Towards an understanding of steric stabilization when using PEO-PS-PEO triblock copolymer as the stabilizer in the non-aqueous emulsion polymerizaton systems.

TOWARDS AN UNDERSTANDING OF STERIC STABILIZATION WHEN USING PEO-PS-PEO TRIBLOCK COPOLYMER AS THE STABILIZER IN THE NON-AQUEOUS EMULSION POLYMERIZATION SYSTEMS

by

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In memory of my father…

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Table of Contents

List of Tables

List of Figures

Abstract

The unique surface activity of PEO-PS-PEO triblock copolymers makes them useful as stabilizers in the preparation of polymer dispersions, either in aqueous or in non-aqueous media.

Sixteen PEO-PS-PEO triblock copolymers were successfully synthesized *via* an anionic polymerization process. They were characterized by means of GPC, NMR, and intrinsic viscosity methods. From the intrinsic viscosity versus temperature data, a transition temperature at 35°C was observed for all the PEO-PS-PEO triblock copolymers in propylene glycol. The transition temperature was interpreted as a conformational change in the copolymer molecule.

An non-aqueous emulsion copolymerization model system, composed of ethyl methacrylate (EMA), and lauryl methacrylate (LMA) monomers, 2,2'-azobis(isobutyronitrile) (AIBN) as initiator in propylene glycol medium, and the PEO-PS-PEO triblock copolymer, was used for evaluating the polymerization, kinetics and stability performance of well-defined PEO-PS-PEO triblock copolymers. The influences of the sizes of the PEO and the PS blocks were studied. Stable latexes were formed when the molecular weights of the PEO blocks were in the range of 5300-7700, and the PS anchor block molecular weight was between 2000 and 4000.

The adsorption of PEO-PS-PEO triblock copolymer on latex particles was measured. A minimum was observed for the amount of PEO-PS-PEO triblock copolymer that was physically adsorbed on the latex particles for a PS block length of about 30 units. The amount of PEO-PS-PEO which is anchored onto the latex particle

surface increases monotonically with the PS block length by virtue of a greater binding energy for longer PS unit lengths. In addition, the effects of stabilizer concentration as well as monomer concentration on the absorption behavior were investigated. It has been found that both the physically adsorbed and anchored molecules decreased with increasing stabilizer concentration. On the other hand, when the monomer concentration was increased, the physically adsorbed molecules as well as the anchored molecules increased. Furthermore, polynomial equations were derived for calculating the total number of PEO-PS-PEO triblock copolymer chains needed for providing stabilization.

Several kinetic parameters including the rate of polymerization, particle density, and total surface coverage were measured independently. The homogeneous nucleation mechanism was supported by all the data, seeded polymerization, kinetics, and monomer partitioning behavior.

Chapter 1

Introduction

1.1 The Need For Non-Aqueous Emulsion Polymerization System

Heterogeneous polymerization includes emulsion, suspension and dispersion polymerization. An emulsion polymerization contains four basic ingredients: monomer, medium (aqueous or non-aqueous), emulsifier (surfactant, stabilizer, or dispersing agent), and catalyst (initiator). The properties of the latex formed and of the polymer or copolymer are dependent on the constituents. Emulsion polymerization has certain advantages over other industrial methods such as bulk or solution polymerization. These advantages are fast reaction rate, ease of control for each stage of the reaction, better heat transfer characteristics and lower viscosity. Therefore, for the above reasons, emulsion polymerization has become very important industrially.

The development of non-aqueous emulsion polymerization systems was stimulated by the surface coating industry. Early research work was mostly carried out in the industrial laboratories in Europe, North American, and Australia and can be dated back to the 1960's. Theoretical principles of the techniques for dispersion polymerization in organic media were systematically reviewed by Barrett [1].

Non-aqueous emulsion polymerization systems have a number of advantages, despite the fact that these systems are not environmentally friendly in comparison to aqueous systems. The advantages of non-aqueous system are summarized as follows. First, most organic liquids have small latent heats of evaporation, corresponding to a smaller heat input for its evaporation during film formation. Second, since its evaporation

rate under ambient conditions is not affected by factors such as relative humidity, the application properties due to variable evaporation rates are much easier to control. Third, organic liquids have a wide range of boiling points, so the required rate of evaporation may be obtained during and after application of the film by selecting the right solvent. Fourth, since the freezing points of most organic liquids are very low, any problems in the storage and transport of non-aqueous emulsion polymers in cold weather will be reduced. Finally, conventional plasticizing aids, which are used to reduce the glass transition temperature of the polymer during application and assist the process of film formation, can be used without any limitations.

Based on the above reasons, non-aqueous emulsion polymerization systems can be industrially important when the environmental issues can be controlled.

1.2 Steric Stabilization in Non-Aqueous Systems

The terms "stabilizers" and "stabilization" are defined to mean a method for producing polymer dispersions which are stable towards the aggregation process. In order to prevent particle aggregation, a stabilizer has to be used since unprotected particles will agglomerate.

Steric stabilization can be described as follows: when two particles, which are each covered by a layer of adsorbed soluble polymer chains, approach each other to form an overlap of their adsorbed layers, a repulsive force is generated to drive them apart.

To be a candidate for steric stabilization, the polymers must consist of long segments, which are soluble in the continuous phase, interspersed by short segments, usually called "anchors" which are strongly adsorbed at the particle-water interface.

When two sterically stabilized particles with adsorbed polymer layers approach one another closely enough for the adsorbed layers to interact, the soluble segments of the polymer chains may either mix or be compressed as the particles approach each other. Mixing of the polymer chains increases polymer concentration between the particles. However, an osmotically driven inflow of solvent between the particles will drive the particles apart. Chain compression causes a decrease in their configuration entropy, which is resisted by the expansion of the polymer chains. Therefore, the loss of configurational freedom will force the particles apart. This explains how polymer surfactants give steric stabilization to provide colloidal stability.

One of the earliest applications for steric stabilization can be found in the preparation of ink in Ancient Egypt and China around 2500 BC [2, 3], which particles of carbon black was dispersed in a solution of a naturally occurring steric stabilizer that includes casein (from milk), albumin (from egg white) and gum arabic (a flexible polysaccharide obtained from the acacia tree). It has been widely used in a variety of products such as paints, emulsions, detergents, oils, lubricants, etc. The utilization of polymeric surfactants as stabilizers in an organic medium started several decades ago as the need for stabilizing particles in non-aqueous systems arose since surfactants used in aqueous systems, i.e. ionic and non-ionic surface active agents are ineffective in organic medium. For instance, Rehbinder et al [4] was a pioneer who demonstrated the long chain carboxylic acids gave stable dispersions in benzene medium. Verwey and de Boer [5] also proved that oleric acid could be a steric stabilizer for several powders (such as iron) in a non-aqueous dispersion medium.

Several factors play a pivotal role in steric stabilization. They include adsorbed layer thickness, polymer chain configuration, fraction of adsorbed segments, and distribution of segment density (both vertical and parallel to the surface) [6-45].

Steric stabilization can provide several significant advantages over electrostatic stabilization. First, it is relatively insensitive to the existence of electrolytes. Second, it is equally effective despite high or low volume fractions of the dispersed phase. Third, it has reversibility of flocculation by means of adjusting the concentration of non-solvent to the dispersion medium. The above reasons help explain why steric stabilization is usually the most favored method of stabilization in non-aqueous dispersion media. This program focuses on steric stabilization.

1.3 The Reason For Choosing PEO-PS-PEO Triblock Copolymer As Stabilizer

Stability generally requires a good solvent for the stabilizer and a minimum layer thickness to mask the dispersion forces. Adsorbing homopolymers only produce full repulsion interaction potentials for strong adsorption at full coverage, when the slowness of desorption retains the polymer within the gap during interactions between particles. Otherwise, macromolecules squeezed between the surfaces desorb, thereby reducing their free energy and the repulsive potential. Indeed, slow flocculation or aging, occurs in dispersions sufficiently concentrated to maintain the layers in contact. Thus, homopolymers can be satisfactory but are not the optimum stabilizers.

Block copolymers offer a simple and versatile method for steric stabilization of colloidal particles suspended in a solution [46-65]. Block copolymers have gained

considerable attention in the past 30 years. However, the theory of steric stabilization of colloid dispersions is still not understood as well as electrostatic stabilization through the theory proposed by Derjaguin and Landau and Verwey and Overbeek (DLVO theory) [66-69].

The best steric stabilizers are the amphipathic block copolymers. One of the blocks should be insoluble in the dispersion medium whereas the others should be soluble in the dispersion medium. The soluble block chains, "stabilizing moieties", extend into the continuous phase to form a cloud around the particles, which prevents the coagulation of the particles. The insoluble block chains, "anchoring moieties", should chemically attach or physically adsorb to the particle such that the anchoring part will not be desorbed or displaced during particle collisions.

Among the many known block copolymers, poly (ethylene oxide)-polystyrene-poly (ethylene oxide) [PEO-PS-PEO] triblock copolymer has a special place due to the marked difference in the properties and behavior of individual components. While PEO is crystallizable, polar and hydrophilic, PS is glassy, non-polar and hydrophobic. Also, PEO-PS-PEO triblock copolymer is more efficient as a stabilizer than polystyrene-poly (ethylene oxide) [PEO-PS] diblock copolymers with the same composition and molecular weight of each block [70].

Many authors [71-95] have investigated the colloidal behavior of PEO-PS-PEO triblock copolymers in aqueous and non-aqueous media. The characteristics of the PEO-PS-PEO triblock copolymers result from their low critical micelle concentration (CMC), their low diffusion coefficient with respect to classical surfactants, and the stability of their micelles. On the other hand, these polymeric surfactants have the ability to promote the

anchoring of the surfactant on a latex particle surface and provide steric stabilization in both aqueous and non-aqueous media.

Piirma [94] studied five well-defined PS-PEO diblock copolymers for using them as stabilizers in the aqueous emulsion polymerization of styrene. The experimental results indicated that 10 PS units were sufficient for the anchoring block length and the minimum molecular weight of stabilizing PEO block was 3000. Also, it was found that stabilizer effectiveness is highly affected by the ratio of PEO/PS blocks. Among the five PS-PEO diblock copolymers that were examined, the diblock copolymers that had a weight ratio of PEO/PS between 75%-90% were effective stabilizers for styrene emulsion polymerization in water.

Riess et. al [95] investigated PS-PEO diblock and PEO-PS-PEO triblock copoiymers as the stabilizers for the dispersion polymerization of styrene in methanol. The effects of the molecular weight of stabilizer, PS/PEO ratio, and stabilizer concentration on particle diameter and polydispersity were examined. The results showed that large (2 μm) monodisperse polystyrene particles were formed when a low molecular weight stabilizer was used. By using higher molecular weight stabilizers, broad bimodal distribution polystyrene particles were generated.

In addition to this, Riess et al [96] also studied a series of PS-PEO diblock and PEO-PS-PEO triblock copolymers, which were used as stabilizers in the emulsion polymerization of styrene and styrene-butyl acrylate in water. The polymerization kinetics and the stabilizing efficiency of these PS-PEO diblock and PEO-PS-PEO triblock copolymers were investigated. The experimental results demonstrated that the stabilizing capability of these block copolymers (diblock, or triblock) decreased with increasing

molecular weight of the block copolymers and increasing PS content of the block copolymers.

Klein et al [70] found that a stable and small particle size (150 nm) latex at 30% solids content could only be made with PEO-PS-PEO triblock copolymers in a latex system composed of ethyl methacrylate and lauryl methacrylate in propylene glycol medium. It is highly important to note that the diblock copolymer PEO-PS with the same composition can not generate stable latex.

Based on a literature survey, PEO-PS-PEO triblock copolymer was chosen as a stabilizer for this research program. The purpose of this study is to evaluate the stabilizing effectiveness of well-defined PEO-PS-PEO triblock copolymers in a model non-aqueous emulsion system. These block copolymers will be studied in terms of variations in their structure. Both the influence of the molecular weight of the PEO blocks to the PS sequence and the effect of the molecular weight of PS sequence to the PEO block will be studied. The effect of the molecular weight of the anchor block (PS), stabilizing blocks (PEO), and the influence of the hydrophobic/hydrophilic ratio on the stabilizing capability of the block copolymers will also be investigated. The stabilizing efficiency of these triblock copolymers in a non-aqueous emulsion polymerization system will be judged by the following criteria:

(1) Monomer conversion and resulting particle size. The triblock copolymer which results in a faster rate of polymerization and smaller particle size is viewed as an efficient stabilizer.

(2) Amount of coagulum. The triblock copolymer that generates the lesser amount of coagulation is viewed as the better stabilizer.

1.4 Objectives

The objectives of this project are:

1. To evaluate the adsorption and kinetic performance of PEO-PS-PEO triblock copolymers as stabilizers in a model non-aqueous emulsion polymerization system and propose a particle formation mechanism.

2. For this, we will need to synthesize well-defined samples of triblock copolymers of styrene (PS) and ethylene oxide (PEO) of the type PEO-PS-PEO with predetermined size of blocks and narrow molecular weight distributions.

3. To correlate the molecular architecture of PEO-PS-PEO with their performance in emulsion polymerization.

In chapter 2, the preparation and characterization of well-defined PEO-PS-PEO triblock copolymers are described and the temperature dependence of the intrinsic viscosity of the different PEO-PS-PEO triblock copolymers in propylene glycol are presented.

In Chapter 3, non-aqueous emulsion polymerization is studied to evaluate the performance of synthesized PEO-PS-PEO triblock copolymers as a stabilizer. Part of this study includes latex preparation, cleaning, and quantification of the adsorption of PEO-PS-PEO triblock copolymer on latex particles.

In Chapter 4, the kinetics of emulsion polymerization in a non-aqueous medium is described. The effect of stabilizer concentration, initiator concentration, and monomer concentration on kinetic rate and number of particles are described. Also, the effect of PEO-PS-PEO triblock composition is discussed. The kinetic studies included seeded polymerization and monomer partitioning behavior between the polymer and continuous phase. A mechanism based on all experimental data is proposed for particle nucleation as

well as particle growth of emulsion copolymerization of ethyl methacrylate / lauryl methacrylate in a non-aqueous (propylene glycol) model system.

Chapter 5 summarizes the conclusions obtained from the whole study and a brief discussion of some extensions for future work is proposed.

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Chapter 2

Poly(Ethyiene Oxide)-Polystyrene-Poly(Ethylene Oxide) Triblock Copolymers

2.1 Introduction

Block copolymers are a novel class of macromolecules, which have remarkable properties from their homopolymers, or a random copolymer of equivalent composition. Although there is a great deal of information in literature [1-24] describing different syntheses of block copolymers. The syntheses of block copolymers for careful physicochemical studies are prepared almost exclusively *via* anionic polymerization.

Anionic polymerization is the most powerful tool for providing convenient and reliable procedures for the synthesis of well-defined block copolymers with a narrow and controlled molecular weight, as well as a low degree of compositional heterogeneity. The outstanding feature of the anionic polymerization in absence of any impurities is the absence of any chain termination step. This feature offers the possibility for synthesis of true block copolymers by sequential addition of different monomers to the linking polymer chains and by obtaining functional polymers by selective termination with the appropriate reagents.

The mechanism of anionic polymerization is generally accepted as follows: The initiation of the carbon-carbon double bond can be done by three types of initiators: (1) alkali metals, (2) aromatic complexes of alkali metals, and (3) organoalkali compounds, mainly organolithium. The growing chain end has a negative charge that also contains a

metallic cation. The propagation is simply a bimolecular reaction between the growing chain and the monomer. Practically, many anionic polymerizations can be kept termination-free.

Three methods can be used for synthesis of ABA type triblock copolymers utilizing an anionic polymerization pathway. They include (1) a three-stage process using a monofunctional initiator; (2) a two-stage process using a difunctional initiator, and (3) a two-stage process using a monofunctional initiator plus a coupling agent. Each method has their pros and cons. The selection of the method used depends on the chemical structures of both A and B blocks, as well as material availability and the experimental conditions.

For a three-stage process with a monofunctional initiator, the requirement is that both A and B blocks be able to initiate each other. The presence of impurities in the monomers will often lead to formation of homopolymer (A) and diblock copolymer (AB).

In the case of a two-stage process, the difunctional initiator, like sodium naphthalene, is used to form the center block B. Consequently, monomer A is added to grow the two end blocks. B block must be able to initiate A block, but not vice versa. The impurities will lead to homopolymer (B) and diblock copolymer (AB) as byproducts.

The two-stage process with a coupling agent is very similar to the case with a difunctional initiator, except that a monofunctional initiator is used instead of the difunctional initiator. In addition to this, a difunctional-coupling agent is needed to link B blocks with an AB diblock to form an ABA triblock copolymer. The two stage process requires that A has the capability to initiate B block, but not the reverse.

The comparison of the three different ways to prepare the ABA triblock copolymers is illustrated in Table 2.1.

Table 2.1: Comparison of Three Different Methods for the Preparation of ABA Triblock Copolymers

	Three-stage process with a monofunctional initiator	Two-stage process with a difunctional initiator	Two-stage process with a monofunctional initiator plus a coupling agent
Initiator	**Organolithium**	**Sodium naphthalene**	**organolithium**
A block initiate B	**Yes**	**No**	**No**
B block initiate A	**Yes**	**Yes**	**Yes**
Advantages	**No limitation for monomers**	**2 increments**	**2 increments**
Disadvantages	**3 increments**	**Limited type of Monomers can be formed**	**Require high precision in the Stoichiometry of the coupling reaction and its efficiency**
Byproducts	**Homopolymer (A) Diblock (AB)**	**Homopolymer (B) Diblock (AB)**	**Homopolymer (B) Diblock (AB)**

Poly (ethylene oxide)-polystyrene-poly (ethylene oxide) (PEO-PS-PEO) triblock copolymer composes polystyrene (PS) as a center block (B) and poly (ethylene oxide) (PEO) as the side blocks (A). These triblock copolymers which were first synthesized by Richards and Szwarc [1], generated considerable interests due to their unique morphology, rheology, and thermal properties. These polymers are polar media soluble and can impart colloidal stability to a dispersed phase.

PEO-PS-PEO triblock copolymers can be made in such a way that the PS part of the macromolecule has affinity for the dispersed phase, and the PEO part is soluble in the dispersion medium. However, the effect of the relative and absolute size of these blocks on colloidal stability is not known, and the amphipathic nature alone does not guarantee efficiency in stabilization of a colloid.

Klein *et al* [25] found that a PEO-PS-PEO triblock copolymer could stabilize a poly (ethyl methyacrlate-co-lauryl methacrylate) emulsion with a particle size of 150 nm in propylene glycol medium. The PEO-PS-PEO triblock copolymers were research samples obtained from Riess in France and were made *via* the anionic polymerization method. Samples of similar composition were not available commercially. An attempt to use commercially available block copolymers as well as co-polymerizable poly (oxyethylene) chains to substitute for the above PEO-PS-PEO triblock copolymer failed to give a stable latex in propylene glycol for the emulsion copolymerization of ethyl methacrylate and lauryl methylacrylate. The efforts to produce stable latex with PEO-PS-PEO triblock copolymers synthesized by using a coupling agent were also unsuccessful. The synthesis pathway *via* a coupling agent includes (1) preparation of the dihydroxy terminated telechelic polystyrene by using a dihydroxy containing initiator species; (2) reaction of the

polystyrene with diisocyanate to terminate the two polymer ends with isocyanate groups; and (3) reaction of the modified polystyrene chains with hydroxy terminated poly (ethylene oxide), which is commercially available.

None of the above PEO-PS-PEO copolymers produced a stable latex of ethyl methylacrylate and lauryl methylacylate when emulsion polymerized in propylene glycol. This further stressed the importance of a systematic synthesis technique to make the ABA stabilizer with well-defined characteristics to study the stability mechanism of this system.

In the present study, all PEO-PS-PEO triblock copolymer samples were made by anionic polymerization technique in an all glass high vacuum system. Potassium naphthalene was used as the difunctional initiator because it ensures a much higher polymerization rate of ethylene oxide than sodium derivatives. Sixteen PEO-PS-PEO triblock copolymers were prepared and characterized by means of proton NMR, gel permeation chromatography and intrinsic viscosity methods. There were a total of four series, which cover the polystyrene (PS) block length from 15 to 40 units with the poly (ethylene oxide) (PEO) block length in the range of 40-100 units.

The stabilization mechanism is known to depend on the anchoring ability and the solution behavior of the blocks in the ABA copolymer. Many researchers [26-51] have studied the conformation of PEO-PS-PEO triblock copolymers in solution. The variation of intrinsic viscosity as a function of the temperature for PEO-PS-PEO triblock copolymer in benzene was reported [52]. Their results showed that a very sharp transition was observed at 35 °C, which was attributed to a conformation change in the solution.

The relationship of the intrinsic viscosity *vs.* temperature in propylene glycol between 20 and 70 °C were studied for different PEO-PS-PEO triblock copolymers along

with two poly (ethylene oxide) (PEO) homopolymers with different molecular weight, for the sake of understanding the conformation profiles of block copolymers in propylene glycol solvent.

2.2 Experimental

2.2.1 Materials

Potassium (99.5%, in mineral oil, Aldrich Chemical Company, Inc.) and naphthalene (99+%, Scintillation grade, Aldrich Chemical Company, Inc.) were used to prepare the initiator (potassium naphthalene). Anhydrous HPLC tetrahydrofuran (THF) (99.9%, Aldrich Chemical Company, Inc.) was used as a solvent for making the initiator. A volumetric standard 0.1N hydrochloric acid (Aldrich Chemical Company, Inc.) was used as the standard to determine the initiator concentration. Methanol (99.9+%, HPLC grade, Aldrich Chemical Company, Inc.) was used in the titration process. A controlled atmosphere chamber (Atmosbag®, Aldrich Chemical Company, Inc.) was used to handle the above air and moisture-sensitive materials.

Styrene (99%, Aldrich Chemical Company, Inc.) and ethylene oxide (99.5+%, Aldrich Chemical Company, Inc.) were used as monomers to prepare PEO-PS-PEO triblock copolymers. Anhydrous toluene (99.8%, Aldrich Chemical Company, Inc.) was used as a solvent for the anionic polymerization. Calcium hydride (powder, -40 mesh, 90-95%, Aldrich Chemical Company, Inc.) was used as drying agent. Acetic acid (99.8%, Aldrich Chemical Company, Inc.) was used to terminate the polymerization. Cyclohexane (99.9+%, HPLC grade, Aldrich Chemical Company, Inc.) was used to separate the

homopolymer (PS) from the raw material mixture, which contains PS homopolymer and PEO-PS-PEO triblock copolymers.

Chloroform (99.9%, HPLC grade, Aldrich Chemical Company, Inc.) was used as an eluant for the gel permeation measurement. Carbon tetrachloride (99.9+%, HPLC grade, Aldrich Chemical Company, Inc.) was used as the solvent for proton NMR measurements. Tetramethylsilane (99.9+%, NMR grade, Aldrich Chemical Company, Inc.) was used as an internal standard. Polystyrene (molecular weight: 11,000; polydispersity: 1.07; made *via* living polymerization) was purchased from Polymer Laboratories, Inc, and was used as an external standard for molecular weight determination. Toluene (99.8%, HPLC grade, Aldrich Chemical Company, Inc.) was used as a solvent for measuring the sample molecular weight *via* the intrinsic viscosity method.

Propylene glycol (99.5+%, Aldrich Chemical Company, Inc.) was used as a solvent to study the temperature dependence of the intrinsic viscosity for different PEO-PS-PEO triblock copolymers as well as the two PEO homopolymers.

Ultra-high purity nitrogen (99.999+%, MG. Industries) was used to provide an inert environment (air-free and moisture-free) in the process for preparation of initiator (potassium naphthalene) and PEO-PS-PEO triblock copolymers.

2.2.2 Glassware Cleaning

All the glassware which was used for preparation of the initiator and anionic polymerization was cleaned with a solution of Chromerge® (solution of chromium oxide and water (CrO_3 + H_2O), Aldrich Chemical Company, Inc.), concentrated sulfuric acid, and followed by a water rinse. The glassware was then left overnight in a potassium

hydroxide and ethanol solution. After that, the glassware was rinsed thoroughly with water, distilled water, and acetone. All cleaned glassware then was kept in the oven at 120 °C for a minimum of 48 hours.

2.2.3 Purification of Reagents

Since the conditions for anionic polymerization are very rigorous, the monomers (styrene and ethylene oxide) had to be purified for successful living polymerization.

Styrene was kept over a slurry of fine calcium hydride powder while under a nitrogen blanket and then stirred for a period of 48 hours. Styrene was cooled with liquid nitrogen during the stirring process, the flask was degassed *via* flashing to the high vacuum line (10^{-3} mm Hg). Before the distillation, the styrene was freeze-thawed to remove air. The monomer was then vacuumed distilled at 40 °C.

The freshly distilled styrene was transferred directly into another flask, which contained calcium hydride powder with a magnetic stirring bar. Upon finishing the vacuum distillation, the collecting flask was then covered with a glass stopper and kept stirring for 24 hours. The above mentioned degassing and vacuum distillation procedure was repeated.

The newly purified styrene monomer (twice vacuum distilled) was immediately used for anionic polymerization.

Ethylene oxide was released from the gas cylinder and condensed into a flask, which contained a fine powder of calcium cooled by a liquid nitrogen and methanol bath. The liquefied ethylene oxide was kept over a slurry of a fine powder of calcium hydride (cooled by liquid nitrogen and methanol bath) for 16 hours. Then, the flask was warmed

up to room temperature, and the condensed ethylene oxide gas was collected into another flask containing fine powder of calcium hydride cooled by the liquid nitrogen and methanol bath. Again, the liquefied ethylene oxide was kept stirring over calcium hydride for a minimum of 8 hours. Finally, the recondensed ethylene oxide was put into another cleaned and nitrogen purged flask. The above purified ethylene oxide was then used immediately for the anionic polymerization.

Solvents (tetrahydrofuran, toluene, and cyclohexane) were used as received. Acetic acid in toluene (10 wt%) was used for easy handling.

2.2.4 Vacuum Line Design and Operation

In order to meet the air and moisture-free requirements, an all glass high vacuum line was designed for the synthesis PEO-PS-PEO triblock copolymers *via* anionic polymerization. A sketch of this system is shown in Figure 2.1.

The main components of this glass vacuum line include: (1) a vacuum/gas double manifold (Chemglass, Inc.), (2) a Pirani gauge (Chemglass, Inc.), (3) a mechanical vacuum pump (Edwards), (4) a vacuum trap (Chemglass, Inc.), and (5) vacuum connecting adapters (Chemglass, Inc.).

The flow of the ultra-high purity nitrogen into the vacuum line and reaction flask was monitored *via* check-valve bubblers (Chemglass, Inc.). The mechanical vacuum pump (10^{-3} –10^{-4} mm Hg) was protected by a liquid nitrogen cooled glass vacuum trap.

