3 to 1/12. The results are given in Table 2-2.

It was found that at a ratio of 1/3, the effective concentration of the stabilizer is increased yielding smaller particle size. However, above a conversion value of 85%, it resulted in coagulation as stirring was found to be less efficient with increasing solid content. In addition, an increase in solvent content (m/s=1/12) results in particles with larger size, in line with a diminution of the stabilizer concentration. As a result, the rate of adsorption of the block copolymer on the PUR particles is reduced. The latter observation is in agreement with that reported by El Aasser *et al.* for methyl methacrylate (MMA) polymerization using poly(vinyl pyrrolidone) (PVP) as the steric stabilizer.[17] Finally, an intermediate ratio of around 1/6 was found to give best results regarding the size and the size span of the final polyurethane particles. This latter m/s ratio of 1/6 was finally selected for all further studies.

2.3. Influence of the stabilizer concentration

The concentration of the stabilizer has a marked effect on the mechanism of the particle formation affecting the final particle size. S4 was used as the stabilizer and its concentration was varied from 1wt.% to 20 wt.%. The data are given in Table 2-3.

S4 wt %	Particle size[a], $D_{(0.5)}$, (μm)	Span[a] $\frac{d(0.9)-d(0.1)}{d(0.5)}$
5	120	9.5
10	51	2.0
15	27	2.8
20	11	1.7

[a] refer to footnote of Table 2-2

Table 2-3 : Effect of the PS-b-PEO block copolymer concentration on the PUR particle size.

As expected, the higher the stabilizer concentration, the lower the particle size. A variation of stabilizer concentration from 5 wt.% to 20 wt.% leads to a particle size decrease from around 100 μm to 10 μm. Indeed, the occurrence of the nucleation step at the earliest stage leads to a maximum number of particles at the very beginning of the polymerization. Once the nuclei are formed, they may aggregate and form bigger particles. This feature is more probable at lower stabilizer concentration than at higher one because of a more pronounced steric barrier effect in the latter situation. Moreover, below a 1 wt. % stabilizer concentration, stabilization is not effective and coagulation of the polymer chains occurs. This is sustained by the work reported by El Aasser *et al.* and is in agreement with the mechanism of dispersion polymerization they have proposed.[19]

Experiments performed in the presence of PS-b-PEO block copolymers as stabilizers reveal that such block copolymers are not well suited for this type of polymerization process. In fact, it is likely that the PEO moiety has a relatively poor affinity towards the polyurethane particles and therefore cannot play its anchor role. This observation prompted us to check the efficiency of functionalized homopolymers such as ω-hydroxy polystyrene as the steric stabilizer for polyurethane synthesis. Indeed, it is known from the literature that functionalized homopolymers mainly based on poly(ethylene oxide) can behave as efficient stabilizers as they form, *in situ*, amphipathic block or graft copolymers.[18,19,20] Similarly, we anticipated that ω-hydroxy polystyrenes could participate through the hydroxy end groups to the urethanization reaction with the isocyanate functions

3 Polyurethane synthesis using ω-hydroxy polystyrene as the reactive stabilizer

A series of well-defined hydroxy-terminated polystyrenes (PS-OH) of different molar masses were prepared by conventional anionic polymerization followed by end-capping the polystyryl lithium chains using ethylene oxide. The characteristics of these polymers are given in Table 2-4.

Stabilizer	$\overline{DPn}$ [a]	$Ip=\frac{\overline{Mw}}{\overline{Mn}}$ [a]	Functionality[b] %
S5	10	1.05	98
S6	20	1.04	96
S7	25	1.05	97
S8	40	1.06	99

[a] determined by SEC

[b] determined by ^1H NMR, calculating the ratio of the area of the signal corresponding to the protons of the methylene group adjacent to the hydroxyl chain ends (I_1, $\delta C\underline{H}_2$-OH=3.5 ppm) to that of the peak arising from the protons of methyl group of the initiator (I_2, $\delta C\underline{H}_3$=0.9 ppm); functionality (%) = $\frac{I1}{\frac{2}{3}I2}\times 100$.

Table 2-4 : Characteristics of ω-hydroxy polystyrenes.

3.1. Manner of addition of the reactants

As previously mentioned, we first studied the effect of the addition manner of the reactants towards the particle formation and their characteristics. PS-OH (10 wt.%) was first added together with TDI and EG at the start of the polymerization. As could be expected, coagulation occurs demonstrating that when this functional homopolymer is added as such, it cannot play the role of a stabilizer. This phenomenon clearly underlines the lesser reactivity of hydroxy functions coming from the polystyrene chain ends compared to the ones of EG monomer.

Therefore, in order to enhance the efficiency of PS-OH as a reactive stabilizer, the reaction between PS-OH and isocyanate functions was carried out in a first stage. PS-OH (1 eq.) was pre-reacted with TDI (2 eq.) in the presence of DBTDL at 60°C in cyclohexane. The following of the reaction by FTIR spectroscopy and SEC reveals that complete derivatization of OH groups occurs within two hours. The resultant polymer was isolated by precipitation in MeOH and then characterized by ^{1}H NMR and SEC. The ^{1}H NMR spectrum of the reaction product is shown in Figure 2-2. The assignment of the peak at 4.4 ppm corresponding to the proton of the N-H group as well as the absence of signal at 3.5 ppm (that would correspond to the protons of $-C\underline{H}_2$-OH group from the PS-OH precursor) argue the complete derivatization of the hydroxy function.

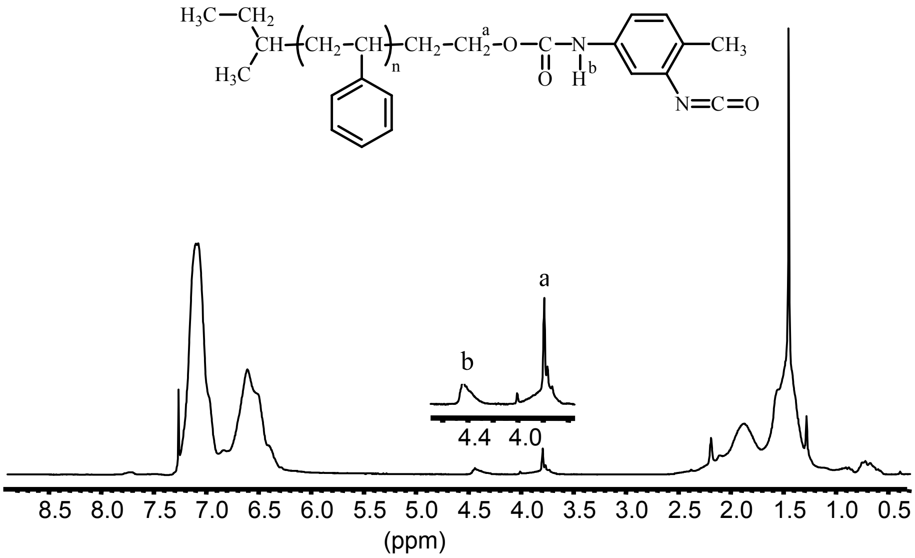


Figure 2-2 : ^{1}H NMR spectrum (200 MHz) of ω-NCO polystyrene in $CDCl_3$.

Interestingly, SEC traces of the isolated polymer shown in Figure 2-3a, reveals a bimodal feature. The shoulder corresponding to nearly 20 % in weight of the whole sample was logically attributed to coupling product (B) along with the formation of the expected main product (A), as presented in Scheme 2-1.

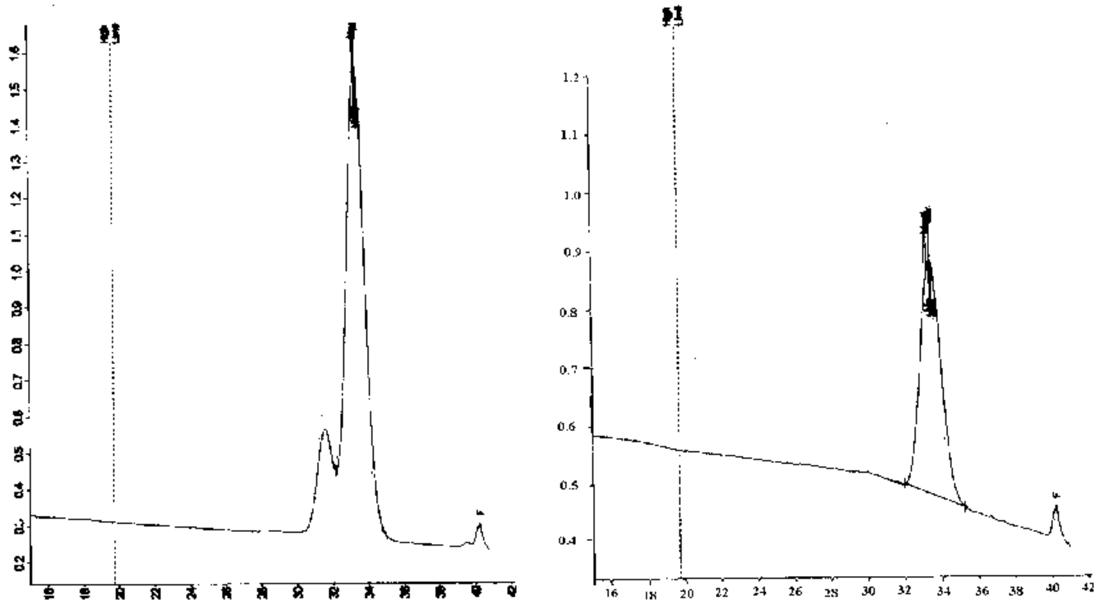
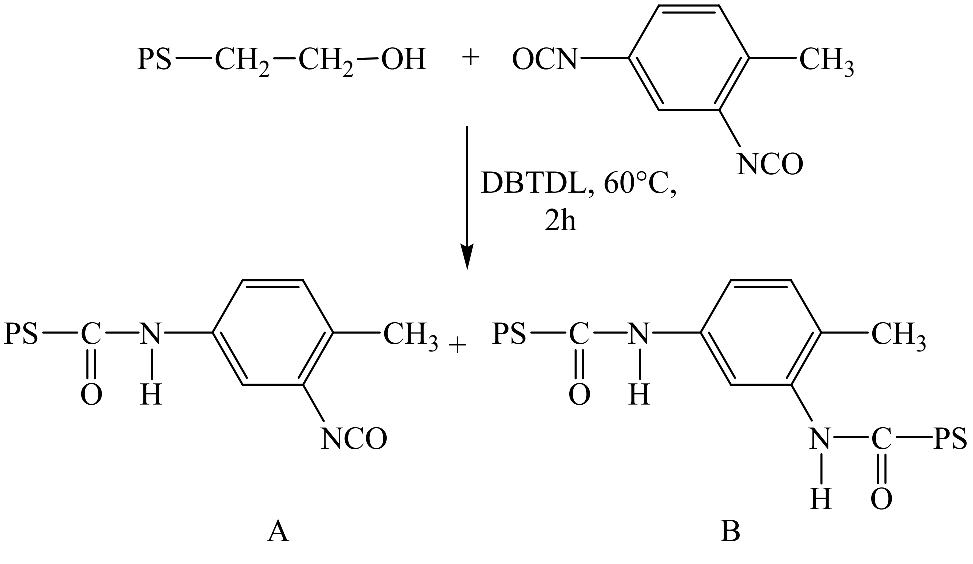


Figure 3a **Figure 3b**

Figure 2-3 : SEC of ω-NCO Polystyrene.



Scheme 2-1 : Reaction between ω-hydroxy polystyrene and TDI.

We succeeded in suppressing the formation of (B) by changing the manner of mixing the two reactants, *i.e.* PS-OH (1 eq.) was added drop-wise over a TDI (2 eq.) solution in cyclohexane in the presence of DBTDL. The total formation of the mono-adduct (A) has notably been confirmed by SEC (see Figure 2-3b). These preliminary investigations finally allowed us to prepare ω-NCO polystyrene (A) with a good efficiency.

The procedure depicted above was thus applied in the following to prepare the ω-NCO polystyrene *in situ*, *i.e.* in the experimental dispersion conditions before addition of the monomers. Therefore, after the formation of (A) is complete within two hours, EG (insoluble in cyclohexane) was first added in one lot (0.010 moles) and the turbid mixture was allowed to react for 30 minutes. TDI (0.012 moles) was then added drop-wise over a variable time period. While the manner of EG monomer addition has no effect on the PUR particle formation, the manner and time of TDI addition was found to be very crucial in order to avoid coagulation and also in order to control the particle size and the particle size distribution, as shown in Figure 2-4.

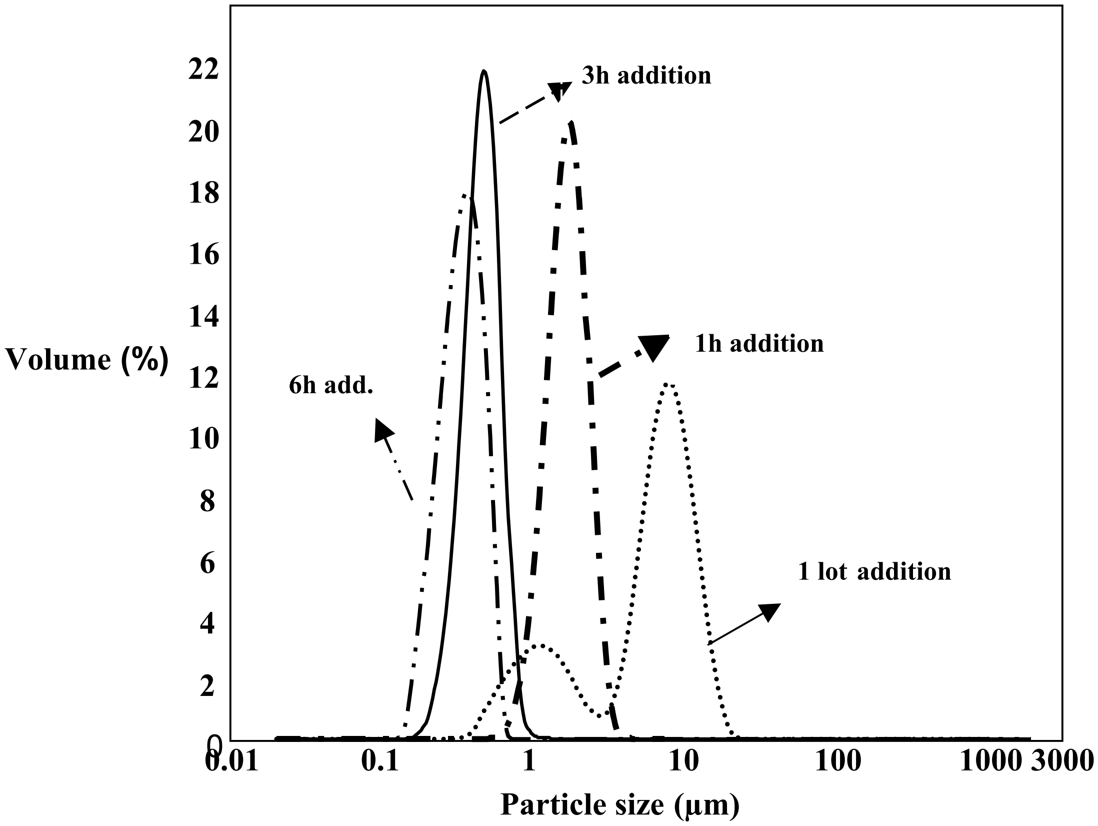


Figure 2-4 : Effect of TDI addition time onto the average size of the PUR particles.

It is worth noting that addition of TDI in one lot yields two populations of particles while a drop-wise addition leads to a single population. In addition, the longer the time of TDI addition, the lower the particle size. The formation of two populations may be the consequence of two nucleation processes, *i.e.* homogeneous and micellar nucleation. The formation of micelles by ω-NCO polystyrene (A) was thus demonstrated by dynamic light scattering (DLS) measurements ; a critical micellar concentration (CMC) value was estimated at around 3,5 mmoles/L and large micelles with a R_H value close to 55 nm could be measured as shown in Figure 2-5. It is important to underline that the stabilizer concentrations used in our experimental conditions (5-8 mmoles/L) are systematically higher than the CMC value, clearly indicating that micelles are formed and play a role in our experimental dispersion conditions.

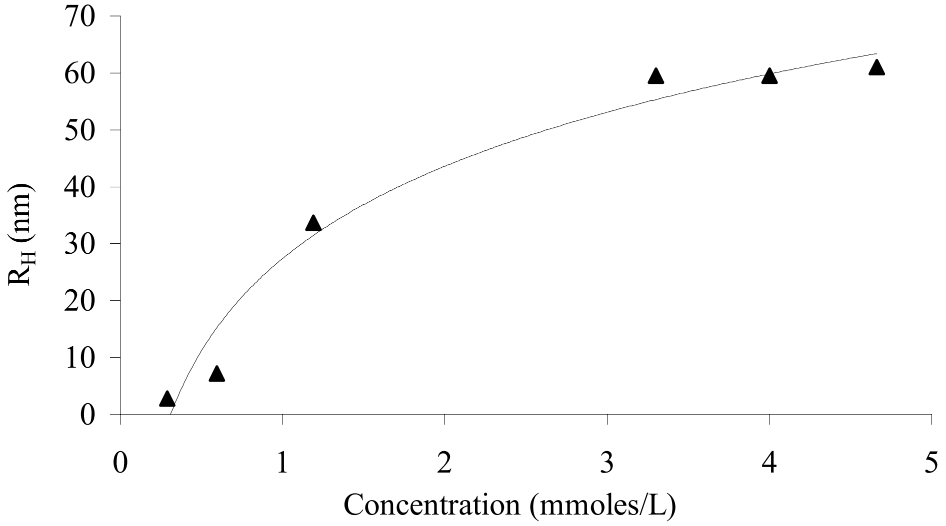


Figure 2-5 : Plot of R_H (nm) vs. concentration (mmoles/L) for ω-NCO polystyrene ($\overline{DP_n} = 20$) in cyclohexane at 25°C.

Surprisingly, it was also observed that when ω-NCO polystyrene (A) -synthesized in a separate experiment then isolated- was added as such into the reactor before EG and TDI, a bimodal particle size distribution was systematically obtained. However, the intensity of the peak corresponding to bigger particles could be lowered and even suppressed by increasing the time of TDI addition.

In addition, the bimodal populations could also be avoided by adding along with ω-NCO polystyrene (A), one equivalent of TDI (vs. OH function). These experiments clearly show that the presence of free TDI at the start of the reaction is essential to avoid the bimodal distribution. It is also worth noting that the particle characteristics obtained in these specific experimental conditions are identical to the ones obtained when ω-NCO polystyrene (A) is synthesized *in situ*. Indeed, in this latter case, some non reacted TDI is present along with (A).

Typical optical microscopy picture of monodisperse polyurethane particles obtained in the presence of S6 used as the stabilizer and for a 1h addition of TDI is shown in Figure 2-6. Many other parameters can influence the main characteristics of the particles. Among them, we mainly investigated the effect attributable to the reactive stabilizer itself, *i.e.* its molar mass and concentration. Indeed, such features have already been described in the literature to drastically govern the formation and stability of the growing particles.[19,21,21]

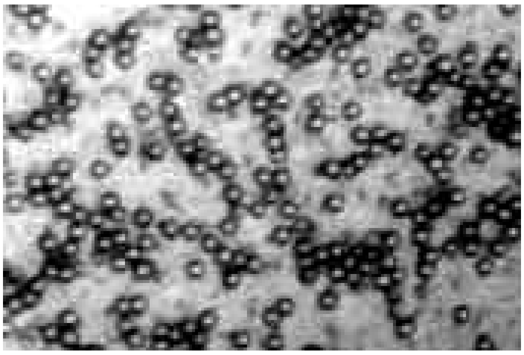


Figure 2-6 : Microscopy picture of PUR particles synthesized using S6 as the stabilizer (Particle size : 1.70 μm) .

3.2. Effect of the stabilizer molar mass

For this study, we varied the molar mass of the stabilizer between 1000 and 4000 g/mole. The results are given in Table 2-5.

Stabilizer, DPn	Stabilizer 10 wt %	Time of TDI addition[a], h	Particle size[b] d $_{(0.5)}$, (μm)	Span[b] $\frac{d(0.9)-d(0.1)}{d(0.5)}$	Observations
10	S5	1	-	-	coagulation
		3	7.30	9.82	multimode
		6	6.70	2.86	multimode
20	S6	1	1.70	0.70	monodisperse
25	S7	1	1.70	0.77	monodisperse
40	S8	1	0.70	2.61	20% coagulation
	S9[c]	1	-	-	Coagulation
		6	-	-	Coagulation

[a] TDI is added drop-wise
[b] refer to footnote of Table 2-2
[c] stabilizer is 1-eicosanol

Table 2-5 : Results of PUR synthesized in cyclohexane using ω-hydroxy polystyrene (10 wt%) as the reactive stabilizer.

As may be observed in Table 2-5, the polymerization in dispersed medium is very sensitive to the length of the stabilizer. Indeed, the results show that keeping the stabilizer concentration constant (10 wt.%) a small change of the molar mass of the stabilizer can cause a dramatic effect such as the flocculation of the polymer. Only polystyrene with a molar mass in the range 2000-3000 g/mol (S6; S7) gives very good latexes, while lower and higher molar mass PS are less efficient using this experimental procedure. We may assume that S5 cannot properly adsorb onto the resultant particles leading to coagulation, except in the case when the addition of TDI is performed over 6h. In the case of S8, it leads to about 20 wt.% coagulation and the resultant particles show a broad span of particle size. A pre-reaction between S8 and TDI was allowed to go for 6h instead of 2h at 60°C but the results obtained were similar. Hence, the reduced efficiency of S8 could be explained on the basis of the restricted mobility of the rigid aromatic polystyrene chains thereby affecting the stabilization process. These behaviors have already been described in the literature by El Aasser and coll.[19] The latter observed that too low molar mass polymeric surfactants were unable to stabilize the growing particles while too high molar mass polymer resulted in diminishing the reactivity of the homopolymers thereby hindering the formation of *in situ* graft copolymers that would have helped in stabilization of the particles.

In addition, it is important to note that eicosanol (S9) is not effective as reactive stabilizer confirming that the chemical structure of the stabilizer is also an important factor to consider.

3.3. Effect of the stabilizer concentration

As predicted, the higher the stabilizer concentration, the lower the particle size (Table 2-6). This is in agreement with the theories of particle formation proposed for example by Barett in case of free radical polymerization.[3] Moreover, it is worth noting that the span values of the polyurethane particles remain narrow indicating the high efficiency of S6 to give monodisperse particles.

S6 Wt. %	Time of addition of TDI, in hour	Particle size[a], $d_{(0.5)}$, µm,	Span[a] $\frac{d(0.9)-d(0.1)}{d(0.5)}$	Observations
2	1	-	-	coagulation
5	1	2.23	2.61	polydisperse
10	1	1.73	0.70	monodisperse
15	1	0.72	0.64	monodisperse
20	1	0.41	0.9	monodisperse

[a] refer to footnote of Table 2-2

Table 2-6 : Effect of ω-hydroxy polystyrene (S6; $\overline{DPn}$=20) concentration on the PUR particle size.