A Pirani transducer (Edwards) serves as an indicator for the vacuum line

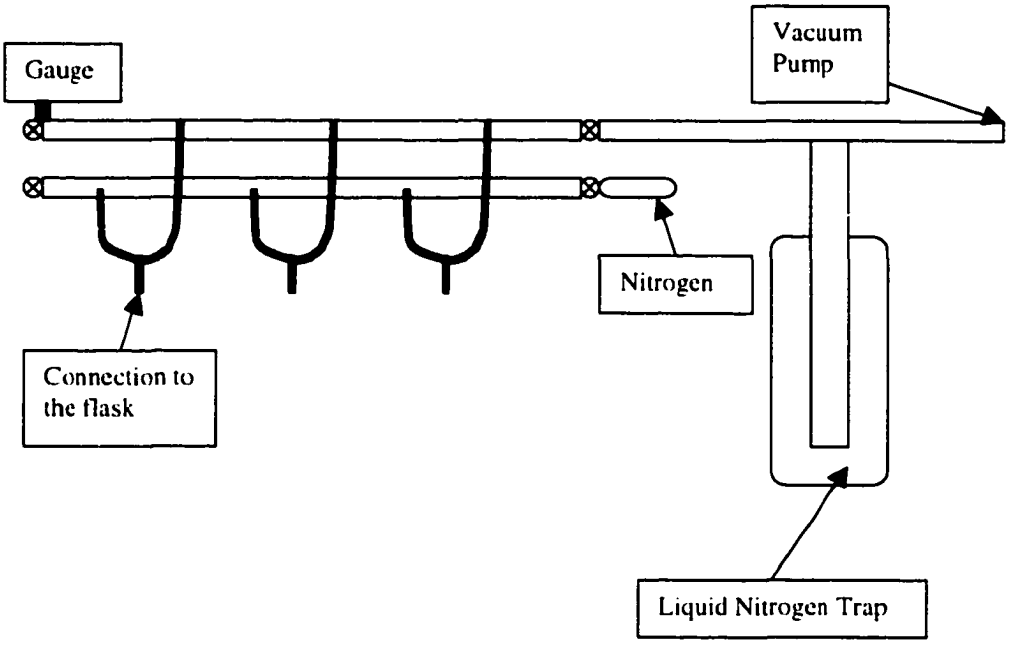


Figure 2.1: Vacuum line for synthesis of PEO-PS-PEO triblock copolymers.

pressure. Any deficiency in the vacuum line was detected occasionally with a Telsa coil (Electro Tech. Product Inc.). The flasks and reactors could be attached to the vacuum line *via* three glass joints.

To ensure that the vacuum line worked properly and efficiently, the mechanical pump oil was changed regularly. The vacuum trap was detached from the vacuum line, cleaned, and dried upon the completion of each reaction, to help prevent the chemical residue from damaging the pump.

When the vacuum line was not in use, vacuum-closing adapters were attached to all three-glass joints to close the vacuum line and help avoid possible outside contamination.

2.2.5 Anionic Polymerization

2.2.5.1 Preparation of Initiator

Load following items into an Atmosbag (Aldrich Chemical Company, Inc.):

(1) One 250 ml Aldrich Schlenk-type round bottom flask with glass stopcock on side arm.

(2) Male joint cap.

(3) 50 ml Hamilton gas tight syringe.

(4) Eight-inch longs needle (18 gauge).

(5) Aldrich techware PP bench tray.

(6) Toploader balance.

(7) Naphthalene container.

(8) Potassium container.

(9) Filter papers.

(10) Weighing dishes.

(11) Utility knife.

(12) Coors mortar.

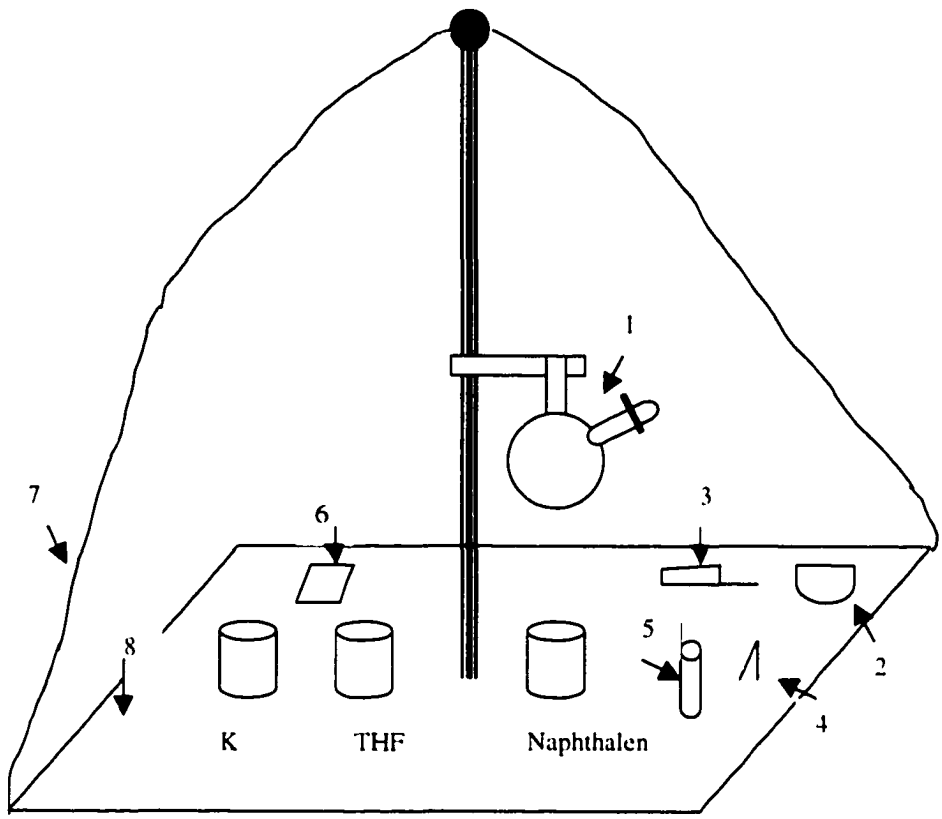
(13) A pair of forceps.

The Atmosbag was attached to the vacuum line via flexible vacuum tubing and kept under vacuum overnight. Then the vacuum line was filled with ultra-high purity nitrogen. Repeat this procedure twice. This operational procedure was used for handling all the air and moisture sensitive chemicals during the course of anionic polymerization. The schematic representation of the above setup is pictured in Figure 2.2.

A small rod of potassium was taken out from the container by forceps and was wrapped thoroughly with filter paper for removing the mineral oil. Soon afterwards, the rod was chopped into small pieces, weighed and charged into the flask. Naphthalene was weighed and transferred into the flask. Tetrahydrofuran was transferred into the flask *via* a Hamilton gas tight syringe. The flask was capped tightly with a male joint cap upon completion of adding reagents (The glass stopcock on side arm was in closed position), and removed from the Atmosbag.

The reaction mixture was stirred for two hours at room temperature. The color of solution appeared dark green. The mixture was then stored in the freezer.

A 2 mL sample of the above green solution was withdrawn from the flask by a Hamilton gastight syringe under nitrogen blanket (transferred in the Atmosbag). Then, it was mixed with 5 mL distilled water and 20 mL of methanol. Standardized



1. Aldrich Schlenk-type flask;
2. Coors mortar;
3. Utility knife;
4. A pair of forceps;
5. 50 ml Hamilton gas tight syringe;
6. Toploader balance;
7. Atmosbag;
8. Aldrich techware PP bench tray.

Figure 2.2: Schematic representation of lab set up for handing the air-free and moisture-free reagents.

hydrochloric acid solution (0.1N) was used to titrate the mixture. This procedure was repeated three times to eliminate the experimental error. Hydrochloric acid solution (0.1N) was used to titrate the mixture. This procedure was repeated three times to eliminate the experimental error.

2.2.5.2 Preparation of PEO-PS-PEO Triblock Copolymers

250 mL Aldrich Schlenk-type reaction flask (with a stopcock on the side arm) was attached to the vacuum line for a minimum of 24 hours before carrying out the polymerization and then filled with ultra pure nitrogen. Freshly distilled styrene and anhydrous toluene were transferred into the flask under a nitrogen blanket (all the operations were performed in the Atmosbag). The flask was capped with a Suba-seal septum and placed in the ice bath with continuous stirring. Two separate Hamilton gas-tight syringes were used to withdraw initiator solution. One syringe was filled with 1mL initiator solution; the other syringe was filled with the desired amount of initiator. First, the syringe containing the 1 mL initiator solution was used. The initiator was added dropwise to the flask until a ruby red color appeared and persisted for 5 minutes. Immediately after this, the desired amount of initiator solution was injected into flask. The mixture was stirred in an ice bath for two hours. The color of the solution was dark red.

Ethylene oxide was recondensed twice over calcium hydride. Then it was diluted with toluene and added to the dark red solution of living polystyrene. The color of the solution changed from dark red to light yellow in a few minutes. This flask was then placed in a sand bath at 60 °C for four days. The color of the resulting mixture was

amber. When the polymerization was nearly complete (after 96 hours), several drops of 10% acetic acid in toluene solution were added to terminate the polymerization. The color of the mixture changed from amber to light yellow.

The solvent was then removed with a Rotavap to dryness, and the product was dried in a vacuum oven overnight at room temperature. The product appeared as white granules. The crude product was dissolved in cyclohexane solvent at the room temperature with stirring for 24 hours. The mixture was vacuum filtered and the filtrate was clear. The white granules that was left on the filter was redissolved into cyclohexane solvent at the room temperature with stirring for 8 hours. Again, the solution was vacuum filtered and the final purified copolymer was a white powder. The yield was 97-99 wt%. The yield of homopolymer polystyrene was 1-3%.

2.2.5.3 Characterization

Gel permeation chromatography (Waters GPC model: 570; Column: 1 × 60cm PLgel 5μ 10^3 Å; Solvent: Chloroform; Flowrate: 1mL/min; Detector: Ultra violet; Injection volume: 20 μL;) was used to determine the number average molecular weight. Chloroform was the eluant solvent. The test sample was dissolved in chloroform (0.05% w/v) and injected into the column. The run time for each sample was 35 minutes. The narrow molecular weight distributions of known molecular weight polystyrene samples were used as the standards for calibration.

Proton NMR spectra were obtained using a 360 MHz Bruker NMR instrument. The samples (20-30mg) were dissolved in carbon tetrachloride using tetramethylsilane (TMS) as the internal standard. In additon, quantitative proton NMR analysis was done to

measure the molecular weight of the samples. Polystyrene (molecular weight 11,000, polydispersity: 1.07) was used as the external standard. First, Proton NMR spectra were obtained for the known amount of polystyrene standard samples in carbon tetrachloride solvent; Second, Proton NMR spectra were obtained with adding known amount of triblock copolymer samples into the same sample NMR test tube, which had a known amount of polystyrene standard samples in carbon tetrachloride solvent; Third, comparisons with integration number for the chemical shift in the region of 6.2-6.8 were made to determine the molecular weight of triblock copolymer samples.

Intrinsic viscosity measurements were used to measure the molecular weights, for comparison to molecular weights that were obtained from the other two methods (GPC, and quantitative proton NMR). Intrinsic viscosity was measured with a conventional Ubbelhode viscometer with the PEO-PS-PEO triblock copolymers dissolved in toluene (99.8% HPLC grade, Aldrich) at constant temperature of 25°C.

2.2.5.4 Temperature Dependence of Intrinsic Viscosity for Different PEO-PS-PEO Triblock Copolymers and Two PEO Homopolymers

The solution properties of the PEO-PS-PEO triblock copolymers were studied in propylene glycol. Intrinsic viscosity [η] at several temperatures (T) in the range of 20 to 70 °C were measured with a conventional Ubbelhode viscometer. The PEO-PS-PEO triblock copolymers and two PEO homopolymers (molecular weight of Mn=5000 and Mn=18500) were dissolved in propylene glycol with the measurement being made at a constant temperature.

2.3 Results And Discussion

2.3.1 Anionic Polymerization

The conditions for anionic polymerization are very rigorous. It is required that all glassware must be oven dried, and all reagents used must be anhydrous. It is essential to use a high vacuum line to ensure the success of the polymerization. Also, ethylene oxide is a gas at room temperature that increases the difficulty of purification and handling. In order to eliminate the moisture from air, all the experiments were carried out under an ultra-pure nitrogen atmosphere. All the reagents were added by means of gas-tight syringes. Styrene and ethylene oxide were purified twice over calcium hydride. The reaction scheme is shown in Figure 2.3.

The initiation of polymerization involves electron transfer to form radical-anions, which have an extra electron in the lowest unoccupied π orbital. The solvent in our case, tetrahydrofuran, assists the transfer of the electron from the potassium to the naphthalene. Complex formation through interorbital exchanges with the electrons available from the oxygen of the ether solvent takes place as shown in Figure 2.3. Therefore, these complexes have entirely different structures from compounds such as naphthylpotassium ($KC_{10}H_7$), where the potassium has actually replaced one of the hydrogen atoms. The stability of these complexes depends on the electron affinity of the hydrocarbons.

The ready dimerization of styrene radical-anion decreases the concentration of this complex species and moves the equilibrium to the right. This ensures the initiation step is completed long before chain growth occurs to any extent. This helps to achieve predictable molecular weights and narrow molecular weight distributions.

The propagation reaction is a two-stage reaction. The first step is a bimolecular reaction between the growing PS $^{\cdot}$ chain and styrene monomers. As the styrene monomer is used up, living polystyrene chain ends are generated. The second step is ring-opening polymerization of ethylene oxide. Since the oxygen is electronegative, the active living PS $^{-}$ chain attacks the carbon atom to grow the polymer chain.

The growing polymer anions live in dynamic equilibrium with ion pair aggregates, contact ion pairs, solvent separated and free ions. This equilibrium can be represented as follows:

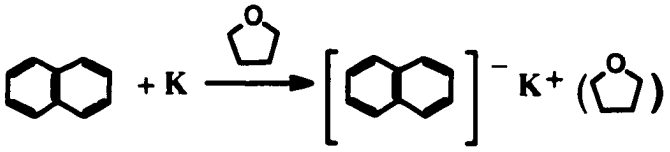
$$(P^{\cdot}, K^{+}) \leftrightarrow (P^{\cdot}, -K^{+}) \leftrightarrow (P^{\cdot}// K^{+}) \leftrightarrow (P^{\cdot}\ K^{+})$$

Ion pair aggregate	Contact ion pair	Solvent separated	Free ion

It was reported [53] that the propagation rate dependence on ethylene oxide *via* naphthalene complex is between one-half and unity. In the case of sodium naphthalene complex, the propagation rate dependence on ethylene oxide is one-half. The difference in their propagation rate dependence is due to the different ion complexes participating in the propagation steps. When potassium naphthalene is used, both the anion and ion pair can participate in the propagation steps. Sodium naphthalene is used, only the free anion can contribute to the polymer chain propagation. This explains why potassium naphthalene has a higher propagation rate dependence on ethylene oxide.

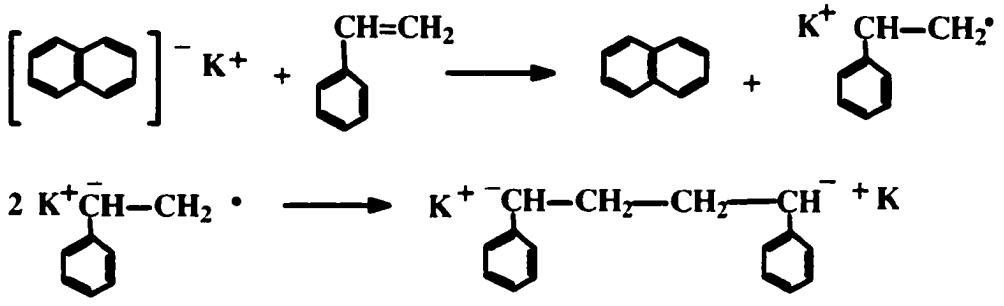
[Reaction Scheme]:

Preparation of initiator (potassium naphthalene):



Complex

Initiation:



Propagation:

Stage 1: form living polystyrene growing chain

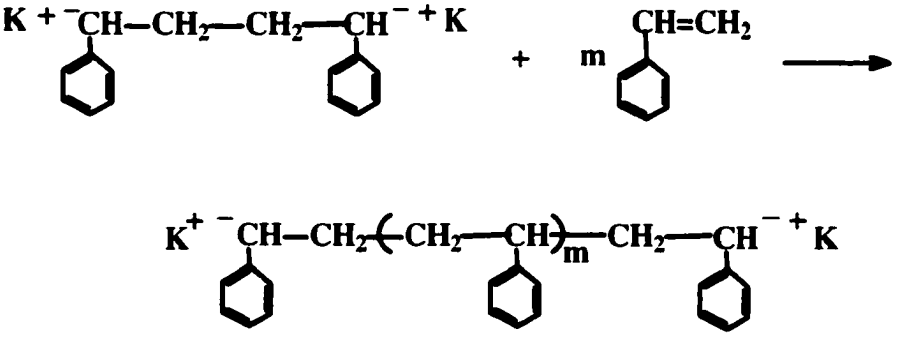
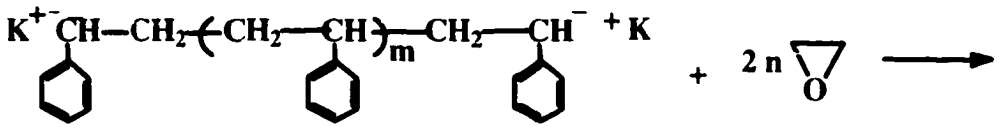
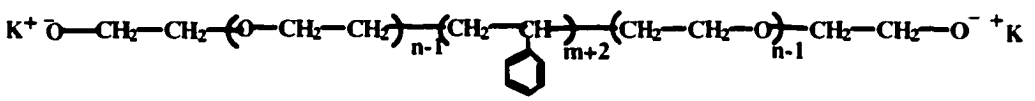


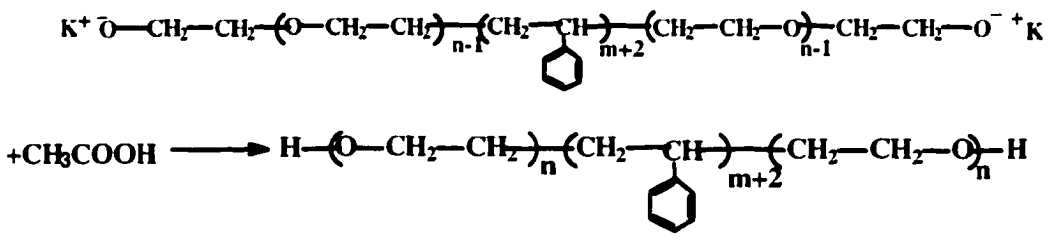
Figure 2.3: Reaction scheme for synthesis of PEO-PS-PEO triblock copolymers.

Stage 2: form PEO-PS-PEO growing chain:





Termination:



PEO-PS-PEO triblock copolymer

Figure 2.3: Reaction scheme for synthesis of PEO-PS-PEO triblock copolymers (continued).

Four series of PEO-PS-PEO triblock copolymers were designed for this research program. They are summarized in Table 2.2. The first series contains four PEO-PS-PEO triblock copolymers. The middle block (PS) is 40 units for all four PEO-PS-PEO triblock copolymers. The PEO block length varies from 40 to 100 at 20 units increment. The second series composes four PEO-PS-PEO triblock copolymers. The PS block length is 30 units for all of them. The PEO block length are 40 units, 60 units, 80 units and 100 units, respectively. The third series has four PEO-PS-PEO triblock copolymers. The PS block length is 20 units for these copolymers. The PEO block length increases from 40 to 100 at 20 unit increments. The fourth series has four PEO-PS-PEO triblock copolymers also. The PS block length is 15 units and the PEO block length changes from 40 to 100 at 20 units apart.

The purpose behind the design of these four series of triblock copolymers was to systematically and fully evaluate the effect of both PS block length and PEO block length on colloidal stability. The influence of the PEO block length can be studied by comparing the data within one series. Similarly, the effect of the PS block length can be investigated by studying the data between different series. These four series PEO-PS-PEO triblock copolymers include PS blocks ranging from 15 to 40 units and PEO block lengths from 40 to100 units.

For a desired PEO-PS-PEO triblock copolymer, the amount of styrene and ethylene oxide can be calculated based on the amount of initiator. The detailed calculation is shown in Appendix I. The actual experimental recipe is shown in Table 2.3.

2.3.2 Characterization

In order to analyze the synthesized samples, gel permeation chromatography was employed to determine the number average molecular weight. Typically, a single peak was observed on the GPC curve, as shown in Figure 2.4.

The proton NMR spectrum was used to verify the block formation. A typical proton NMR spectrum is shown in Figure 2.5. The chemical shift for the protons in the $-CH_2-CH_2-$ group repeat unit is a single peak at 3.2 ppm. The aromatic protons in polystyrene are two peaks at 6.2-6.8 ppm. The peak at 1.1 ppm indicates the non-aromatic protons in the $Ar-CH_2-CH_2-$ group. Also, quantitative data can be obtained by integrating the chemical shifts for the aromatic protons and the protons in the oxyethylene repeat unit. Therefore, the block composition for each block can be calculated according to the molecular weight and ratio of PEO/PS blocks. An example calculation is shown in Appendix II. The measured characteristics of all sixteen PEO-PS-PEO triblock copolymers are listed in Table 2.4.

In order to confirm the measured molecular weight accuracy which were obtained from gel permeation chromatography, two additional methods were used. One was quantitative proton NMR analysis, the other was intrinsic viscosity measurement.

For quantitative proton NMR analysis, a narrow molecular weight distribution and known molecular weight polystyrene sample was used as the external standard to determine the molecular weight of the synthesized samples. For example, 0.0285 g polystyrene (MW=11,000, Polydisperisity=1.07) was dissolved in carbon tetrachloride in the NMR test tube. Then, 0.0357 g sample (xyd34) was added into the same test tube. The ratio of the aromatic protons to the protons in $-CH_2-CH_2-$ repeating units is 1.1011

The aromatic protons that arise from the polystyrene standard

= (0.0285/11000) × 5

The aromatic protons that presented in sample (xyd34)

=(0.0357/MW xyd34) × 5

The non-aromatic protons in the $-CH_2-CH_2-$ repeating units

=(0.0357/MW xyd34) × 4×2

X={[(0.0357/MW xyd34) × 5] + [(0.0285/11000) × 5]}/

[(0.0357/MW xyd34) × 8]=1.1013

Therefore, MW xyd34 =10,500

For the intrinsic viscosity study, since the characteristic constants for the PEO-PS-PEO triblock copolymers as well as for PEO were not available, the constants K (1.7×10^{-4}) and α (0.69) for polystyrene in toluene at 25 °C were used for the molecular weight calculations. The Mark-Houwink relationship[54] ($[\eta] = K \cdot Mv^{\alpha}$) was applied for the calculations.

The comparison of the molecular weight data *via* three different methods is listed in Table 2.5. These data show reasonably good correlation with each other. The polydisperisity of all these PEO-PS-PEO triblock copolymers were between 1.03-1.07 as determined by gel permeation chromatography. The compositions of these PEO-PS-PEO triblock copolymers were within the design range for each block.

Table 2.2: Summary of the Compositions of Four Series of PEO-PS-PEO Triblock Copolymers Designed with Various Ratios of Anchoring to Branch Blocks

Series	Units of S	Mn (PS)	Total Units of EO	Mn (PEO)	Mn (PEO-PS-PEO)	Target Composition (PEO-PS-PEO)
1	**40**	**4166**	**80**	**3524**	**7690**	**40PEO-40PS-40PEO**
1	**40**	**4166**	**120**	**2643**	**9452**	**60PEO-40PS-60PEO**
1	**40**	**4166**	**160**	**7048**	**11214**	**80PEO-40PS-80PEO**
1	**40**	**4166**	**200**	**8810**	**12976**	**100PEO-40PS-100PEO**
2	**30**	**3125**	**80**	**3524**	**4449**	**40PEO-30PS-40PEO**
2	**30**	**3125**	**120**	**2643**	**8411**	**60PEO-30PS-60PEO**
2	**30**	**3125**	**160**	**7048**	**10173**	**80PEO-30PS-80PEO**
2	**30**	**3125**	**200**	**8810**	**11935**	**100PEO-30PS-100PEO**
3	**20**	**2083**	**80**	**3524**	**5607**	**40PEO-20PS-40PEO**
3	**20**	**2083**	**120**	**5286**	**7369**	**60PEO-20PS-60PEO**
3	**20**	**2083**	**160**	**7048**	**9131**	**80PEO-20PS-80PEO**
3	**20**	**2083**	**200**	**8810**	**10893**	**100PEO-20PS-100PEO**
4	**15**	**1562**	**80**	**3524**	**5086**	**40PEO-15PS-40PEO**
4	**15**	**1562**	**120**	**5286**	**6858**	**60PEO-15PS-60PEO**
4	**15**	**1562**	**160**	**7048**	**8610**	**80PEO-15PS-80PEO**
4	**15**	**1562**	**200**	**8810**	**10372**	**100PEO-15PS-100PEO**

Table 2.3: Recipe for Synthesis of PEO-PS-PEO Triblock Copolymers

Ingredient	Amount
toluene	100 mL
potassium naphthalene (0.4738mol/l)	8 mL
styrene	7.90-15.79 g (variable)
ethylene oxide	13.7-33.39 g (variable)
cyclohexane	300 mL
acetic acid (10% toluene solution)	2.28 mL

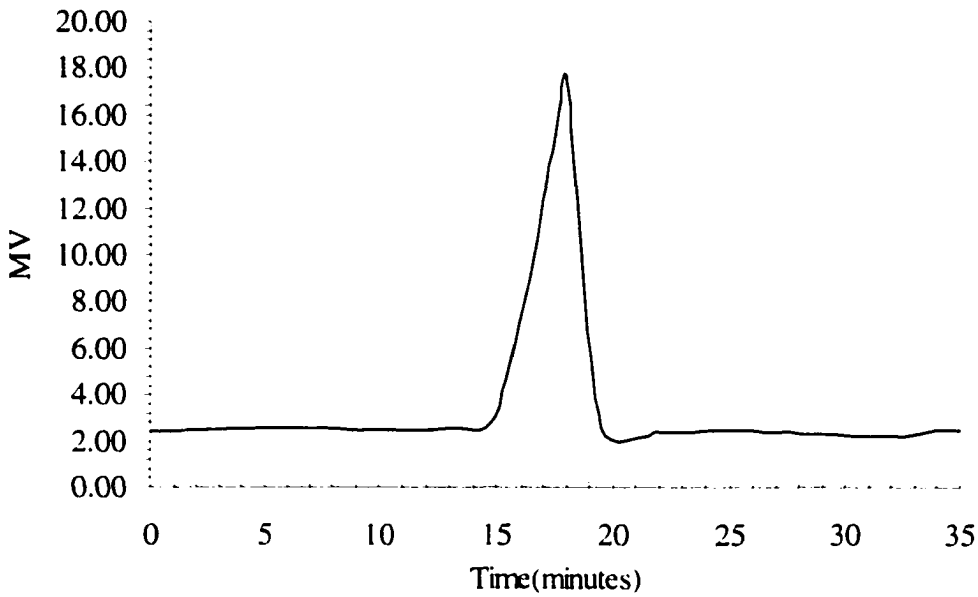


Figure 2.4: A typical GPC curve for a synthesized PEO-PS-PEO triblock copolymer.