4 Kinetic study and characterization of the polyurethane sample

4.1. Kinetics

Kinetic theories treat dispersion polymerization essentially as a micro-bulk polymerization with monomer conversion being largely within the particles.[3] The polymerization kinetic was followed by sampling out at regular intervals of 30 min for 6h and determining the solid content using the equation given in the experimental section. Whatever the stabilizer used, the block copolymers or the reactive homopolymers, the conversion curve showed the same trend as shown in Figure 2-7.

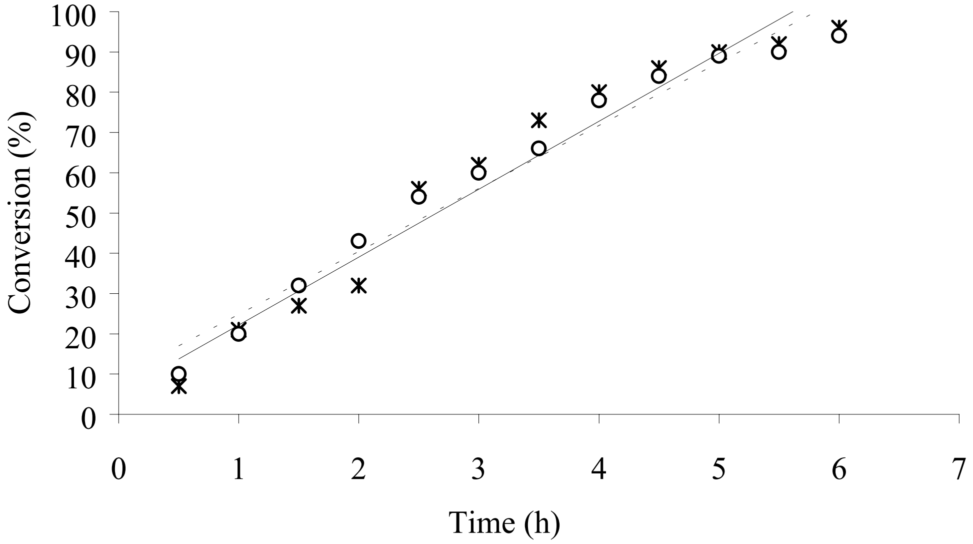


Figure 2-7 : Plot of conversion (%) vs. time (h): o= S4 as the stabilizer; ✳= S6 as the stabilizer, (10 wt.% stabilizer; time of addition: 1h).

4.2. Growth of particles

The particle growth with time was followed by optical microscopy. It was found that a steady growth in particle size took place till a conversion of about 80 % after which there was only a slight increase as shown in Figure 2-8.

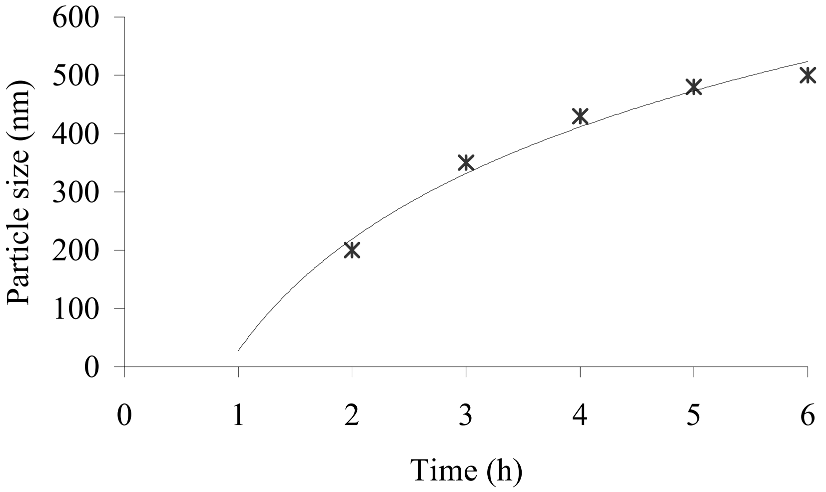


Figure 2-8 : PUR particle size vs. time ; (Stabilizer = S6; time of TDI addition=6h).

4.3. Molar mass determination

The molar mass of the PUR samples could be determined by SEC using DMF as the eluant (see Table 2-7).

S6 wt %	$d_{(0.5)}$[a] (μm)	Span[a]	$\overline{Mn}$[b]	$Ip=\frac{\overline{Mw}}{\overline{Mn}}$[b]
2	-	-	-	-
5	2.23	2.61	8400	1.59
10	1.72	0.70	11500	1.50
15	0.5	0.64	11600	1.81
20	0.41	0.96	nd	nd

[a] refer to footnote of table 2-2

[b] determined by SEC using *N,N*-dimethylformamide (DMF) as eluant

Table 2-7 : Effect of ω-hydroxy polystyrene (S6; $\overline{DPn}=20$) concentration on the molar mass of the resultant PUR particles.

As shown in Table 2-7, the molar mass of the PUR samples slightly increases with the wt % of stabilizer used while in the mean time the particle size decreases. The observed trend may be explained if we consider that the contribution of the reactive stabilizer with respect to the global molar mass of the PUR sample is quite high. Indeed, the theoretical number of monomer units constituting the polyurethane moiety, calculated considering the non-stoichiometry between OH and NCO functions as well as the presence PS-OH as a chain stopper remains close to 10 whatever the PS-OH concentration.

4.4. PUR characterization

Earlier discussions and results indicate that the ω-hydroxy polystyrene took part in the stabilization process by formation of an *in situ* block copolymer. We tried to explore the evidence of grafting of the stabilizer on the resultant particles by performing ^{1}H NMR and thermo mechanical analysis. Samples in the form of powders were then recovered by washing several times with cyclohexane and by filtration before being characterized using both ^{1}H NMR as well as DMA techniques.

The ^{1}H NMR spectrum of one PUR sample, prepared in the presence of 10wt% of PS-OH (S6; $\overline{DPn}$=20), is shown in Figure 2-9.

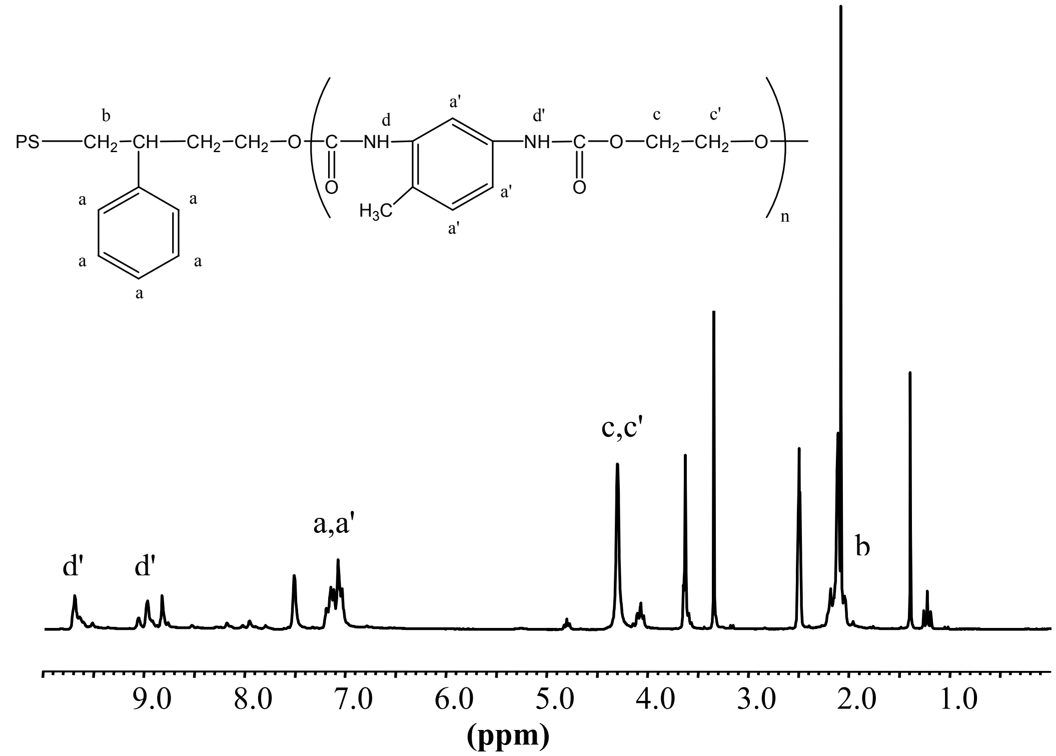


Figure 2-9 : ^{1}H NMR (400 MHz, DMSO) spectrum of PUR synthesized using PS-OH (S6; $\overline{DPn}$=20 /10wt%) as the stabilizer

The assignment of signals located at around 7 ppm to the aromatic protons of styrene and TDI units and at 8.8-9.7 ppm to the proton of the NH group, allowed us to estimate that the amount of grafted stabilizer onto the particle was close to 100%. This characterization proves the participation of the stabilizer as a reactive molecule in the process. To further give clear evidence of the core-shell type of these materials, DMA analysis were implemented.

The DMA traces show the presence of two transitions (see Figure 2-10). The two glass transition temperatures which could be attributed to polystyrene and polyurethane parts were found at 65°C and 98°C respectively. These data were counter-checked by measuring the Tg of polystyrene (S6) and of the polyurethane sample synthesized in the presence of PS-b-PEO block copolymer as stabilizer. Interestingly both show a single Tg at 77°C and 85°C respectively. These results confirm that hydroxy-polystyrene has taken part in the PUR synthesis.

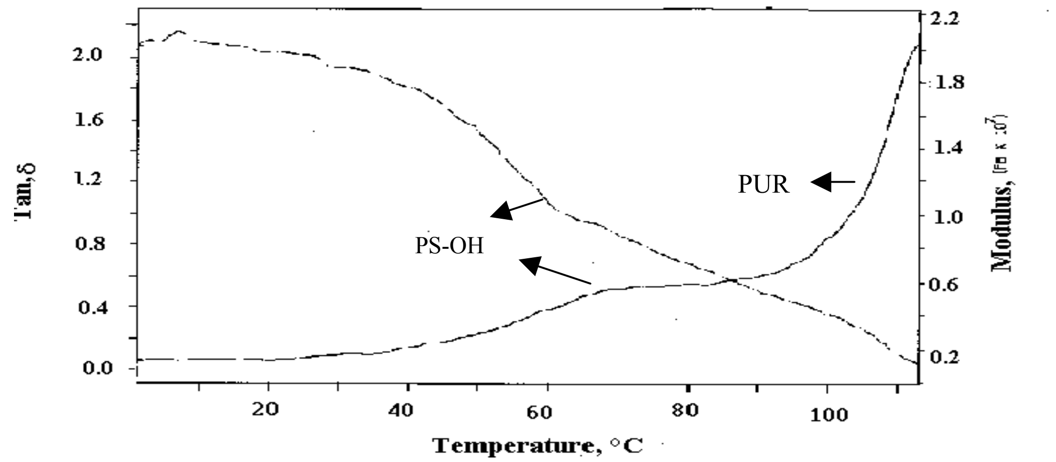


Figure 2-10 : DMA curve of PUR synthesized using PS-OH (S6; $\overline{\text{DPn}}$=20) as the stabilizer.

5 Conclusion

The preparation of polyurethane particles could be achieved successfully in dispersed medium. Block copolymers as well as reactive homopolymers were tried as stabilizers for the polyurethane synthesis.

We have demonstrated, for the first time, that polyurethane synthesis in organic dispersed medium could be readily carried out using functional homopolymer such as ω-hydroxy polystyrene. The stabilization of the particles was obtained by formation of an *in situ* PS-*b*-PUR block copolymer. The ability of the hydroxy-terminated PS to play the role of steric reactive stabilizer depends not only on its concentration and dimension but also on the way of monomers addition.

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Nous avons démontré dans le chapitre 2 la possibilité de préparer des particules polyuréthane de taille contrôlée par polymérisation par étapes en milieu dispersé. En outre les résultats obtenus ont mis clairement en évidence les avantages à utiliser des agents de stabilisation réactifs en comparaison des copolymères à blocs "conventionnels" tels les poly(styrène)-b-poly(oxyde d'éthylène). Les résultats prometteurs obtenus en présence de polystyrènes ω-hydroxyle, PS(OH), s'expliquent par la formation *in situ* de copolymères à blocs PS-b-PUR qui permettent la stabilisation colloïdale du latex. Pour ce faire, il s'est avéré essentiel de faire pré-réagir le polystyrène ω-OH avec deux équivalents de TDI pour aider l'étape de nucléation.

La masse molaire et la concentration en agent stabilisant, le mode et le temps d'addition du TDI sont quelques uns des paramètres que nous avons faits varier pour contrôler et moduler la taille des particules PUR. La taille des particules diminue avec une augmentation de la concentration en agent stabilisant (jusqu'à 20 %, m/m) ou encore un allongement du temps d'addition du TDI.

Même si l'utilisation de polystyrène ω-OH comme agent stabilisant réactif s'est avérée intéressante, la mono-valence de cet oligomère lui confère le rôle de limitateur de chaîne dans un processus de polyaddition. C'est pour pallier cet inconvénient que nous avons mis au point la synthèse de polystyrène porteur de deux fonctions hydroxyle en position géminée, $PS(OH)_2$. Le chapitre 3 discute ainsi l'influence de la valence de l'oligomère réactif sur son aptitude à jouer le rôle d'agent stabilisant. Pour également tester l'influence des propriétés physico-chimiques et thermo-mécaniques de l'agent stabilisant de la dispersion, les analogues polybutadiène mono- et divalents PBut-OH et $PBut\text{-}(OH)_2$, ont été synthétisés et testés en dispersion.

CHAPTER 3:

NOVEL MACROMONOMERS AS REACTIVE STABILIZERS FOR POLYURETHANE SYNTHESIS IN DISPERSED MEDIUM

GLOSSARY

1 Introduction

Heterogeneous polymerization processes enable the preparation of polymer in the form of particles. Such materials find varied applications in synthetic rubber, paints, adhesives, binders for non-woven fabrics and also in biomedical and pharmaceutical applications such as diagnostic tests and drug delivery systems.[1] These polymers can be produced through several processes including emulsion, mini-emulsion, dispersion, suspension as well as by emulsification of preformed polymers.[2,3]

Stabilizers play a crucial role in the production of polymer in particle form by dispersion technique. Indeed, they stabilize the resultant particle during the polymerization process and also help in the long shelf life of the final products. Usually block copolymers are used to stabilize the resultant particles by steric effect. However since the latter are not covalently bonded to the particles, they can be desorbed and their stabilizing properties may be lost under the influence of high shear stress. Typically in coating applications, the stabilizers can migrate through the film and segregate,[4] leading to the loss of the film properties. The stabilizer migration to the 'film-air surface' of the film can also affect the gloss.[5] It can also migrate to the 'film-substrate' interface reducing adhesion.

In order to overcome these drawbacks, two main strategies have been described in literature. The first one reports the use of functionalized monomers such as (meth)acrylic acid, (meth)acrylamide and their derivatives,[1] or sulfonated monomers such as sulfopropyl acrylamide and styrene sulfonate.[6] However, large amounts of these comonomers are needed to obtain sufficient stabilization effect. This can change the properties of the final polymers, which may not be advantageous most of the time. In addition, the hydrophilic nature of these comonomers leads to highly water soluble polymer which can also have negative effect.

The second strategy consists of using reactive stabilizers such as functionalized homo- and co-polymers or macromonomers. The latter have reactive moieties that bind covalently to the polymer material, leading to an increased stability of the resultant latexes.[7] The desorption from the polymer particles or migration in the polymer film is therefore impeded. It also can make the latexes re-dispersible.

Functionalized stabilizers and macromonomers differ by their valence. The reactive stabilizers are monovalent and they stabilize the resultant particles by formation of *in situ* block copolymers by a grafting reaction, mainly involving chain transfer to the growing polymer.[8] Homopolymers such as poly(vinylpyrrolidone), poly(acrylic acid) and hydroxy propyl cellulose were found able to stabilize dispersion polymerization of styrene in aqueous ethanol solution.[9,10,11,12] Bourgeat-Lami *et al.* also studied the dispersion polymerization of styrene using thiol end-capped polyethylene oxide as the reactive stabilizer.[13] The macromonomers have a valence higher or equal to two in nature and can act as the monomer itself. The use of macromonomers in dispersion polymerization was pioneered by ICI.[14] Sivaram *et al.*[15,16] reported the use of a polycondensable macromonomer based on dihydroxy-terminated poly(dodecylmethacrylate) for the preparation of polyurethane microspheres by dispersion as well as by suspension polymerization in aliphatic solvents.

In the previous chapter, we have reported the use of *ω*-hydroxy polystyrene as the reactive stabilizer[17] for the preparation of PUR particles with narrow particle size distribution. In continuation with our previous studies, the objectives are to evaluate the chemical nature and valence of the reactive stabilizer onto the stabilization process and final particle properties – by comparing the behavior of ω-hydroxy polybutadiene and ω-hydroxy polystyrene on one hand, and ω,ω'-dihydroxy polybutadiene and ω,ω'-dihydroxy polystyrene macromonomers on the other hand.

2 Polyurethane synthesis using ω-hydroxy polybutadiene as a stabilizer

A comparison of the solubility parameters of polystyrene (δ=18.6 MPa$^{1/2}$) and polybutadiene (δ=17.2 MPa$^{1/2}$) with the one of cyclohexane (δ= 16.8 MPa$^{1/2}$) indicates that polybutadiene has a better solubility in cyclohexane than polystyrene. Therefore, it may be anticipated that the use of ω-hydroxy polybutadiene instead of ω-hydroxy polystyrene as reactive stabilizer could be more favorable for the preparation of PUR particles, via dispersion process.

2.1. Synthesis of polyurethane particles

2.1.1. Mode of addition of the reagents

In the first attempt, the polymerization of TDI and EG was performed by addition of all the reagents at the start of the reaction. As could be expected and similar to the results obtained with ω-hydroxy polystyrene,[17] coagulation occurred whatever the concentration of ω-hydroxy polybutadiene used from 1 wt. % to 20 wt. %. This behavior may be explained by the absence of participation of ω-hydroxy polybutadiene as a reactive stabilizer in these experimental conditions. Therefore, in order to force ω-hydroxy polybutadiene to participate in the reaction, 1eq. of it was pre-mixed with an excess of TDI (2 eq.) in the presence of DBTDL at 60°C in cyclohexane for 2h to form *in situ* ω-NCO polybutadiene. EG (0.635g, 0.010 mole) was then added and the turbid mixture was allowed to react for 30 minutes. The rest of TDI (0.012 moles) was then added drop-wise over a variable time period. This procedure similar to the one developed with ω-hydroxy polystyrene[17] was maintained in all experiments to study the effect of different parameters such as the concentration of the stabilizer and the time of TDI addition on the resultant particle characteristics.

2.1.2. Effect of the stabilizer concentration

As indicated in Table 3-1, the polyurethane particle size decreases from 7.5 μm to 0.70 μm when the stabilizer concentration is increased from 2 wt. % to 20 wt. %. This phenomenon may be interpreted by the fact that nucleation occurs at the earlier stages of the polymerization. Therefore, the particle number reaches a maximal value at the beginning of the polymerization. The presence of large amount of stabilizers will enable a larger surface to be stabilized, leading to large number of smaller particles. It is worth noting that a ω-hydroxy polybutadiene concentration of 1 wt .% is not sufficient to stabilize the latex. The size distribution of the particle is also very narrow (span ≅ 0.6 - 0.8), whatever the stabilizer concentration. It indicates that ω-hydroxy polybutadiene stabilizer plays efficiently its role.

Wt% of PB-OH	SEC[c]		$d_{(0.5)}$, (µm)[a]	Span[b] $\frac{d(0.9)-d(0.1)}{d(0.5)}$	Observation
	$\overline{Mn}$	$Ip=\frac{\overline{Mw}}{\overline{Mn}}$			
1	-	-	-	-	coagulation
2	4500	1.77	7.5	2.08	broad dispersity
5	11370	1.53	1.8	0.8	monodisperse
10	10600	1.72	1.5	0.6	monodisperse
15	13850	2.19	1.0	0.6	monodisperse
20	nd	nd	0.7	0.7	monodisperse

[a] particle size obtained by performing light scattering measurements on a Malvern Master sizer 2000 (Hydro 2000S) apparatus
$d_{(0.5)}$ =50 % particles have size lower than the given value,
[b] particle size distribution or "span" = $\frac{d(0.9)-d(0.1)}{d(0.5)}$
where: $d_{(0.9)}$ =90 % particles have size lower than the given value,
$d_{(0.5)}$ =50 % particles have size lower than the given value,
$d_{(0.1)}$ =10 % particles have size lower than the given value.
[c] determined by SEC using *N,N*-dimethylformamide (DMF) as eluant

Table 3-1 : Effect of the stabilizer concentration, PB-OH ($\overline{Mn}$ = 4100 g/mol), on the PUR particle size. (TDI addition time = 1h).

2.1.3. Effect of TDI addition time on the dispersion process

A variation of TDI addition time was found to have an effect on the final polyurethane particle size. The slower the addition of TDI, the smaller the polyurethane particles. Indeed, a variation of TDI addition time from 1h to 6h for a ω-hydroxy polybutadiene concentration of 10 wt. % leads to a particle size reduction from 1.5 µm to 1µm, as shown in Table 3-2. In addition, the particle size distribution remains narrow whatever the time of TDI addition. Moreover, it was observed that addition of TDI in one lot leads to complete coagulation of the system.

Time of TDI addition	$d_{(0.5)}$, (µm)[a]	Span	Observation
1 lot	-	-	Coagulation
1h	1.50	0.69	Monodisperse
3h	1.20	0.61	Monodisperse
6h	1.06	0.6	Monodisperse

a = refer to footnote of Table 3-1

Table 3-2 : Effect of TDI addition time on the PUR particle size.
(PB-OH : 10 wt.%)

In Figure 3-1 is shown the optical microscopy picture of the PUR particles synthesized using ω-hydroxy polybutadiene as the stabilizer. The average particle size was measured to be 1.5 µm, which is in close agreement with the data obtained from Malvern measurements.

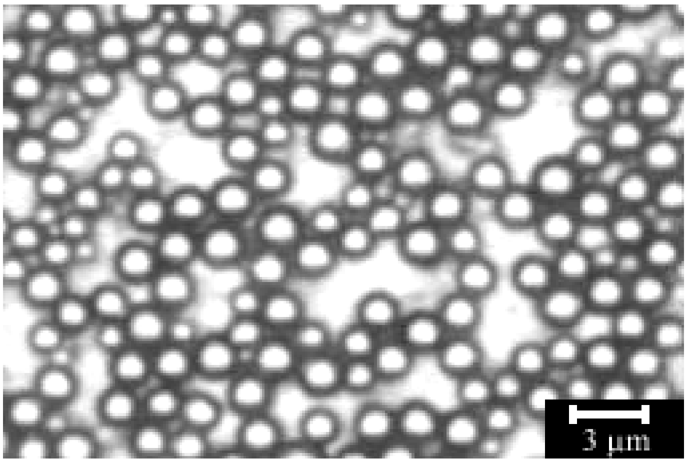


Figure 3-1 : Optical microscopy of PUR particles synthesized using PB-OH (10 wt. %) as the stabilizer

2.1.4. Molar mass determination

The molar masses of the polyurethane samples were determined by SEC using DMF as the eluant (see Table 3-1). As already observed (see previous chapter), the molar mass of the PUR particle increases with the amount of stabilizer used while in the mean time the particle size decreases. The inverse relationship between the particle size and the PUR sample molar mass is explained by considering that the stabilizer contribution with respect to the molar mass is very sensitive in our experimental conditions. In addition, two stages occur in step-growth process in dispersed medium. In the first stage, the chains grow in the bulk of the solvent and as conversions increases, a critical chain length is achieved whereby even low molar mass oligomers / polymers precipitate out. During the final stage, as the polymeric precipitate are reactive as shown by Morgan,[18] further chain growth takes place within the particle resulting in higher molar masses without affecting the size of the particles.

2.1.5. PUR thermo-mechanical analysis

We explored the evidence of the polybutadiene stabilizer anchorage on the PUR particles by performing thermo-mechanical analysis. Since the stabilizers have good solubility in cyclohexane, it should be easily removed if present in the free form by washing the PUR particles several times with cyclohexane. The washing procedure was implemented and followed by filtration. The PUR powder was recovered and characterized using thermo-mechanical analysis.

The DMA trace shows the presence of two transitions (see Figure 3-2). The two glass transition temperatures could be attributed to the stabilizer moiety i.e. polybutadiene and to the polyurethane segment. These transitions were found at –75°C for polybutadiene and 95°C for the polyurethane respectively. These data were counter checked by measuring the Tg of polybutadiene and that of the polyurethane particle synthesized in the presence of unreacted stabilizer such as PS-b-PEO block copolymer. As expected, the latter showed single Tg respectively at -77°C and 100°C. These results support the fact that the stabilizer is covalently linked to the PUR microspheres and has taken part in the condensation process.

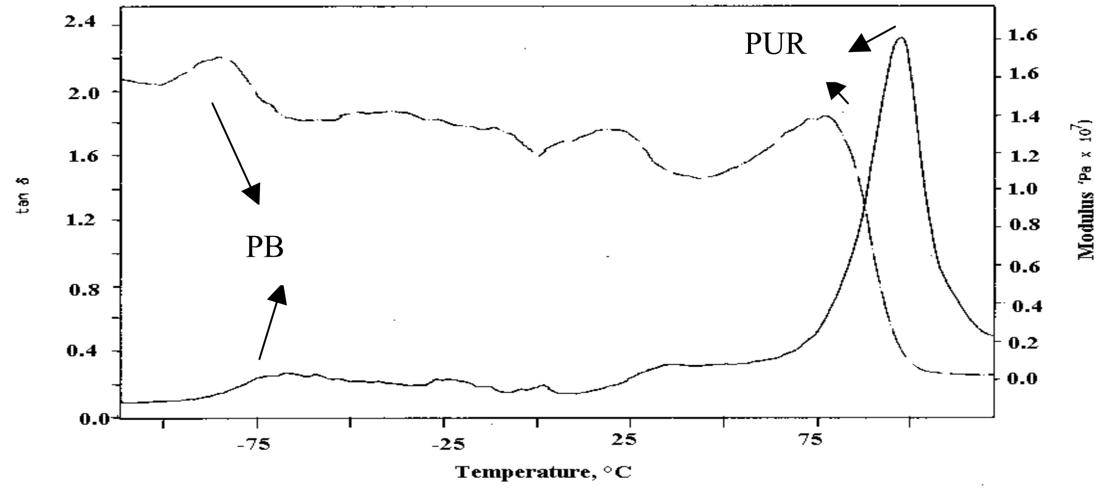


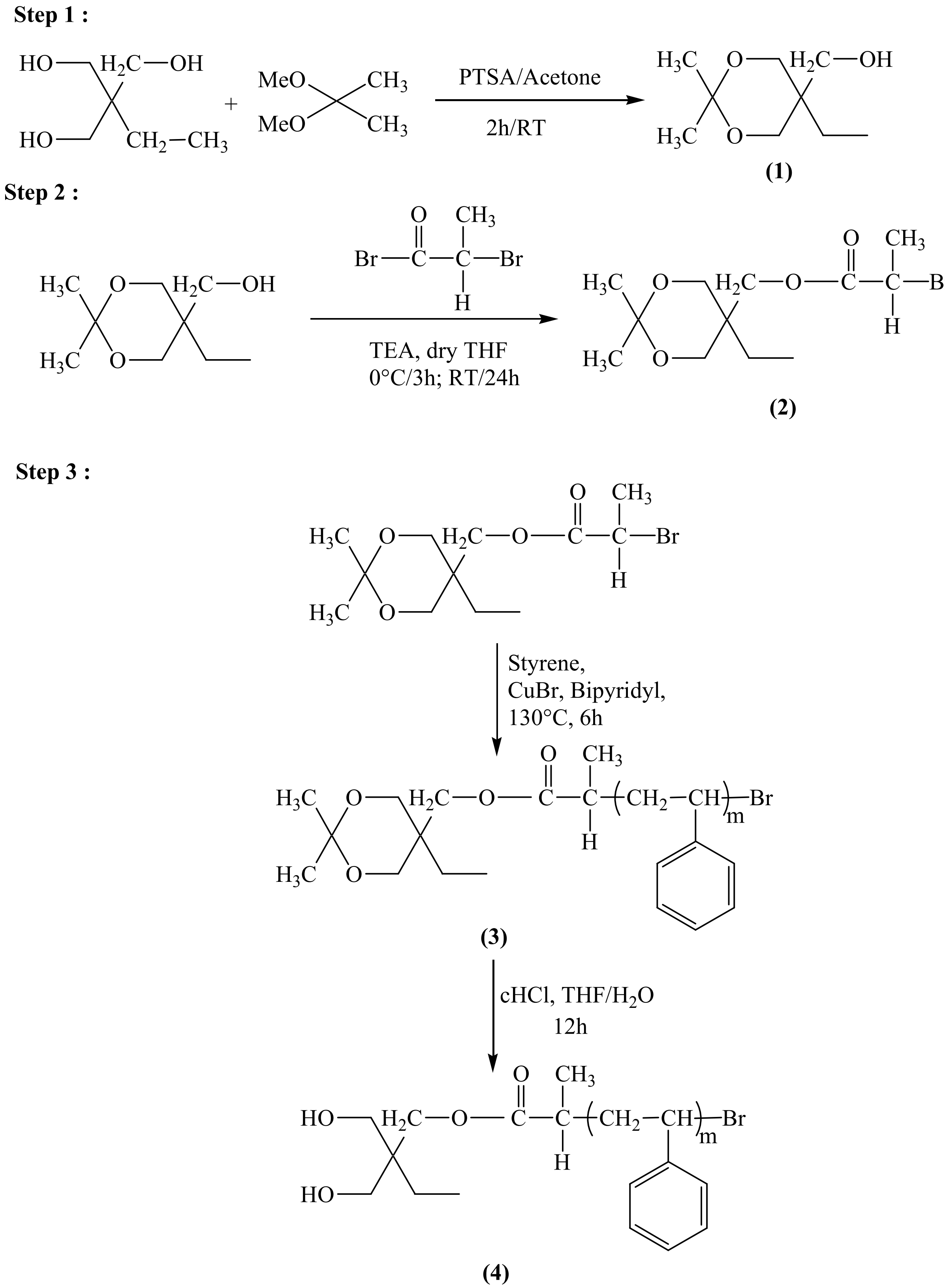
Figure 3-2 : DMA trace of PUR synthesized using PB-OH as the stabilizer.

The use of ω-hydroxy polybutadiene and ω-hydroxy polystyrene[17] as reactive stabilizers was found efficient for the preparation of uniform PUR particles by dispersion technique. Nevertheless, these reactive stabilizers are monovalent and may be considered as "chain stoppers" towards the addition process. To overcome this drawback, we investigated the possibility to use ω,ω'-dihydroxy polybutadiene and polystyrene as reactive stabilizers also called macromonomers. The preparation of such difunctional stabilizers as well as their use for the preparation of PUR particles is described below.

3 Polyurethane synthesis using ω,ω'-dihydroxy polystyrene as a reactive stabilizer

3.1. Synthesis of ω,ω'-dihydroxy polystyrene

A multiple step process involving ATRP technique was used for synthesizing this macromonomer. The synthetic pathway is shown in Scheme 3-1



Scheme 3-1: Synthesis of ω,ω'-dihydroxy polystyrene $PS(OH)_2$ via initiation.

3.1.1. Synthesis of 5-ethyl 5-hydroxymethyl-2,2-dimethyl 1:3 dioxane

The protection of the hydroxyl groups of trimethylol propane was performed using 2,2-dimethoxy propane in the presence of PTSA as the catalyst. The product of the reaction (a) was characterized by ^{1}H NMR (Figure 3-3). The ^{1}H NMR spectrum is in good agreement with the structure of (**1**).

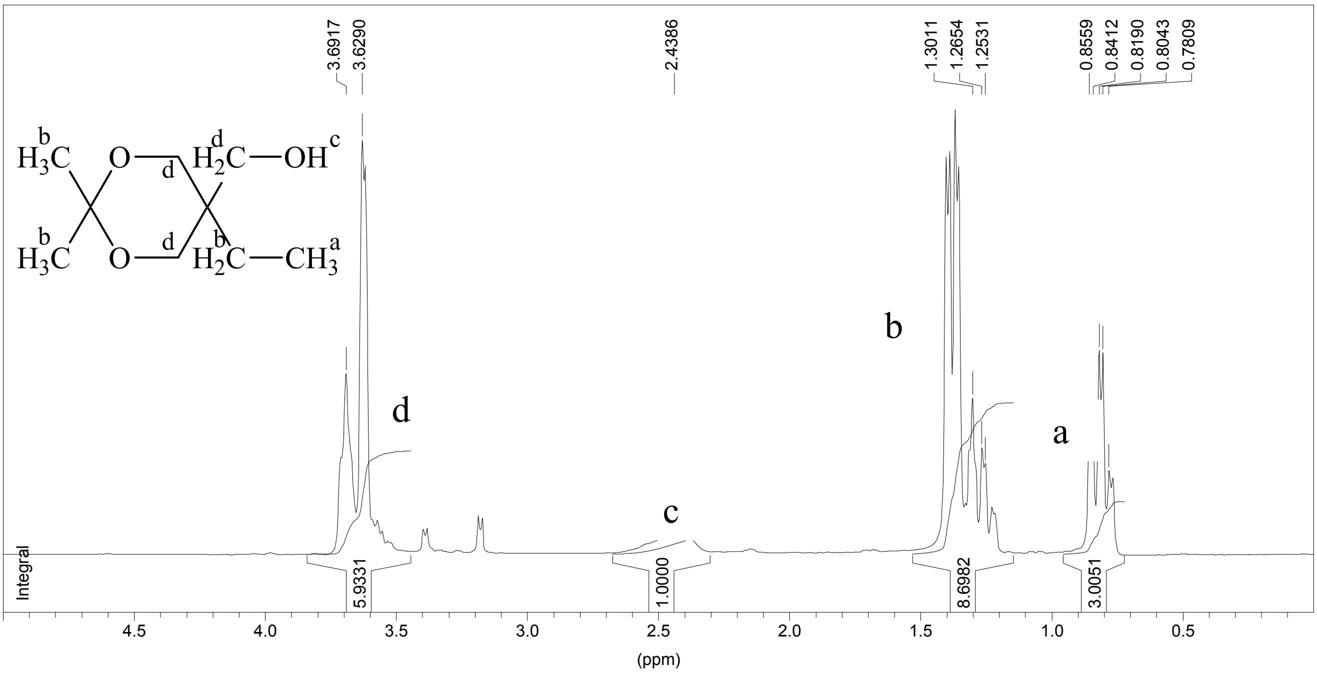


Figure 3-3 : ^{1}H NMR spectrum of 5-ethyl, 5-hydroxy methyl-2,2-dimethyl-1,3-dioxane (**1**).

3.1.2. Synthesis of 5-ethyl 5-(2-methyl,2-bromo propionate) methyl-2,2-dimethyl-1,3-dioxane

We designed a novel ATRP initiator, (**2**), bearing an acetal ring as a protected hydroxyl group and a secondary bromine. This initiator was synthesized by esterification of (a) using 2-bromo propionyl bromide in the presence of triethyl amine as the base to trap the acid liberated during the reaction. The product (**2**) was characterized by ^{1}H NMR (Figure 3-4). The disappearance of the hydroxy peak and the presence of a multiplet at δ = 4.2 ppm assigned for the proton attached to the secondary carbon indicate the complete esterification of (**1**) to give the ATRP initiator (**2**).

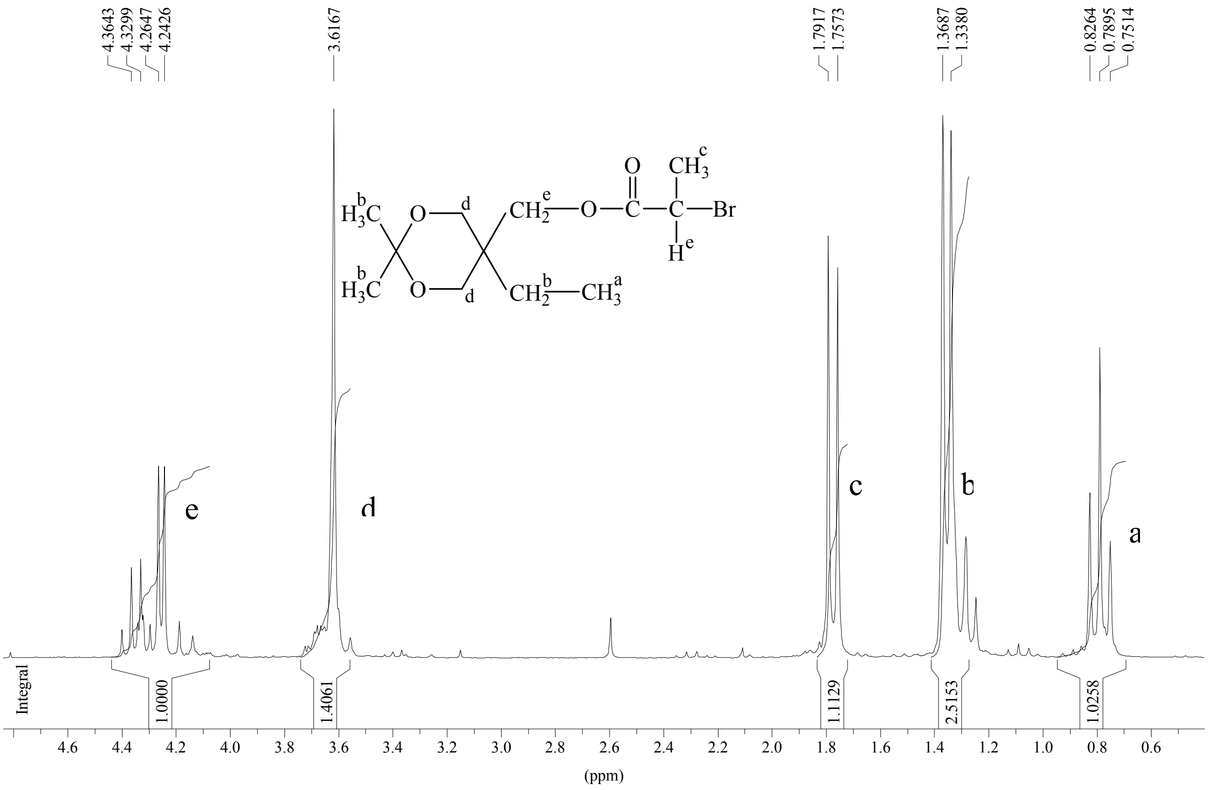


Figure 3-4 : ^{1}H NMR spectrum of 5-ethyl 5-(2-methyl, 2-bromo propionate) methyl-2,2-dimethyl 1:3 dioxane (2).

3.1.3. Atom transfer radical polymerization of styrene followed by deprotection of the acetal function

Styrene polymerization was performed using (2) as the ATRP initiator. We prepared a series of ω,ω'-dihydroxy polystyrene (4) of various molar masses to be used for polyurethane synthesis. Different ligands were used to achieve a controlled polymerization and to obtain well-defined polymers. The use of bipyridine as the ligand resulted in rather large polydispersity indices (I_p >1.3). However, when PMDETA was used as the ligand, and at low monomer conversion, a better control of the polymerization was achieved. This protected polystyrene was subsequently deprotected by acid treatment. The deprotected polymer characterized by ^{1}H NMR was found to be in good agreement with the structure of the ω,ω'-dihydroxy polystyrene as expected. The characteristics of the polymer are given the Table 3-3. These ω,ω'-dihydroxy polystyrenes were then used for the dispersion polymerization of polyurethane.

Stabilizer	Ligand	Temp, °C	Time, h	Conv, %	SEC		
					$\overline{M}_{n,th}$	$\overline{M}_{n,exp}$	$I_p = \frac{\overline{M}_w}{\overline{M}_n}$
S-1	Bipyridyl	100	1	20	10000	1600	1.60
S-2	Bipyridyl	100	2	36	10000	3681	1.46
S-3	PMDETA	80	1	40	10000	3793	1.10
S-4	PMDETA	80	20 min	6	25000	1500	1.14
S-5	PMDETA	80	40 min	20	25000	2100	1.2

Table 3-3 : ATRP polymerization of styrene using (**2**) as the initiator.

3.2. Polyurethane synthesis using $PS(OH)_2$ as a stabilizer

As was reported earlier,[17] ω-hydroxy polystyrene of $\overline{DP}_n = 20$ was found to be the most efficient to stabilize the PUR particles. For comparison, ω,ω'-dihydroxy polystyrene (S-5) of the same $\overline{DP}_n$ was used as the macromonomer for the polyurethane synthesis.

3.2.1. Synthesis of the "precursor"

The reactivity of the ω,ω'-dihydroxy polystyrene towards TDI was evaluated. To that purpose, both the monomers (S-5 and TDI) were mixed together at an equimolar ratio at 60°C for 24h. The resultant product was precipitated in MeOH and analyzed by ^{1}H NMR. The NMR spectrum of the product (Figure 3-5) shows the presence of unreacted –OH functions along with –NH group from the urethane linkages. From these NMR data as well as SEC measurements, the formation of a dimer, as shown in Scheme 3-2, was postulated. Indeed, it may be suggested that the reactivity of the second hydroxyl group is affected due to a steric hindrance coming from the more rigid polystyrene backbone.

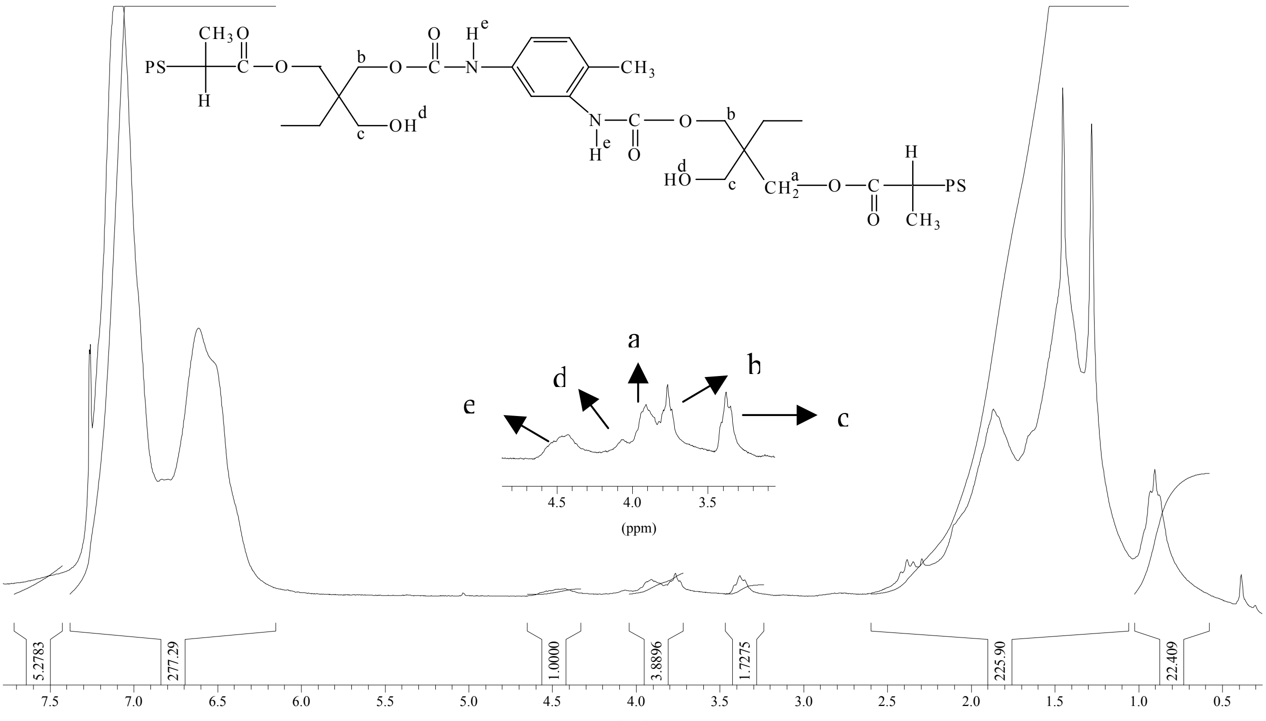
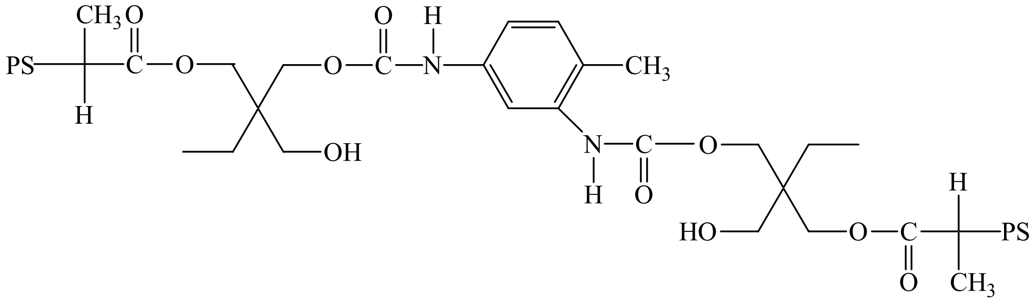


Figure 3-5 : ^{1}H NMR spectrum of the reaction product of TDI with ω,ω'-dihydroxy polystyrene ($\overline{DP}_n = 20$).



Scheme 3-2 : Hypothetic structure of the dimer formed after reaction of PS(OH)$_2$ with TDI at 60°C in cyclohexane.

The preparation of PUR particles carried out at 60°C even in the presence of high stabilizer concentration (20 wt.%), and for a slow addition of TDI (6h), results in coagulation.

In order to enhance the reactivity of ω,ω'-dihydroxy polystyrene, the polymerization temperature was elevated to 80°C, value higher than the Tg of this oligomeric polystyrene. The same method of monomer addition and "precursor" synthesis was adopted as reported for the ω-hydroxy polybutadiene and ω-hydroxy polystyrene. The temperature increase allowed us to prepare polyurethane particles for a 10 wt. % stabilizer concentration only when TDI is added slowly in the reaction medium over 6h time. Nevertheless, the particle size range is from 100 nm to 500 nm, with a majority of particles having a size close to 250 nm as shown in Figure 3-6.