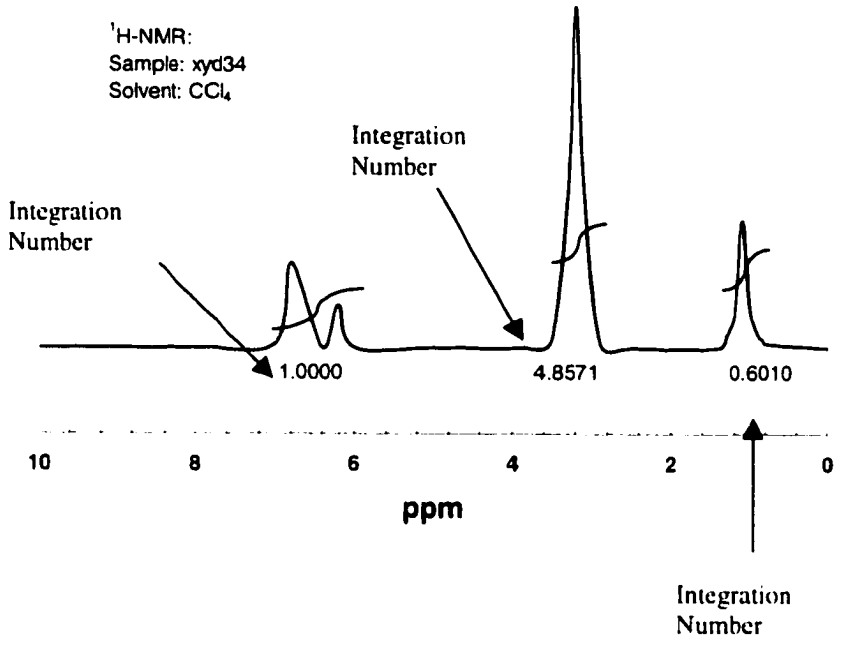


Figure 2.5: A typical proton NMR spectrum for synthesized PEO-PS-PEO tiblock copolymer.

Table 2.4: Characteristics of PEO-PS-PEO Triblock Copolymers

Sample	MW(total) (1)	MW(PS) (2)	PS Block	MW(PEO) (2)	PEO Block	Composition
xyd32	6.7E+03	3.1E+03	30	3.6E+03	82	41-30-41
xyd33	9.1E+03	3.0E+03	29	6.1E+03	138	69-29-69
xyd34	1.04E+04	2.9E+03	28	7.5E+03	170	85-28-85
xyd35	1.21E+04	3.2E+03	31	8.9E+03	202	101-31-101
xyd36	5.5E+03	1.9E+03	18	3.6E+03	82	41-18-41
xyd37	7.4E+03	2.0E+03	19	5.5E+03	124	62-19-62
xyd38	9.7E+03	2.0E+03	19	7.8E+03	176	88-19-88
xyd39	1.14E+04	2.1E+03	20	9.3E+03	212	106-20-106
xyd41	7.9E+03	4.3E+03	41	3.6E+03	82	41-41-41
xyd42	9.5E+03	4.1E+03	39	5.5E+03	124	62-39-62
xyd43	1.14E+04	4.2E+03	40	7.2E+03	164	82-40-82
xyd44	1.33E+04	4.3E+03	41	9.0E+03	204	102-41-102
xyd45	5.1E+03	1.5E+03	14	3.6E+03	82	41-14-41
xyd46	7.0E+03	1.6E+03	15	5.5E+03	124	62-15-62
xyd47	8.6E+03	1.5E+03	14	7.1E+03	162	81-14-81
xyd48	1.03E+04	1.4E+03	13	8.9E+03	202	101-13-101

(1) GPC data; (2) calculated data;

2.3.3 The Relationship of Temperature Versus Intrinsic Viscosity in Propylene Glycol for Different PEO-PS-PEO Triblock Copolymers and Two PEO Homopolymers

The intrinsic viscosity of different PEO-PS-PEO triblock copolymers and two PEO homopolymers were measured between 20-70 °C to study the conformation of PEO-PS-PEO triblock copolymers in propylene glycol. It was found that all these triblock copolymers behave similarly. Transition temperatures appear around 35°C and 50°C as shown in Figure 2.6. Two PEO homopolymers with molecular weights of 5000 and 18500 behaved differently. The intrinsic viscosity was independent of the temperature. These results were consistent with reported data on PEO-PS-PEO triblock copolymers in benzene solvent [52].

The intrinsic viscosity is related to the hydrodynamic volume of the triblock copolymer in the solvent (propylene glycol), which depends on both the conformation and molecular weight of the PEO-PS-PEO triblock.

Two factors can affect the miscibility of the different blocks of the copolymer: temperature and selectivity of the solvent. The second factor strongly influences the conformation of the copolymers.

For a triblock copolymer of PEO-PS-PEO in solution, if one of the blocks of the copolymer occupies a volume in which the other block does not enter, this block copolymer is in a segregated conformation. On the other hand, if the different blocks of the copolymer interpenetrate with each other, this block copolymer is in a nonsegregated conformation.

Since propylene glycol is a polar solvent, it is a good solvent for the PEO block regardless of the temperature range. Below 35°C, the PEO-PS-PEO block copolymer is in a non-segregated conformation. The attractive force between the PEO blocks and propylene glycol molecules overcomes the non-polar character of the PS block.

As the temperature increases, the polymer chain becomes more flexible, (semi-coil to coil), the intrinsic viscosity decreases. However, the non-polar/polar interaction of the PS blocks in the polar solvent increases. Above 35°C, propylene glycol becomes a poor solvent for the PS block, and remains a good solvent for the PEO block. PS block forms a swollen core surrounded by a flexible fringe of the soluble PEO block. Thus, propylene glycol becomes selective for PS block in the triblock copolymer and the block copolymer PEO-PS-PEO is in a segregated conformation. Consequently, the minimum in the plot of intrinsic viscosity vs. temperature is observed due to the transition of the conformation.

As the temperature increases (between 35-50°C), the PS block becomes more swollen. The hydrodynamic volume of the whole polymer chain increases, so the intrinsic viscosity increases. Above 50°C, the core PS block must shrink to explain the decrease in the overall hydrodynamic volume of the polymer. A schematic representation of the above explanation is illustrated in Figure 2.7.

As propylene glycol is a good solvent for PEO blocks, the conformation of two PEO homopolymers (random coil) remains the same during the entire testing temperature range. Therefore, the intrinsic viscosity of these PEO homopolymers is independent of the temperature.

Table 2.5: Comparison of molecular weight data that were obtained *Via* three different methods

Sample	Molecular weight *Via* GPC	Molecular weight *Via* NMR	Molecular weight *Via* Intrinsic viscosity
Xyd33	**9100**	**9300**	**9600**
Xyd34	**10400**	**10500**	**10800**

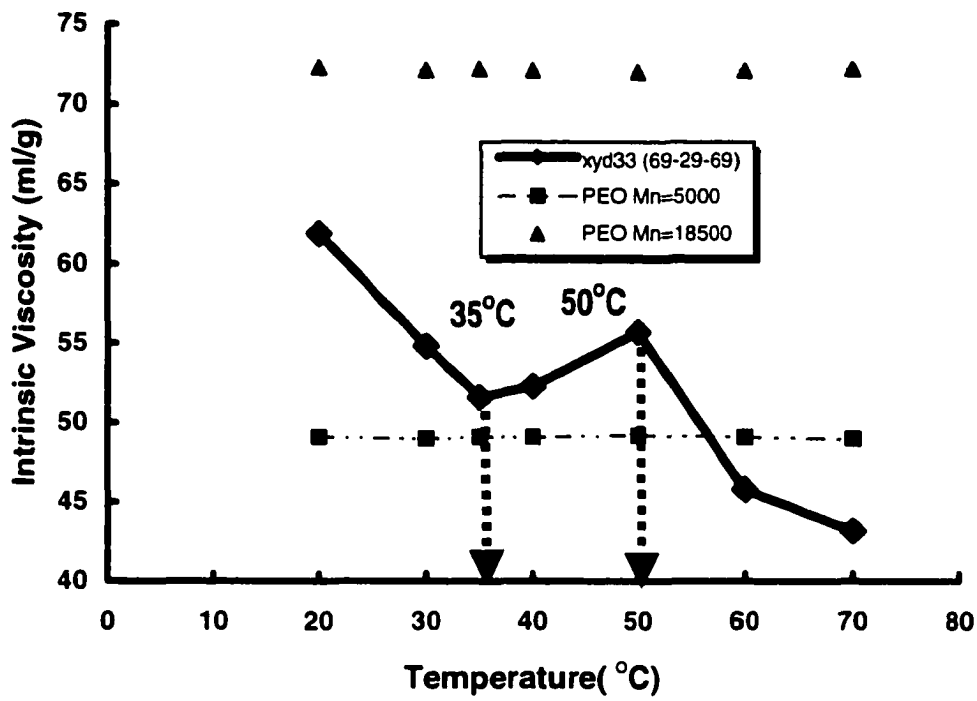


Figure 2.6: Variation in the intrinsic viscosity of PEO-PS-PEO triblock copolymer and PEO homopolymers in propylene glycol.

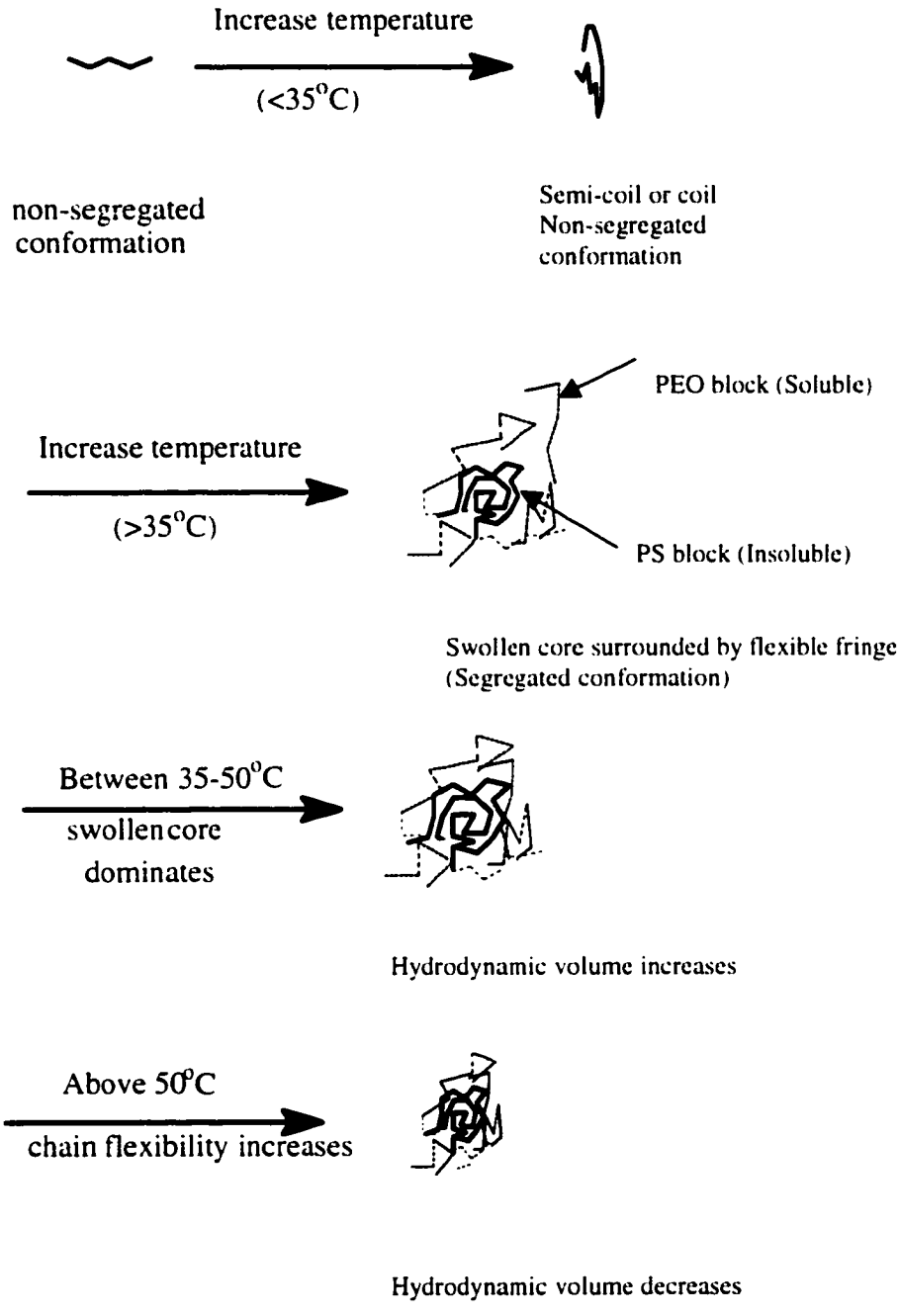


Figure 2.7: Schematic explanation for the conformation change of PEO-PS-PEO triblock copolymers in the propylene glycol within the temperature range of 20 to 70 °C.

2.4 Summary

The anionic polymerization technique was chosen for synthesizing PEO-PS-PEO triblock copolymer stabilizers since it was the most effective way to give predictable molecular weight and narrow molecular distribution of the A-B-A type block copolymers. The conditions of anionic polymerization were very stringent. All the glassware was cleaned thoroughly and oven dried 48 hours. In order to minimize impurities that cause premature termination of the polymerization, the integrity of the all glass high vacuum line was crucial for the success of the polymerization. All reagents were transferred *via* gas tight syringes under a nitrogen blanket.

Sixteen PEO-PS-PEO triblock copolymers were successfully synthesized *via* the anionic polymerization process. They were characterized by means of gel permeation chromatography, proton NMR, and intrinsic viscosity methods. The molecular weight of these sixteen PEO-PS-PEO triblock copolymers ranged from 5100 to 13300. The polystyrene (PS) block length was between 13 and 41. The PEO block length was between 41 and 106. The polydispersities of these PEO-PS-PEO triblock copolymers were 1.03-1.07.

These sixteen PEO-PS-PEO triblock copolymers were divided into four series. Each series contained four PEO-PS-PEO triblock copolymers that have the same polystyrene block length but with varying poly (ethylene oxide) block lengths. Different series have different polystyrene block length. Therefore, these four series of PEO-PS-PEO triblock copolymers were the foundation for the evaluation of the influence of polystyrene block length as well as poly (ethylene oxide) block length on colloidal

stability. All the PEO-PS-PEO triblock copolymers synthesized correlated well with the design or theoretical block length.

An intrinsic viscosity transition temperature at 35°C was observed for all the PEO-PS-PEO triblock copolymers in propylene glycol. A conformational change on the two sides of the transition temperature is hypothesized. The variation of the intrinsic viscosity represents the different conformations of the PEO-PS-PEO triblock copolymer in the solvent (propylene glycol). This information was useful in determining the stabilizing ability of the PEO-PS-PEO triblock copolymers.

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Chapter 3

Non-Aqueous Emulsion Polymerization

3.1 Introduction

Emulsion polymerization has been a very successful industrial process since the 1930's and has many advantages over other polymer synthesis methods. It has three major steps: initiation, propagation and termination. Also, transfer reactions to polymers, monomers, transfer agents, and emulsifier molecules may take place during the polymerization. Emulsion polymerization can be carried out in three different ways that are generally classified as batch, semi-continuous, or continuous.

The stability of polymer latex is due to the presence of surface-active materials at the interface between the polymer particle and the aqueous phase. The utilization of a polymeric surfactant as the stabilizer in non-aqueous media began several decades ago and was stimulated by the need for stabilizing materials in non-aqueous systems where an ionic surfactant can not work efficiently. The mechanism for the preparation of a polymer colloid in a non-aqueous dispersion was reviewed by Barrett [1]. However, the development of polymeric surfactants as stabilizers in non-aqueous colloid systems has not been as widespread as their use in non-aqueous dispersion systems. With increasing interest to fully understand the colloidal properties of the latex that is prepared in a non-aqueous emulsion polymerization, a non-aqueous emulsion system is proposed for this research project.

As described in Chapter 2, sixteen PEO-PS-PEO triblock copolymers had been successfully synthesized *via* an anionic polymerization process. These PEO-PS-PEO

triblock copolymers have narrow molecular weight distributions and designed block lengths. They are large molecules, which contains PEO and PS homopolymer subchains that are interconnected by chemical bonds. This structural design results in the unique behavior of PEO-PS-PEO triblock copolymers both in solution and in the bulk. The molecular interaction between PEO and PS subchains may occur within the same molecule or between different molecules. In addition to these interactions, entropic effects must be considered when viewing the conformations of these molecules. The situation becomes more complex in solvent since interactions between solvent molecules and the PEO/PS subchains of the copolymer molecules exist along with the interaction between the PEO/PS polymer chains. Therefore, the outcome of these multiple interactions presents a wide spectrum of colloidal and morphological properties for PEO-PS-PEO triblock copolymers.

PEO-PS-PEO triblock copolymer coils at the solid-liquid interface are of technological interest for many reasons. When PEO-PS-PEO triblock copolymers are employed in colloidal systems, the adsorbed layers alter surface forces and interfacial hydrodynamics in a manner directed by the adsorbed chain conformation. Adsorption is driven primarily by the poor solvent quality for the anchor block. Adsorbed layers can control particle flocculation rates or rates of particle deposition on surfaces. So, adsorption is vital parameter for determining the stabilizing efficiency of PEO-PS-PEO triblock copolymers.

Many studies of PEO-PS diblock copolymers or PEO-PS-PEO triblock copolymers investigate their behavior at the solid-liquid interface [2-21]. For instance, Piirma [23] reported the use of a series of PEO-PS-PEO triblock copolymers as stabilizers

in polystyrene aqueous emulsion. Riess et al [24, 25] investigated a number of PEO-PS diblock and PEO-PS-PEO triblock copolymers as stabilizers in polystyrene non-aqueous dispersion polymerization as well as an aqueous emulsion system. Furthermore, Klein et al. [26], who attempted developing a slow-drying art paint, discovered that the PEO-PS-PEO triblock copolymers were good stabilizers in poly (ethyl methacrylate-co-lauryl methacrylate) latex in non-aqueous (propylene glycol) solvent.

The adsorption process for these triblock molecules is generally understood by viewing the polymer chains attached by the strongly adsorbed anchored block, while the soluble block extends from the surface as a single tail, forming an extended polymer brush. Both the scaling laws and self-consistent field theory were applied to develop these theoretical models for adsorption. This adsorption mechanism was supported not only by experimental evidence but also by theoretical modeling.

For the purpose of a thorough appraisal of stabilizing efficiency of the sixteen synthesized PEO-PS-PEO triblock copolymers, a non-aqueous emulsion polymerization model system was proposed. The criteria for selection of ingredients had to obey the following rules:

(1) Triblock copolymer should have good solubility in this organic solvent.

(2) The generated polymer should be soluble, or at least swellable in its monomers. The resulting particles remain swollen throughout the entire reaction.

(3) The organic medium should have a reasonable boiling point and freezing point. It should be environmentally friendly, and commercially available.

(4) The initiator should have a reasonable half-live to guarantee a practical rate of initiation.

(5) The reaction temperature should be selected to assure that the polymerization would proceed at a modest rate and in a controlled manner.

(6) Triblock copolymer is the only stabilizer.

As a natural extension of what has been done by Klein *et al* [26], propylene glycol is chosen as the continuous medium for the model system. Propylene glycol is a good solvent for PEO-PS-PEO triblock copolymers. It is a high boiling (b.p=187 °C), polar, non-toxic and viscous solvent.

This model system has five ingredients and can be schematically represented in Figure 3.1. Ethyl methylacrylate and lauryl methylacrylate are the monomers. PEO-PS-PEO triblock copolymers are the only stabilizers. 2,2'-azobis(isobutyronitrile) (AIBN) is the free radical initiator. Propylene glycol serves as the continuous phase in the non-aqueous emulsion polymerization.

The emulsion polymerizations were carried out in the proposed non-aqueous model system. Latex stability was used as the criterion, with varying PEO-PS-PEO triblock copolymers to map out regions of operability. This stability phase diagram was created to study the regions for stabilization and non-stabilization. The latexes were cleaned *via* a serum replacement cell for investigating the adsorption behavior of different PEO-PS-PEO triblock copolymers. Contour graphing methods were used to analyze the partitioning and variation of the adsorbed and anchored PEO-PS-PEO triblock copolymers on the latex particles.

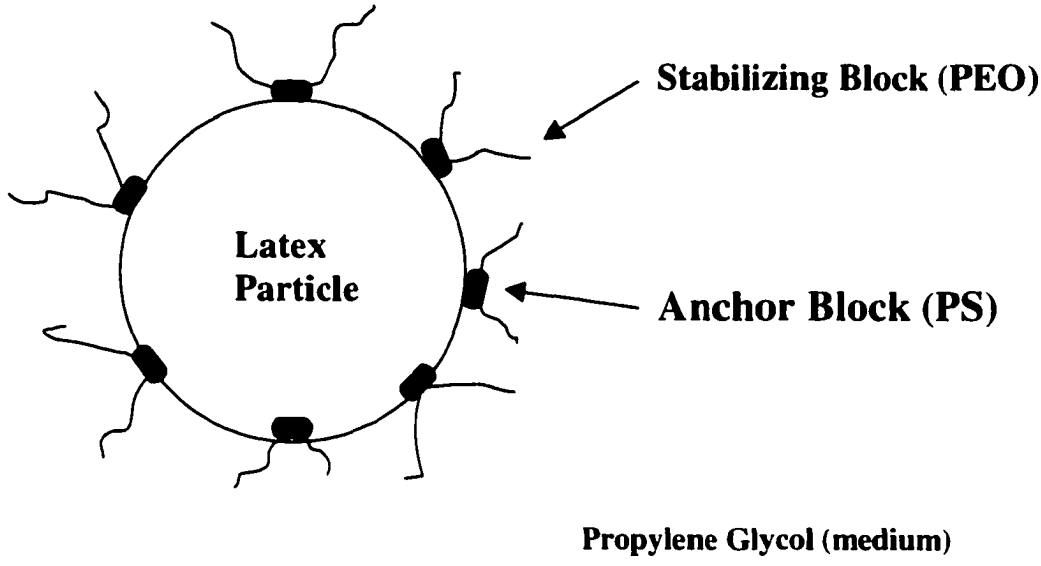


Figure 3.1: Schematic Representation of Model System.

3.2 Experimental

3.2.1 Materials

Ethyl methacrylate (EMA) (99%, Aldrich Chemical Company, Inc.) and lauryl methacrylate (LMA) (96%, Aldrich Chemical Company, Inc.) were used as monomers. They were purified by passing through inhibitor-removal columns (HQ, or MEHQ) (Aldrich Chemical Company, Inc.).

All other materials were used as received, including propylene glycol (99.5+%, A.C.S. reagent, Aldrich Chemical Company, Inc.), 2,2'-azobis(isobutyronitrile) (AIBN) (98%, Aldrich Chemical Company, Inc.), hydroquinone (99%, Aldrich Chemical Company, Inc.), iodine (99.8+%, A.C.S. reagent, Aldrich Chemical Company, Inc.) and potassium iodide (99+%, A.C.S. reagent, Aldrich Chemical Company, Inc.). PEO-PS-PEO triblock copolymers were synthesized according to the method described in Chapter 2.

3.2.2 Emulsion Polymerization in Non-Aqueous Model System

The emulsion polymerization of ethyl methylacrylate / lauryl methacrylate was carried out in a non-aqueous model system at 60°C for a period of twenty-four hours. The recipe was given in Table 3.1. A small glass vial (16 mL) was charged with the desired amount of propylene glycol, 2,2'-azobis(isobutyronitrile) (AIBN), PEO-PS-PEO triblock copolymers and magnetic stir bar. Ethyl methylacrylate and lauryl methacrylate were mixed well in a separate beaker and poured into the small glass vial which contained the mixture of propylene glycol, 2,2'-azobis(isobutyronitrile) (AIBN), PEO-PS-PEO triblock copolymers and magnetic stir bar. Then, the small glass vial was

purged with nitrogen, capped, sealed, and placed in a 60°C constant temperature water bath with continuous stirring. A drop of solution was withdrawn from the mixture at various reaction times and added to the 1 mL of 1% hydroquinone / propylene glycol solution. The sample was placed in ice.

The conversion was measured by gravimetry. After polymerization was completed, the latex was filtered through 200-mesh screen. The amount of coagulum was determined based on the residue on the screen. The particle size was measured by a light scattering method (Nicomp 370).

3.2.3 Determination of the Amount of Adsorbed PEO-PS-PEO Triblock Copolymer on Latex Particles

The PEO-PS-PEO stabilizer, after emulsion polymerization, could be located on the particle surface by anchoring or adsorption, entrapped in the particle, or free in the continuous phase. The overall procedure for the determination of the distribution of the PEO-PS-PEO triblock copolymer in the latex system is given schematically in Figure 3.2. Latex was prepared according to the recipes described in Table 3.1. A serum replacement cell was used to clean the latex and collect all of the free and adsorbed PEO-PS-PEO triblock copolymer. The eluant used was propylene glycol. The latex was cleaned until the refractive index of the serum was the same as that of propylene glycol.

Iodine-Iodide (I_2) titration [27, 28] was used to determine the concentration of the PEO-PS-PEO triblock copolymer in the serum according to the following procedures that are represented schematically in Figure 3.3.