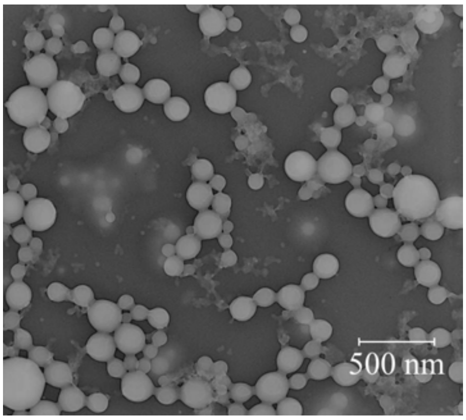


Figure 3-6 : TEM micrograph of PUR particles synthesized using $PS(OH)_2$ ($\overline{DP}_n = 20$) as the stabilizer (Stabilizer concentration 10 wt. %; time of addition : 6h).

In addition to S-5, a low molar mass ω,ω'-dihydroxy polystyrene ($\overline{M}_n$ = 1500g/mol^{-1}) (S-4) was also used as reactive stabilizer. However, coagulation occured whatever the concentrations of S-4 used. The inefficiency of S-4 to stabilize the particles can be attributed to the too short chain length of the stabilizer. This observation is in agreement with that observed by Guyot[19] *et al.* whereby maleate based PEO macromonomers were used as stabilizers for the dispersion polymerization of styrene in ethanol-water mixture.

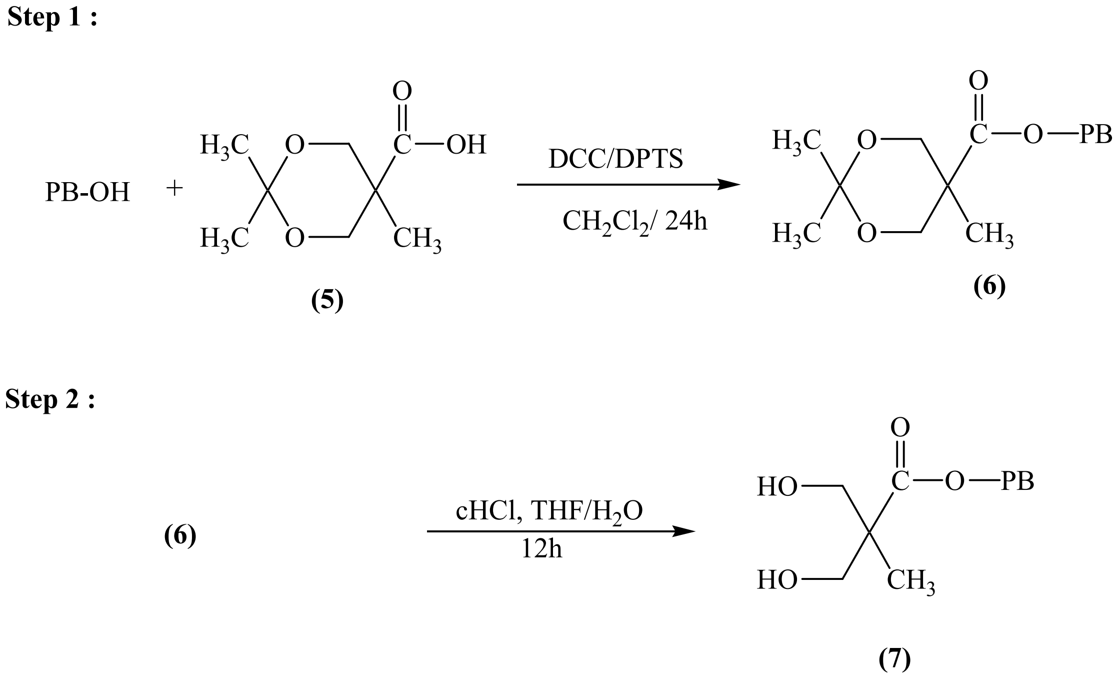
3.2.2. Effect of the stabilizer concentration

The stabilizer concentration was varied at the reaction temperature of 80°C from 1 wt. % to 10 wt. %. As anticipated, 1 wt. % S-5 stabilizer concentration was not enough to achieve efficient dispersion. An increase in stabilizer concentration from 5 wt. % to 10 wt. % leads to a particle size decrease from 3.20 µm to 250 nm. In both cases, the particle size distribution is rather large as already discussed.

4 Polyurethane synthesis using ω,ω'-dihydroxy polybutadiene (PB(OH)$_2$) as a stabilizer

4.1. *Synthesis of ω,ω'-dihydroxy polybutadiene*

The ω,ω'-dihydroxy polybutadiene was synthesized by esterificaton of the corresponding hydroxy-terminated polybutadiene ($\overline{M_n}$ = 4000g/mol) with the bis-methoxy propionic acid in the presence of DPTS and DCC at room temperature.[20] The protected polymer (6) obtained was thereafter deprotected by acid treatment in water/THF mixture (Scheme 3-3). This macromonomer (7) was then used for the polyurethane synthesis in dispersed medium.



Scheme 3-3 : Synthesis of ω,ω'-dihydroxy polybutadiene (PB(OH)$_2$).

4.2. *Polyurethane synthesis using PB(OH)$_2$ as a stabilizer*

ω,ω'-dihydroxy polybutadiene of the same molar mass (4100g/mole) as ω-hydroxy polybutadiene was chosen as reactive stabilizers for PUR synthesis in dispersed medium. The procedure of "precursor" synthesis, followed by the monomer addition was similar as the previous studies. Parameters such as the concentration of the stabilizer and time of TDI addition were varied to achieve efficient dispersion.

4.2.1. Effect of TDI addition time

For the purpose, the concentration of ω,ω'-dihydroxy polybutadiene was maintained at 10 wt. % and TDI was added over a variable time period (from 1 h to 6 h). As shown in the Table 3-4, a fast addition of TDI either leads to coagulation phenomenon or to PUR particles with a rather large size distribution. Conversely, monodisperse PUR particles with a size around 1 µm are obtained for longer time of TDI addition. It is worth noting that the particle size remains constant over a TDI addition time of 3 h. This phenomenon is different than the one observed with polystyrene and highlights the efficiency of ω,ω'-dihydroxy polybutadiene in the nucleation step of the process.

Time of TDI addition	$d^{a}_{(0.5)}$, (µm)	Span	Result
1 lot	-	-	Coagulation
1h	3.21	6.7	Bimodal
3h	1.1	1	Monodisperse
6h	0.9	0.9	Monodisperse

a = refer to footnote of Table 3-1

Table 3-4 : Effect of TDI addition time on the PUR particle size (Stabilizer: 10 wt.%).

4.2.2. Effect of stabilizer concentration

A series of polyaddition in dispersed medium for variable ω,ω'-dihydroxy polybutadiene concentrations proved the efficiency of the latter as a surfmer. Indeed, even a very low stabilizer concentration (1 wt %) enables the preparation of PUR particles. The results given in Table 3-5, also show that the PUR particle size remains rather constant whatever the concentration (5 or 10 wt %) of ω,ω'-dihydroxy polybutadiene.

Wt.%	$d^{a}_{(0.5)}$, (µm)	Span	Result
1	3.42	13.24	15% coagulation
5	1.02	1.0	Monodisperse
10	0.98	0.9	Monodisperse

a = refer to footnote of Table 3-1

Table 3-5 : Effect of the stabilizer $PB(OH)_2$ concentration on the PUR particle size.

4.2.3. Comparison of ω-hydroxy polybutadiene and ω,ω'-dihydroxy polybutadiene behavior as the stabilizers

The kinetics of the polymerizations were compared using mono- and dihydroxy-terminated polybutadiene stabilizers. Kinetic was followed by sampling out aliquots at regular intervals of 30 min during 6h time. A plot of the conversion with time is shown in Figure 3-7. The conversion using both the stabilizers was always close to 100 % and there was no much difference in the conversion curves whatever the stabilizers used.

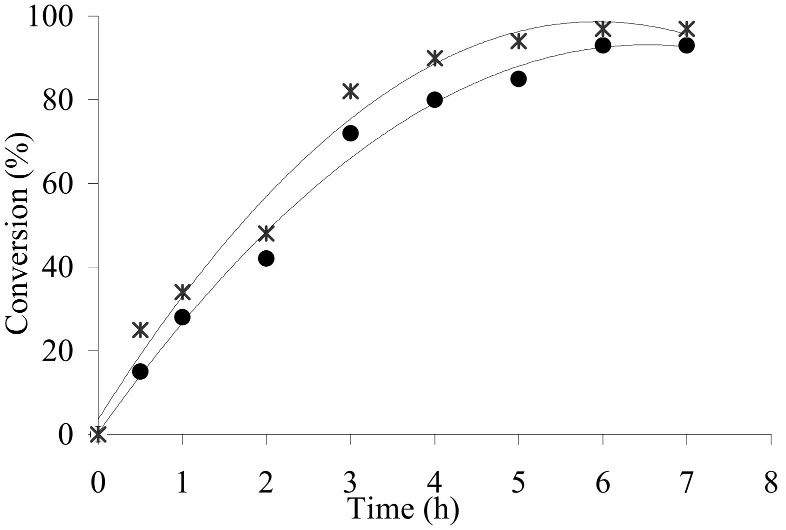


Figure 3-7 : Plot of conversion (%) *vs* time (h): •= PB(OH) as the stabilizer; ✳= $PB(OH)_2$ as the stabilizer (10 wt.% stabilizer; time of addition = 6h).

It was found for both stabilizers that an *in situ* synthesis of the "precursor" is essential to achieve stable dispersions. In agreement with literature data,[20,21] the concentration of the stabilizer required to form PUR particles was found to be much lower in the presence of the macromonomer than with the corresponding mono-hydroxy homopolymer. In addition, at the same stabilizer concentration and time of TDI addition, PB(OH)$_2$ gives smaller particles of 0.9 µm diameter as compared to 1.1 µm with PB(OH).

The growth of the particles with time was followed by optical microscopy. It was found that a steady growth in particle size took place till a conversion of about 80 % in both cases (Figure 3-8). As clearly shown in Figure 3-8, the use of macromonomer as the stabilizer yields smaller PUR particles. This suggests that the critical chain length to get precipitation occurs sooner in the case of PB(OH)$_2$ compared to PB(OH).

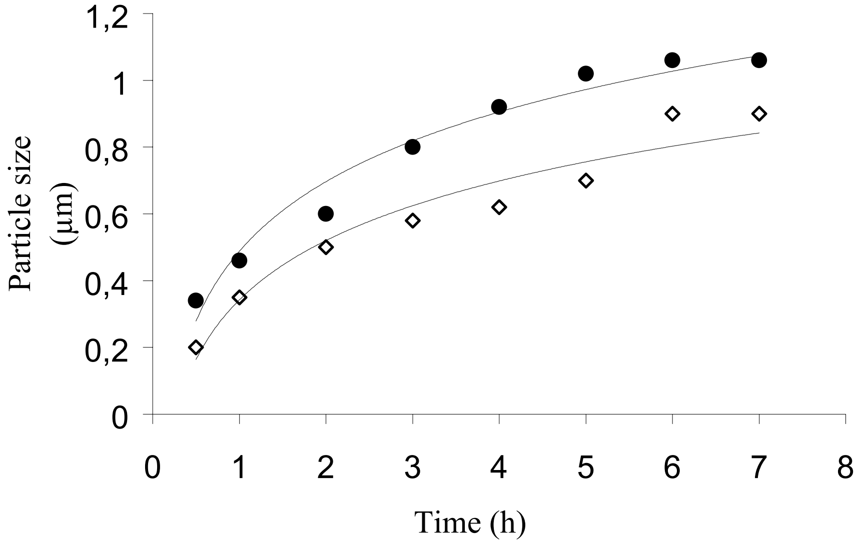


Figure 3-8 : Plot of particle size (µm) *vs*. time (h); PB(OH) (•) and PB(OH)$_2$ (◊)as the stabilizer, and time of TDI addition = 6h.

4.2.4. Comparison of ω,ω'-dihydroxy polystyrene and ω,ω'-dihydroxy polybutadiene as the stabilizers

The main difference between both these macromonomers is their polymer skeleton. The polybutadiene backbone is highly flexible as compared to the rigid polystyrene chains.

The dispersion polymerization points out the importance of flexible stabilizer backbone to obtain stable dispersion. The higher is the chain mobility, the greater is the anchoring/grafting of the reactive stabilizer onto the growing particles, resulting in well controlled particles.

5 Conclusion

Reactive stabilizers based on polystyrene and polybutadiene were synthesized using anionic, and ATRP polymerization techniques. Detailed characterizations of these stabilizers were performed to confirm the well-defined structures.

Polyurethane synthesis by dispersion technique was carried out using these reactive stabilizers. Although all these stabilizers did prove to be efficient for the polyurethane synthesis, polybutadiene-based stabilizers give better results regarding the uniformity of the PUR particles. It is noteworthy that the stabilizer based on polystyrene backbone worked only at a temperature higher than the Tg of the oligomeric polystyrene used. Studies were performed to confirm the covalent bond formation of the stabilizer with the resultant PUR particles using DMA techniques. It was clearly proved that the stabilizer has indeed stabilized the particles by reaction with the PUR particles giving a core-shell structure to the particles. This led us to study the mechanical properties of these materials along with the ability of film formation in view for coating applications. The behavior of such films as well as their careful physical characterizations is under investigation.

6 References

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Il ressort du chapitre précédent que les caractéristiques physico-chimiques de l'agent stabilisant utilisé sont déterminantes pour préparer des particules polymères. Ainsi les polybutadiènes mono et divalents se sont avérés plus aptes à stabiliser des dispersions de polyuréthane en comparaison de leurs homologues polystyrène. Dans le cas particulier de $PS(OH)_2$ utilisé comme macromonomère, l'absence de réactivité d'une des deux fonctions hydroxyle vis-à-vis des isocyanates - liée à la structure relativement rigide de la chaîne polystyrène qui induit une forte gène stérique - ne permet pas l'utilisation de cet oligomère comme un agent stabilisant de la dispersion. Dans ce cas, une coagulation du latex est observée.

C'est dans l'objectif de préparer des matériaux polyuréthane présentant des propriétés adhésives que nous avons pensé utiliser des poly(acrylate de *n*-butyle)s, porteurs de une ou deux fonctions hydroxyle en bout de chaîne, comme agents stabilisants réactifs de la dispersion. Leur faible température de transition vitreuse laisse entrevoir un comportement comparable à celui du polybutadiène. Le chapitre 4 est scindé en deux parties. La première traite d'une part de la synthèse par polymérisation radicalaire contrôlée des poly(acrylate de *n*-butyle)s ω-OH et ω-$(OH)_2$ et, d'autre part, de leur utilisation comme agents stabilisants de la dispersion. La deuxième partie discute l'aptitude des latex préparés à former des films bien structurés puis évalue les propriétés adhésives de ces nouveaux matériaux constitués d'un cœur "dur" polyuréthane et d'une écorce "souple" polyacrylate.

CHAPTER 4:

SYNTHESIS OF CORE-SHELL POLYURETHANE PARTICLES WITH ADHESIVE PROPERTIES

GLOSSARY

1 Introduction

Polymerization in heterogeneous conditions such as in dispersed medium is an attractive route for the preparation of polymeric particles in the micron size range. In such a process, the continuous phase is selected as a non-solvent for the growing polymer. As the polymerization proceeds, nuclei constituted of oligomeric species are formed but the coagulation of the precipitated polymer is prevented by the presence of steric stabilizers leading to the formation of polymer particles.

Among all the polymeric stabilizers described so far, two main categories can be distinguished. Amphipathic block copolymers such as PS-b-PEO have extensively been described in the literature for this purpose.[1,2] They enable the stabilization of the particle by physical adsorption. Another class of steric stabilizers that have received wide attention are reactive polymers,[3] surfmers,[4] macromonomers,[5] etc... The latter react with the growing polymer, giving rise to the *in situ* formation of block or graft copolymers and remain attached to the final particle which exhibit a core-shell structure. The main advantage in using such reactive stabilizers lies with the formation of covalent links between the core and the shell of the particles, which enhances the stability with time of the resultant latexes. Homopolymers such as poly(vinyl pyrollidone), poly(acrylic acid), hydroxy propyl cellulose[6,7,8,9] and thiol end-capped polyethylene oxide[10] were used to stabilize the dispersion polymerization of styrene in aqueous/ethanol solution by this process.

The preparation of "polycondensate" particles by dispersion techniques is less documented in the literature. Recently, we investigated the possibility to elaborate PUR particles in dispersed medium in the presence of different steric stabilizers. To that purpose, we could demonstrate that ω-hydroxyl polystyrene, PS(OH) and ω-hydroxyl polybutadiene, PBu(OH), exhibited higher stabilization ability compared to PS-b-PEO block copolymers.[11,12].

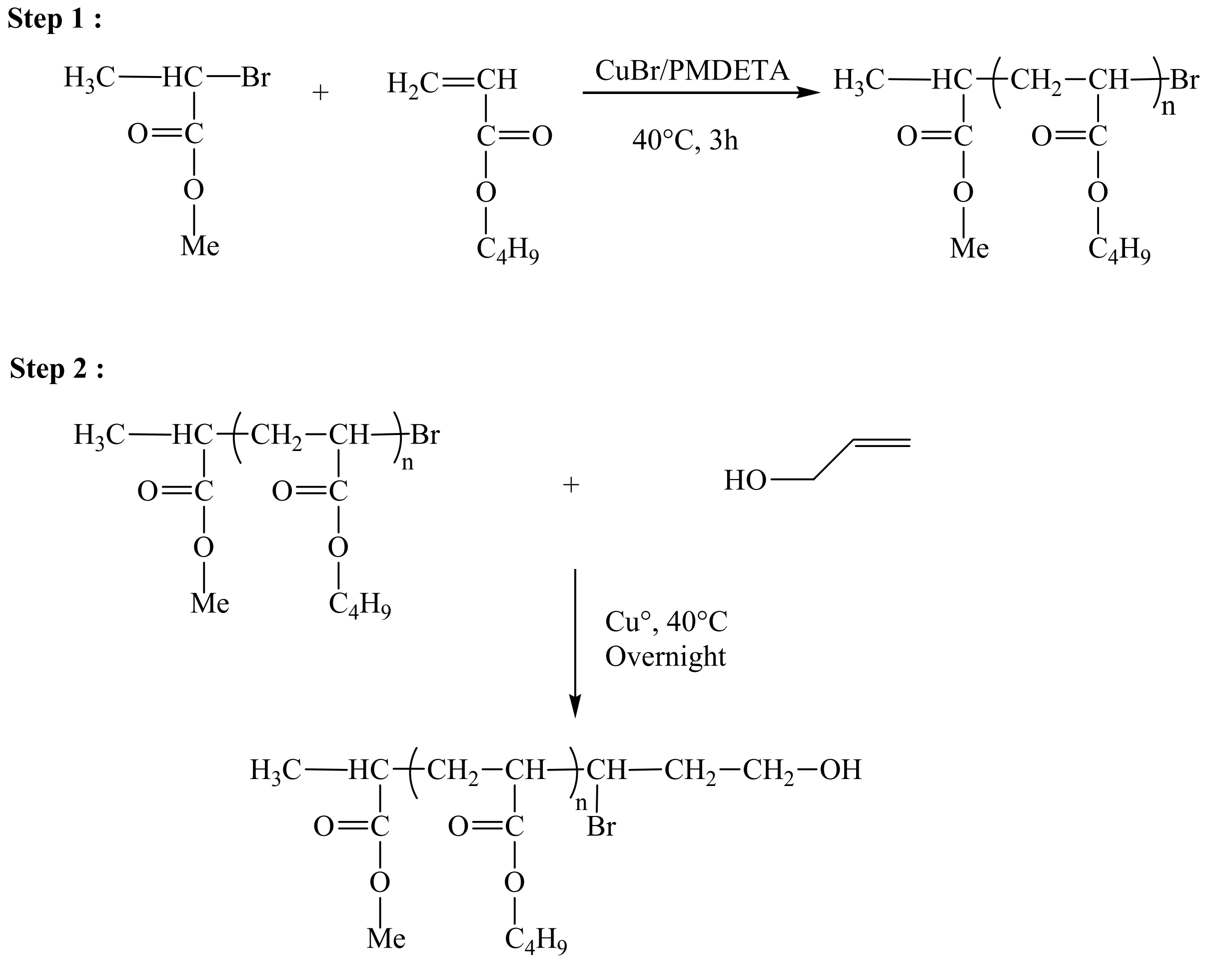
One of the objectives of the present study is to evaluate the influence of the stabilizer valence on its capacity to act as a steric stabilizer for PUR synthesis in dispersed medium. Only few papers report the synthesis and the use of polycondensable macromonomers in dispersed medium. Sivaram *et al.*[13,14] described the synthesis of polyurethane microspheres by dispersion as well as by suspension polymerizations in aliphatic solvents using polycondensable macromonomers based on dihydroxy-terminated poly(dodecylmethacrylate).

This chapter mainly focuses on the synthesis of two kinds of poly(*n*-butyl acrylate)s fitted with one or two hydroxyl groups at their end. The synthesis of these stabilizers was carried out using atom transfer radical polymerization (ATRP). Regarding the synthesis of the macromonomer, P*n*BuA$(OH)_2$, two routes have been explored depending on the way of functionalization, either through initiation or by chain end functionalization. The behaviors of P*n*BuA$(OH)_2$ and P*n*BuA-OH, as steric stabilizers towards the synthesis of PUR particles in dispersed medium (EG and TDI being kept as monomers) are compared and discussed.

2 Synthesis of hydroxy and dihydroxy end-capped poly(*n*-butyl acrylate)s and use as reactive stabilizers for the preparation of polyurethane latexes

2.1. Synthesis of ω-hydroxyl poly(n-butyl acrylate), PnBuA(OH)

The synthesis of hydroxy-terminated poly(*n*-butyl acrylate) was realized according to the procedure reported by Matyjaszewski *et al.*[15] As shown in Scheme 4-1, the synthesis proceeds by ω-functionalization of the poly(*n*-butyl acrylate) chains (obtained by ATRP) with an excess of allyl alcohol (30 eq.) together with copper(0) at high conversion of the acrylate polymerization. The characteristics of the prepared P*n*BuA(OH) are listed in Table 4-1.



Scheme 4 –1 : Synthesis of P*n*BuA(OH) by chain-end functionalization.

As shown below in Table 4-1, the molar masses determined by size exclusion chromatography (SEC) are in good agreement with the targeted ones, and the SEC traces exhibit a narrow molar mass distribution. This confirms the efficiency of the initiating system composed of methyl 2-bromopropionate with the $Cu^{I}Br$/PMDETA metal/ligand catalyst at rather low temperature (40°C). In addition, the incorporation of an allyl alcohol molecule -a less reactive functional monomer- at the chain end of poly(n-butyl acrylate) was confirmed by NMR spectroscopy. Indeed, the ^{1}H NMR spectrum of P*n*BuA(OH) revealed the presence of a characteristic signal at $\delta \approx 3.75$ ppm that was assigned to the resonance of the methylene protons adjacent to the hydroxyl group.