Table 3.1: Non-aqueous Emulsion Polymerization Recipe

Ingredients	Amount (g)
Propylene Glycol	**2.80-3.67**
Triblock copolymer PEO-PS-PEO	**0.10-0.20**
Ethyl methacrylate	**0.57-1.15**
Lauryl methacylate	**0.41-0.85**
AIBN (g)	**0.04-0.07**

AIBN: 2,2'-azobis(isobutyronitrile)

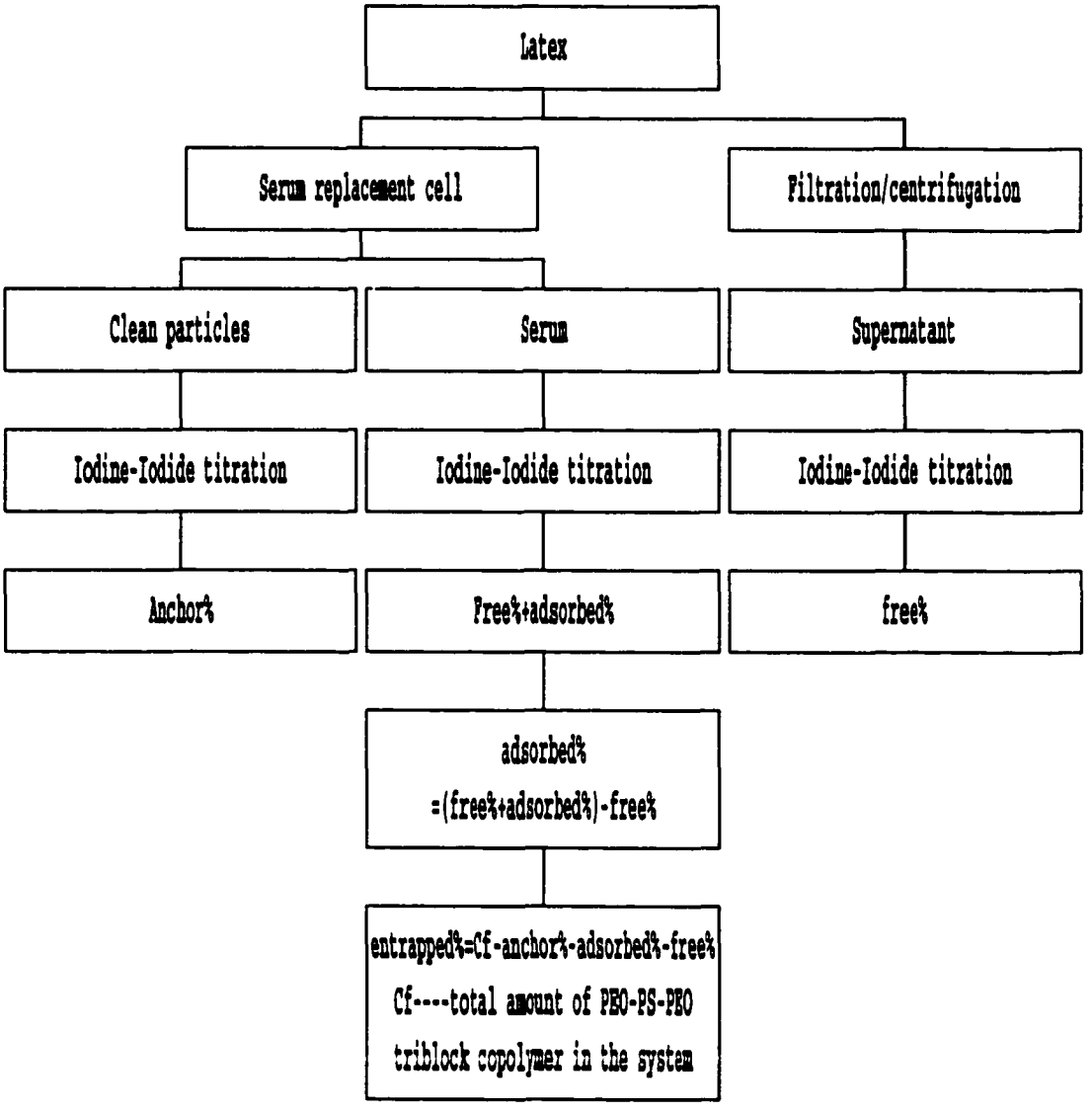


Figure 3.2: Procedure for measuring the partitioning of the PEO-PS-PEO triblock copolymer stabilizer.

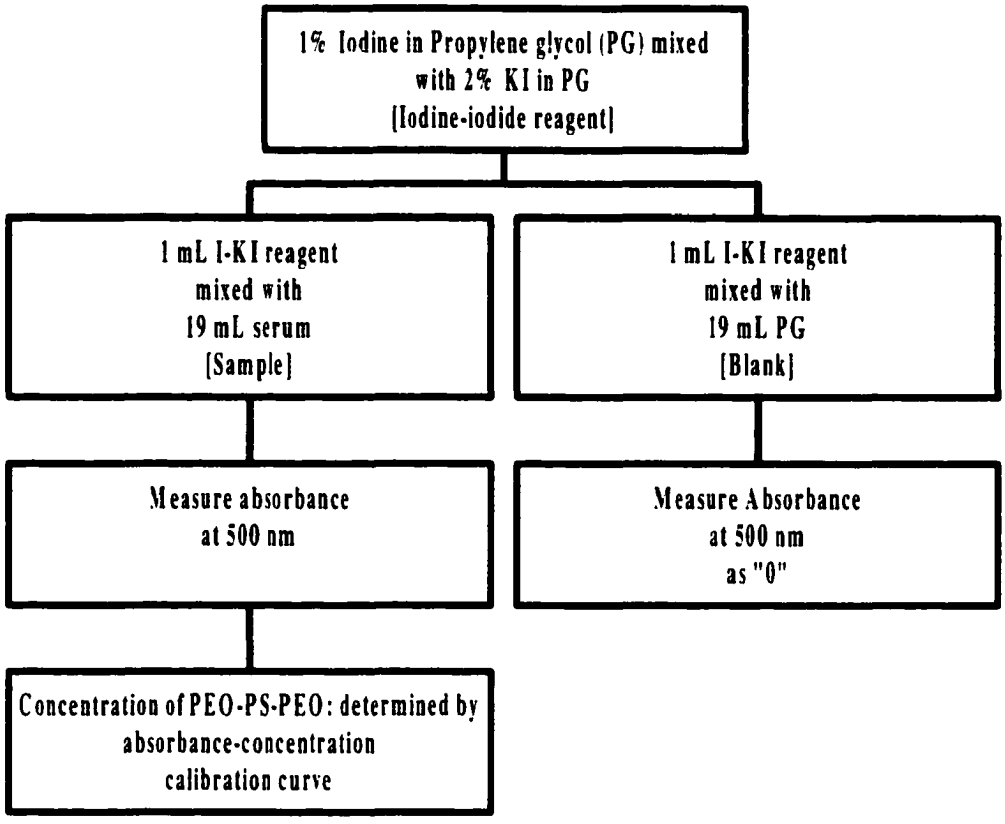


Figure 3.3: Schematic representation of the I_2 titration procedure.

(1) The free and desorbed PEO-PS-PEO triblock copolymers were collected from the serum replacement cell and analyzed by the I_2 titration procedure (described below) in order to determine the total amount of free and adsorbed copolymer ($C_f + C_{ads}$);

(2) The free copolymer was determined by I_2 titration of the supernatant obtained from filtration/ centrifugation (C_f);

(3) The difference between the results of step (1) and step (2) represents the amount of adsorbed copolymer (C_{ads});

(4) The cleaned latex was titrated with Iodine-Iodide to determine the amount of anchored (grafted) copolymer (C_{anc});

(5) The amount of entrapped (buried) copolymer (C_{ent}) was calculated by mass balance using the following equation (1):

$$\text{Entrapped amount of copolymer } (C_{ent}) = C_t - C_f - C_{ads} - C_{anc} \qquad (1)$$

Where: C_{ent} is the entrapped amount of copolymer in the latex particles;

C_t is the total amount of PEO-PS-PEO triblock copolymer in the system;

C_f is the free copolymer in the propylene glycol medium;

C_{ads} is the amount of adsorbed copolymer on the latex surface;

C_{anc} is the amount of anchored copolymer on the particle surface.

(6) Control experiments were carried out where a known amount of PEO-PS-PEO triblock copolymer was used with no latex present to determine if any triblock copolymer remains adsorbed on the serum replacement membrane.

1 wt% iodine and 2 wt% potassium iodide were mixed together in propylene glycol. 19 mL of the serum sample containing PEO-PS-PEO triblock copolymer was mixed with 1 mL of the iodine-iodide reagent. The absorbance of this solution at a

wavelength of 500 nm was compared with a blank solution containing 19 mL propylene glycol and 1mL iodine-iodide reagent (yellow). The concentration of the PEO-PS-PEO triblock copolymer was determined from a previously measured absorbance-concentration calibration curve.

An UV-Vis spectrophotometer (Bausch and Lomb Spectronic 20) was used to determine the concentration of the absorbing species (PEO-iodine complex) in solution. The absorbance of solutions with known concentrations of PEO-PS-PEO triblock copolymer were determined to generate a calibration curve (a plot of absorbance vs. concentration) from which the concentration of an unknown solution could be determined once its absorbance was measured. The blank solution was used to set the absorbance to zero (100% transmittance).

The absorbance was calculated based on Beer's Law:

$$A = \text{Log}(1/T) = \varepsilon bc \qquad (2)$$

Where: A is the absorbance;

T is the transmittance;

b is the path length (the "thickness" of the solution expressed in cm);

C is the concentration of the absorbing species, expressed in molarity;

ε is the molar absorbance coefficient, a constant at any given wavelength for a particular absorbing species.

The experimental results are listed separately in Table 3.2, Table 3.3, and Table 3.4 respectively. No residual was remained on the serum replacement membrane for all six PEO-PS-PEO triblock copolymers. Only six PEO-PS-PEO triblock copolymers produced stable emulsions in this non-aqueous (propylene glycol) EMA-LMA emulsion

copolymerization system. The stable latexes were used to determine the partitioning behavior for these PEO-PS-PEO triblock copolymers (TBC) on latex particles. The compositions of these PEO-PS-PEO triblock copolymers were as follows. The PEO end-blocks ranged from 62 to 88 units, while the PS middle-block varied in length from 19 to 40 units. The molecular weights (Mn) ranged from 7,400 to 11,400 g mol^{-1}. Sample xyd37 had the lowest molecular weight, and xyd43 had the highest molecular weight.

The total number of molecules of PEO-PS-PEO triblock copolymer in the reactor for a given polymerization was calculated using the following equation (3):

$$\text{Total molecules of TBC in the reactor} = (W_{TBC} / M_{TBC}) \cdot N \qquad (3)$$

Where: W_{TBC} is the total amount PEO-PS-PEO triblock copolymer added in the reactor;

M_{TBC} is the molecular weight of PEO-PS-PEO triblock copolymer added to the reactor;

N is Avogadro's number (6.023×10^{23}).

All the latexes listed in Table 3.2 had 30% solid content and 0.1g PEO-PS-PEO triblock copolymer as stabilizer. For every latex listed in Table 3.3, it contained 30% solid content and 0.2g PEO-PS-PEO triblock copolymer as stabilizer. In the latexes included in Table 3.4, the solid content of each latex was 40%, and the amount of PEO-PS-PEO triblock copolymer was 0.2g. As different PEO-PS-PEO triblock copolymers had different molecular weights, the total number of molecules of PEO-PS-PEO triblock copolymer in the reactor was different in each case. This leads to the different triblock copolymer molar concentrations since the total solution volume was constant for all six latexes in each table.

The particle density, number of particles per mililiter, (N/cc) was calculated using the following equation (4) and (5):

$$W_{pol} = (W_{EMA} + W_{LMA}) \cdot x = (\pi /6) \cdot D^3 \cdot d \cdot (N/cc) \quad (4)$$

Thus,

$$N/cc = [(W_{EMA} + W_{LMA}) \cdot x] / [(\pi /6) \cdot D^3 \cdot d] \quad (5)$$

Where: W_{EMA} is the amount of monomer (EMA) in 1 mL latex (g/mL);

W_{LMA} is the amount of monomer (LMA) in 1 mL latex. (g/mL);

D is the particle diameter (cm);

d is the latex density (1.19 g/mL);

x is the percentage of monomer converted to polymer.

3.3 Results and Discussion

3.3.1 Reaction Scheme of Emulsion Polymerization in Non-Aqueous Model System

Emulsion polymerization in propylene glycol is a three-step free radical polymerization, which involves initiation, propagation, and termination. Unstable free radical initiator (AIBN) is thermally decomposed into two free radials which can rapidly react with monomers (EMA, or LMA) to begin the propagation of a polymer chain. There are four propagation steps involved in the chain growth. The rate of addition of a monomer (EMA or LMA) is influenced not only by the radical end type but also by the monomer type in the penultimate position. Termination reactions involve two living polymer chains as well as the living polymer chains with inhibitor (Hydroquinone). The termination reaction between two living polymer chains is a diffusion-controlled process. The rate of termination depends on conversion and copolymer chain microstructure.

Table 3.2: Partitioning Behavior of Different PEO-PS-PEO Triblock Copolymers (TBC) on Latex Particles for the Systems in which 0.1 g TBC was used in Non-aqueous Propylene Glycol in the Emulsion Copolymerization of EMA-LMA at 30% Solids

Sample ID	**xyd33**	**xyd34**	**xyd38**	**xyd37**	**xyd43**	**xyd42**
Composition of triblock copolymer (TBC) (PEO-PS-PEO)	69-29-69	85-28-85	88-19-88	62-19-62	82-40-82	62-39-62
Number of PS units	29	28	19	19	40	39
Number of PEO units	138	170	176	124	164	124
Molecular weight of TBC	9100	10400	9700	7400	11400	9500
Total number of TBC molecules in reactor	6.62×10^{18}	5.79×10^{18}	6.21×10^{18}	8.14×10^{18}	5.28×10^{18}	6.34×10^{18}
Total solution volume (ml)	4.97	4.97	4.97	4.97	4.97	4.97
Avg. TBC molecules/ml soln.	1.33×10^{18}	1.17×10^{18}	1.25×10^{18}	1.64×10^{18}	1.06×10^{18}	1.28×10^{18}
Particle no. / ml soln.	1.1×10^{14}	1.1×10^{14}	1.1×10^{14}	1.1×10^{14}	1.1×10^{14}	1.1×10^{14}
% Phys. Adsorbed TBC on particle surface	27.2	35.2	52.9	37.8	51.3	50.1
% Anchored TBC on particle surface	27.0	29.1	21.5	20.2	45.2	44.8
% Entrapped TBC in particles	9.5	8.9	10.1	13.7	2.9	3.8
% Free TBC in soln.	36.3	26.8	15.5	28.3	0.7	1.3
TBC molecules phys. Adsorbed on each particle	3235	3629	5852	5529	4829	5660
TBC molecules anchored on each particle	3213	3003	2378	2957	4250	5062
TBC molecules entrapped in each particle	1130	918	1117	2005	273	429
Free TBC molecules in medium	4320	2769	1716	4142	61	146
Total TBC adsorbed (phys. + anchored) on each particle	6448	6632	8230	8486	9090	10722

Table 3.3: Partitioning Behavior of Different PEO-PS-PEO Triblock Copolymers (TBC) on Latex Particles for the Systems in which 0.2 g TBC was used in Non-aqueous Propylene Glycol in the Emulsion Copolymerization of EMA-LMA at 30% Solids

Sample ID	xyd33	xyd34	xyd38	xyd37	xyd43	xyd42
Composition of triblock copolymer (TBC) (PEO-PS-PEO)	69-29-69	85-28-85	88-19-88	62-19-62	82-40-82	62-39-62
Number of PS units	29	28	19	19	40	39
Number of PEO units	138	170	176	124	164	124
Molecular weight of TBC	9100	10400	9700	7400	11400	9500
Total number of TBC molecules in reactor	1.32×10^{19}	1.16×10^{19}	1.24×10^{19}	1.63×10^{19}	1.06×10^{19}	1.27×10^{19}
Total solution volume (ml)	4.97	4.97	4.97	4.97	4.97	4.97
Avg. TBC molecules/ml soln.	2.67×10^{18}	2.33×10^{18}	2.50×10^{18}	3.28×10^{18}	2.13×10^{18}	2.55×10^{18}
Particle no. / ml soln.	1.5×10^{14}	1.5×10^{14}	1.5×10^{14}	1.5×10^{14}	1.5×10^{14}	1.5×10^{14}
% Phys. Adsorbed TBC on particle surface	17.7	22.3	30.9	22.0	32.4	28.1
% Anchored TBC on particle surface	17.1	18.3	13.6	13.1	29.7	27.2
% Entrapped TBC in particles	10.3	9.7	13.2	15.6	5.3	5.9
% Free TBC in soln.	54.8	49.7	42.3	49.3	32.7	38.8
TBC molecules phys. Adsorbed on each particle	3193	3508	5256	4868	4622	4880
TBC molecules anchored on each particle	3080	2884	2313	2901	4241	4727
TBC molecules entrapped in each particle	1855	1529	2245	3455	757	1025
Free TBC molecules in medium	9869	7837	7195	10922	4669	6736
Total TBC adsorbed (phys. + anchored) on each particle	6273	6392	7569	7769	8863	9607

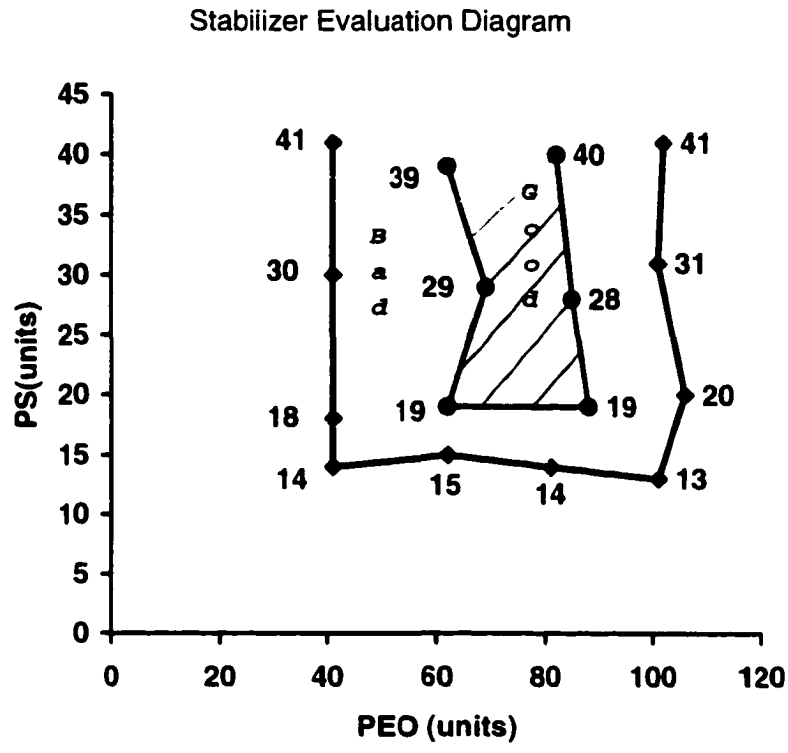
Table 3.4: Partitioning Behavior of Different PEO-PS-PEO Triblock Copolymers (TBC) on Latex Particles for the Systems in which 0.2 g TBC was used in Non-aqueous Propylene Glycol in the Emulsion Copolymerization of EMA-LMA at 40% Solids

Sample ID	xyd33	xyd34	xyd38	xyd37	xyd43	xyd42
Composition of triblock copolymer (TBC) (PEO-PS-PEO)	69-29-69	85-28-85	88-19-88	62-19-62	82-40-82	62-39-62
Number of PS units	29	28	19	19	40	39
Number of PEO units	138	170	176	124	164	124
Molecular weight of TBC	9100	10400	9700	7400	11400	9500
Total number of TBC molecules in reactor	1.32×10^{19}	1.16×10^{19}	1.24×10^{19}	1.63×10^{19}	1.06×10^{19}	1.27×10^{19}
Total solution volume (ml)	4.93	4.93	4.93	4.93	4.93	4.93
Avg. TBC molecules/ml soln.	2.68×10^{18}	2.35×10^{18}	2.52×10^{18}	3.30×10^{18}	2.14×10^{18}	2.57×10^{18}
Particle no. / ml soln.	1.06×10^{14}	1.06×10^{14}	1.06×10^{14}	1.06×10^{14}	1.06×10^{14}	1.06×10^{14}
% Phys. Adsorbed TBC on particle surface	15.3	19.8	28.5	19.9	35.6	32.1
% Anchored TBC on particle surface	14.1	15.3	12.8	11.9	24.6	22.4
% Entrapped TBC in particles	15.8	14.5	17.8	19.6	9.2	10.1
% Free TBC in soln.	54.8	50.4	40.9	48.6	30.8	35.4
TBC molecules phys. Adsorbed on each particle	3864	4393	6778	6191	7200	7930
TBC molecules anchored on each particle	3569	3389	3039	3705	4970	5535
TBC molecules entrapped in each particle	3999	3211	4227	6101	1859	2496
Free TBC molecules in medium	13871	11154	9701	15130	6223	8750
Total TBC adsorbed (phys. + anchored) on each particle	7433	7782	9818	9896	12170	13465

3.3.2 Evaluation of Stabilizing Efficiency for PEO-PS-PEO Triblock Copolymers

Among sixteen PEO-PS-PEO triblock copolymers that were tested, only six gave stable latex. The compositions of these six PEO-PS-PEO triblock copolymers are xyd33 (69PEO-29PS-69PEO), xyd34 (85PEO-28PS-85PEO), xyd37 (62PEO-19PS-62PEO), xyd38 (88PEO-19PS-88PEO), xyd42 (62PEO-39PS-62PEO), and xyd43 (82PEO-40PS-82PEO). The corresponding molecular weights are as follows: xyd33 (Mn=9100), xyd34 (Mn=10400), xyd37 (Mn=7400), xyd38 (Mn=9700), xyd42 (Mn=9500), and xyd43 (Mn=11400). It seems that the minimum polystyrene block (PS) length for giving latex stability is 19 units (Mn=2000 g/mol) and the maximum PS block length for imparting stabilization is 40 units (Mn=4000 g/mol). Similarly, the minimum poly (ethylene oxide) (PEO) block length for offering efficient steric hindrance is 124 units (62 units on each side) (Mn=5300) and the maximum PEO block length for avoiding bridging flocculation is 176 units (88 units on each side). This can be pictured in the phase diagram shown in Figure 3.4.

It seems that a narrow region exists for PEO-PS-PEO triblock copolymer composition acting as good stabilizer in the emulsion polymerization of ethyl methacrylate and lauryl methacrylate in propylene glycol solvent. The structural variations of each PEO-PS-PEO triblock copolymer lead to different behavior in the solution[29]. The change in the molecular conformation effects their stabilizing efficiency. Thus, the stabilizing capability of each PEO-PS-PEO triblock copolymer can be evaluated by examining their molecular conformation profile in solution.



Good Stabilizer:

Latex was made without coagulum during polymerization.

Bad stabilizer:

Latex can not be made. Polymer particles coagulate during polymerization.

Figure 3.4: Stabilizing phase diagram for PEO-PS-PEO triblock copolymers in emulsion polymerization of EMA/LMA in propylene glycol at a polymerization temperature of 60 °C.

It is hypothesized that for triblock copolymers xyd32 (41PEO-30PS-41PEO) and xyd41 (41PEO-41PS-41PEO), the soluble PEO block is very short and forms a very thin layer of fringe around the insoluble PS block swollen core. Thus the hydrodynamic volume of the molecule is small. When this triblock copolymer is dissolved in the solvent (propylene glycol), the PEO block can not form an efficient protective layer around the polymer particles. Therefore, they are not good stabilizers.

Similar to the above situation, triblock copolymers xyd36 (41PEO-18PS-41PEO) and xyd45 (41PEO-14PS-41PEO) have also very short soluble PEO blocks. The PS blocks are very short too, and can not absorb or anchor strongly to the polymer particles. Therefore, these triblock copolymers can not provide good stabilization.

The PS blocks of the triblock copolymers xyd46 (62PEO-15PS-62PEO) and xyd47 (81PEO-14PS-81PEO) are very short and the volume of the swollen cores is relatively small. Thus, the hydrodynamic volume of the molecule is small. When these triblock copolymers are dissolved in the solvent (propylene glycol), PS block can not absorb or anchor strongly to the polymer particles. Thereupon, they do not have the capability to be good stabilizers.

It is believed that triblock copolymer xyd35 (101PEO-31PS-101PEO), xyd39 (106PEO-20PS-106PEO), xyd44 (102PEO-44PS-102PEO) and xyd48 (101PEO-13PS-101PEO) have a different status. The soluble PEO block is very long, and the hydrodynamic volume of the molecule is large. When these triblock copolymers are dissolved in the solvent (propylene glycol), PEO chain bridging favors the coagulation of the particles. Hence, they are not good stabilizers.

The six PEO-PS-PEO triblock copolymers, [xyd33 (69PEO-29PS-69PEO), xyd34 (85PEO-28PS-85PEO), xyd37 (62PEO-19PS-62PEO), xyd38 (88PEO-19PS-88PEO), xyd42 (62PEO-39PS-62PEO), and xyd43 (82PEO-40PS-82PEO)], have relatively moderate hydrodynamic size and a balance between hydrophilic / hydrophobic block lengths. The PS blocks are long enough to be strongly adsorbed or anchored to the particles, and the PEO soluble block forms an efficient layer around the particles to offer stability. Thus, these triblock copolymers can be efficient stabilizers.

The mechanism of colloid stabilizing ability for these triblock polymers is presented below. They are based on conformation arguments that will be supported by experimental data in the next section. In brief, the conformation of these sixteen PEO-PS-PEO triblock copolymers can be divided into three groups. The first group contains four copolymers [xyd32 (41PEO-30PS-41PEO), xyd36 (41PEO-18PS-41PEO), xyd41 (41PEO-41PS-41PEO), and xyd45 (41PEO-14PS-41PEO). The common character of this group is the non-overlap "island" type conformation, which is caused by the short PEO chains. This can be schematically described as in Figure 3.5.

The PEO block of two copolymers in the second group [xyd46 (62PEO-15PS-62PEO) and xyd47 (81PEO-14PS-81PEO) can adsorb on the surface to form a "pancake" type conformation. However, it is not enough to form full coverage by reason of the relatively small overall hydrodynamic volume, which is the result of the short PS block length. The adsorption energy is not sufficient to provide the copolymers enough contact time on the particles and assure full coverage which would prevent coagulation by collision of particles. This can be portrayed as in Figure 3.6.

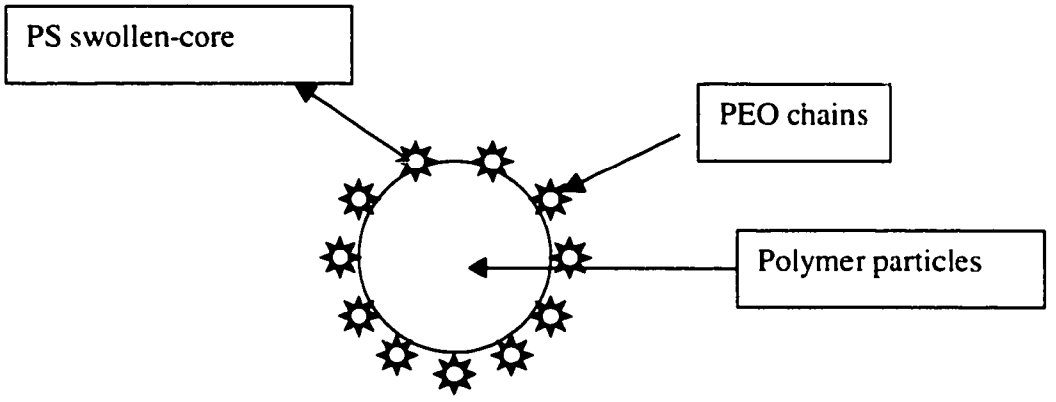


Figure 3.5: Schematic representation of the no-overlap "island" conformation of PEO-PS-PEO triblock copolymers in propylene glycol.