Stabilizer	$\overline{M_n}$ (g/mole)		$I_p=\frac{\overline{M_w}}{\overline{M_n}}$	Functionality[c] %
	Targeted[a]	SEC[b]		
S1	6250	6000	1.23	96
S2	8160	8600	1.22	95
S3	10225	10000	1.18	92
S4	15380	15000	1.15	95

[a] Molar masses calculated from $\{([n\text{-BuA}]_0/[\text{initiator}]_0)M_{nBuA}\} + M_{\alpha\text{-end}} + M_{\omega\text{-end}}$, M_{nBA} being the molar mass of the n-butyl acrylate units, $M_{\alpha\text{-end}}$ and $M_{\omega\text{-end}}$ the molar masses corresponding to the methyl propionate at one end and to the ethylene hydroxy-methyl at the other end respectively;

[b] Average molar masses determined by SEC equipped with refractive index (RI)/UV dual detections and calibrated with narrow PS standards;

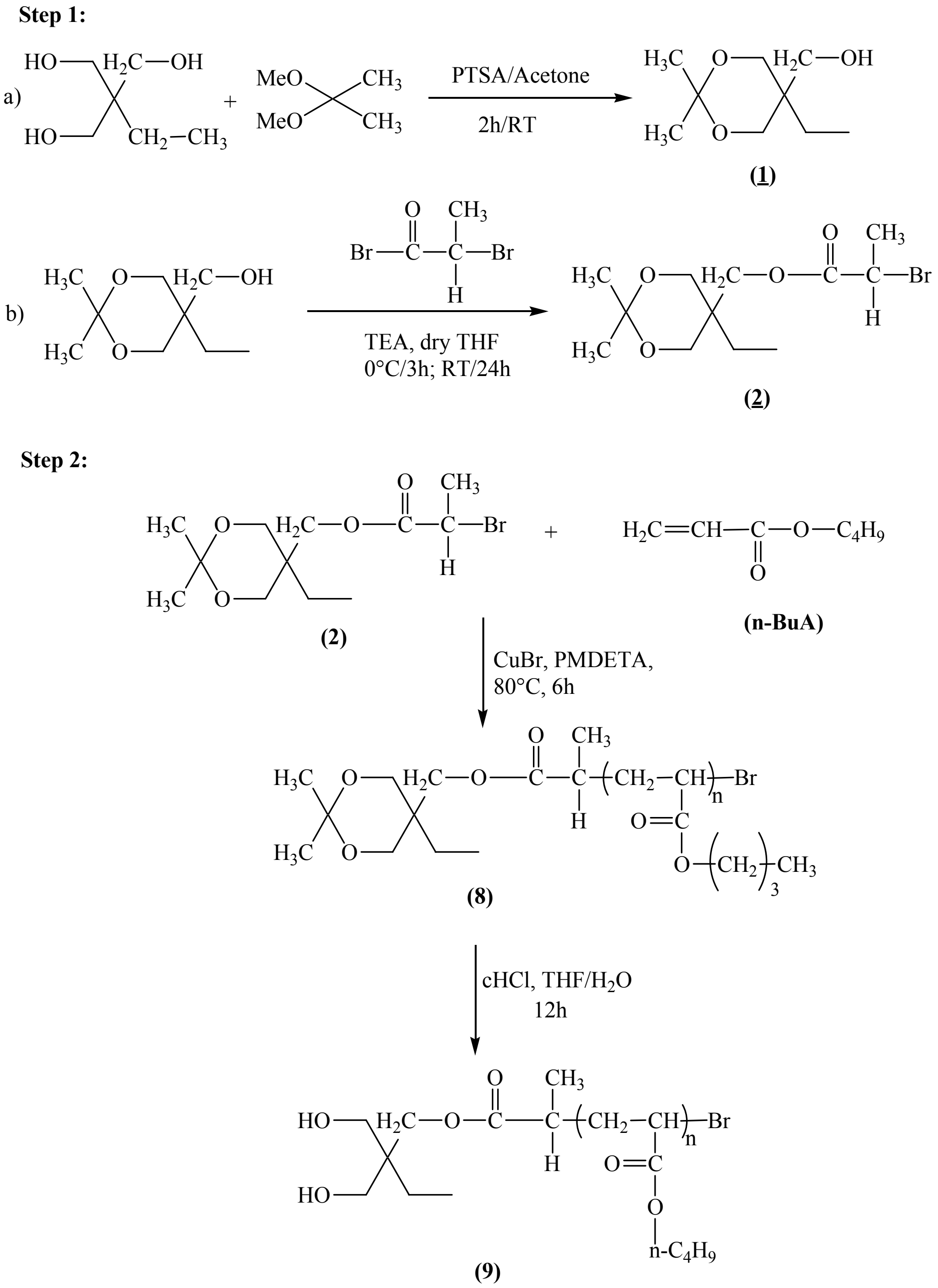
[c] Determined by ^{1}H NMR, calculating the ratio of the area of the signal corresponding to the protons of the methylene group adjacent to the hydroxyl chain ends (I_1, $\delta C\underline{H}_2\text{-OH}=3.7$ ppm) to that of the peak arising from the protons of methyl group of the initiator (I_2, $\delta C\underline{H}_3\text{-CH}(CO_2CH_3)\text{-}=1.1$ ppm); functionality (%) = $\frac{I1}{\frac{2}{3}I2}\times 100$

Table 4-1 : Characteristics of ω-hydroxy poly(*n*-butyl acrylate)s, P*n*BuA(OH).

2.2. Synthesis of gemini-type dihydroxy poly(n-butyl acrylate), PnBuA(OH)$_2$ macromonomers

2.2.1. Via initiation

A first series of gemini-type poly(*n*-butyl acrylate)s macromonomers fitted with two hydroxyl groups at the end were obtained according to Scheme 4-2.



Scheme 4-2 : Synthesis of gemini-type P*n*BuA(OH)$_2$ macromonomers *via* initiation.

In a first step, a Janus-type molecule, (2), which carries both an initiating moiety and two protected hydroxyl groups as an acetal ring is synthesized. (2) was obtained by nucleophilic substitution between an acid bromide and a cyclic acetal (1) in the presence of triethylamine in THF. It is noteworthy that the addition of the acid bromide had to be performed drop wise in order to get a good efficiency and yield up to 90%. The structure of (2) was checked by ^{1}H NMR (see Chapter 3; Figure 3.4).

All signals were assigned and had proved the structure of molecule (2), *e.g.* the signals at $\delta\approx3.61$ ppm and at $\delta\approx1.77$ ppm corresponding to the resonance of the protons from the methoxy of the acetal ring $(-C\underline{H}_2-O-)_2$ and of the proton adjacent to the bromine atom $(-C\underline{H}(CH_3)-Br)$ respectively. The second step involved the ATRP polymerization of *n*-butyl acrylate using (2) as initiator in similar conditions as described with methyl 2-bromopropionate. All polymerizations were performed in bulk with Cu^IBr/PMDETA as the metal/ligand catalyst, and molar masses ranging from 1000 g/mole to 6000 g/mole were targeted. Unfortunately, the polymers obtained were showing broad and multiple molar mass distributions. A low efficiency of the initiator (2) was speculated to explain this phenomenon. Therefore it was decided to work either at higher temperature or during longer reaction time. In Table 4-2 the characteristics of samples S5 to S7 prepared at 80°C instead of 40°C are shown.

Stabilizer	Polymerization system	$\overline{M_n}$ (g/mole)		$Ip=\frac{\overline{M_w}}{\overline{M_n}}$	Functionality[c] %
		Targeted[a]	SEC[b]		
S5	**Route 1**: Molecule (2) /Cu^IBr/PMDETA/BuA/80°C	1000	960	1.4	95
S6		3000	3100	1.3	96
S7		6000	5400	1.1	95
S8	**Route 2**: Methyl 2-bromopropionate/Cu^IBr/ PMDETA/BuA/80°C + functionalizing molecule (**10**)	1000	1200	1.1	97
S9		3000	3100	1.1	95
S10		6000	5800	1.1	96

[a] Molar masses calculated from $\{([nBA]_0/[initiator]_0)M_{nBA}\} + M_{\alpha\text{-end}} + M_{\omega\text{-end}}$, M_{nBA} being the molar mass of the n-butyl acrylate units, $M_{\alpha\text{-end}}$ and $M_{\omega\text{-end}}$ the molar masses corresponding to the molar masses of the end groups;

[b] Average molar masses determined by SEC equipped with refractive index (RI)/UV dual detections and calibrated with narrow PS standards;

[c] Determined by ^1H NMR, according to the molar mass determined by SEC and comparing the area of the signals corresponding to the protons of the methylene group adjacent to the hydroxyl chain ends ($\delta C\underline{H}_2-OH=3.6$ ppm) to that of the peak arising from the protons of methyl group of the repeating units ($\delta C\underline{H}_3-(CH_2)_3-=0.9$ ppm).

Table 4-2 : Characteristics of ω,ω'-dihydroxy poly(*n*-butyl acrylate)s

As expected, the experimental molar masses are in good agreement with the targeted ones. The preparation of poly(n-butyl acrylate)s fitted with two gemini-type primary alcohol functions was finally achieved after cleavage of the acetal head of the polyacrylate under strong acid conditions, *i.e.* with concentrated hydrochloric acid. The functionality of thus formed end-functionalized polyacrylates was checked by ^{1}H NMR and was found close to 100 % by comparing the signal area of methylene groups adjacent to the hydroxyl chain ends ($\delta(C\underline{H}_2\text{-OH})\sim3.6$ ppm) with that of the protons of the methyl groups of the repeating units ($\delta(-(CH_2)_3C\underline{H}_3)\sim1.1$ ppm) (see Figure 4-1).

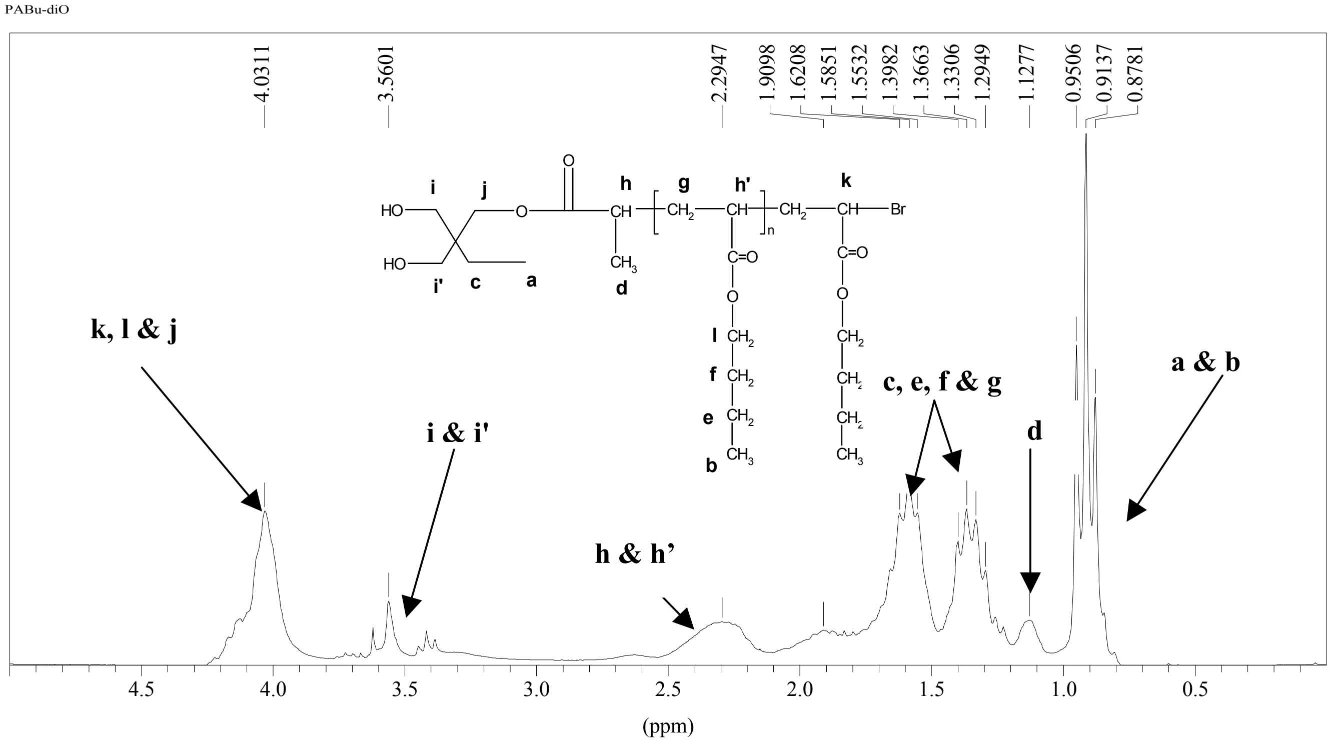
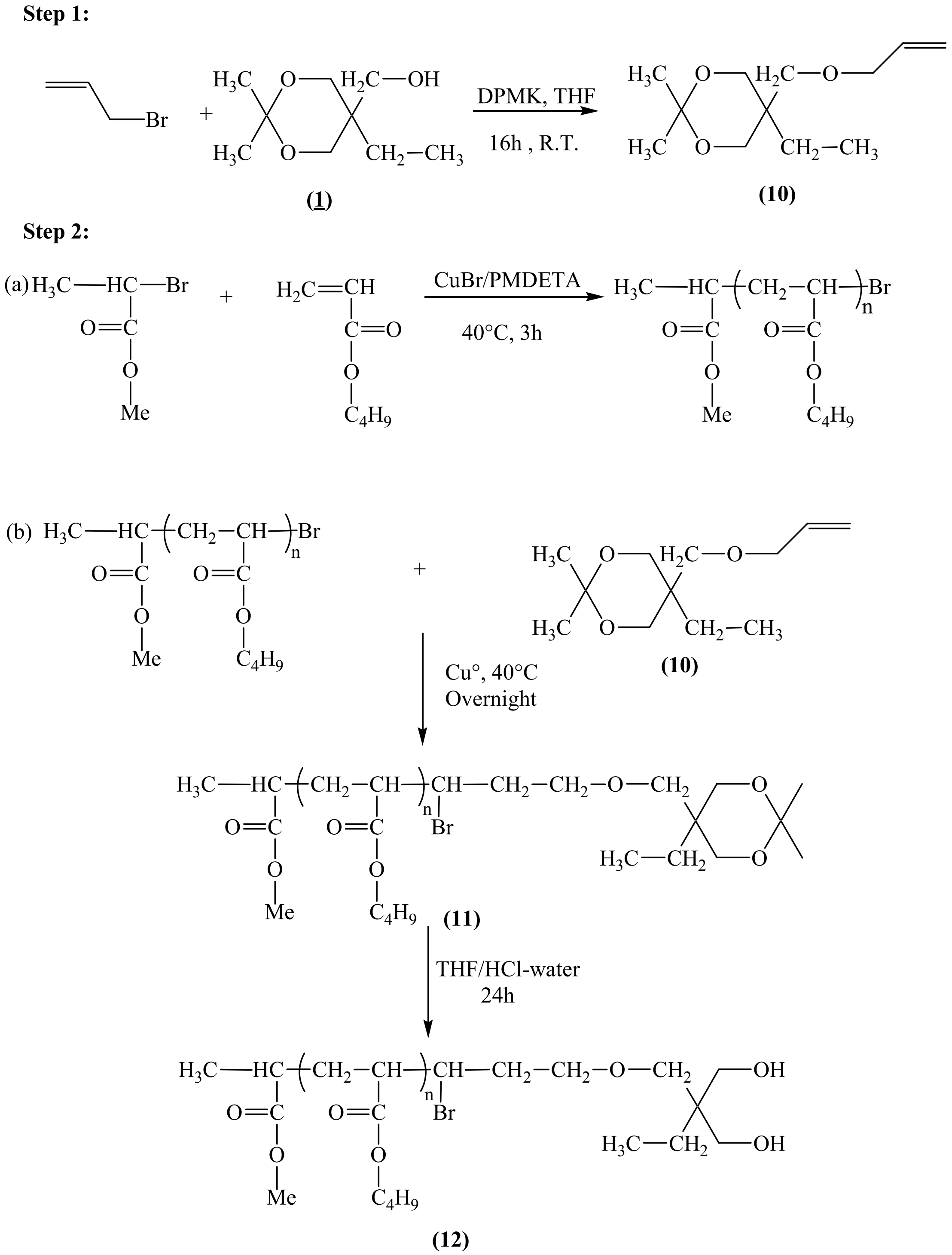


Figure 4-1 : ^{1}H NMR spectrum of P*n*BuA(OH)$_2$ macromonomer (**9**) obtained via initiation ($\overline{M_n}\approx1000$g/mole)

2.2.2. Via chain end-functionalization

In order to prepare gemini-type dihydroxy-terminated poly(*n*-butyl acrylate)s in milder conditions, we explored the possibility to end-functionalize the poly(*n*-butyl acrylate) chains with a newly designed functionalizing agent bearing two protected hydroxyl groups. Actually, for this procedure, we took advantage of the data obtained from the synthesis of monohydroxy-terminated poly(*n*-butyl acrylate)s. Therefore, instead of using the allyl alcohol as a chain-end functionalizing agent, we prepared, in a first step, a functional molecule (**10**) bearing both a vinylic unsaturation and an acetal ring (see Scheme 4- 3).



Scheme 4-3 : Synthesis of gemini-type P*n*BuA$(OH)_2$ macromonomers via chain-end functionalization

Starting from molecule (**1**), the substitution of the alcoholic proton by an allyl group was achieved in the presence of diphenyl methyl potassium (DPMK) as strong base and by using a small excess (1.5 eq.) of allyl bromide as the alkylating agent. Pure molecule (**10**) was finally obtained by performing the column chromatography of the crude product. It was noticed that (**10**) could be separated from the byproduct (*i.e.* diphenyl methane) after a two-stage chromatography. The removal of diphenyl methane was achieved after an important elution with hexane, and a subsequent elution with dichloromethane gives pure (**10**). The overall yield of (**10**) from (**1**) was found around 40 %. This rather low value could be explained by the procedure itself. Indeed, the reaction yield could be increased by controlling the amount of DPMK used for the oxanion formation from the molecule (**1**). The structure of (**10**) has been confirmed by NMR (see Figure 4-2).

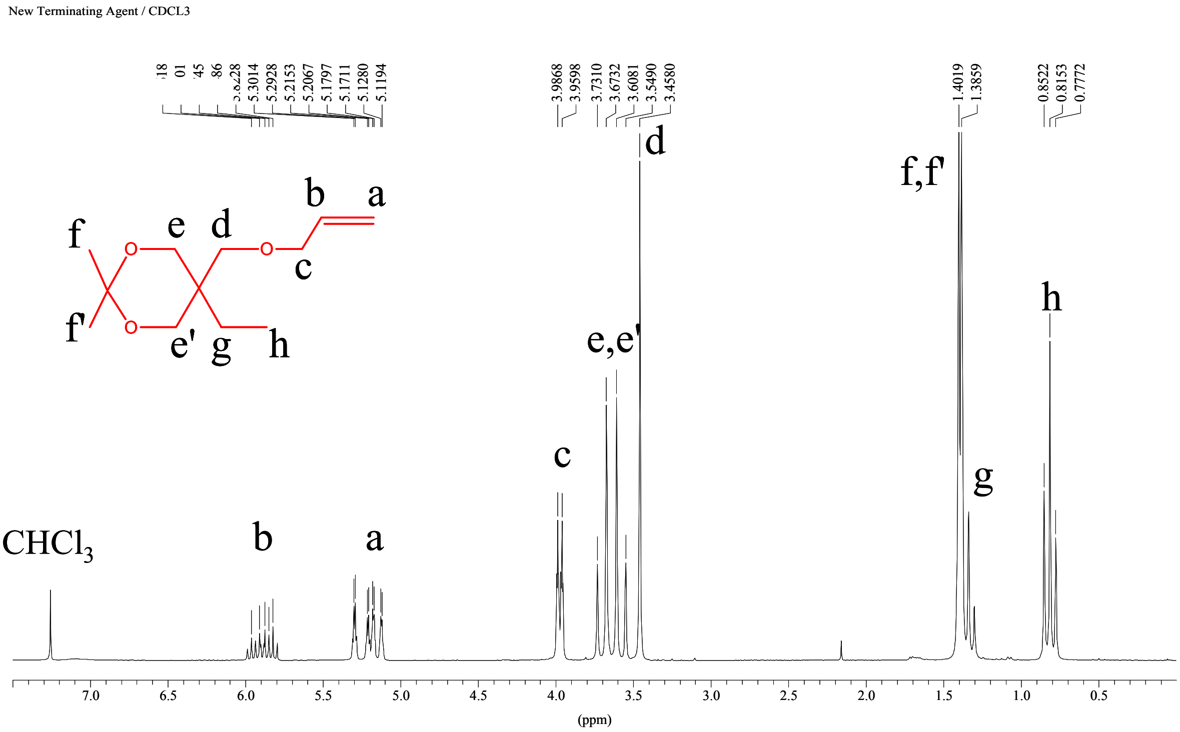


Figure 4-2 : ^{1}H NMR spectrum of a novel functionalizing agent: 5-ethyl 5-(methoxy allyl ether) methyl-2,2'-dimethyl-1,3-dioxane (**10**)

Figure 4-2 exhibits the presence of characteristic signals at $\delta \approx 5.2$ ppm and $\delta \approx 5.8$ ppm due to the resonance of allylic protons (CH_2 and CH from CH_2=CH– respectively).

This novel molecule (**10**) was therefore added at high conversion of *n*-butyl acrylate polymerization. A complete and efficient chain-end functionalization by (**10**) was obtained in a few hours at 40°C. The preparation of the dihydroxy-terminated poly(*n*-butyl acrylate) was finally achieved by cleavage of the acetal ring under strong acidic conditions. This gemini-type P*n*BuA$(OH)_2$ macromonomer (**12**) was characterized by ^{1}H NMR spectroscopy and SEC (see Table 4-2, samples S8 to S10). As expected, the molar mass of the poly(*n*-butyl acrylate)s as well as their functionality are in agreement with the theoretical ones. In addition, the SEC traces of the final product exhibit narrow molar mass distributions. It must be mentioned that similar results could be obtained when performing the cleavage of the acetal ring prior to the chain-end functionalization process.

2.3. Preparation of polyurethane (PUR) particles by step-growth polymerization in dispersed medium

2.3.1. Use of P*n*BuA(OH) as a reactive steric stabilizer

The experimental procedure was similar to the one described in the previous chapters.[11,12] Indeed, the step-growth polymerization between tolylene-2,4-diisocyanate (TDI) and ethylene glycol (EG) was performed at 60 °C in cyclohexane in the presence of dibutyl tin dilaurate (DBTDL) as the catalyst. As already described, a pre-reaction between the steric stabilizer (P*n*BuA(OH)) with two equivalents of TDI was carried out for 2h to enhance the stabilizer reactivity. EG is then added over a 30 minutes period followed by TDI, which is added drop-wise at regular intervals over a 6h. The effects of the molar mass and the weight concentration of the steric stabilizer onto the PUR particle formation were mainly investigated.

2.3.1.1. Influence of the stabilizer concentration

The influence of PBuA(OH) concentration on the PUR particle formation was studied in cyclohexane at 60 °C. S1 ($\overline{M_n} \approx 6000$ g/mole) was selected for this study and its weight concentration was varied from 2 wt. % to 20 wt. %. Data are gathered in Table 4-3.