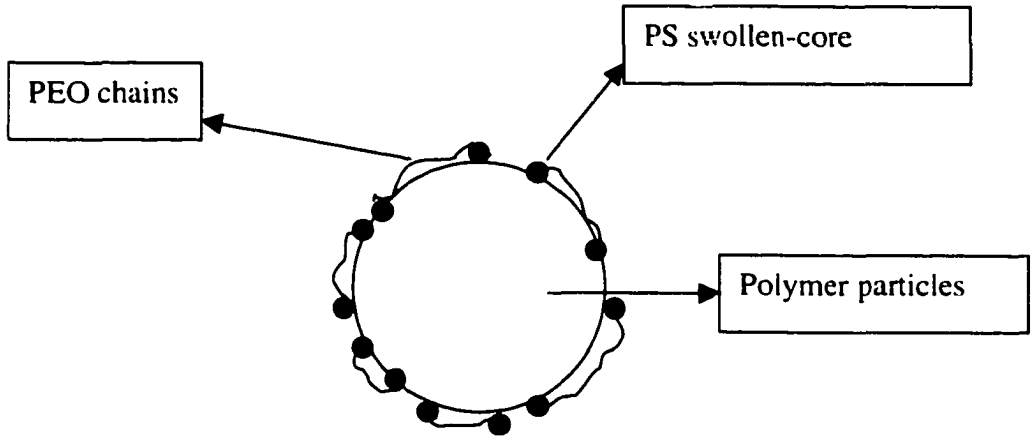


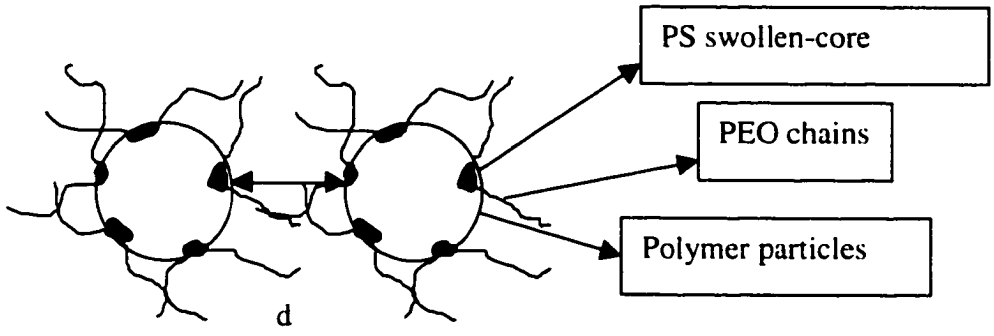
Figure 3.6: Schematic representation of the "pancake" conformation of PEO-PS-PEO triblock copolymers in propylene glycol.

The four triblock copolymers in the third group [xyd35 (101PEO-31PS-101PEO), xyd39 (106PEO-20PS-106PEO), xyd44 (102PEO-44PS-102PEO), and xyd48 (101PEO--13PS-101PEO)] are marked by long PEO chain and bridging flocculation. This can be visualized in Figure 3.7.

In summary, the hydrodynamic volume of the PEO-PS-PEO triblock copolymer has to be in a given range for them to be eligible as a good stabilizer. The ratio of PEO/PS block is proposed as one of the independent variables contributing to colloidal stability.

3.3.3 Effect of the Composition of the PEO-PS-PEO Triblock Copolymers on the Conformation of These Triblock Copolymers in Propylene Glycol

The intrinsic viscosity of these sixteen PEO-PS-PEO triblock copolymers in propylene glycol at 60°C were examined in an attempt to understand the relationship between intrinsic viscosity and the ratio of PS/PEO blocks. In propylene glycol solvent at 60 °C, the PEO-PS-PEO triblock copolymer is in a segregated conformation as shown previously in Figure 2.6 and Figure 2.7. Intrinsic viscosity is related the hydrodynamic volume of the polymer chains. The hydrodynamic volume of the PEO-PS-PEO triblock copolymer depends on both molecular weight of the polymer and the hydrophilic / hydrophobic ratio of the polymer molecule. So, the intrinsic viscosity of these PEO-PS-PEO triblock copolymers in propylene glycol represents the relative conformation of these PEO-PS-PEO triblock copolymers in solvent (propylene glycol). The results are shown in Figure 3.8 as a three-dimensional plot in PEO, PS and conformation as determined by intrinsic viscosity. If the composition of the triblock copolymer falls in



Where d represents the distance between two particles.

Figure 3.7: Schematic representation of the "bridging" conformation of PEO-PS-PEO triblock copolymers in propylene glycol.

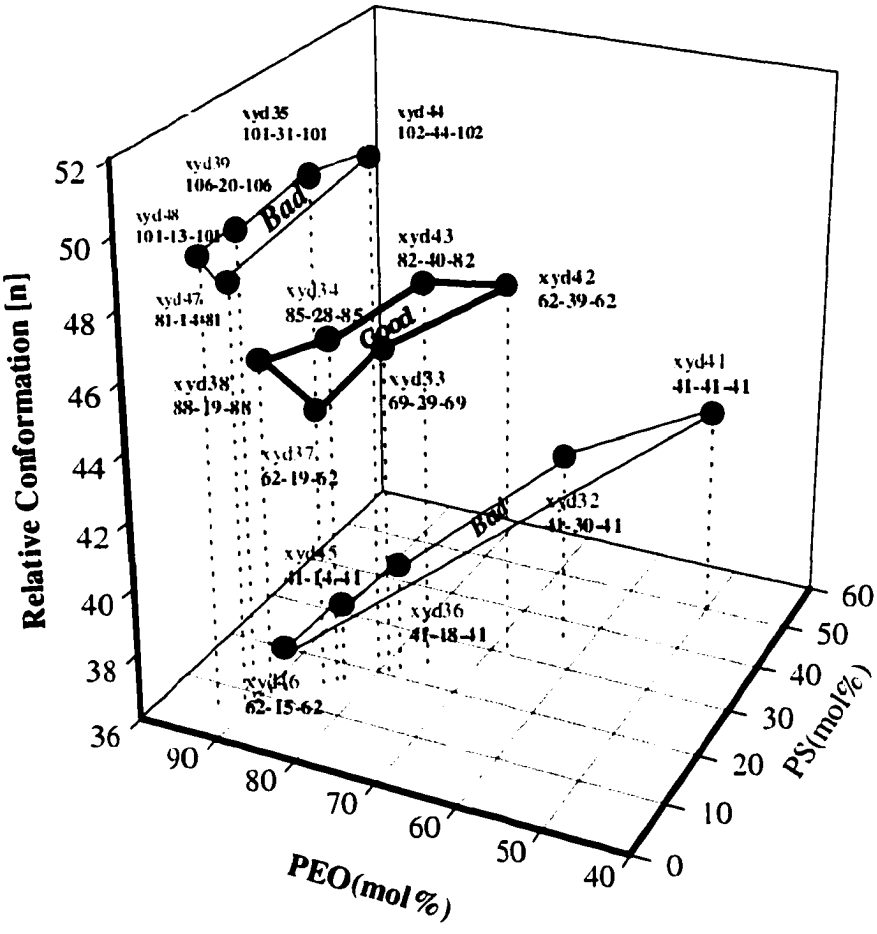


Figure 3.8: Relative conformation *vs.* composition at 60°C for several PEO-PS-PEO triblock copolymers in propylene glycol.

the low conformation region, the triblock copolymer either can not be strongly adsorbed on the particles or the entropic contribution to stabilization is inadequate. Therefore, these low hydrodynamic volume PEO-PS-PEO triblock copolymers can not provide good stability. On the other hand, when the composition of triblock copolymer is located in the upper conformation area, the triblock copolymer PEO chains become too long and may cause bridging to the neighboring particles. A narrow zone in conformation located between the above two zones (upper and lower), is observed to yield stable colloids. In this domain, the triblock copolymer chains are just the right size to adsorb strongly to the particles and provide a long enough PEO chain for entropic stability.

In order to support the above statement, the distance between two particles was calculated to give feasibility to the bridging flocculation hypothesis. The schematic for this calculation is shown in Figure 3.9.

As the volume of a close packed spherical particle (Vc) is 0.74 time of total volume (polymer + stabilizer), the radius of poly (EMA-co-LMA) latex particles with a PEO-PS-PEO triblock copolymer protecting layer (R) can be determined based on the value of the latex particle radius (r) and latex particle density (N). The calculation is shown as follows.

In 1 mL of latex,

$Vc = (4\pi/3)\cdot R^3\cdot N = 0.74$ mL

Therefore, $R=[(0.74\cdot 3)/ 4\pi N]^{1/3}$

In this case, since the particle density (N) is 1.13×10^{14} particles /mL, the radius of poly (EMA-co-LMA) latex particles with the PEO-PS-PEO triblock copolymer protecting layer (R) is 116 nm. Consequently, as the particle radius (r) is 81.5 nm, the

distance between the particles in the close packed situation 2(R-r) is 69 nm. This must be compared with the PEO length calculated from the hydrodynamic volume of the stabilizer.

For a PEO-PS-PEO triblock copolymer random coil shown in Figure 3.10, the hydrodynamic volume (Ve) can be calculated according to the equation (6):

From the intrinsic viscosity one can determine the volume of the equivalent hydrodynamic sphere of the PEO-PS-PEO triblock copolymer chain according to equation (7):

$$[\eta] = 2.5[(N \times Ve) / M] \qquad (7)$$

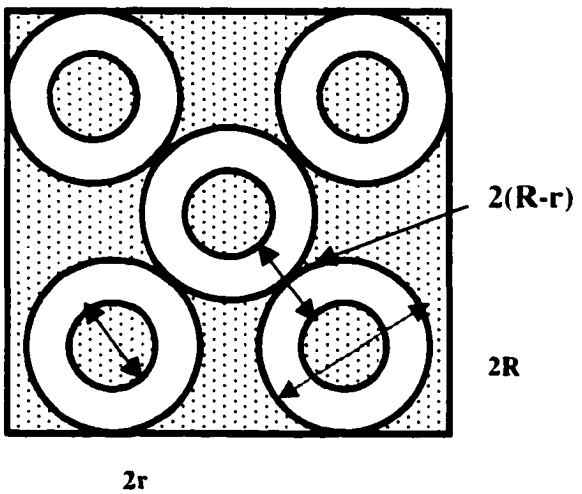
Where $[\eta]$---- intrinsic viscosity of PEO-PS-PEO triblock copolymer chain in propylene glycol at 60 °C;

M---- the molecular weight of PEO-PS-PEO triblock copolymer;

N----Avogadro constant (6.023×10^{23}).

Consequently, the radius of the equivalent hydrodynamic sphere of the PEO-PS-PEO triblock copolymer chain (Re) can be calculated according to equation (6). The results are listed in Table 3.5. The results demonstrate that the radius of the equivalent hydrodynamic sphere of the PEO-PS-PEO triblock copolymer chain (Re) in the upper region is greater than the distance between the particle surfaces, which is 69 nm. Therefore, bridging flocculation will occur while these PEO-PS-PEO triblock copolymers are used as the stabilizers. When the PEO hydrodynamic length is shorter than the distance of separation between particle surfaces, no flocculation takes place.

All these calculations point to the critical importance of the PEO/PS block length and the PEO/PS block ratio.



Where: r---- radius of poly (EMA-co-LMA) latex particles;

R----radius of poly (EMA-co-LMA) latex particles with PEO-PS-PEO triblock copolymer protecting layer;

2(R-r)----distance between the latex particle surfaces in a close packed situation.

Assumption: (1) the particle radius (r) is 81.5 nm;

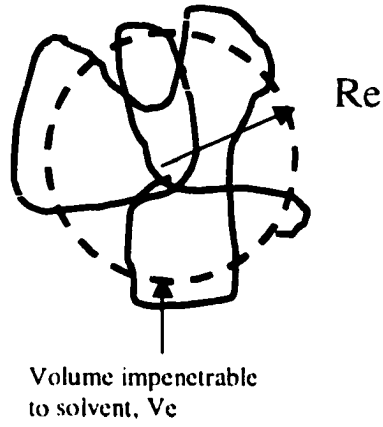
(2) the particle density (N) is 1.13×10^{11} particles /ml;

(3) in the close packed particle conformation

Vc (total polymer + stabilizer volume)

=0.74 Vt (total volume)

Figure 3.9: Schematic representation of close packed particles in non-aqueous emulsion polymerization model system.



$$Ve = (4\pi/3) \cdot Re^{3} \qquad (6)$$

Where Re----radius of the equivalent hydrodynamic sphere of the PEO-PS-PEO triblock copolymer chain;

Ve----the volume of the equivalent hydrodynamic sphere of the PEO-PS-PEO triblock copolymer chain.

Figure 3.10: Schematic representation of the equivalent sphere model for PEO-PS-PEO triblock copolymer chains.

Table 3.5: Comparison of the radius of the equivalent hydrodynamic sphere of the PEO-PS-PEO triblock copolymer chain (Re) for three different levels in Figure 3.8

Sample	2Re (nm)	[2Re-2(R-r)] (nm)	Result
Lower level	**51**	**51<69**	**No bridging**
Middle level	**64**	**64<69**	**No bridging**
Upper level	**76**	**76>69**	**bridging**

3.3.4 Adsorption of PEO-PS-PEO Triblock Copolymer on Latex Particles

The PEO-PS-PEO triblock copolymer stabilizer in the latex system could possibly be found at four locations: (1) entrapped within the latex copolymer particles; (2) anchored (grafted) on the surface of the copolymer particles; (3) physically adsorbed on the copolymer particles; and (4) as free triblock copolymer in the propylene glycol solution. Among these four locations, only the anchored and adsorbed PEO-PS-PEO triblock copolymers can provide stability to the latex particles. The fractions of physically adsorbed and anchored PEO-PS-PEO copolymers are strongly affected by the composition of the triblock copolymers.

A contour plotting technique [30] was used to analyze the partitioning in three dimensions, with respect to PS and PEO block length. Variation of the adsorbed and anchored PEO-PS-PEO triblock copolymer on the latex particles, for instance, is shown in Figures 3.12 and 3.14. The procedure used to construct the contour plot is as follows:

1. Obtain the points for the six PEO-PS-PEO triblock copolymers in the plot of the number of PEO units *vs.* the number of PS units.

2. Assign the corresponding number of adsorbed triblock copolymer molecules (or anchored molecules) to the corresponding PEO-PS-PEO triblock copolymer. For example, in the case of sample xyd33 there are 3235 triblock copolymer molecules adsorbed on each latex particle, which corresponds to the point where there are 29 PS units and 138 PEO (69 units on each side of the chain) units present in the triblock copolymer molecule. The same approach was utilized for the other 5 triblock copolymer samples. The assumption is made that between experimental points, linear extrapolation

can be used to obtain intermediate values and those similar values can be connected to yield isocontour lines.

3. The data are thus interpolated with an increment of 500 triblock copolymer molecules. The small diamond symbols given in Figure 3.11 between two experimental data points are the interpolated values. All the points are used then to obtain the contour plots.

Contour plots showing the number of PEO-PS-PEO triblock copolymer molecules, which were physically adsorbed on the latex particles, are given in Figures 3.12, 3.16, and 3.20 respectively. Contour plots displaying the number of PEO-PS-PEO triblock copolymer molecules, which were anchored (grafted) on the latex particles, are presented in Figures 3.14, 3.18, and 3.22, separately.

From the contour plots of the number of adsorbed PEO-PS-PEO triblock copolymer molecules on a latex particle (Figures 3.12, 3.16, and 3.20), it appears that the PS block length effect dominates and a transition with a minimum value in adsorption is observed at a PS block length of about 30 units. For those PEO-PS-PEO triblock copolymers where the PS block length is less than 30 units, the PEO chains most likely adsorb on the surface of the particles to form a "brush" type of layer which confers stability to the particles. As the PS block length increases, the binding energy between the PS block and the particle increases. Thus, anchoring of more segments of the PS block to the particle surface increases. The PEO brush on the particle surface must be rearranged in order to make space for the PS block to become anchored on the particle surface. Consequently, the overall number of adsorbed PEO-PS-PEO triblock copolymer molecules on the latex particle decreases.

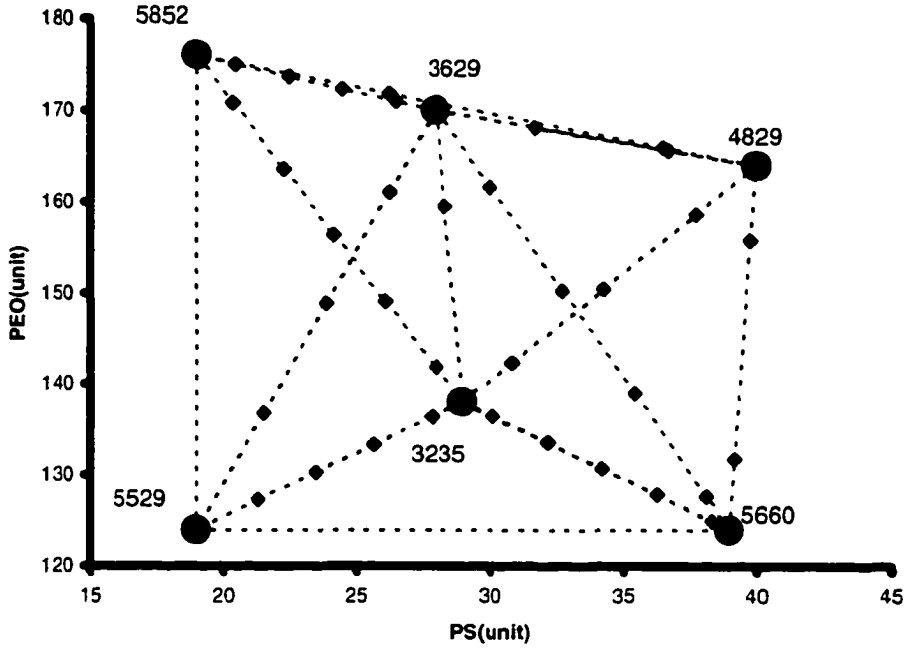


Figure 3.11: Construction of contour plot showing the number of PEO-PS-PEO triblock copolymer (TBC) molecules adsorbed on each latex particle. The six numbers on the plot represent the actual number of TBC molecules adsorbed on the copolymer particles as shown in Table 3.2.

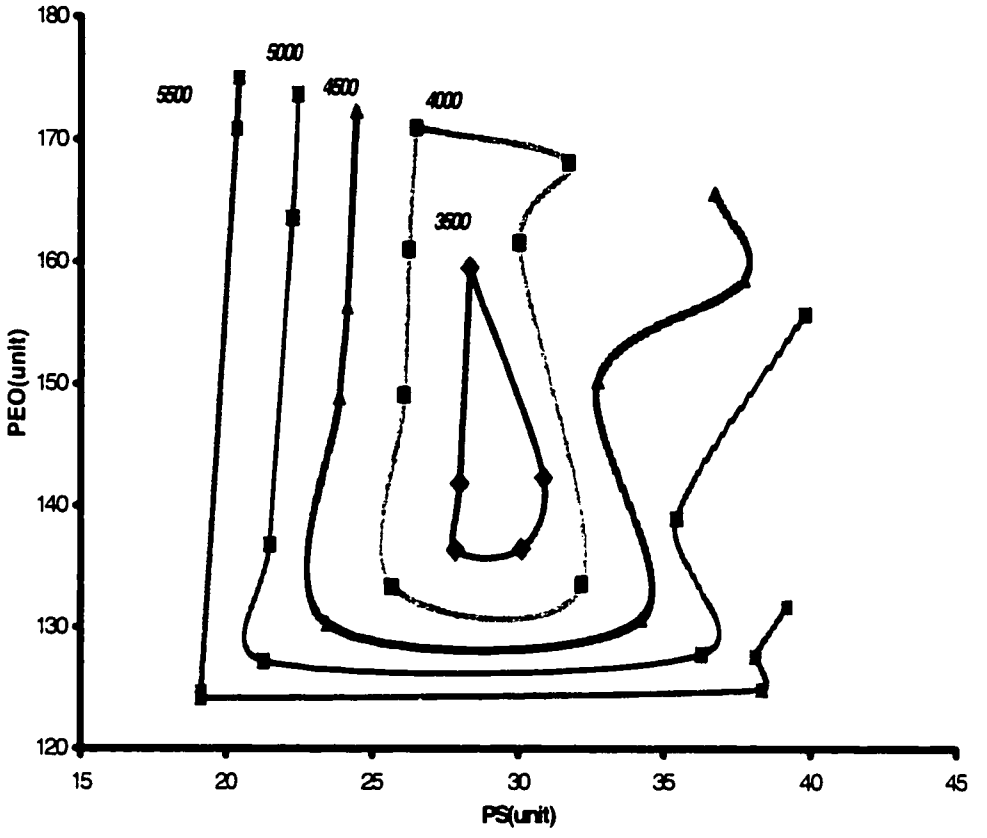


Figure 3.12: Contour plot showing the number of PEO-PS-PEO triblock copolymer (TBC) chains adsorbed on each latex particle. The numbers on the plot represent the number of TBC molecules adsorbed on a latex particle based on connecting the interpolated data, which have the same value (from Figure 3.11).----30% solids latex prepared with 0.1 g TBC.

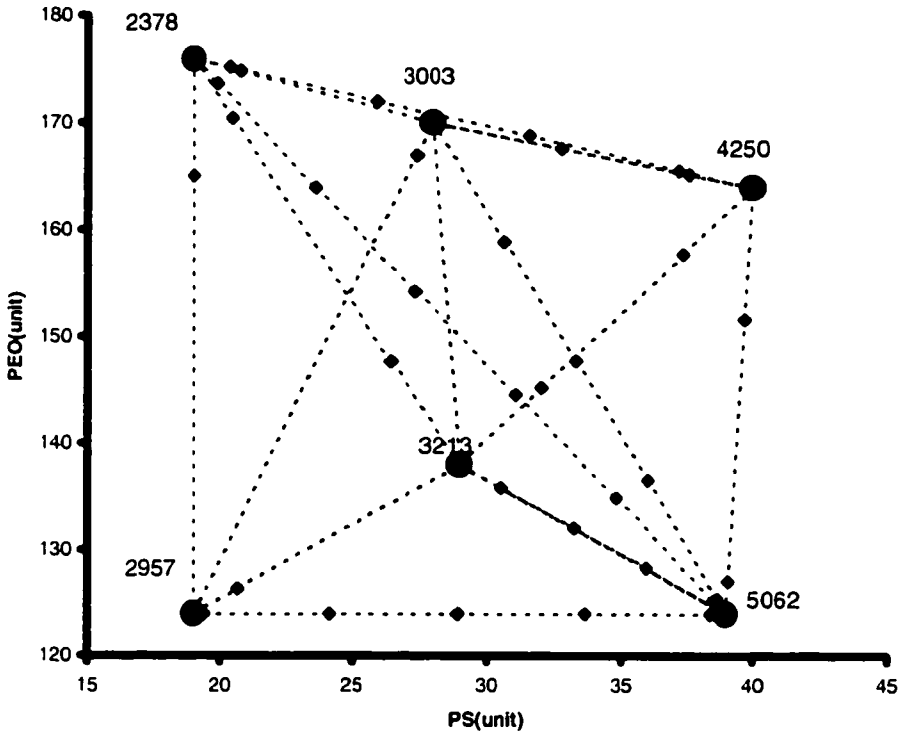


Figure 3.13: Construction of contour plot showing the number of PEO-PS-PEO triblock copolymer (TBC) molecules anchored on each latex particle. The six numbers on the plot represent the actual number of TBC molecules anchored on the copolymer particles as shown in Table 3.2.

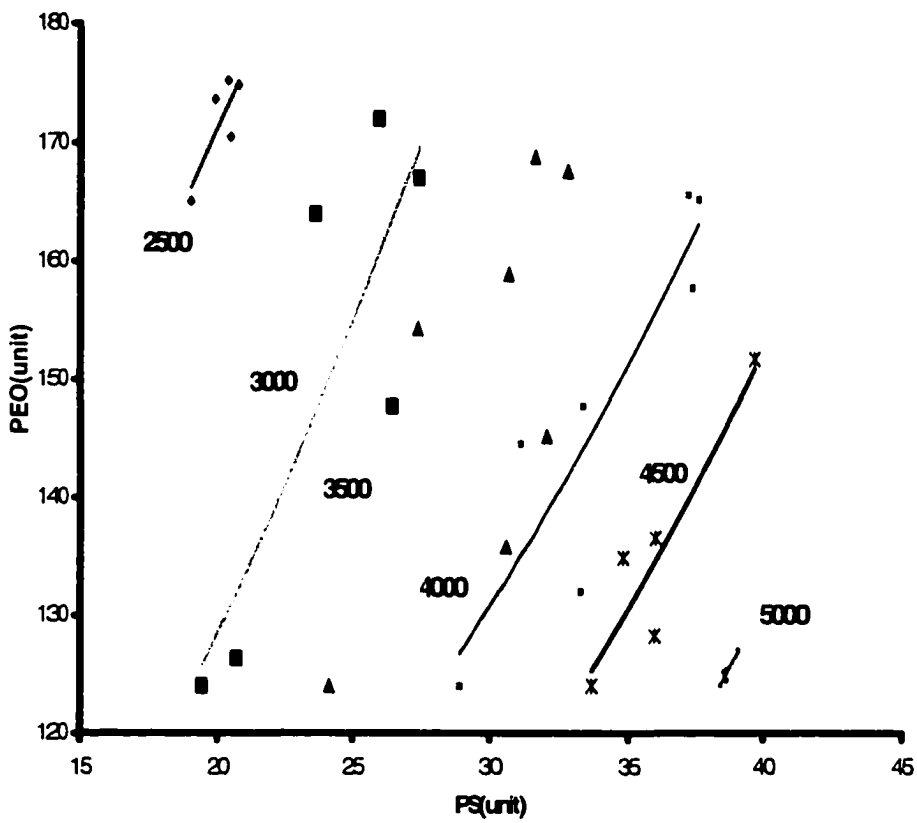


Figure 3.14: Contour plot showing the number of PEO-PS-PEO triblock copolymer (TBC) chains anchored on each latex particle. The numbers on the plot represent the number of TBC molecules anchored on the latex particle based on connecting the interpolated data, which have the same value (from Figure 3.13).----30% solids latex prepared with 0.1 g TBC.

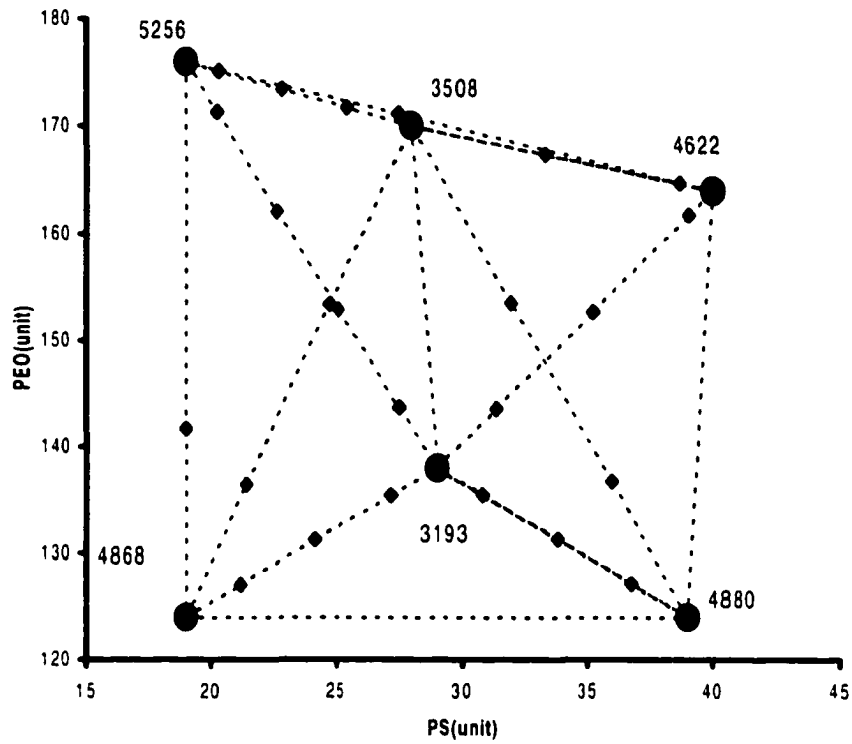


Figure 3.15: Construction of contour plot showing the number of PEO-PS-PEO triblock copolymer (TBC) molecules adsorbed on each latex particle. The six numbers on the plot represent the actual number of TBC molecules adsorbed on the copolymer particles as shown in Table 3.3.