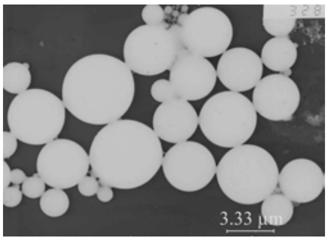
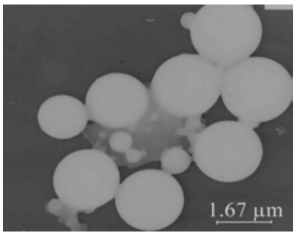
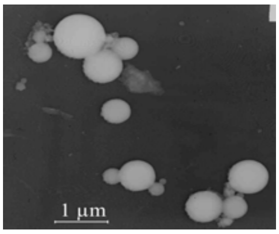
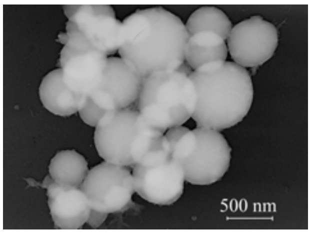
Weight concentration of S1 (wt. %)	TEM micrographs	Average diameter (µm)	Remarks
2 %		3	Multimode (large polydispersity)
5 %		2	Multimode (large polydispersity)
10 %		0.8	Multimode (large polydispersity)
20 %		0.5	Monodisperse

Table 4-3 : Effect of the P*n*BuA(OH) (S1, $\overline{M_n} \approx 6000$ g/mole) weight concentration on the PUR particle formation (TEM analysis)

The results listed in Table 4-3 are in good agreement with the prediction on the particle formation discussed by Barret.[16] The higher the weight concentration of the steric stabilizer, the lower the particle size. Indeed, the TEM micrographs show that the particle size decreases from 3 μm to 500 nm when the stabilizer concentration of hydroxy-terminated poly(n-butyl acrylate) increased from 2 wt.% to 20 wt.%. Although one should mention that though the dispersions showed polydispersity, the PUR particles showed perfect spherical shape. In addition, better control of the PUR particle size distribution could be obtained in the presence of 20 wt.% S1. This observation can be explained by the occurrence of the nucleation at the earlier stage of the polymerization. The higher stabilizer concentration enables high surface coverage of all nuclei formed and prevents growth of the particles by a coalescence effect.

2.3.1.2. Effect of the stabilizer molar mass

We also studied the influence of the P*n*BuA(OH) molar mass on the PUR particle formation (see Table 4-4). Thus, while keeping constant its weight concentration equal to 10 wt.%, the molar mass of P*n*BuA(OH) samples was varied from 6000 g/mole to 15000 g/mole (S1 to S4).

The TEM pictures displayed in Table 4-4 clearly unveil the steric stabilizing efficiency of the polyacrylates. All latexes obtained in these conditions show particle size lower than 1.5 μm. In addition, the longer the steric stabilizer length, the lower the particle size. For instance, PUR particles as small as 500 nm average diameter were obtained in the presence of S4 ($\overline{\mathrm{Mn}} \approx 15000$ g/mole). This phenomenon can be explained if we consider the P*n*BuA(OH) steric stabilizer length. Indeed coagulation of the particles is avoided because the stabilizers surround the particles. The longer the stabilizer, the better the particles surrounding. This interpretation is confirmed by the TEM pictures that clearly show particles with a core-shell structure ; the core and the shell being the PUR and the polyacrylate moieties respectively. Due to the low glass transition temperature of the polyacrylate chains, one was able to observe also that some particles were linked to each others by interpenetration of the polyacrylate shells. Indeed, the DSC analysis of a PUR sample obtained from the system S4 (10%)/TDI/EG/DBTDL in cyclohexane at 60°C showed two glass transition temperatures at – 50°C and 100°C corresponding to the polyacrylate and the polyurethane parts respectively. These features clearly support the formation of *in situ* block copolymers between P*n*BuA(OH) and PUR.

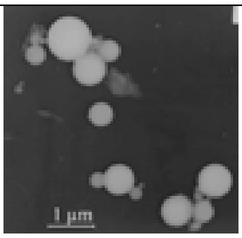
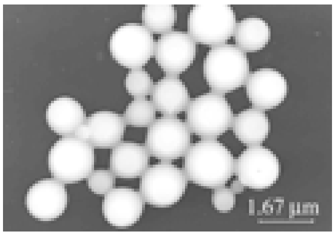
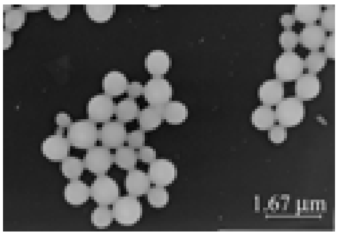
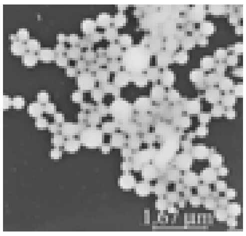
PBuA(OH) 10 wt. %	TEM micrographs	Average diameter (µm)	Remarks
S1 ($\overline{M_n} \approx$ 6000 g/mole)		0.8	Multimode (large polydispersity)
S2 ($\overline{M_n} \approx$ 8600 g/mole)		1.3	Multimode (large polydispersity)
S3 ($\overline{M_n} \approx$ 10000 g/mole)		0.8	Multimode (large polydispersity)
S4 ($\overline{M_n} \approx$ 15000 g/mole)		0.5	Monodisperse

Table 4-4 : Effect of the PBuA(OH) (10 wt. %) molar mass on the PUR particle formation

These results and previous studies demonstrate that hydroxyl-terminated homopolymers are efficient in the stabilization process for the preparation of PUR latexes. However, it is obvious that such reactive stabilizers with a valence equal to 1 act as "chain stoppers" during the polyurethane formation. In the following, we decided to explore the role and the influence of ω,ω'-dihydroxy poly(*n*-butyl acrylate) (P*n*BuA(OH)$_2$) macromonomers -with a valence equal to 2- on the PUR particle formation.

2.3.2. Use of P*n*BuA(OH)$_2$ as a stabilizing macromonomer

We first investigated the ability of the two primary alcohol functions to react with isocyanates. Indeed, it is important to recall that the reactivity of PS-(OH)$_2$ towards TDI was found very poor. The latter could not be used as a steric stabilizer for PUR dispersion (see previous chapter).[17] Therefore, the reaction between P*n*BuA(OH)$_2$ (S8, $\overline{Mn} \approx 1200$g/mol) macromonomers and TDI was performed in cyclohexane (in the presence of DBTDL) and at 60°C at the [OH]/[NCO] 1/1 stoichiometry. As shown in Figure 4-3, the molar mass of the resultant polyurethane increases as expected from a polyaddition process. This shows that both hydroxyl functions are reactive towards isocyanate functions and proves the true macromonomer character of P*n*BuA(OH)$_2$.

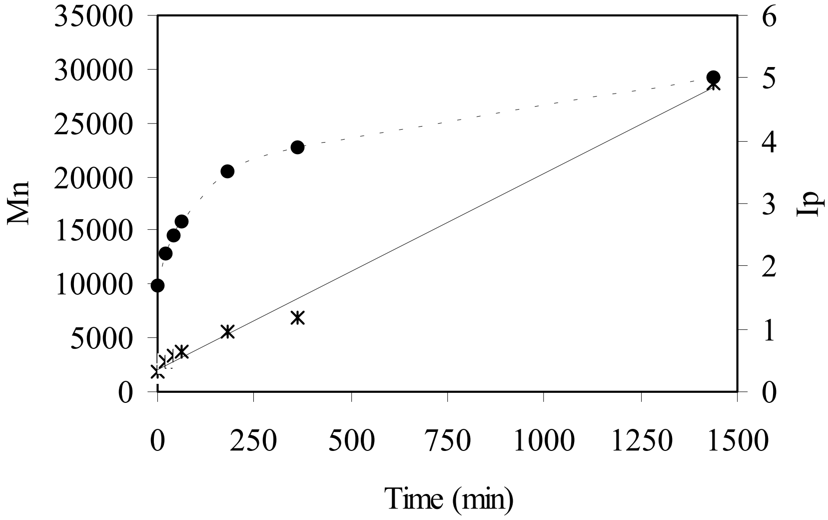


Figure 4-3 : Kinetic study of the polyurethane formation using the system: P*n*BuA(OH)$_2$ (S8)/TDI, in cyclohexane at 60 °C; • = Ip and * = $\overline{Mn}$

OH/NCO ratio is equal to 1/1

Therefore, preparation of PUR particles in dispersed medium in the presence of the well-defined P*n*BuA(OH)$_2$ macromonomers (S8 to S10) was investigated using the procedure previously described. The influence of both the weight concentration and the molar mass of the P*n*BuA(OH)$_2$ macromonomers was investigated.

2.3.2.1. Influence of the stabilizer concentration

The weight concentration of sample S9 ($\overline{M_n}\approx$3100g/mole) was varied from 2 wt.% to 10 wt.% as shown in Table 4-5.

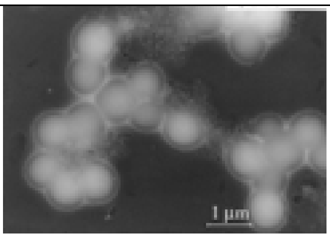
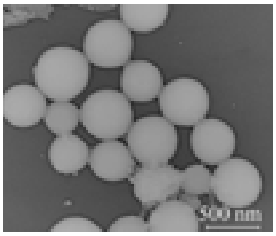
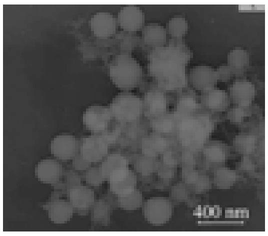
Weight concentration of S9 (wt. %)	TEM micrographs	Average diameter (µm)	Remarks
2 %		1	Low polydispersity
5 %		0.50	Low polydispersity
10 %		0.25	Low polydispersity

Table 4-5 : Effect of the P*n*BuA(OH)$_2$ (S9, $\mathbf{\overline{M_n} \approx 3100}$ g/mole) weight concentration on the PUR particle formation

As shown in Table 4-5, the higher the weight concentration of S9, the lower the particle size. Indeed, the size of the PUR particles decreases from 1 µm to 250 nm when the weight percentage of S9 increases from 2 wt. % to 10 wt. %. This trend was already observed in the case of P*n*BuA(OH) and may be explained by the larger surface coverage of the particles at higher steric stabilizer weight concentration. However, the gemini-type P*n*BuA(OH)$_2$ macromonomer S9 shows a slightly different behavior as compared to monohydroxy-terminated poly(*n*-butyl acrylate) in the sense that quite monodisperse samples were obtained. In addition, the particles formed in the presence of P*n*BuA(OH)$_2$ are much smaller than the ones obtained in the presence of P*n*BuA(OH).

These observations led to the conclusion that the macromonomer is more efficient as a steric stabilizer towards the dispersion process compared to its monofunctional analog.

2.3.2.2. Effect of the stabilizer molar mass

The molar masses of the P*n*BuA(OH)$_2$ were varied from 1200 to 6000 g/mole (samples S8 to S10), keeping constant its weight percentage at 10 wt. % (see Table 4-6).

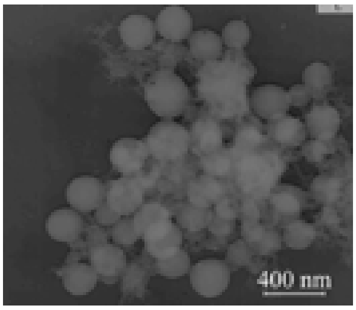
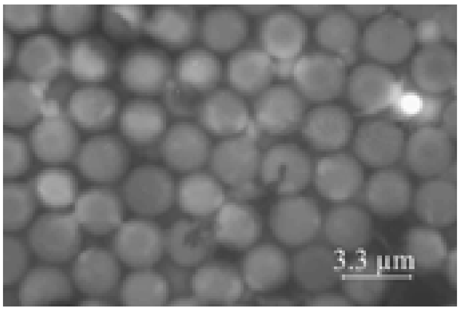
P*n*BuA(OH)$_2$ 10 wt. %	TEM micrographs	Average diameter (μm)	Remarks
S8 ($\overline{M_n} \approx 1200$ g/mole)	-	-	Coagulation
S9 ($\overline{M_n} \approx 3100$ g/mole)		0.25	Low polydispersity
S10 ($\overline{M_n} \approx 6000$ g/mole)		2.3	Monodisperse

Table 4-6 : Effect of the P*n*BuA(OH)$_2$ (10 wt. %) molar mass on the PUR particle formation.

Results gathered in Table 4-6 confirmed the good efficiency of the gemini-type P*n*BuA(OH)$_2$ steric stabilizers. Except for S8 -probably with a too short chain length to stabilize a growing PUR particle- dispersions in the presence of S9 and S10 allowed us to prepare well-defined and monodisperse spherical PUR particles.

Interestingly, PUR particles of average diameter of 2.3 μm obtained with S10 tend to pack under a honey comb structure, which is a characteristic of monodisperse particles.

However, it is difficult to explain the effect of the P*n*BuA(OH)$_2$ molar mass onto the average size of the particles formed.

The higher efficiency of the P*n*BuA(OH)$_2$ macromonomers compared to P*n*BuA(OH) could be explained by a better repartition of the polyacrylate chains at the surface of the PUR particles as expected from the insertion of polyacrylate macromonomers in the polyurethane main chain. Indeed, while the macromonomer S9 (10 wt .%, $\overline{M}_n \approx 3100$g/mole) gave rise to quite monodisperse PUR particles of 250 nm average diameter, the monofunctional analog P*n*BuA(OH) of 3000 g/mole led to coagulation.

2.3.3. PUR particles characterization

The polyurethane particles were characterized with the main objective to prove the participation of the reactive stabilizers (either PnBuA-OH or PnBuA-(OH)$_2$) in the polyaddition reaction and thus to demonstrate that the core and the shell of the particle are covalently linked. To that purpose, ^{1}H and ^{13}C NMR of the PUR samples were carried out in DMSO at 50°C. Before analysis, the samples were washed several times with cyclohexane to eliminate any free stabilizer. The ^{1}H NMR spectrum of PUR sample prepared in the presence of S10 is shown Figure 4.4.

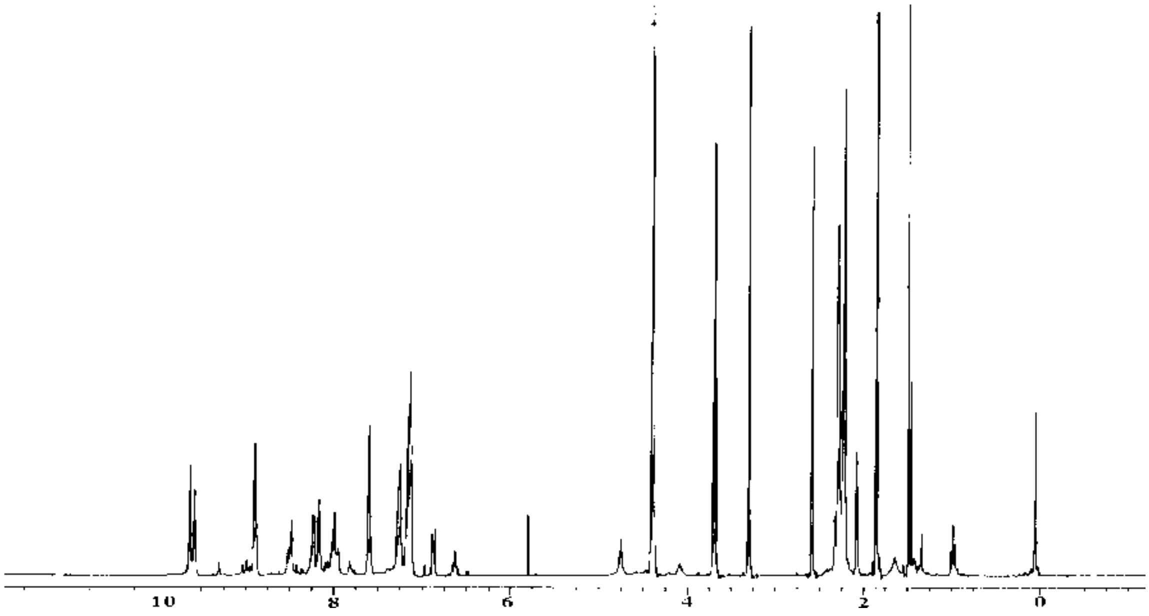


Figure 4-4: ^{1}H NMR spectrum of PUR particles prepared via the system: S10 (10 wt %, $\overline{M}_n \approx 5800$ g/mole)/TDI/EG/DBTDL in cyclohexane at 60°C.

The assignment of signals located at around 7 ppm to the aromatic protons of TDI units and at 8.8-9.7 ppm to the proton of the NH groups as well as at 0.9 ppm to the CH_3 group of the n-butyl acrylate units allowed us to estimate that 10wt% of n-butyl acrylate units were present in agreement with an efficiency of the reaction close to 1.

Surprisingly, the polyurethane samples were found insoluble or slightly soluble in DMF at 80°C and the determination of their molar mass was found quite difficult.

Characterization of the PUR particles with respect to their thermo-mechanical properties, was achieved by DSC and DMA analyses. For instance, the DSC trace of system S4 - (10 %)/TDI/EG/DBTDL - showed two glass transition temperatures at – 50 °C and 100 °C attributed to the polyacrylate and the polyurethane parts respectively. These data also support the core-shell structure of the particle.

2.4. Conclusion

The synthesis of new reactive steric stabilizers based on poly(*n*-butyl acrylate)s using exclusively atom transfer radical polymerization techniques has been described. We designed well-defined mono- and dihydroxy-terminated poly(*n*-butyl acrylate)s (P*n*BuA(OH) and P*n*BuA$(OH)_2$ respectively.

The behavior of P*n*BuA(OH) and P*n*BuA$(OH)_2$ was investigated regarding their steric stabilizing character in the preparation of polyurethane (PUR) particles by polyaddition in dispersed medium. The best results were obtained in the case of gemini-type P*n*BuA$(OH)_2$ which behaves as a true macromonomer or a surfmer. For example, well-defined and monodisperse particles characterized by average diameters of 250 nm to 2.3 μm could be obtained when varying the molar mass of the macromonomer from 3100 g/mole to 6000 g/mole (the weight concentration in macromonomer being equal to 10 wt. %). This peculiar feature encountered with P*n*BuA$(OH)_2$ macromonomer was explained by the formation of graft copolymers. Finally, it was clearly proved that the stabilizers based on polyacrylate reacted with the PUR core giving rise to core-shell type structure.

3 Application of the PUR particles as adhesive materials

3.1. Introduction

One important and far-reaching applications of polymers is their use as adhesives. Adhesive bounding is a method by which materials can be joined together to generate assemblies. Although adhesive applications of polymers seem to be a rather new development of technology, it is interesting to note that polymers coming from the biomass such as clay or bitumen or cellulose or casein derivatives have been used for joining purpose since long before the advent of industrial revolution. Many examples of veneered furniture from Egyptian and Roman times are found in museums. Adhesives are also used for the generation of wooden musical instruments. Since then a vast number of polymeric systems including epoxies, urethanes, acrylates, neoprene and ethylene-vinyl acetate copolymers have been developed to join various materials such as wood, metal and polymers.

It is important to distinguish structural adhesive bounding, used essentially in the aerospace industry and non-structural assemblies, such as pressure-sensitive adhesives (PSA). PSA's exhibit tack properties which result from the association of two opposite behaviors, instantaneous adhesion and cohesion. Instantaneous adhesion of the adhesive film is expected in the sticking step, whereas cohesion gets involved in the release step, when the adhesive film splits off completely (without any stuck mark) from the surface of the substrate. In the sticking step, quite instantaneous wetting of the substrate surface and spreading under weak shearing stress are required from the adhesive film, which implies high flow ability. On the contrary, as the adhesive film dissipates the deformation energy in the release step, viscoelastic properties are involved, implying convenient bulk cohesion. The bulk properties depend on the characteristics of the adhesive material such as glass transition temperature Tg, average molar mass $\overline{M}$, molar mass between entanglements, $\overline{Me}$, molar mass distribution, structure and morphology.[18,19,20,21,22] .Tack is an important property for the manufacture of many rubber goods like belts, tires, etc... Tacky adhesives are used as a coating on various substrates to make pressure sensitive tapes, labels, stickers, etc…

Polyacrylates are inherently known to show good tack properties. They are predominantly copolymers of acrylates and methacrylates which contain a few acrylic acid monomers. Glass transition and elastic modulus of the copolymer is controlled by the type and amount of the comonomers.

Another class of non-crosslinked adhesives called hot-melt is defined as a family of adhesive applied from the melt, gaining strength upon solidification and crystallisation. Polyurethanes composed of flexible (polyester or polyether) segments alternating with rigid frequently crystalline urethane blocks are widely used as hot-melt. They show excellent adhesion to rubber, plastics, metals, wood and leather.[23] These adhesives are generally prepared by a two-step method using a prepolymer. In this case, adhesion properties are governed by the microphase separation and the morphology.

In this study, we prepared polyurethane (PUR) particles with a core-shell structure. Various functionalized homopolymers such as ω-hydroxy polystyrene, ω-hydroxy polybutadiene, and ω-hydroxy poly(butyl acrylate) were used as reactive stabilizers. The latter are covalently bonded to the particles, and form the shell of the particle. It was anticipated that the particles with a poly (butyl acrylate) shell would exhibit some tack properties. Hence, the PUR particles were tested to elucidate the relationship between the structure and the adhesive properties of these PUR particles. Thermodynamic and tack properties were also investigated to evaluate the participation of the soft poly(butylacrylate) shell to adhesion phenomena.

3.2. Structure-property relationship of polyurethane particles

3.2.1. Film formation

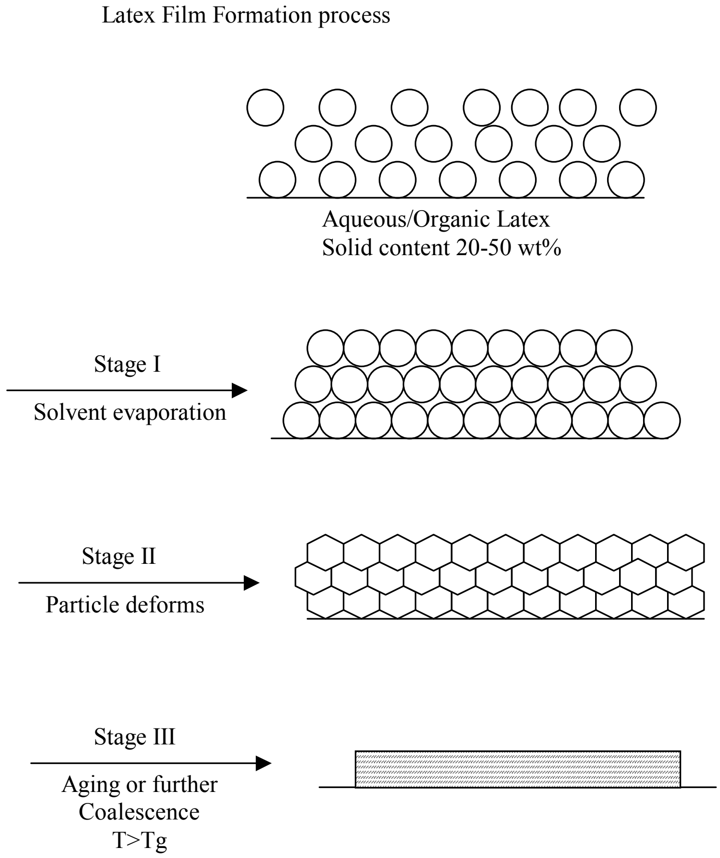
Different theories have been put forward to describe the film formation mechanism. The proposed theories follow the three stages described below.[24] (Scheme 4-4)

a. Stage I : The particles are dispersed in the solvent. The sample is casted on a support and the solvent is evaporated gradually at room temperature. Evaporation of the solvent brings the particles into close contact. At certain distance between particles, Van-der-Waals attractive forces compensate the steric and/or the electrostatic forces which give rise to the flocculation of the particles.

b. Stage II : As more solvent is evaporated, the particles undergo deformation from a void-free structure which is still mechanically weak. During this stage, the spherical particles take the dodecahedral form; it is the combination of different phenomena

- i. dry sintering where the decrease of the interfacial tension between the polymer hair takes place
- ii. wet sintering where the decrease of the interfacial tension between polymer and solvent occurs
- iii. Capillary phenomena

c. Stage III : is referred to as the ageing or maturation of the film. In this stage, coalescence of the particles takes place. The fusion occurs among the adjacent particles to give a mechanically strong film. The key phenomenon is the inter-diffusion between the chains. This inter-diffusion is favored when low molar mass polymers are used or at high temperature above the Tg of the polymer.



Scheme 4-4 : Pictorial view of the formation of a film produced by solvent evaporation from a dispersion of latex particles.

3.2.2. Kinetic of solvent evaporation from the latex

In literature, models for the drying process are based on the measurement of the solvent evaporation rate from the latex dispersion. To that purpose, PUR particles dispersed in cyclohexane were casted over a glass slide and let to dry at room temperature. As shown in Figure 4-5, the loss of solvent weight with time was measured. The initial rate of solvent evaporation is calculated as the initial slope of the curve. It was found that the rate of solvent evaporation depends on the stabilizer used, which formed the outer shell of the polyurethane.

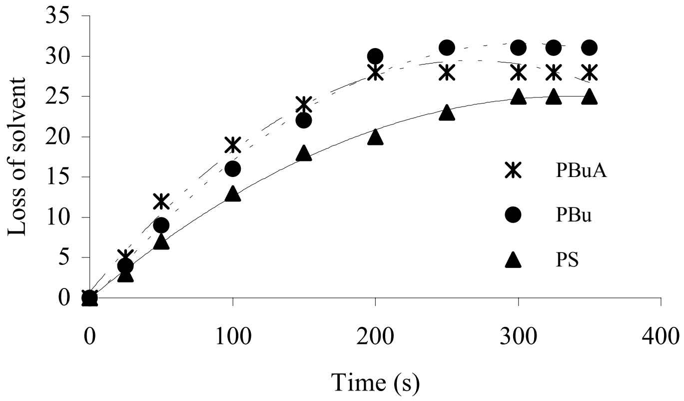


Figure 4-5 : Graphical representation of the solvent loss with time from the latex film using different stabilizers.

This result is in partial agreement with the classical model dealing with the drying process of latex dispersion given by Vander-hoff *et al.*[25]

This trend of solvent evaporation could be explained by the difference in the solubility parameter (Table 4-7) of the stabilizer compared to the one of cyclohexane. Indeed, the closer the polymer solubility parameter value with respect to that of the solvent (PS, PB ; $\Delta\delta \approx 0.4$, 1.8), the better the polymer solubility and the slower the rate of solvent evaporation from the film.

Polymer	δ (MPa$^{1/2}$)	$\Delta\delta$
Polystyrene	18.6	1.8
Polybutadiene	17.2	0.4
Poly(butyl acrylate)	20.4	3.6
Cyclohexane	16.8	

Table 4-7 : Solubility parameters of different polymers and of cyclohexane.

3.2.3. Observation of films by optical microscopy

The film obtained with the particles synthesized using P*n*BuA(OH) ($\overline{M_n}$ = 6000 g.mol^{-1}) as the stabilizer S1 is shown in Figure 4-6.

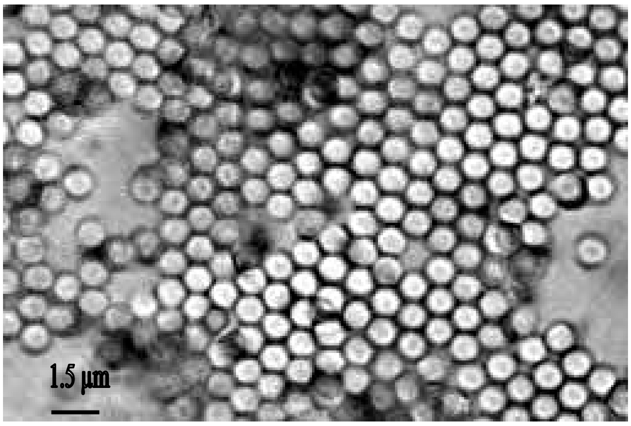


Figure 4-6 : PUR film synthesized using the latex obtained with ω-hydroxyl poly(n-butyl acrylate) (S1, $\overline{M_n}$ = 6000 g.mol^{-1}) as the stabilizer.

After evaporation of the solvent, the particles spontaneously aggregate to form hexagonal structures like a "bee-hive". This phenomenon is due to the difference of rheology between the 'rigid-like' core and 'viscous-like' shell. Many parameters influence the topology of the films such as the nature, the concentration and the molar mass of the stabilizer. After cyclohexane evaporation, no coalescence of the core occurs and the adhesion between each particle, governed by the interpenetration of P*n*BuA hairs, insures the stability of the hexagonal organization.

3.2.4. Thermal properties of the films

All the films were subjected to heating up to 150°C. It was observed that above the Tg (95°C) of the PUR particles, the film showed a tendency to coagulate as shown in Figure 4-7.

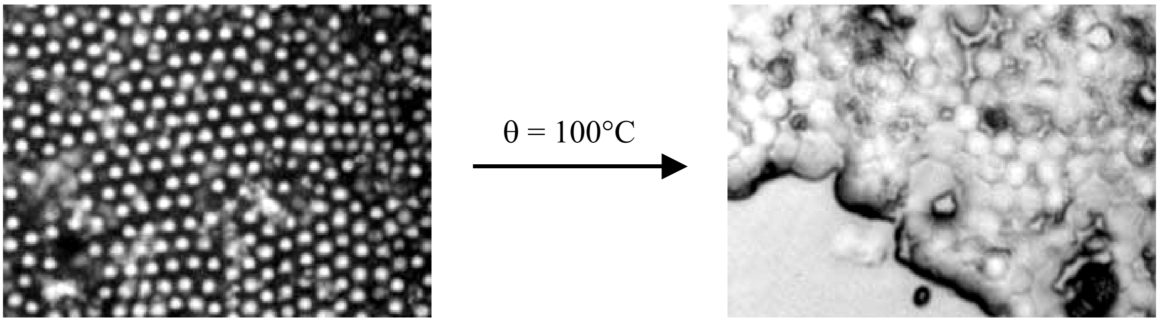


Figure 4-7 : Coalescence of PUR film on heating.

Up to 150°C, the particle coagulation can be explained by the high mobility of PUR chains which control their interpenetration.

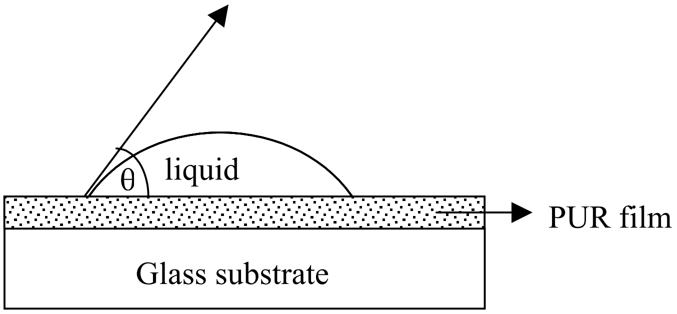
3.3. Adhesive Properties

Films of PUR latexes prepared using poly(*n*-butyl acrylate) as the stabilizer were coated on different substrates (glass, aluminum or PET films) to check their thermo-dynamical surface properties and the tacky behavior.

3.3.1. Wettability

The thermodynamic adhesion is based on information on the wetting of solid surfaces. Thermodynamic work of adhesion is the relevant parameter which allows to qualify a solid polymer surface as polar or non-polar. Contact angles measurements are required to evaluate the wettability ; typically, a contact angle value of water less than 90° means a good spreading of this liquid, in agreement with the establishment of Lifshitz-Van der Waals or donor-acceptor interactions.

The wettability of the films was determined as shown in Scheme 4-5 using a goniometer and measuring the contact angle between the film and the liquid. The liquids used for this purpose include polar solvents like water or ethylene glycol and non-polar solvent like tricresylphosphate.



Scheme 4-5 : Contact angle measurement.

The wetting property for all the polyurethane films coated on glass sheet have been studied. Measurements of the contact angle for the PUR films, at room temperature and at 120°C are shown in Figure 4-8. Data indicate that the contact angles for the non-polar liquid (TCP) are low while they are rather high for polar liquids (water and ethylene glycol). It is worth noting that :

i. the non-polar behavior seems to be rather independent of the chemical structure of the shell, probably due to a global behavior of the surface,

ii. the polar character of the surface is poor whatever the film tested ($\theta_{H_2O} > 120°C$). However the polarity increases (decreasing of θ_{H_2O}) after heating all the PUR films. This may be explained by the loss of particle nature after coalescence. The stabilizer hairs are no more available on the surface of the film which exhibits a "normal" PUR character.

To conclude, the true influence of the chemical nature of the films on wettability requires the development of a systematic approach based on the calculation of a non-polar part of the surface free energy and of the work of adhesion.

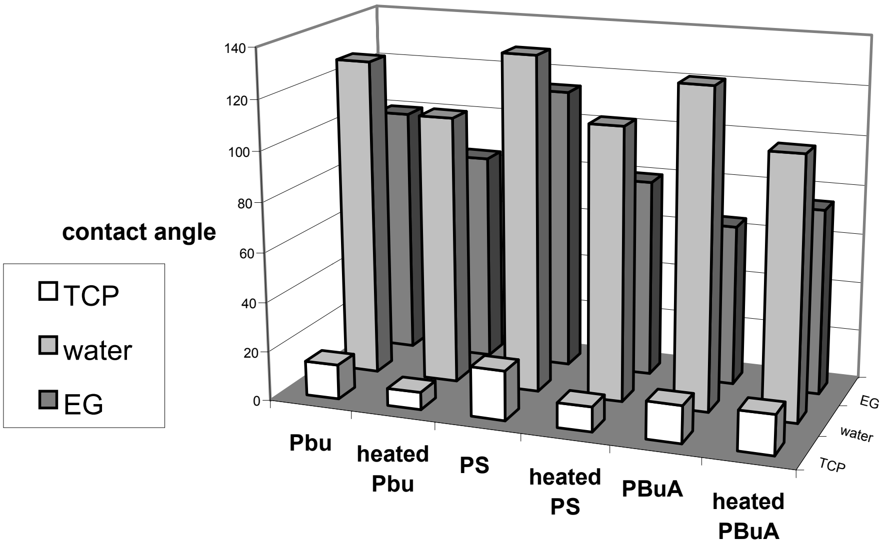


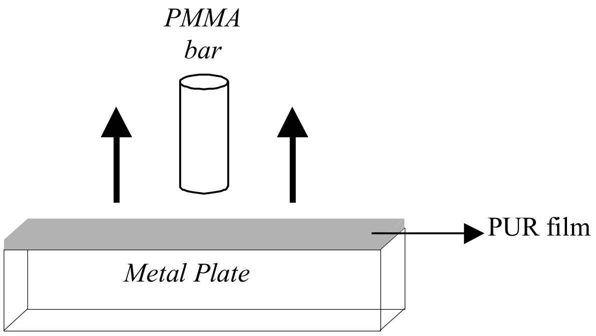
Figure 4-8 : Effect of the stabilizer nature on the contact angle values for a series of PUR films.

3.3.2. Probe tack test

In the domain of adhesives and especially pressure-sensitive adhesives, good adhesion after short times of contact and under low pressure is required. To evaluate tack strength or tack energy, probe tack test (ASTM D2979) is usually carried out (Scheme 4-6). By controlling the contact pressure and the separation rate (instrumented MTS dynamometer), this test simulates the light finger application on a post-it.

The films are obtained by casting the latex over a flat rigid plate of stainless steel. The solvent is evaporated at room temperature in order to coagulate the particles.

Tack test is a good indicator for the adhesive property of a material. The probe is in our case made of PMMA which must be cleaned before the test. The key features of the probe tack device are the controlled rate of approach as well as the rate of detachment. The results are reported as force per area of probe tip at a specific rate of attachment and detachment and at a specific temperature. Since PSA performance is determined by viscoelasticity character, the probe tack parameters must be carefully controlled to obtain meaningful data. To complete probe tack results, cross-analysis by shear test and peel test must be carried out.



Scheme 4-6 : Experimental set-up for the determination of tack.

The probe tack test for the PUR synthesized using P*n*BuA(OH) as the steric stabilizer was then performed. PUR particles synthesized using ω-hydroxy polystyrene and ω-hydroxy polybutadiene as the stabilizer did not show any tack properties.

For P*n*BuA(OH) as a stabilizer, preliminary results on the effect of the stabilizer molar masses on tack properties were deduced.

P*n*BuA(OH) stabilizer (g/mol)	Tack force at room temperature (N)	
	Coalescence at 25°C	Coalescence at 120°C
8600	0,5	0
10000	2,5	0

Table 4-8 : Effect on tack properties of the molar mass of the ω-hydroxy poly(*n*-butyl acrylate) stabilizer.

The results shown in Table 4-8 indicate the presence of weak tack property at room temperature. It may be recalled that this PUR particles have a core-shell structure, the shell comprising of poly(*n*-butyl acrylate) chains which contributes to the tack property. The tack property increases with the increasing molar mass of the poly(*n*-butyl acrylate). This property seems to be related to the ability of P*n*BuA chains with a low Tg to create a high surface contact. However this tack property is lost after heating at 120°C, value above the

Tg of the PUR particles. The heating treatment at 120°C leads to coagulation of the particles and migration of the poly(*n*-butyl acrylate) hairs into the PUR bulk. This leads to a total loss of the tack property at this temperature, in agreement with the rigid viscoelastic behavior of PUR (Tg ≥ 80°C) and the disappearance of P*n*BuA moiety from the surface.

These preliminary results are the advent for a new research onto the relation between tack properties and structured films based on original core-shell particles.

4 Conclusion and perspectives

PUR particles synthesized using ω-hydroxy polystyrene and ω-hydroxy polybutadiene as the stabilizer did not show any tack properties. However when ω-hydroxy poly(*n*-butyl acrylate) is used as reactive stabilizer, the resulting PUR films show some adhesive properties due to the ability of the low Tg P*n*BuA chains to create a high contact surface. The tack properties disappeared after heating which is a proof of the P*n*BuA hair participation on the surface behavior. Further investigations have to be performed on a more homogeneous and thicker films. More emphasis should be laid on tack properties at a nanometric scale using atomic force microscopy. The AFM tip can be used to indent and excite mechanically one single latex particle and provide an adhesion test which resembles macroscopic probe tack test, but at nanometric scale. Such a study is currently under investigation.

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CHAPTER 5:

EXPERIMENTAL

GLOSSARY

1 Materials

1.1. Solvents

Cyclohexane (J. T. Baker, 99%), for anionic polymerization was first distilled over CaH_2 and then cryo-distilled over polystryl lithium and cyclohexane (J. T. Baker, 99%) for dispersion polymerization was used as received. Tetrahydrofuran, THF (J. T. Baker, 99%) was first distilled over CaH_2 and then distilled over sodium-benzophenone. Acetone was cryo-distilled over magnesium sulphate. Dry dichloromethane was obtained by cryo-distillation over calcium hydride.

1.2. Monomers

Styrene (Aldrich, 99%) was distilled over CaH_2 and stored over dibutyl magnesium. It was then cryo-distilled just before polymerization. Ethylene Oxide (Fluka, Purity 99.8%) was transferred from its steel tank into a three-neck flask in which it was stirred over sodium at –30°C for 3h and then cryo-distilled. n-Butyl acrylate (Aldrich, 99%) was distilled over CaH_2 Ethylene glycol (EG) (Aldrich), tolylene-2,4-diisocyanate (TDI) (Aldrich, 98%), were used as received.

1.3. Catalysts and initiators

1,1-diphenyl ethylene (Aldrich, 97%) was stored over CaH_2 and cryo-distilled. A THF solution of the deprotonating agent, diphenylmethyl potassium (Ph_2CHK or DPMK) was prepared according to a reported procedure.[1] Trimethylol propane (TMP), (Aldrich, 99%), bis–(hydroxymethyl) propionic acid (Aldrich, 99%), 2-bromo propionyl bromide (Aldrich, 99%), Bipyridine (Aldrich, 99%), N,N,N',N',N''-Pentamethyl diethylene triamine (PMDETA) (Aldrich, 99%), copper bromide (Aldrich, 99%), 1,3-dicyclohexylcarbodiimide (DCC) (Aldrich, 99%), p-toluene sulphonic acid monohydrate (PTSA) (96%, Aldrich), 2,2-dimethoxy propane (Lancaster, 98%), triethylamine (Lancaster, 99%), were all used as received. 4-(Dimethylamino)pyridinium 4-toluenesulfonate (DPTS) was synthesized using reported procedure.[2]

Allyl alcohol were purified by distillation over CaH_2. Cu(I)Br was purified by stirring in acetic acid, washing with methanol and then drying. Cu(0) (Aldrich) was used as received.

Dibutyl tin dilaurate (DBTDL) (Aldrich, 98%), was used as received. A 1% stock solution of it was prepared by dissolving 2.48×10^{-3} mole of DBTDL in 25 g of paraffin.

2 Synthesis of the stabilizers

All anionic polymerizations used for the synthesis of the stabilizers were performed under an inert atmosphere using a reactor equipped with a nitrogen inlet, magnetic stirrer, burettes meant to introduce solvents, monomers etc...

All atom transfer radical polymerizations (ATRP) were performed in a schlenk equipped with a nitrogen inlet.

2.1. Synthesis of PS-b-PEO copolymer

A series of PS-b-PEO block copolymers were synthesized using anionic techniques according to the well-known reported procedure.[3] The molar mass of the PS-block was determined by SEC and that of the second PEO block was determined by ^{1}H NMR. SEC of the block copolymer was then performed to determine the molar mass distribution. The characteristics of the block copolymer are given in Table 2-1.

2.2. Synthesis of ω-hydroxy polystyrene PS(OH)

The end-functionalization of the polystyrenes synthesized by anionic polymerization was performed by end-capping with ethylene oxide followed by terminating with methanol. ω- hydroxy polystyrenes were characterized by SEC and by ^{1}H NMR. The characteristics of the polymer are given in Table 2-4.

2.3. Synthesis of ω, ω'- dihydroxy polystyrene PS(OH)$_2$

(Scheme 3-1)

2.3.1. Synthesis of 5-ethyl 5-hydroxymethyl-2,2-dimethyl- 1, 3-dioxane

Trimethylol propane, (10g, 74.62 mmol), 2, 2-dimethoxy propane (11.64g, 11.1 mmol), and p-toluene sulfonic acid monohydrate 0.71g (37.3 mmol) were dissolved in 50 mL of acetone. The reaction mixture was stirred for 2h at room temperature. The acid catalyst was then neutralized by adding approximately 1mL of NH_3/EtOH (50:50) solution. After evaporation of the solvent at room temperature, the residue was then dissolved in 250 mL of CH_2Cl_2 and washed with two portions of 20 mL water. The organic phase was dried with $MgSO_4$ and evaporated to give (**1**) as a colorless oily liquid, Yield: 12g, (90%). Characterization: ^{1}H NMR ($CDCl_3$): δ in ppm 0.8 (t, 3H, -CH_3) 1.30 (q, 2H, -CH_2), 1.39 (m, 6H, -CH_3), 2.5 (s, 1H, -OH), 3.65 (d, 4H, -CH_2O), 3.7 (s, 2H, -CH_2O).

2.3.2. Synthesis of 5-Ethyl 5-(2-methyl,2-Bromopropionate) methyl-2,2-dimethyl-1,3-dioxane

A 500 mL three-neck round-bottom flask was charged with 20g (1.14 x10^2 mmol) of compound (**1**), 13.9g (1.37 x 10^2 mmol) of triethylamine and 150 mL of THF. The flask was cooled to 0°C in an ice/water bath. The flask was fitted with a pressure equalizing addition funnel and was charged with a solution of 30g (1.37 x 10^2 mmol) of 2-bromopropionyl bromide in 100 mL of THF. The content of the addition funnel was added drop-wise under nitrogen atmosphere. The reaction was stirred overnight, warming to room temperature of its own accord. The salt formed was removed by filtration. The solvent was removed by rotary evaporation. The oily liquid obtained was re-dissolved in 200 mL dichloromethane and extracted twice with 5 wt. % NaOH (aq) solution followed by water. The organic phase was dried over $MgSO_4$ and the solvent removed. The product was further purified by performing column chromatography on an alumina column using petroleum ether as the eluant. Pure product (**2**) was obtained as a yellow oily liquid. Yield: 29g, (82%), Characterization: ^{1}H NMR ($CDCl_3$): δ in ppm 0.8 (t, 3H, -CH_3) 1.30 (q, 2H, -CH_2), 1.39 (m, 6H, -CH_3), 1.8 (d, 3H,-CH_3), 3.65 (s, 4H, -CH_2O), 4.2 (s, 2H, -CH_2OCO), 4.1-4.4 (m, 1H, -CH-Br).

2.3.3. ATRP of Styrene followed by deprotection of the acetal function

All polymerizations were carried out in bulk using either CuBr/Bipyridine or CuBr/ PMDETA system at 100°C / 80°C respectively. In a typical reaction, the initiator (0.09g, 0.3 mmol), CuBr (0.044g, 0.3 mmol) and bipyridine (0.097g, 0.62 mmol) were taken in a schlenk. After three freeze-thaw cycles, styrene (3.23g, 31.05 mmol), was added, and the polymerization was allowed to proceed at 100°C / 80°C for variable reaction time. The

CuBr catalyst was removed from the polymer by re-dissolving the polymer in small amount of CH_2Cl_2 and passing it over a small column of neutral alumina using CH_2Cl_2 as the eluant. The protected polymer (**3**) was then recovered by precipitation in MeOH. The deprotection of the acetal functionalized polystyrene was performed by dissolving the polymer (2g) in 5 mL (50/50, v/v) solution of THF/HCl-water mixture. It was stirred overnight at room temperature. The dihydroxy polymer (**4**) was recovered by precipitation in MeOH. Yield: 1.5g, (82%).