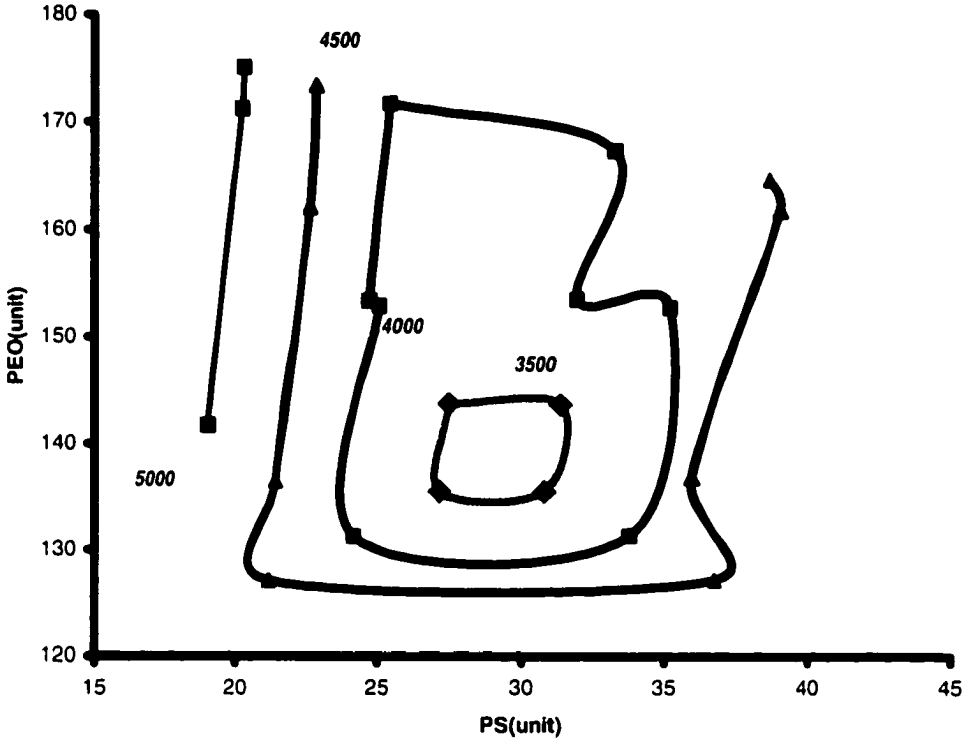


Figure 3.16: Contour plot showing the number of PEO-PS-PEO triblock copolymer (TBC) chains adsorbed on each latex particle. The numbers on the plot represent the number of TBC molecules adsorbed on a latex particle based on connecting the interpolated data, which have the same value (from Figure 3.15).----30% solids latex prepared with 0.2 g TBC.

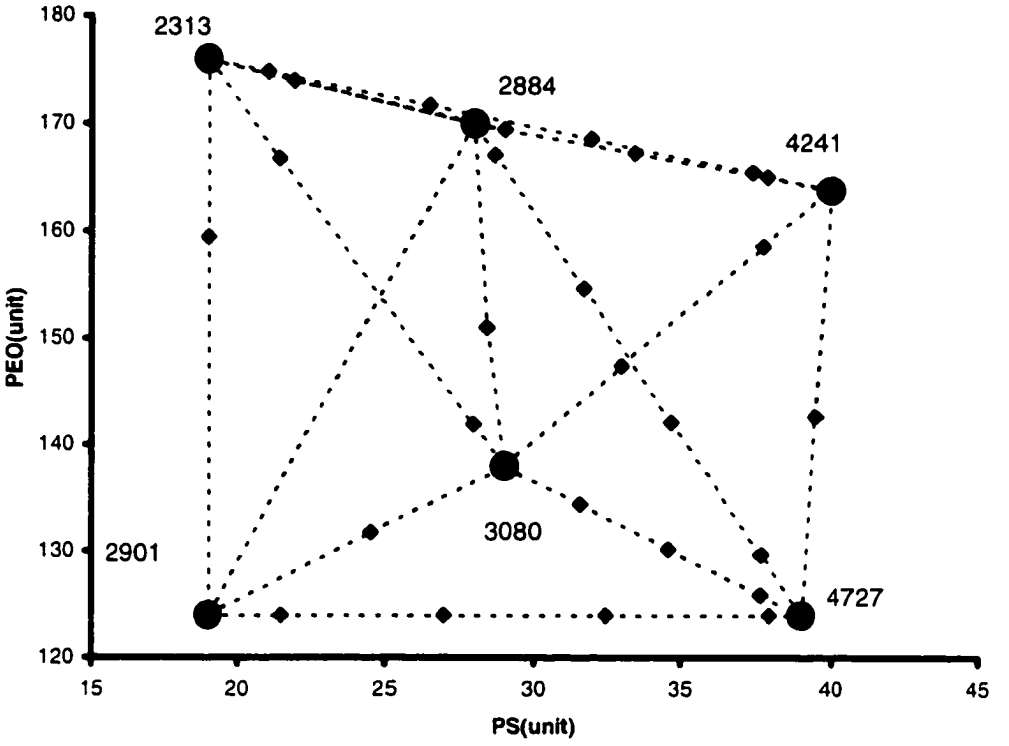


Figure 3.17: Construction of contour plot showing the number of PEO-PS-PEO triblock copolymer (TBC) molecules anchored on each latex particle. The six numbers on the plot represent the actual number of TBC molecules anchored on the copolymer particles as shown in Table 3.3.

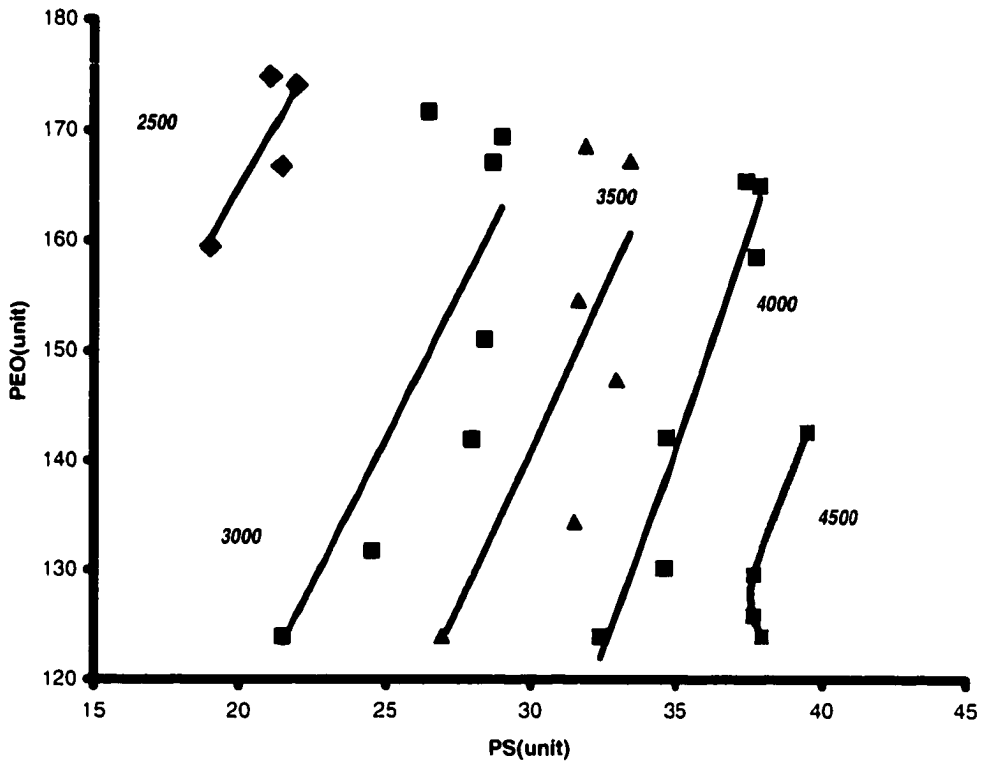


Figure 3.18: Contour plot showing the number of PEO-PS-PEO triblock copolymer (TBC) chains anchored on each latex particle. The numbers on the plot represent the number of TBC molecules anchored on the latex particle based on connecting the interpolated data, which have the same value (from Figure 3.17).----30% solids latex prepared with 0.2 g TBC.

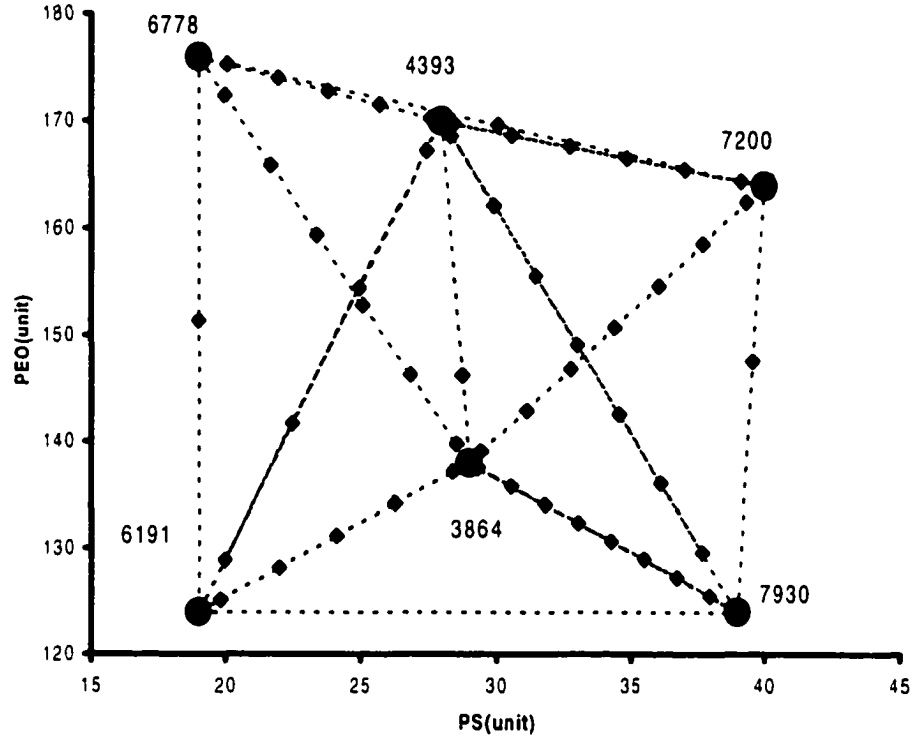


Figure 3.19: Construction of contour plot showing the number of PEO-PS-PEO triblock copolymer (TBC) molecules adsorbed on each latex particle. The six numbers on the plot represent the actual number of TBC molecules adsorbed on the copolymer particles as shown in Table 3.4.

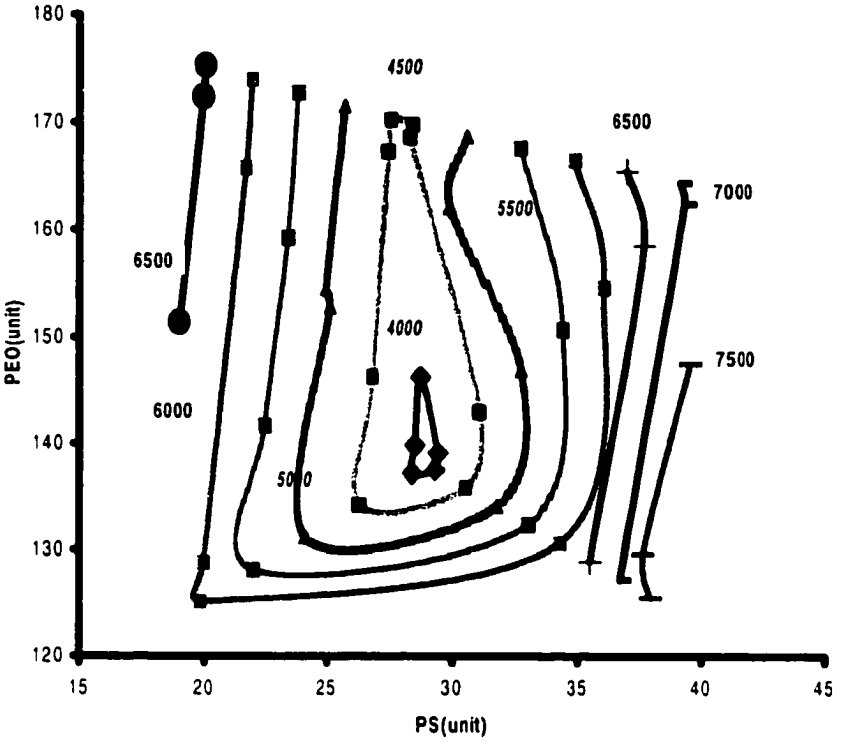


Figure 3.20: Contour plot showing the number of PEO-PS-PEO triblock copolymer (TBC) chains adsorbed on each latex particle. The numbers on the plot represent the number of TBC molecules adsorbed on a latex particle based on connecting the interpolated data, which have the same value (from Figure 3.19).----40% solids latex prepared with 0.2 g TBC.

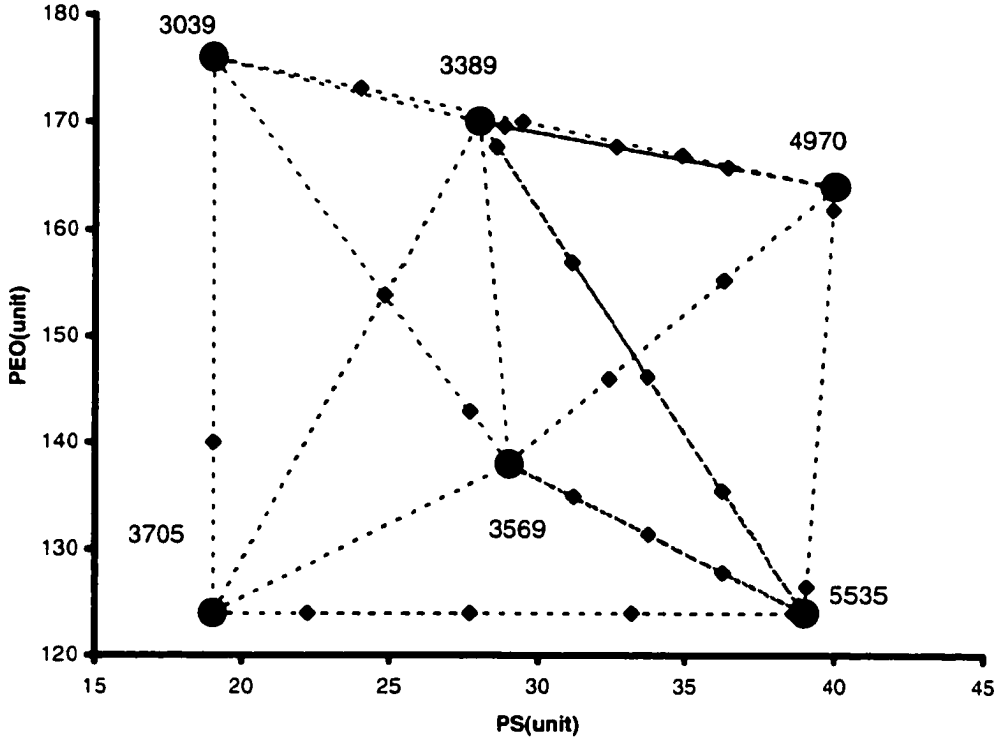


Figure 3.21: Construction of contour plot showing the number of PEO-PS-PEO triblock copolymer (TBC) molecules anchored on each latex particle. The six numbers on the plot represent the actual number of TBC molecules anchored on the copolymer particles as shown in Table 3.4.

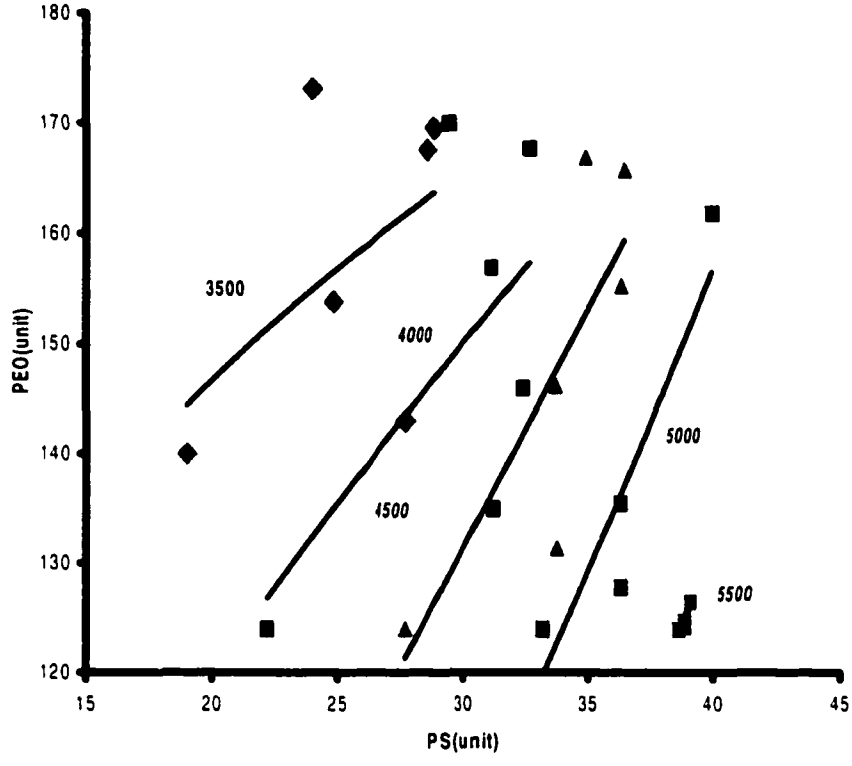


Figure 3.22: Contour plot showing the number of PEO-PS-PEO triblock copolymer (TBC) chains anchored on each latex particle. The numbers on the plot represent the number of TBC molecules anchored on the latex particle based on connecting the interpolated data, which have the same value (from Figure 3.21).----40% solids latex prepared with 0.2 g TBC.

For those PEO-PS-PEO triblock copolymers where the PS block length is longer than 30 units. the PS block collapses and is swollen in the propylene glycol medium as the PS block length increases. The large swollen PS core creates a free volume for the PEO block. Therefore, the PEO chains can reside inside the PS core. Since propylene glycol is a poor solvent for the PS block, the PEO-PS-PEO triblock copolymer chains prefer to remain on the particle surface rather than desorbing into the medium due to the unfavorable environment (poor solvency) for the PS block. This can be confirmed from the concentration of the free PEO-PS-PEO triblock copolymer in the continuous phase, which was found to be close to zero for the two PEO-PS-PEO triblock copolymers that have 40 PS units (0.7% and 1.3%, see Table 3.2). However, the anchored and adsorbed PEO-PS-PEO triblock copolymer molecules saturate the particle surface. The copolymer molecules are in a dynamic equilibrium between adsorbed and desorbed triblock copolymer molecules on the particle surface.

As the PS block chain length increases, the area occupied by each triblock copolymer increases and the number of chain packed decreases to a minimum around 30 unit PS block. After this point, the PS block collapsed and therefore larger number of triblock copolymer chains can be packed on the same particle. The data on intrinsic viscosity presented in Table 2.4 also confirm the proposed mechanism of triblock copolymers adsorption. For similar values of total (PS+PEO) molecular weights (TBC xyd39 and xyd43) but with different PS block chain length 20 and 40 PS units respectively, intrinsic viscosity is lower for the triblock copolymer with larger PS block. This demonstrates that the polymer chain is in a collapsed configuration and therefore with a reduced hydrodynamic volume of the random coil. Thus, the amount of adsorbed

PEO-PS-PEO triblock copolymer molecules increases as the PS block length increases. A schematic representation of the scenario described above is shown in Figure 3.23.

From the contour plot of the anchored PEO-PS-PEO triblock copolymer on each particle (Figures 3.14, 3.18, and 3.22), it seems that the PS block length significantly affects the amount of the anchored triblock copolymer chains on each particle. As the PS block length increases, the binding energy between the PS block and the polymer particle increases; therefore, the number of the anchored triblock copolymer chains increases continuously. With increasing number of PS segments in contact with the particle surface during polymerization reaction, the probability for grafting also increases. But, the PS block length also affects the solubility of the triblock copolymer in the propylene glycol medium. In one extreme one may think that when the length of the PS block exceeds a critical length, the triblock copolymer is no longer soluble in the medium (propylene glycol), and it can no longer act as a stabilizer. On the other hand, when the PS block length is below a lower limit of critical chain length, the adsorbing energy between the PS block and the polymer particles are not sufficient to yield the PS segment concentration to allow irreversible anchoring of chains on the surface of the polymer particles. To summarize, both the upper critical PS block length and the lower critical PS block length are envisioned to be important parameters for a triblock copolymer to act as a stabilizer.

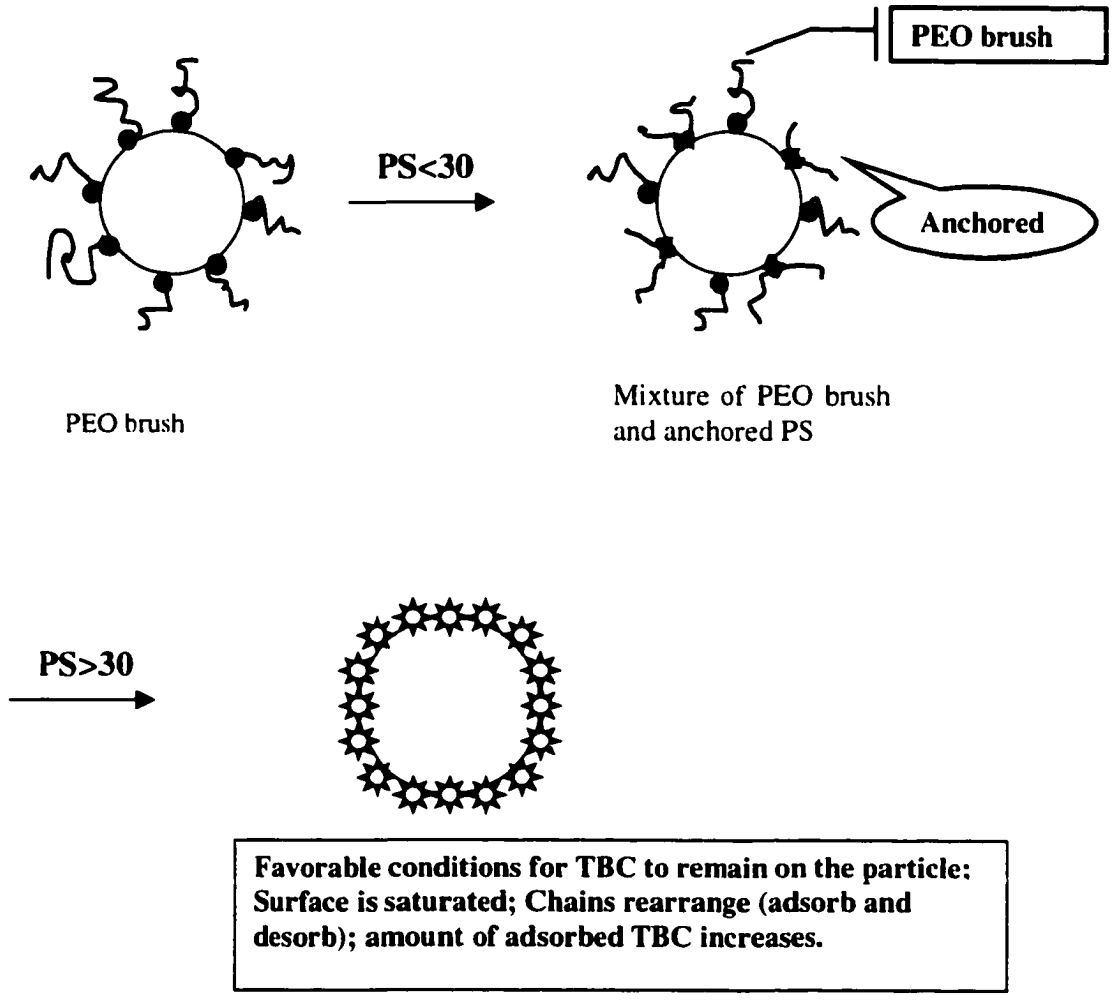


Figure 3.23: Schematic representation of adsorbed PEO-PS-PEO triblock copolymer on latex particles.

3.3.5 Effect of Stabilizer Concentration on the Partitioning Behavior of PEO-PS-PEO Triblock Copolymer on Each Latex Particle

As the amount of stabilizer increases from 0.1g to 0.2g, the adsorbed or anchored PEO-PS-PEO triblock copolymer on each latex particle decreases consistently. The effect of stabilizer concentration on the adsorbed portion of PEO-PS-PEO triblock copolymer on each latex particle is shown in Figure 3.24. Figure 3.25 displays the influence of stabilizer concentration on the anchored portion of PEO-PS-PEO triblock copolymer on each latex particle. The above results can be understood by examining the effect of the stabilizer concentration on the particle surface area generated. The particle surface area was determined based on the particle size data, which was measured by means of light scattering. When the amount of stabilizer increased, the particle size decreased from 163 nm to 149 nm and the surface area of each particle decreased from 8.34×10^{-14} m^2 to 6.99×10^{-14} m^2. The surface area occupied by a single PEO-PS-PEO triblock copolymer molecule in which 0.1 g triblock copolymer was used in non-aqueous propylene glycol in the emulsion copolymerization of EMA-LMA at 30% solid for the different PEO-PS-PEO triblock copolymer compositions is shown in table 3.6. Similarly, the surface area occupied by a single PEO-PS-PEO triblock copolymer molecule in which 0.2 g triblock copolymer was used in non-aqueous propylene glycol in the emulsion copolymerization of EMA-LMA at 30% solid for the different PEO-PS-PEO triblock copolymer compositions is shown in table 3.7.

As the amount of stabilizer increased from 0.1 g to 0.2 g, the surface area occupied by a single triblock copolymer increased from 15% to 3% for the different triblock copolymer compositions. This is due to particle curvature effect. Stutman[31]

observed similar trend in mono-dispersed polystyrene latex system using sodium lauryl sulfate as surfactant.

3.3.6 Effect of Monomer Concentration on the Partitioning Behavior of PEO-PS-PEO Triblock Copolymer on Each Latex Particle

When the monomer concentration was changed to yield from 30% to 40% solid content, the adsorbed or anchored PEO-PS-PEO copolymer on each latex particle also increased. This was true for all six triblock copolymers. Again, Figure 3.26 demonstrates the influence of monomer concentration on adsorbed portion of PEO-PS-PEO triblock copolymer on each latex particle. The efficacy of monomer concentration on the anchored portion of PEO-PS-PEO triblock copolymer on each latex particle is illustrated in Figure 3.27. The above results can be understood by examining the effect of the monomer concentration on the particle surface area generated. The particle surface area was determined based on the particle size data, which was measured by means of light scattering. When the amount of monomer concentration increased, the particle size increased from 149 nm to 199 nm, particle number density decreased from 1.46×10^{14} to 8.26×10^{13}, the surface area of each particle increased from 6.99×10^{-14} m^2 to 1.24×10^{-13} m^2. Therefore, larger surface area needs more PEO-PS-PEO triblock copolymers to provide stabilization. This explains why both physically adsorbed and anchored PEO-PS-PEO triblock copolymers latex particle increase with increasing the monomer concentration.

3.3.7 Entrapped and Free Partitions of Different PEO-PS-PEO Triblock Copolymer on Latex Particles for the Emulsion Copolymerization of EMA-LMA in Non-Aqueous Propylene Glycol

As mentioned in section 3.3.4, each PEO-PS-PEO triblock copolymer has four locations in a latex system, which is affected by the composition of PEO-PS-PEO triblock copolymer, stabilizer concentration, and monomer concentration. Figure 3.28 shows the partitioning behavior of different PEO-PS-PEO triblock copolymers (TBC) on latex particles for the systems in which 0.1 g TBC was used in non-aqueous propylene glycol in the emulsion copolymerization of EMA-LMA at 30% solids. The PEO-PS-PEO triblock copolymers xyd43 [82-40-82] and xyd42 [62-39-62] had minimum amount of entrapped partition due to the large volume of PS swollen core. Similarly, the PEO-PS-PEO triblock copolymers xyd38 [88-19-88] and xyd37 [62-19-62] had maximum amount of entrapped partition since the small volume of PS swollen core. The "free" partitions of the PEO-PS-PEO triblock copolymers xyd43 [82-40-82] and xyd42 [62-39-62] were almost near zero because large PS swollen core preferred to stay on the particle surface. For the rest of PEO-PS-PEO triblock copolymers (xyd33 [69-29-69], xyd34 [85-28-85], xyd38 [88-19-88], and xyd37 [62-19-62]), significant amount of triblock copolymers existed in the continuous phase.

Figure 3.29 illustrates the partitioning behavior of different PEO-PS-PEO triblock copolymers (TBC) on latex particles for the systems in which 0.2 g TBC was used in non-aqueous propylene glycol in the emulsion copolymerization of EMA-LMA at 30% solids. Figure 3.30 depicts the partitioning behavior of different PEO-PS-PEO triblock copolymers (TBC) on latex particles for the systems in which 0.2 g TBC was used in

non-aqueous propylene glycol in the emulsion copolymerization of EMA-LMA at 40% solids. Correspondingly, the PEO-PS-PEO triblock copolymers xyd43 [82-40-82] and xyd42 [62-39-62] had minimum amount of entrapped partition despite of the stabilizer concentration and monomer concentration. As increasing monomer concentration and stabilizer concentration, large amount of triblock copolymer were "free" in the medium regardless of composition of the triblock copolymers.

In summary, the entrapped partition is mainly determined by the composition of PEO-PS-PEO triblock copolymers, and slightly affected by the monomer concentration as well as stabilizer concentration. The "free" partition is decided by the monomer concentration, the stabilizer concentration, and the composition of PEO-PS-PEO triblock copolymer.

3.3.8 Mathematical Extension

For the purpose of providing an empirical correlation for calculating the total PEO-PS-PEO triblock copolymer chains (anchored + adsorbed) on each latex particle, polynomial equations were derived and applied to the adsorption experimental data. The result is shown in Appendix III.

Table 3.6: The Surface Area Occupied by A Single PEO-PS-PEO Triblock Copolymer Molecule in Which 0.1 g TBC Was Used In Non-Aqueous Propylene Glycol in The Emulsion Copolymerization of EMA-LMA At 30% Solid for the Different TBC Compositions

Sample ID	**xyd33**	**xyd34**	**xyd38**	**xyd37**	**xyd43**	**xyd42**
Composition of triblock copolymer (TBC) (PEO-PS-PEO)	69-29-69	85-28-85	88-19-88	62-19-62	82-40-82	62-39-62
Number of PS units	29	28	19	19	40	39
Number of PEO units	138	170	176	124	164	124
Molecular weight of TBC	9100	10400	9700	7400	11400	9500
Particle no. / ml soln.	1.1×10^{14}	1.1×10^{14}	1.1×10^{14}	1.1×10^{14}	1.1×10^{14}	1.1×10^{14}
TBC molecules phys. Adsorbed on each particle	3235	3629	5852	5529	4829	5660
Total surface area (m^2/cc)	9.34	9.34	9.34	9.34	9.34	9.34
Surface area $(A^o)^2$/TBC	2578	2298	1425	1508	1727	1473

Table 3.7: The Surface Area Occupied by A Single PEO-PS-PEO Triblock Copolymer Molecule in Which 0.2 g TBC Was Used In Non-Aqueous Propylene Glycol in The Emulsion Copolymerization of EMA-LMA At 30% Solid for the Different TBC Compositions

Sample ID	**xyd33**	**xyd34**	**xyd38**	**xyd37**	**xyd43**	**xyd42**
Composition of triblock copolymer (TBC) (PEO-PS-PEO)	69-29-69	85-28-85	88-19-88	62-19-62	82-40-82	62-39-62
Number of PS units	29	28	19	19	40	39
Number of PEO units	138	170	176	124	164	124
Molecular weight of TBC	9100	10400	9700	7400	11400	9500
Particle no. / ml soln.	1.5×10^{14}	1.5×10^{14}	1.5×10^{14}	1.5×10^{14}	1.5×10^{14}	1.5×10^{14}
TBC molecules phys. Adsorbed on each particle	3193	3508	5256	4868	4622	4880
Total surface area (m^2/cc)	10.21	10.21	10.21	10.21	10.21	10.21
Surface area $(A^o)^2$/TBC	3193	3508	5256	4868	4622	4880

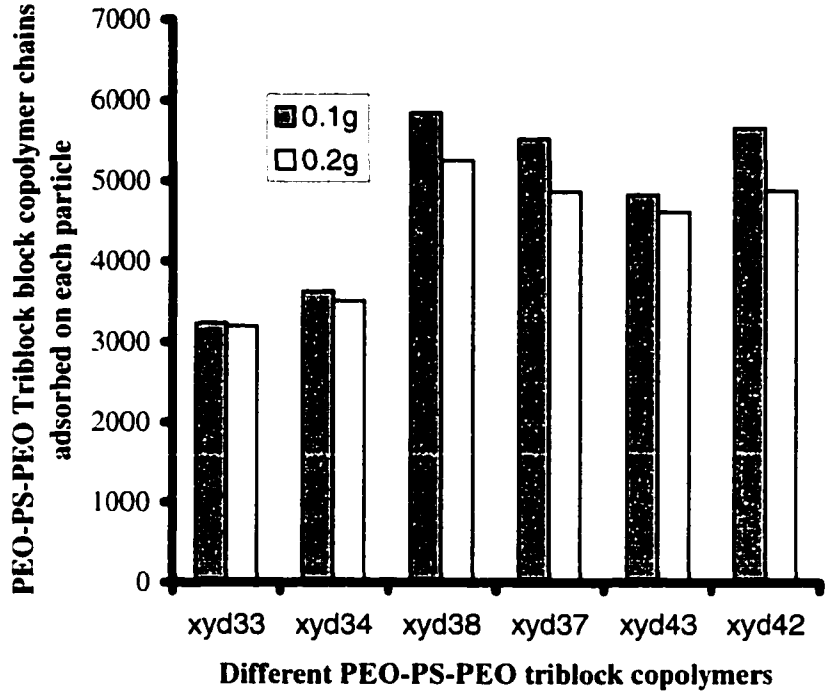


Figure 3.24: Effect of stabilizer concentration on the adsorbed portion of PEO-PS-PEO triblock copolymer on each latex particle

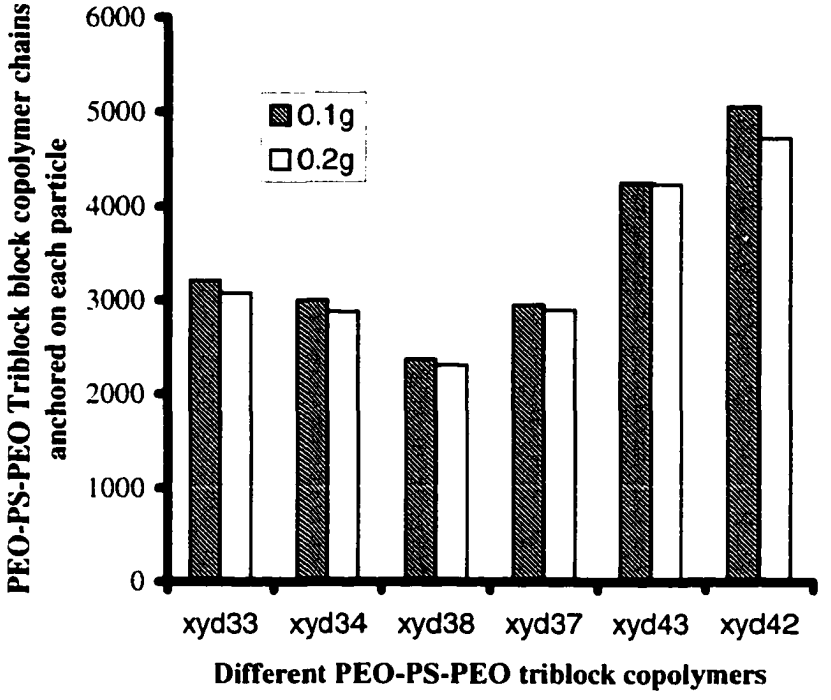


Figure 3.25: Effect of stabilizer concentration on the anchored amount of PEO-PS-PEO triblock copolymer on each latex particle

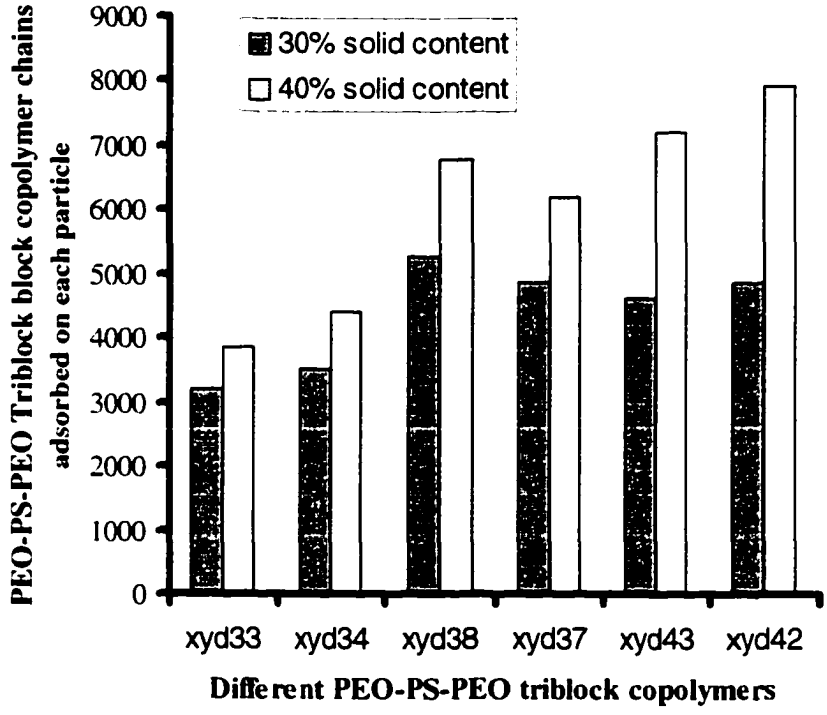


Figure 3.26: Effect of monomer concentration on the adsorbed portion of PEO-PS-PEO triblock copolymer on each latex particle

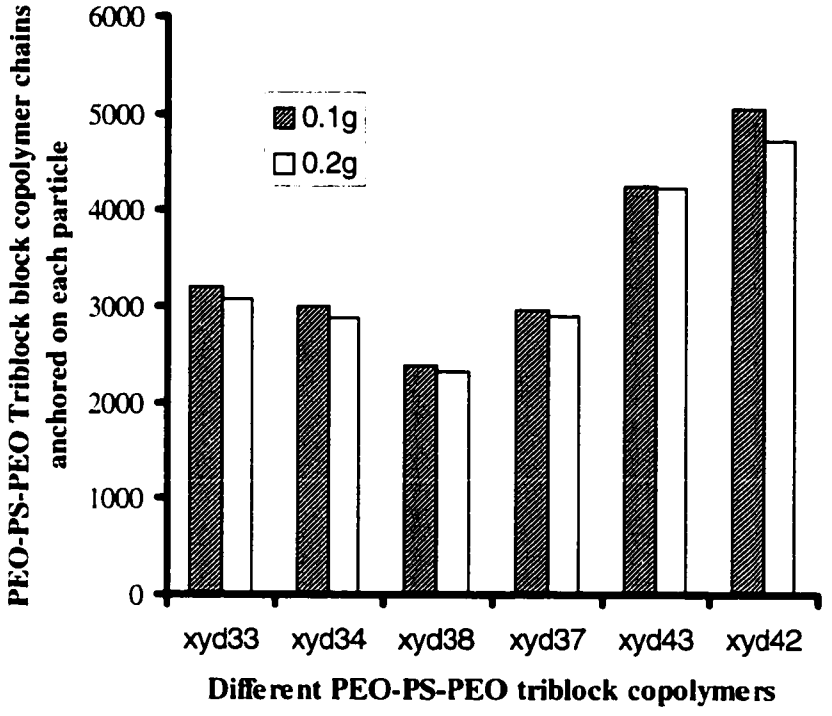


Figure 3.27: Effect of monomer concentration on the anchored amount of PEO-PS-PEO triblock copolymer on each latex particle

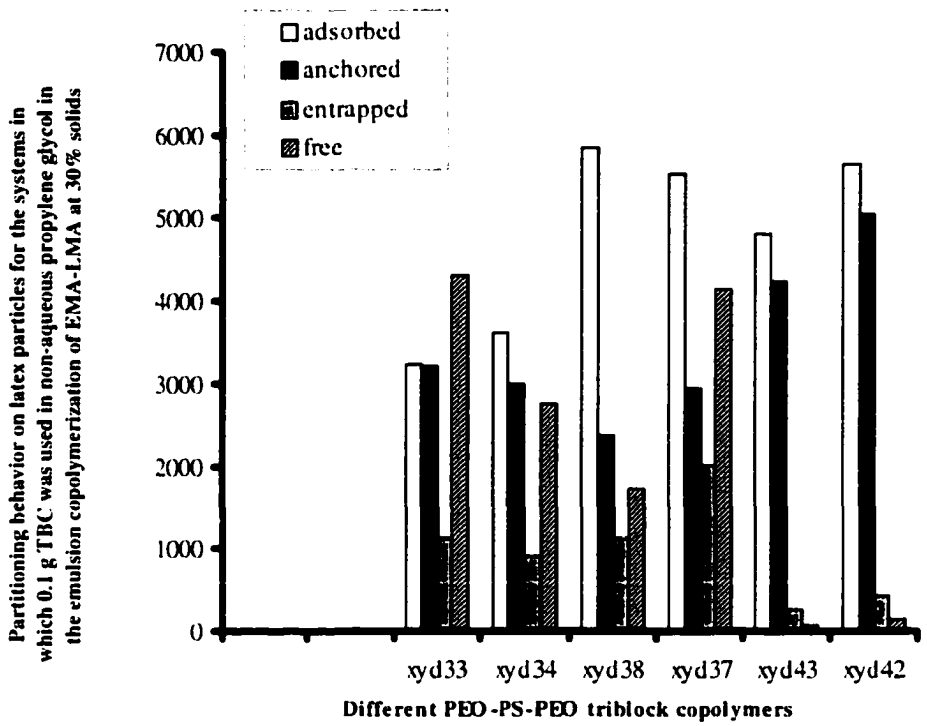


Figure 3.28: Partitioning behavior of different PEO-PS-PEO triblock copolymers (TBC) on latex particles for the systems in which 0.1 g TBC was used in non-aqueous propylene glycol in the emulsion copolymerization of EMA-LMA at 30% solids.

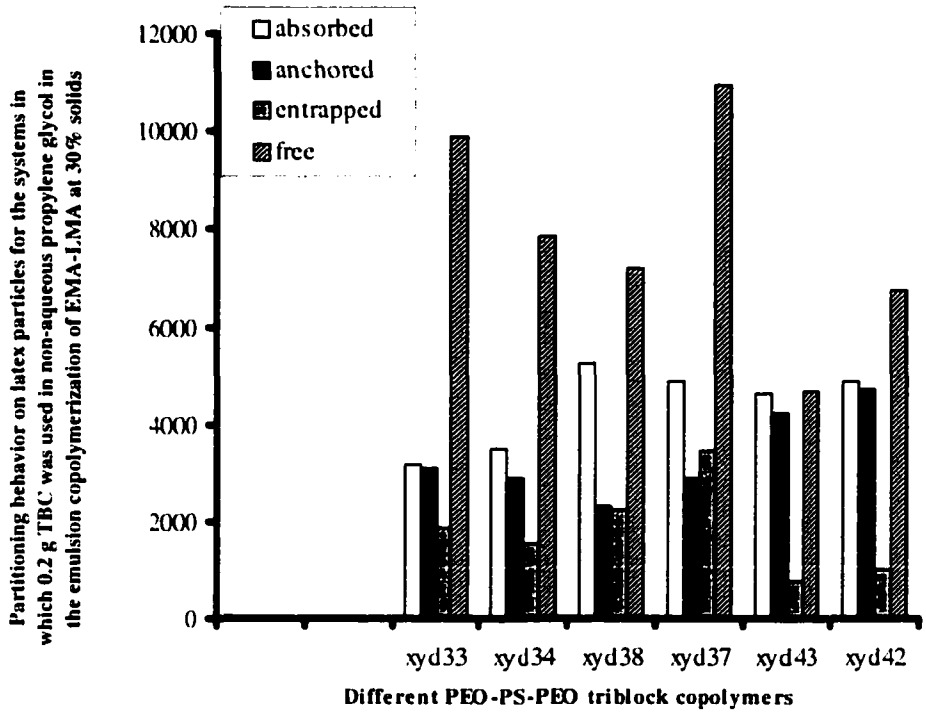


Figure 3.29: Partitioning behavior of different PEO-PS-PEO triblock copolymers (TBC) on latex particles for the systems in which 0.2 g TBC was used in non-aqueous propylene glycol in the emulsion copolymerization of EMA-LMA at 30% solids.

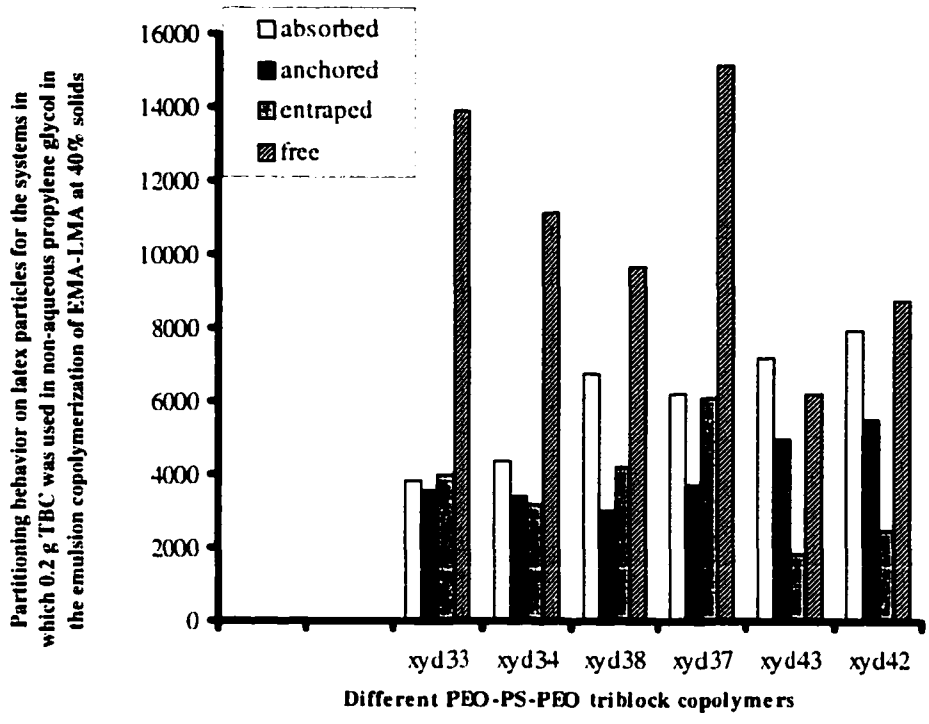


Figure 3.30: Partitioning behavior of different PEO-PS-PEO triblock copolymers (TBC) on latex particles for the systems in which 0.2 g TBC was used in non-aqueous propylene glycol in the emulsion copolymerization of EMA-LMA at 40% solids.

3.4 Summary

A non-aqueous emulsion polymerization model system was proposed for evaluating the performance of well-defined PEO-PS-PEO triblock copolymers as stabilizer. This model system contains five ingredients, ethyl methacrylate and lauryl methacrylate are the monomers, 2,2'-azobis(isobutyronitrile) (AIBN) is the initiator, propylene glycol is the continuous phase, and the PEO-PS-PEO triblock copolymer is the only stabilizer.

Due to the high solubility of ethyl methacrylate and lauryl metharylate in propylene glycol (5wt%), homogeneous nucleation is anticipated during the entire emulsion polymerization process.

Both the influence of PEO blocks and the PS blocks were studied as a function of structural variations. To be an effective stabilizing group, the molecular weight of the PEO blocks should be in the range of 5300-7700. For the anchor group, the molecular weight of the PS block should be between 2000 and 4000. In this range, stable latexes were formed.

In order to understand the mechanism of PEO-PS-PEO triblock copolymer as stabilizer in a model non-aqueous emulsion polymerization system consisting of ethyl methacrylate (EMA) and lauryl methacrylate (LMA) comonomers, a method was developed to measure the adsorption of PEO-PS-PEO triblock copolymer on latex particles. The PEO-PS-PEO triblock copolymer could be found at four different locations in the latex system: (1) entrapped inside the copolymer particles; (2) anchored to the surface of the copolymer particles; (3) physically adsorbed onto the particles; and (4) as "free" triblock copolymer in the propylene glycol continuous phase. The location of the triblock copolymers was determined *via* I_2 titration of the serum (obtained from a serum

replacement cell), the clean latex and a supernatant (obtained by centrifugation of the latex).

A minimum was observed in the amount of PEO-PS-PEO triblock copolymer that was physically adsorbed on the latex particles for a PS block length of about 30 units. When the PS block size is increasing up to 30 units, adsorption is decreased due to the rearrangement of mixed PEO brush and adsorbed PS block. When the PS block length is greater than 30 units, adsorption is increased again since the PS swollen core prefers to remain on the particle surface as opposed to desorbing into the propylene glycol medium. Also, the lower limit for the PS unit length is controlled by the binding energy between the PS block and the latex surface. The upper limit of the PS block length is governed by the solubility of the PS block in propylene glycol.

The amount of PEO-PS-PEO, which is anchored onto the latex particle surface, increases monotonically with the PS block length by virtue of a greater binding energy for longer PS unit lengths.

It has been found that both the physically adsorbed and anchored molecules decreased with increasing stabilizer concentration. On the other hand, when the monomer concentration was increased, the physically adsorbed molecules as well as the anchored molecules increased.

Polynomial equations were derived for calculating the total PEO-PS-PEO triblock copolymer chains needed for providing stabilization. These equations could be used for calculating the stabilizing capabilities of PEO-PS-PEO triblock copolymers.

3.5 References

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Chapter 4

Kinetics Study of Emulsion Copolymerization In Non-Aqueous System

4.1 Introduction

Classical emulsion polymerization involves three intervals. During interval I, the particle formation is generally completed. In interval II, the monomer droplets disappear from the continuous phase. The particle volume increases as the polymerization proceeds, and the particle number is kept constant. The monomer concentration in the particles remains constant. Interval III begins when the monomer phase separate disappears. The initial conversion of polymerization in interval I depends on the type of monomers. Generally speaking, particle nucleation involves three different mechanisms, which include micellar, homogeneous, and droplet nucleation. All these mechanisms may compete and coexist in the same system. However, one mechanism usually dominates at a given time in most cases.

The smith-Ewart theory[1] is the generally accepted starting point for kinetic studies. It is the quantification of the Harkins[2] micellar theory. Based on this theory, the rate of polymerization (Rp) at any instant can be expressed as equation (1):

$$Rp=kp\cdot[M]\cdot[P\bullet] \quad (1)$$

Where [P•] is the concentration of active particles, containing a free radical;

[M] is monomer concentration in the particle.

The concentration of active particles [P•] can be represented as equation (2):

$$[P\bullet]= [10^3\cdot N'\cdot \bar{n}]/N_A \quad (2)$$

Where N' is the concentration of micelles plus particles;

$\bar{n}$ is the average number of radicals per micelle plus particle;

N_A is the Avogadro number.

Insert equation (2) into (1),

$$Rp = [10^3 \cdot N' \cdot \bar{n} \cdot kp \cdot [M]] / N_A \quad (3)$$

At the commencement of interval I, $\bar{n}$ is zero. So, the product of $N' \cdot \bar{n}$ is zero. During interval I, the product of $N' \cdot \bar{n}$ increases with time by reason of the increasing $\bar{n}$ despite N' is decreasing.

At the starting point of interval II, N' has reached its steady-state value N. $\bar{n}$ remains approximately constant. The equation (3) is equal to equation (4):

$$Rp = [10^3 \cdot N \cdot \bar{n} \cdot kp \cdot [M]] / N_A \quad (4)$$

The value of $\bar{n}$ in interval II is the key factor to determine the rate of polymerization. Three cases can be classified as case 1, case 2, and case 3. The main difference between the three cases are the probability of radical desorption, the particle size, manner of termination, and the rates of initiation and termination relative to each other and to the other reaction parameters.

Case 2 is the most often used case, as it describes styrene emulsion polymerization. If the absorption of the radicals in the particles is much higher than the desorption of radicals, and particle size is too small to accommodate more than one radical, then the radical located inside the particle will continue the propagation until it is terminated by the entry of another radical. Hence, half of the polymer particles contain one radical and are growing while the other half are inactive in the overall system. In this case, the average number of radicals per particle $\bar{n}$ is 0.5.