2.4. Synthesis of ω, ω'- dihydroxy polybutadiene PB(OH)$_2$

(Scheme 3-3)

2.4.1. Esterification of Polybutadiene (acetal terminated polybutadiene)

0.12g, (0.73 mmol) of isopropylidene-2, 2-bis(methoxy) propionic acid (**5**) protected using reported procedure,[4] 3g (0.73 mmol) of ω-hydroxy polybutadiene, and 0.025g, (0.087 mmol) of DPTS was mixed with 15 mL of CH_2Cl_2. The reaction flask was flushed with nitrogen and 0.18g (0.87 mmol) of DCC was added. The reaction mixture was stirred at room temperature for 15h under nitrogen atmosphere. Once the reaction was complete, the DCC-urea formed was filtered off in a glass filter and washed with a small volumes of CH_2Cl_2. The solvent was then evaporated at room temperature and the protected polymer (**6**) was precipitated in acetone. The protected polymer (**6**) was characterized by ^{1}H NMR. Yield: 2.5 g (82%). ^{1}H NMR ($CDCl_3$): δ in ppm 1.20 (s, 3H, -CH_3), 1.39 (s, 3H, -CH_3), 1.42 (s, 3H, -CH_3), 2.1 (s, 3H, -CH_2, -CH-CH=CH_2), 3.65 (d, 2H, -CH_2O), 4.18 (d, 2H, -CH_2O), 5.0 (m, 2H, CH_2=C), 5.5 (m, 3H, -CH=CH-, -CH=CH_2) .

2.4.2. Deprotection of the acetal group of the polybutadiene

2g of the polymer (**6**), was dissolved in 5 mL (50/50, v/v) solution of THF/HCl-water mixture. It was stirred overnight at room temperature. The dihydroxy polymer (**7**) was recovered by precipitation in acetone. The polymer was characterized by ^{1}H NMR. ^{1}H NMR ($CDCl_3$): δ in ppm 1.20 (s, 3H, -CH_3), 3.65 (d, 2H, -CH_2O), 4.18 (d, 2H, -CH_2), 5.0 (m, 2H, CH_2=C), 5.5 (m, 3H, -CH=CH-, -CH=CH_2) .

2.5. Synthesis of ω-hydroxy poly(n-butyl acrylate) PnBuA(OH)

For this synthesis, we followed the procedure that has been recently described by Matyjaszewski *et al.*[5] as shown in Scheme 4-1

A dried three-neck round-bottom flask reactor equipped with a stirrer bar was charged under nitrogen with 11.9 mg (0.083 mmole) of Cu(I)Br, 18 µL (0.083 mmole) of *N,N,N',N'',N''*-pentamethyldiethylenetriamine, and 0.09 mL (0.830 mmole) of methyl 2-bromopropionate following the molar ratios $Cu^{I}Br$/PMDETA/Initiator = 0.1/0.1/1. After adding the required amount of n-butyl acrylate, *i.e.* 5.59 mL (39 mmoles) in the case of a targeted molar mass of 6 250 g/mole (S1), the reaction solution was submitted to three freeze-vacuum-thaw cycles to remove evacuated gases. The flask was then placed in an oil bath at 40°C and kept under stirring during 3 hours. Then, the functionalization was carried out by adding 1.693 mL (25 mmoles) of allyl alcohol and 158 mg (2.5 mmoles) of Cu(0) and left under vigorous stirring overnight at 40°C. The flask was cooled down at room temperature, the content was dissolved in chloroform and then passed through a column of neutral alumina to remove copper salts. The final ω-hydroxyl poly(n-butyl acrylate) (PBuA(OH)) was recovered by precipitation in a large volume of hexane, and the polymer was dried in a vacuum oven. All PBuA(OH) were characterized by SEC and by NMR. The characteristics of the polymers are given in Table 4-1.

2.6. Synthesis of ω,ω'-dihydroxy poly (n-butyl acrylate) PnBuA(OH)₂

(Scheme 4-2)

2.6.1. Initiation method

2.6.1.1. Synthesis of 5-ethyl 5-hydroxymethyl-2,2-dimethyl- 1,3-dioxane (1)

Trimethylol propane, (10 g, 74.62 mmol), 2,2'-dimethoxy propane (11.64 g, 11.1 mmol), and p-toluene sulfonic acid monohydrate 0.71 g (37.3 mmol) were dissolved in 50 mL of acetone. The reaction mixture was stirred for 2h at room temperature. The acid catalyst was then neutralized by adding approximately 1 mL of NH_3/EtOH (50:50) solution. After evaporation of the solvent at room temperature, the residue was then dissolved in 250 mL of CH_2Cl_2 and washed with two portions of 20 mL water. The organic phase was dried with $MgSO_4$ and evaporated to give (**1**) as a colorless oily liquid; yield:

12 g (90 %). Characterization: ^{1}H NMR ($CDCl_3$): δ in ppm 0.8 (t, 3H, $-CH_3$) 1.30 (q, 2H, $-CH_2$), 1.39 (m, 6H, $-CH_3$), 2.5 (s, 1H, -OH), 3.65 (d, 4H, $-CH_2O$), 3.7 (s, 2H, $-CH_2O$).

2.6.1.2. Synthesis of 5-Ethyl 5-(2-methyl,2-Bromopropionate) methyl-2,2-dimethyl-1,3-dioxane

A 500 mL three-neck round-bottom flask was charged with 20 g (1.14 x10^2 mmol) of compound (**1**), 13.9 g (1.37 x 10^2 mmol) of triethylamine and 150 mL of THF. The flask was cooled to 0 °C in an ice/water bath. The flask was fitted with a pressure equalizing addition funnel, and was charged with a solution of 30 g (1.37 x 10^2 mmol) of 2-bromopropionyl bromide in 100 mL of THF. The content of the addition funnel was added drop-wise under nitrogen atmosphere. The reaction was stirred overnight, warming to room temperature of its own accord. The salt formed was removed by filtration. The solvent was removed by rotary evaporation. The oily liquid obtained was re-dissolved in 200 mL dichloromethane and extracted twice with 5 wt. % NaOH (aq) solution followed by water. The organic phase was dried over $MgSO_4$ and the solvent removed. The product was further purified by performing column chromatography on an alumina column using petroleum ether as the eluant. Pure product (**2**) was obtained as a yellow oily liquid; yield: 29 g (82 %). Characterization: ^{1}H NMR ($CDCl_3$): δ in ppm 0.8 (t, 3H, $-CH_3$) 1.30 (q, 2H, $-CH_2$), 1.39 (m, 6H, $-CH_3$), 1.8 (d, 3H,$-CH_3$), 3.65 (s, 4H, $-CH_2O$), 4.2 (s, 2H, $-CH_2OCO$), 4.1-4.4 (m, 1H, -CH-Br).

2.6.1.3. ATRP of n butyl acrylate followed by deprotection of the acetal function

All polymerizations were carried out in bulk, using copper (I) bromide (Cu^IBr) as the catalyst and either 2,2'-bipyridine (bpy) or N,N,N',N",N"-pentamethyldiethylene triamine (PMDETA) as the ligand at 100°C and 80°C respectively. In a typical reaction, the initiator (**2**) (0.09 g, 0.3 mmol), Cu^IBr (0.044 g, 0.3 mmol) and 2,2'-bipyridine (0.097 g, 0.62 mmol) were taken in a schlenk. After three freeze-thaw cycles, styrene (3.23 g, 31.05 mmol) was added, and the polymerization was allowed to proceed at 80°C for variable reaction time. The Cu^IBr catalyst was removed from the polymer by re-dissolving the polymer in small amount of CH_2Cl_2 and passing it over a small column of neutral alumina using CH_2Cl_2 as the eluant. The protected polymer (**8**) was then recovered by precipitation in methanol. The cleavage of the acetal functionalized polystyrene was performed by dissolving 2 g of the polymer in 5 mL (50/50, v/v) solution of THF/HCl-water mixture. It was stirred overnight at room temperature. The dihydroxy-terminated poly(n-butyl acrylate) (**9**) was recovered by precipitation in MeOH; yield: 1.5 g (82 %).

2.6.2. Chain end-functionalization method

(Scheme 4-3)

2.6.2.1. Synthesis of 5-ethyl 5-(methyl allyl ether) methyl-2,2-dimethyl-1,3-dioxane (10)

A 250 mL three-neck round bottom flask was charged under nitrogen with 10 g (55.8 mmole) of acetal molecule (**1**) and 100 mL of freshly distilled THF. Then, with the help of a graduated burette, the deprotonating agent DPMK was added drop wise at 25 °C until the mixture turned a persistent dark orange color that is characteristic of the formation of an oxanion. To this mixture was added drop wise 7.5 mL (86.7 mmole) of allyl bromide. The reaction was allowed to stir overnight at room temperature. After filtration of the white powder (KBr salts formed), and removal of the solvent under reduced pressure, the residue was dissolved in 250 mL of dichloromethane and washed several times with water. The organic phase was dried with Na_2SO_4, filtrated over a filter paper, and evaporated at the rotary evaporator to give an oily liquid as a mixture of two products, the targeted one and diphenylmethane. In order to get the pure targeted product (**10**), it was necessary to perform a column chromatography. An important elution with hexane gave only the diphenylmethane, then a subsequent elution with dichloromethane gave the product (**10**) as a colorless oil; yield: 3.82 g (31 %). (**10**) has been characterized by NMR (see Figure 4-3).

2.6.2.2. Synthesis of poly(n-butyl acrylate) and chain extension using the functionalizing agent (10) via ATRP

The incorporation of the molecule (**10**) at the end of the poly(n-butyl acrylate) was performed following the same procedure as described earlier in the case of the addition of allyl alcohol. Indeed, at the end of the polymerization of n-butyl acrylate using the system comprising of methyl 2-bromopropionate/Cu^IBr/PMDETA (following the molar ratio: 1/0.1/0.1) at 40 °C, the molecule (**10**) was added in excess (30 eq. towards the end groups). After passing a solution of polymer (**11**) in THF over a column of neutral alumina, the polymer (**11**) was recovered by precipitation in cold methanol. Then, the cleavage of the acetal end was performed by dissolving 1 g of polymer (**11**) in THF and adding HCl

(36 wt. %) and water following the volume ratio 1/0.1/0.1 (THF/HCl/distilled water). It was stirred vigorously overnight at room temperature. The organic phase was then diluted with dichloromethane and washed several times with water until neutral pH. After drying the organic phase with Na_2SO_4, filtration and evaporation of the solvent under reduced pressure, the dihydroxy-terminated poly(n-butyl acrylate) (**12**) was recovered by precipitation in cold methanol. The viscous polymer is dried in a vacuum oven before further characterization and use.

3 Polyurethane synthesis

Polyurethane synthesis was carried out in a 250 mL jacketed glass reactor as shown in Figure 5-1 fitted with a reflux condenser, a stainless steel half-moon type stirrer, a sampling device and nitrogen inlet tube. Different procedures were followed according to the stabilizer used.

3.1. Typical procedure using the block copolymers as stabilizers

The reactor was charged with the required amount of stabilizer, (0.288g, 10 wt %), DBTDL, (0.1g of 1% solution in paraffin), and half the amount of solvent, (10g), heated at 60°C and stirred at 500 rpm for 1h. Then to it, the monomers EG (0.635g, 0.010 moles), and TDI (2.25g, 0.012 moles), were added with the remaining amount of solvent (10g).

3.2. Typical procedure using functionalized homopolymers or macromonomers as stabilizers

The reactor was charged with the stabilizer (0.288 g, 10 wt% *vs* monomers), 2eq. (x moles) of TDI with respect to the OH functions and all of the solvent (20 g). This was allowed to react in the presence of DBTDL as the catalyst (0.1 g of 1 % solution in paraffin) for 2h at 60°C at a stirring speed of 500 rpm. EG (0.635 g, 0.010 mole) was then added in one lot and let to react for 30 minutes. Then (0.012 – x) mole of TDI was added over a variable time period.

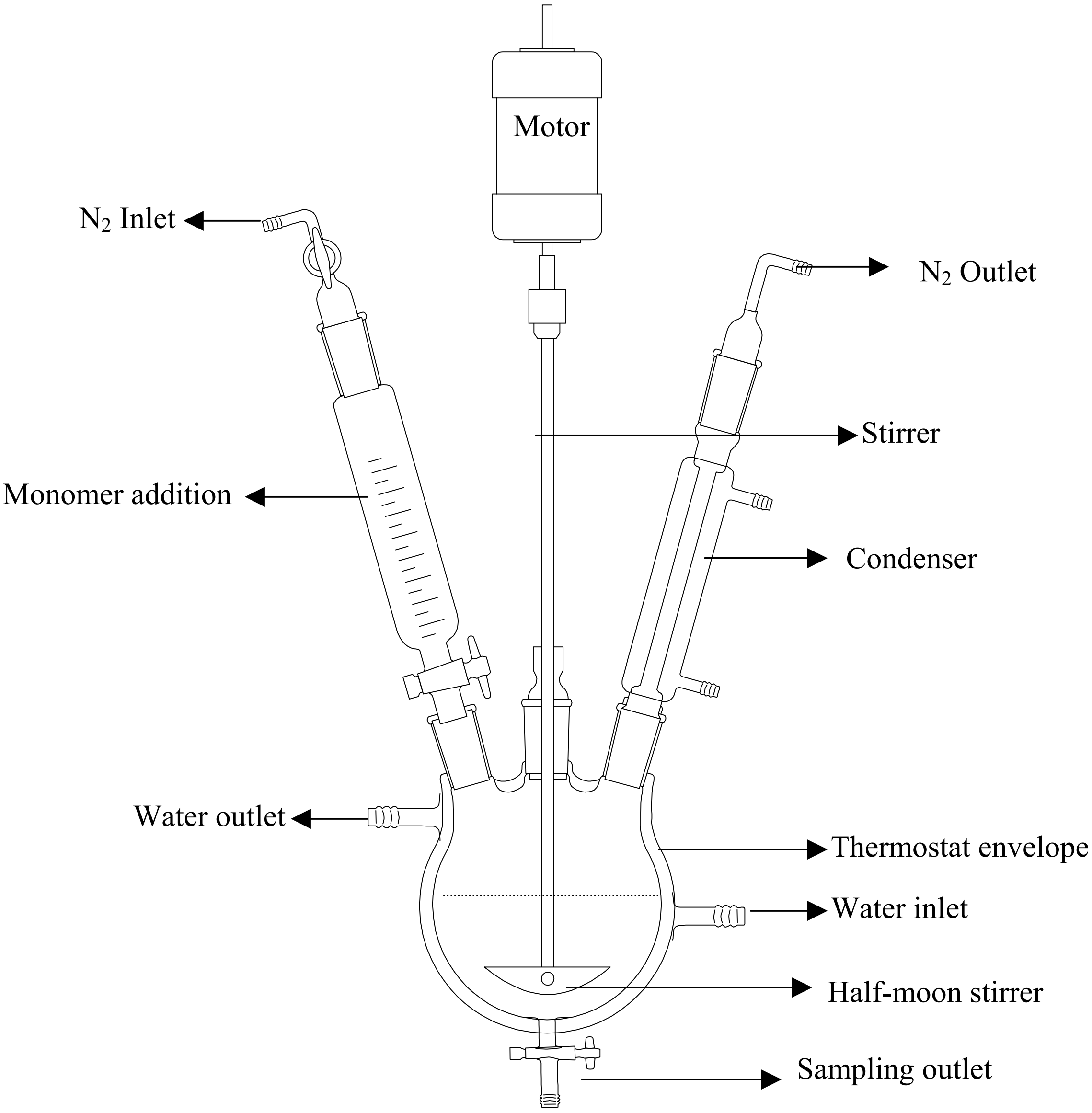

Figure 5-1 : Dispersion polymerization reactor.

4 Characterization

4.1. Polymerization kinetics

Aliquots were taken out at regular intervals to monitor the kinetics of the reaction. The kinetics was followed by solid content measurements to determine the conversion. Conversion for the polymerization reaction was calculated using the following equation:

$$\text{Conversion\%}=\frac{\text{experimentalSC\%}}{\text{theoriticalSC\%}}\times 100$$

where SC% is the solid content.

The theoretical SC% is calculated using the equation:

$$\text{TheoriticalSC\%}=\frac{\text{monomer(g)+stabilizer(g)}}{\text{monomer(g)+stabilizer(g)+solvent(g)}}\times 100$$

The experimental solid content is the mass of solid obtained after evaporation of the solvent and monomers.

Growth of the particles with time was observed by various microscopy techniques.

4.2. Techniques

^{1}H & ^{13}C NMR spectra were recorded using a Brüker AC-200 and 400 MHz NMR spectrometer.

Size exclusion chromatography (SEC) of the stabilizers were performed using a JASCO HPLC pump type 880-PU, TOSOHAAS TSK gel columns, a Varian (series RI-3) refractive index detector and a JASCO 875 UV/vis absorption detector, with THF as the mobile phase. The system was calibrated by means of narrow polystyrene standards. In a same manner, we performed SEC measurements for the PUR samples in dimethylformamide (DMF) as the mobile phase.

IR spectra of the PUR samples were recorded on a Perkin Elmer 16 PC-FT-IR spectrometer.

Dynamic light scattering (DLS) measurements were performed on a Malvern Zetasizer 3000HS$_{A}$ instrument to observe the formation of micelles. The analyses were performed at 25°C in cyclohexane at an angle of 90°.

PUR particle size and particle size distribution or span were measured using a Malvern Master sizer 2000 (Hydro 2000S) fitted with a flow cell that passes the sample/dispersant beam of the optical unit. The solvent used was cyclohexane and the measurements were performed at 25°C at a stirring speed of 2100 rpm.

Optical microscopy data were collected on a Olympus BX 50 microscope equipped with a Sony Power Had camcorder.

Differential scanning calorimetry (DSC) was conducted on powder specimens on a Perkin-Elmer DSC System 7 in flowing nitrogen. Calibration was made with indium (T_m = 156.6 °C and ΔH_m = 28.4 J/g). Glass transition temperatures were recorded at the half height of the corresponding heat capacity jumps. A heating rate of 10 °C/min was used.

Transmission electron microscopy (TEM) was performed on a JOEL, JEM-100S electron microscopy. The sample was placed on a copper grid and was let to dry at room temperature

5 References

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Conclusion

La préparation de matériaux polyuréthane sous la forme de particules sphériques calibrées de taille comprise entre 250 nm et 10 µm était le but principal des études menées dans le cadre de cette thèse. Cet objectif a pu être atteint grâce à l'utilisation de différents agents stabilisants polymères réactifs tels des homopolymères fonctionnels ou des macromonomères, synthétisés à dessein, par les méthodes de polymérisation anionique vivante et radicalaire contrôlée.

Il a ainsi été démontré, pour la première fois, que des polystyrène, polybutadiène et poly(acrylate de *n*-butyle) de dimensions contrôlées, et porteurs d'une fonction hydroxyle en bout de chaîne (position ω) pouvaient être avantageusement employés comme agents stabilisants réactifs pour la préparation, en milieu dispersé organique, de particules polyuréthane. Ces oligomères réactifs prennent part à la réaction d'uréthanisation par leur extrémité hydroxyle conduisant à la formation de copolymères à blocs qui permettent la stabilisation colloïdale du latex. Ainsi, le produit de la réaction est une particule de type "coeur-écorce", constituée d'un cœur polyuréthane et d'une écorce dont la nature chimique varie avec l'agent stabilisant utilisé.

Dans l'objectif de ne pas limiter la masse molaire des polyuréthanes synthétisés et de mieux contrôler la taille et la stabilité des latex préparés, nous avons conçu de nouveaux macromonomères – de structure chimique identique à celle des homopolymères fonctionnels précédents - porteurs de deux fonctions hydroxyle en position géminée. Une étude comparative entre ces deux familles d'agents stabilisants réactifs nous a permis de mettre en évidence que l'utilisation des macromonomères comme agents stabilisants réactifs permettaient de préparer des particules polyuréthanes de taille inférieure à celle obtenue en présence d'agents stabilisants monovalents. Ce phénomène peut s'expliquer par le fait que l'étape de précipitation/nucléation intervient plus tôt au cours du processus lorsque des macromonomères sont employés.

L'ensemble des travaux réalisés a permis de clairement identifier les paramètres à maîtriser pour préparer des latex de polyuréthane. L'ordre et le mode d'addition des réactifs se sont avérés particulièrement déterminants dans le procédé de synthèse. Ainsi, l'agent stabilisant, qu'il soit mono- ou divalent, doit réagir préliminairement avec le monomère di-isocyanate pour faciliter l'étape de nucléation et assurer la formation des particules. Les tendances observées, s'agissant notamment de l'effet de la masse molaire ou de la concentration en agent stabilisant sur la taille des particules formées, sont en accord avec les données existantes de la littérature. Ainsi, la taille des particules décroît lorsque la concentration en agent stabilisant croît ou lorsque la masse molaire de l'agent stabilisant augmente. De façon plus spécifique à ce travail, il a été démontré que les oligomères réactifs dont le paramètre de solubilité était le plus éloigné de celui du solvant de dispersion permettaient la préparation des particules les plus petites.

La structure « cœur-écorce » des particules synthétisées a été bien caractérisée par des techniques thermiques et microscopiques. Le lien chimique entre le cœur et l'écorce est primordial car il assure une stabilité pérenne du latex formé. De tels matériaux possèdent des propriétés originales qui permettent d'envisager leur emploi dans de diverses applications comme par exemple, le renforcement au choc de matrices thermodurcissables (ce thème fait l'objet d'une étude contractuelle qui démarre). Dans le cas particulier des particules constituées d'une couronne poly(acrylate de *n*-butyle), ces matériaux manifestent des propriétés de tack à température ambiante, rendant ces derniers potentiellement attractifs dans le domaine des adhésifs sensibles à la pression, au vu des premiers tests effectués.

Ce travail de thèse est l'amorce de recherches qui devraient se développer davantage au cours des prochaines années. A ce jour, il est envisagé de concevoir la réalisation de particules polymères de nature polyuréthane ou autre (polyester, polyurée, polyépoxyde,…) en dispersion dans l'eau. Un second volet consistera également à fonctionnaliser ces particules afin de leur conférer une réactivité chimique de surface.

Résumé:

Des particules polyuréthane (PUR) de type "cœur-écorce" ont été élaborées par des techniques dispersives en présence d'agents stabilisants polymères réactifs (surfmers). Ces derniers de nature chimique polystyrène, polybutadiène ou poly(acrylate de *n*-butyle) et porteurs d'une ou deux fonctions hydroxyle en bout de chaîne ont été synthétisés par polymérisations anionique "vivante" et radicalaire "contrôlée". L'influence de la masse molaire, de la valence et de la concentration en agent stabilisant, sur la taille moyenne des particules PUR obtenues, a été analysée et discutée. Les particules constituées d'un cœur polyuréthane et d'une écorce poly(acrylate de *n*-butyle) trouvent des applications originales dans le domaine des adhésifs sensibles à la pression (PSA).

Summary:

Monodisperse polyurethane (PUR) particles having core-shell structures have been successfully synthesized using reactive stabilizers. These reactive stabilizers viz ω-$(OH)_x$ (with $x = 1$ or 2) polystyrene, polybutadiene and poly(*n*-butyl acrylate) were synthesized using living anionic and controlled radical methods. The influence of the molar mass, the valence and the concentration of the stabilizers were varied to study the effect on the particle size and the particle size distribution of the resultant polyurethane. The particles having a core of PUR and a shell of poly(*n*-butyl acrylate) showed some adhesive properties.

Mots clés:

Polyurethane, Reactive stabilizers, Core-shell particles, Adhesives