In case 1, the radical desorption from the particles and termination in the continuous phase are relative high. Consequently, the average number of radicals per particle is less than 0.5.

In case 3, if the particle size is large or the termination rate constant is low, some of the polymer particles contain two or more radicals per particle. The average number of radicals per particle is larger than 0.5.

The quantitative treatment of the particle number as a function of emulsifier concentration, initiation, and polymerization rates were also developed according to the Smith-Ewart theory. The number of particles (N) depends on the total surface area of surfactant ($a_s \cdot S$), which is available for particle stabilization. This is the product of the interfacial surface area occupied by a surfactant molecule on the particle surface and the total concentration of surfactant in the system. The location of the surfactant involves micelles, solution and monomer droplets. The number of particles depends on the rate of radical generation (Ri).

The predicted dependence of N on ($a_s \cdot S$) and Ri for the formation of polymer particles varies with the nucleation mechanism. For micellar nucleation, N is given by equation (5):

$$N = k \cdot (Ri/\mu)^{0.4} \cdot (a_s \cdot S)^{0.6} \qquad (5)$$

where μ is the rate of volume increase of a polymer particle, which can be determined from r_p and geometric considerations;

a_s is the interfacial surface area occupied by a surfactant molecule;

S is the total concentration of surfactant in the system (micelles, solution, and monomer droplets);

Ri is the rate of radical initiation;

k is between 0.37 and 0.53. The value of k depends on the relative efficiencies of radical capture by micelles versus polymer particles and physical properties of the particles.

If coagulation is considered during the particle formation process, the particle number can be expressed by equation (6):

$$N \propto Ri^{0.4} S^{0.4\text{-}1.2} \qquad (6)$$

Smith-Ewart theory has been successful in describing the particle formation process for monomers with low water solubility. Nonetheless, large discrepancies exist in the more water-soluble monomer system such as vinyl acetate.

Another important particle creation mechanism is homogeneous nucleation, which the initiator radical propagates in the continuous phase to form an oligomer. These oligomers grow until they reach insolubility and then collapse and form the nucleus for the new particles. This theory was proposed by Fitch and co-workers [4]. Fitch and Tsai applied this theory to the emulsion polymerization of methyl methacrylate, for which homogenous particle formation is dominant. The experimental results had reasonably good correlation with the theoretically predicted data.

A homogeneous process can also be treated as a chain reaction, which was proposed by several researchers [5-9]. Each chain has its own probability for propagation, termination, and absorption. New particles are formed by the most probable mechanism.

No quantitative treatment has been available for the mixed-micelle nucleation mechanism, due to the complex interfacial interactions in the system. Several models[10-11]

have been developed for a given particular system, which requires modifications in general for applying them to other emulsion polymerization systems.

Particle formation *via* initiation in the monomer droplets is not usually the dominating particle nucleation mechanism as the absorption rate of radicals into the droplets is low. However, it can become an important particle formation source when the monomer droplets are made very small such as in miniemulsions.

The course of emulsion polymerization depends on the solubility of monomers in the medium [12-17]. When the monomers are insoluble in the solvent, the polymerization rate can sometimes surpass the mass transfer rate of the monomer, which renders the polymerization diffusion controlled. The viscosity within the particles is increasing throughout the process of the reaction.

In the previous three chapters, sixteen well-defined and narrow molecular weight distribution PEO-PS-PEO triblock copolymers were synthesized by an anionic polymerization process. The stabilizing efficiency of these sixteen PEO-PS-PEO triblock copolymers was examined in a model non-aqueous emulsion copolymerization system, using propylene glycol, ethyl methacrylate and lauryl methacrylate as monomers, 2,2'-azobis(isobutyronitrile) (AIBN) as free radical initiator, and the PEO-PS-PEO triblock copolymer was the sole stabilizer.

Among these PEO-PS-PEO triblock copolymers, only six of them gave stable latexes. The rest of them could not generate a latex at all. For the purpose of fully understanding the mechanism of emulsion copolymerization and gaining better control of the emulsion copolymerization process, it is crucial to investigate important parameters

such as particle size, particle number, surface coverage by the stabilizer, and polymerization rate during the entire emulsion copolymerization process.

The current system is analogous to emulsion polymerization using highly water-soluble monomers. Ethyl methacrylate and lauryl methacrylate have relatively high solubility (5%) in propylene glycol. Homogeneous nucleation therefore plays an important role in this non-aqueous emulsion polymerization. It can be predicted that the kinetic behavior of emulsion copolymerization of ethyl methacrylate / lauryl methacrylate in propylene glycol would deviate from the traditional Smith-Ewart theory, which was proposed based on water-insoluble monomers.

The purpose of the present work is to study the kinetics of the batch emulsion copolymerization of ethyl methacrylate / lauryl methacrylate in propylene glycol. The effect of stabilizer, initiator concentration, monomer concentration on the particle size, rate of polymerization, and surface coverage were investigated. All of these studies focus on the mechanistic aspects of emulsion polymerization and mathematical modeling is beyond the scope of this research.

4.2 Experimental

4.2.1 Materials

Ethyl methacrylate (EMA) (99%, Aldrich Chemical Company, Inc.) and lauryl methacrylate (LMA) (96%, Aldrich Chemical Company, Inc.) were used as monomers. They were purified by passing through the inhibitor-removal columns (HQ, or MEHQ) (Aldrich Chemical Company, Inc.).

All other materials were used as received, including propylene glycol (99.5+%, A.C.S. reagent, Aldrich Chemical Company, Inc.), 2,2'-azobis(isobutyronitrile) (AIBN) (98 %, Aldrich Chemical Company, Inc.), and hydroquinone (99%, Aldrich Chemical Company, Inc.). PEO-PS-PEO triblock copolymers were synthesized according to the method described in Chapter 2.

4.2.2 Emulsion Copolymerization In Non-Aqueous Model System

The emulsion polymerization of ethyl methacrylate / lauryl methacrylate were carried out in a non-aqueous model system at 60°C for a period of twenty-four hours. A small glass vial (16 mL) was charged with desired amount of propylene glycol, 2,2'-azobis(isobutyronitrile) (AIBN), PEO-PS-PEO triblock copolymers and magnetic stir bar. Ethyl methacrylate and lauryl methacrylate were mixed well in a separate beaker and poured into the small glass vial which contained the mixture of propylene glycol, 2,2'-azobis(isobutyronitrile) (AIBN), PEO-PS-PEO triblock copolymers and magnetic stir bar. The small glass vial was purged with nitrogen, capped, sealed, and placed in the 60°C constant water bath with continuous stirring.

4.2.2.1 Effect of Stabilizer Concentration

The recipe for studying the effect of stabilizer concentration is given in Table 4.1. The variable is the amount of the stabilizer. The conversion-time curve was measured *via* a dilatometry method and a gravimetric method. The dilatometer was filled with a mixture of monomers (ethyl methacylate and lauryl methacrylate), initiator (AIBN), PEO-PS-PEO triblock copolymer, and propylene glycol to a point where part of the capillary was filled and the assembly was immersed in a 60 °C constant bath. The

Table 4.1: Recipe for studying effect of stabilizer concentration

Ingredient	Amount (g)
Propylene Glycol(g)	**3.41**
xyd33(g)	**0.10-0.15-0.20**
Ethyl methacrylate (g)	**0.87**
Lauryl methacylate (g)	**0.63**
AIBN (g)	**0.07**

AIBN: 2,2'-azobis(isobutyronitrile)

capillary height was measured at regular time intervals during the polymerization. The reaction mixture is degassed before transferring into the dilatometer in order to prevent air bubble formation during the polymerization.

A drop of solution was withdrawn from the mixture (a separate vial) at regular intervals and added to 1 mL of 1% hydroquinone / propylene glycol solution. The sample was placed in an ice bath for measuring the conversion by means of gravimetric methods, and the particle size through the light scattering method (Nicomp 370).

4.2.2.2 Effect of Initiator Concentration

The recipe for studying the effect of initiator concentration is given in Table 4.2. The variable is the amount of the initiator. The conversion-time curve was measured *via* a dilatometry method and a gravimetric method. Again, the reaction mixture, which contains monomers (ethyl methacylate and lauryl methacrylate), initiator (AIBN), PEO-PS-PEO triblock copolymer, and propylene glycol, was degassed and filled into the dilatometer. Then, the assembly was placed in a 60 °C constant bath. The capillary height was measured at regular time intervals during the polymerization.

A small sample was withdrawn from the same mixture at regular intervals, terminated with 1 mL 1% hydroquinone / propylene glycol solution, and placed in ice for measuring the conversion by means of gravimetric methods, and particle size through the light scattering method (Nicomp 370).

Table 4.2: Recipe for studying effect of initiator concentration

Ingredient	Amount (g)
Propylene Glycol(g)	**3.41**
xyd33(g)	**0.10**
Ethyl methacrylate (g)	**0.87**
Lauryl methacylate (g)	**0.63**
AIBN (g)	**0.07-0.055-0.04**

AIBN: 2,2'-azobis(isobutyronitrile)

4.2.2.3 Effect of Monomer Concentration

The recipe for studying the effect of monomer concentration is given in Table 4.3. The variable is the amount of the monomers. The conversion-time curve was measured *via* a dilatometry method and a gravimetric method. Once again, the dilatometer was charged with monomers (ethyl methacylate and lauryl methacrylate), initiator (AIBN), PEO-PS-PEO triblock copolymer, and propylene glycol. Then, the assembly was placed in a 60 °C constant bath. The capillary height was measured at regular time intervals during the polymerization.

A small sample was taken from the same mixture at regular intervals. The polymerization was stopped with 1 mL 1% hydroquinone / propylene glycol solution and cold condition. The conversion was measured by gravimetric methods, and particle size was determined *via* the light scattering method (Nicomp 370).

4.2.3 Seeded Polymerization

Seed latex (1 mL) was made using the recipe in Table 4.1. The stabilizer was xyd33 (69PEO-29PS-69PEO) and the amount used was 0.2g. The emulsion polymerizations of ethyl methacrylate / lauryl methacrylate were carried out in a non-aqueous model system at 60°C for a period of eight hours. The recipe for the seeded polymerization is given in Table 4.4. A small glass vial (16 mL) was charged with the desired amount of propylene glycol, 2,2'-azobis(isobutyronitrile) (AIBN), seed latex, PEO-PS-PEO triblock copolymers, and magnetic stir bar. Ethyl methacrylate and lauryl methacrylate were mixed well in a separate beaker and poured into the small glass vial

Table 4.3: Recipe for Studying Effect of Monomer Concentration

Ingredient	Amount (g)
Propylene Glycol(g)	**3.67-3.41-2.80**
xyd33(g)	**0.20**
Ethyl methacrylate (g)	**0.57-0.87-1.15**
Lauryl methacylate (g)	**0.41-0.63-0.85**
AIBN (g)	**0.07**

AIBN: 2,2'-azobis(isobutyronitrile)

Table 4.4: Recipe for Seeded Polymerizations

Ingredient	Amount (g)
Propylene Glycol	3.41
PEO-PS-PEO triblock copolymer	0-0.1-0.2
Ethyl methacylate (EMA)	0.87
Lauryl methacrylate (LMA)	0.63
Seed latex*	1 ml
AIBN**	0.07

* Seed latex was made using the recipe in Table 4.1. The stabilizer was xyd33 (69PEO-29PS-69PEO) and the amount used was 0.2g.

****AIBN:** 2,2'-azobis(isobutyronitrile)

which contained the mixture of propylene glycol, 2,2'-azobis(isobutyronitrile) (AIBN), seed latex, PEO-PS-PEO triblock copolymers, and magnetic stir bar. The small glass vial was purged with nitrogen, capped, sealed and placed in the 60°C constant temperature water bath with continuous stirring.

The variable in this series of experiments was the amount of stabilizer (xyd33). Three emulsion copolymerizations were studied with the amount of stablizer which ranged from 0, 0.1 g, and 0.2 g. Sample was withdrawn every two hours, and the reaction was terminated with 1 mL 1% of cold hydroquinone/propylene glycol solution. The particle size and distribution were measured through a light scattering method. The experimental results are summarized in Table 4.5.

4.2.4 Monomer Partitioning Behavior in the Latex

Latex sample (1g), comprised of 29.96 wt% poly (ethyl methacrylate-co-lauryl methacrylate), 3.86 wt% PEO-PS-PEO triblock copolymer (xyd33), and 65.83 wt% propylene glycol, was mixed with 0.5 g of the monomer mixture (weight ratio of EMA to LMA was 0.87:0.63). The ratio of the two monomers is the same as that used before. The mixture was stirred for 24 hours, and then centrifuged. The top layer (supernatant) consists of propylene glycol and monomers. The bottom layer consists of swollen polymer. Both layers were separated, weighed, and the partitioning of the monomers in the polymer was calculated. The flow chart of the above experimental process and the result obtained is illustrated in Figure 4.1. As seen in this Figure, 90% of the monomer prefers the continuous medium.

Table 4.5: Experimental Results of Seeded Polymerizations

Concentration of stabilizer (g)	0	0.1	0.2
Particle size distribution (<2h)	Coagulum	Bimodal	Bimodal
Particle size distribution (>4h)	Coagulum	Single Peak	Single Peak

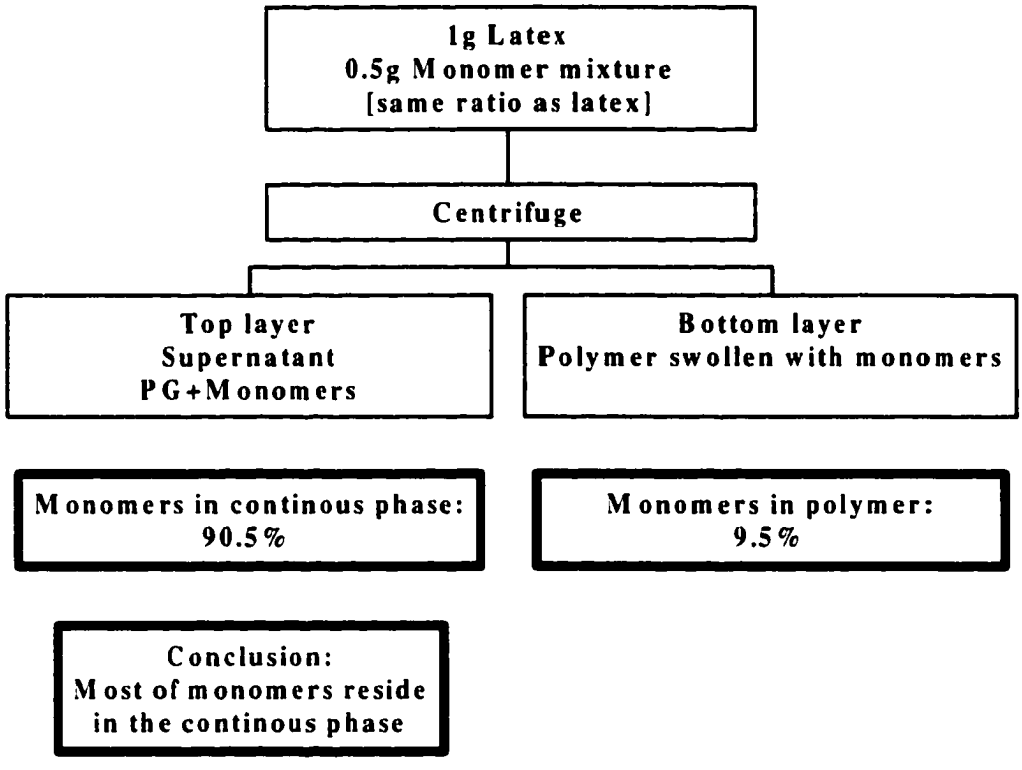


Figure 4.1: Flow chart of the experimental process for measuring monomer partitioning behavior.

4.3 Results and Discussion

4.3.1 Effect of Stabilizer Concentration

The emulsion copolymerizations of ethyl methacrylate/lauryl methacrylate were carried out according to the recipe given in Table 4.1. In the recipe, the variable is the amount of stabilizer, which was changed as follows: 0.10g (1.97wt%), 0.15g (2.92wt%), and 0.20g (3.86 wt%) respectively. The conversion-time curve was measured by means of dilatomery, which takes advantage of the density differences between monomers and their polymers.

Two effects should be accounted for the initial movement of the meniscus in the capillary. They include: (1) thermal expansion of the monomers; (2) contraction due to polymerization. After 5-8 minutes the meniscus height change by reason of the thermal expansion of monomers becomes negligible. Any further change is on account of the polymerization. Since the capillary cross sectional area is known, the volume as a function of length is easily computed. Thus the slope of a plot of meniscus height *vs.* time ($\Delta H/\Delta t$) can easily be converted to a volume to give $\Delta V/\Delta t$. This is shown in detail in Appendix IV.

The effect of stabilizer concentration on conversion of emulsion polymerization is shown in Figure 4.2. It can be seen that the initial rate of polymerization is independent of stabilizer concentration initially (up to 8% conversion), but slightly dependent on stabilizer concentration at high conversions.

The high solubility of ethyl methacrylate and lauryl methacrylate in propylene glycol suggests that homogeneous nucleation is the dominant mechanism. The loci of nucleation are in the medium instead of the monomer micelles. In the beginning of the

polymerization, free radicals initiate the monomers in the propylene glycol to form oligomeric radicals. These oligomers keep propagating until reaching their critical precipitation length. At that time, PEO-PS-PEO triblock copolymer adsorbs on these oligomeric chains to form the particles. Therefore, the rate of polymerization has zero dependence on PEO-PS-PEO triblock copolymer stabilizer concentration at the start of the polymerization.

Figure 4.3 displays the effect of PEO-PS-PEO triblock copolymer stabilizer concentration on particle number density. Three regions are observed. In region I, the particle density decreases sharply at the beginning. Then, it declines gradually during region II. Finally, it reaches a steady state at the region III. The particle density was calculated based on the particle diameter, which was obtained via light scattering method. The effect of stabilizer concentration on final particle size and distribution is shown in Table 4.6.

Assuming the particle diameter is Dv

The volume of each particle V is equal to

$V=(\pi \cdot Dv^{3})/6$

If the density of polymer particle d is 1.19 g/ml,

The particle density N/cc is equal to:

$N/cc = \{([M] \cdot X)/d\}/[(\pi \cdot Dv^{3})/6]$

Where [M] is the monomer concentration;

X is the fraction conversion of polymerization;

d is density of polymer particles;

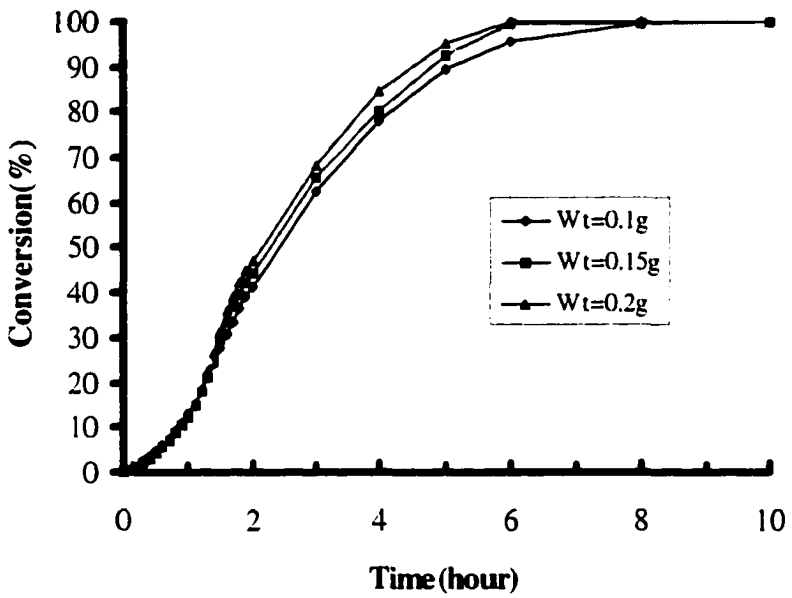
Dv is the particle volume average diameter;

Table 4.6: Effect of Stabilizer Concentration on Particle Size and Distribution

Stabilizer Concentration (g)	Dn (nm)	Dw (nm)	Polydispersity
0.10	**163**	**171**	**1.05**
0.15	**156**	**161**	**1.03**
0.20	**149**	**156**	**1.05**

*Dn: number average particle size

*Dw: weight average particle size



$$Ri \propto [E]^0$$

Figure 4.2: Conversion *vs.* time curves for the model EMA/LMA non-aqueous emulsion polymerization system showing the effect of the variation in the concentration of PEO-PS-PEO triblock copolymer stabilizer at 60° C.

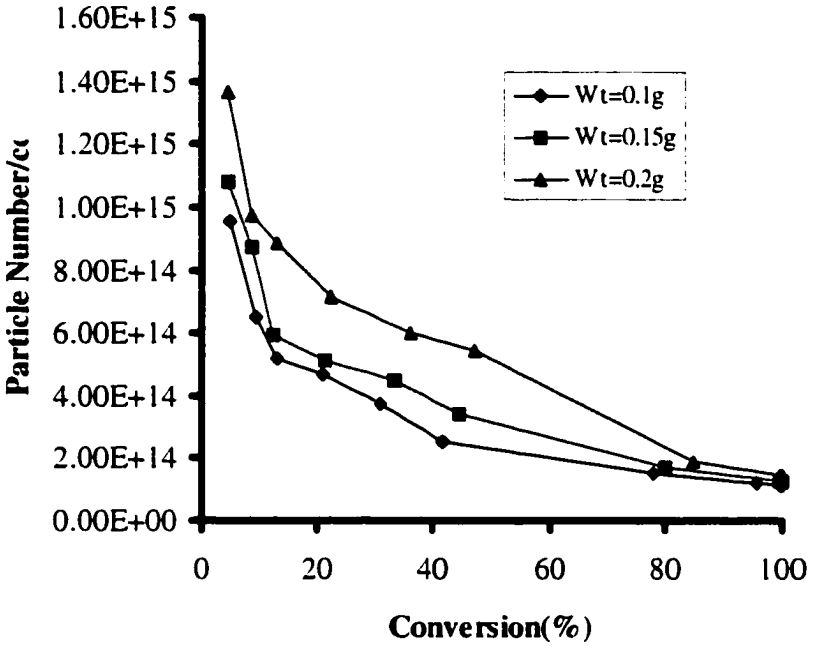


Figure 4.3: Particle density *vs.* conversion curves for the model EMA/LMA non-aqueous emulsion polymerization system showing the effect of the variation in the concentration of PEO-PS-PEO triblock copolymer stabilizer at 60° C.

N/cc is the particle number density.

At the early stage of the polymerization (region I), which is assisted with the homogeneous nucleation stage, the PEO-PS-PEO triblock copolymer stabilizer is initially adsorbed on the oligomeric polymers to form particles. The main feature of this interval is adsorption without rearrangement. The particle density is high due to the small particle nucleus requires less amount of PEO-PS-PEO triblock copolymer stabilizers.

During region II, the particle volume increases as polymerization proceeds. Additional PEO-PS-PEO triblock copolymer stabilizers are required for stabilization. This can be accommodated by a rearrangement of the PEO-PS-PEO triblock copolymer stabilizers on the surface. Thus the characteristics of region II is adsorption with rearrangement on primary particles.

The transition from region II to region III occurs when the maximum adsorbed amount of PEO-PS-PEO triblock copolymer stabilizers is reached. The net flux of adsorbed polymer is zero. However, a slow rearrangement of triblock copolymers on the particle surface is expected since the polymer arriving in region II has fewer attached PS segments on average per molecule than did the existing layer.

With high concentration of PEO-PS-PEO triblock copolymer stabilizer, more particles can be stabilized initially, but they must undergo limited flocculation to yield almost the same particle number at the end. Hence, the particle density still increases with the concentration of PEO-PS-PEO triblock copolymer stabilizer. It suggests 0.4 power dependence on stabilizer concentration (see Figure 4.4).

The effect of the concentration of PEO-PS-PEO triblock copolymer stabilizer on the total surface area is illustrated in Figure 4.5. From the particle diameter and particle density, the total surface area is determined. It can be expressed in the equation:

$S = \pi \times (Dv)^2 \times (N/cc)$

Where S is the total surface particle area;

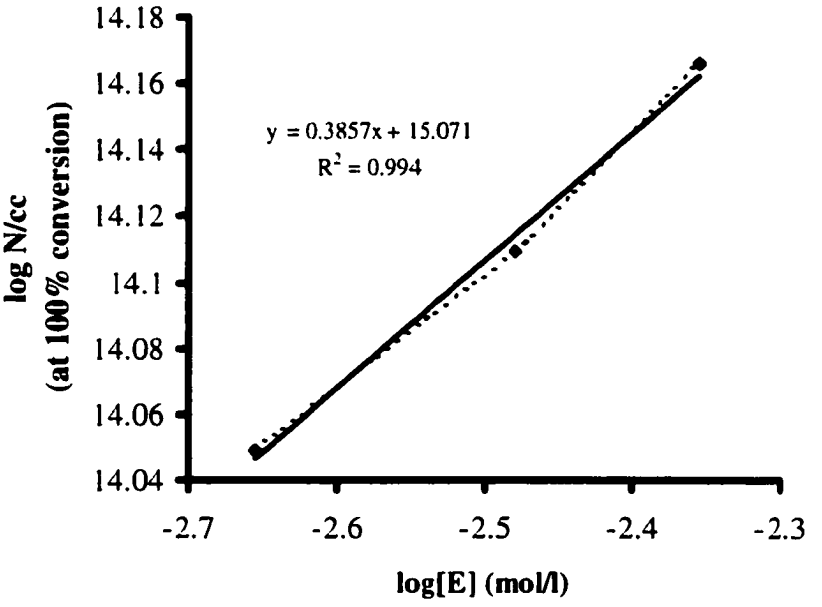
Dv is the average volume diameter;

N/cc is the particle number density.

The experimental results indicate that the total particle surface area increases until it reaches total conversion, despite the decreasing particle number density. This is because the particle growth rate is faster than the limited rate of flocculation. Thus more stabilizer molecules are required to provide steric stabilization on the particles, while the separate monomer phase is present. Once the separated monomer phase disappears, the particles should shrink in volume and decrease in area. This should increase the adsorbed stabilizer concentration and hence increase particle stability. Higher stabilizer concentration yields slightly larger total surface area. The 0.13 power dependence of the total surface area on the concentration of PEO-PS-PEO triblock copolymer is suggested experimentally (see Figure 4.6).

As expected, the particle size decreases with high concentration of PEO-PS-PEO triblock copolymers. It indicates (-0.13) power dependence on the stabilizer concentration (shown in Figure 4.7).

In summary, as the solubility of monomers in propylene glycol is relatively high (5%), homogeneous nucleation is the dominant mechanism in the beginning. At high stabilizer concentration, more particles are stabilized at the start. This accelerates the



$$Np \text{ -}[E]^{0.39}$$

Figure 4.4: Dependence of final particle number density *vs.* the concentration of PEO-PS-PEO triblock copolymer stabilizer for the model EMA/LMA non-aqueous emulsion polymerization system at 60° C.

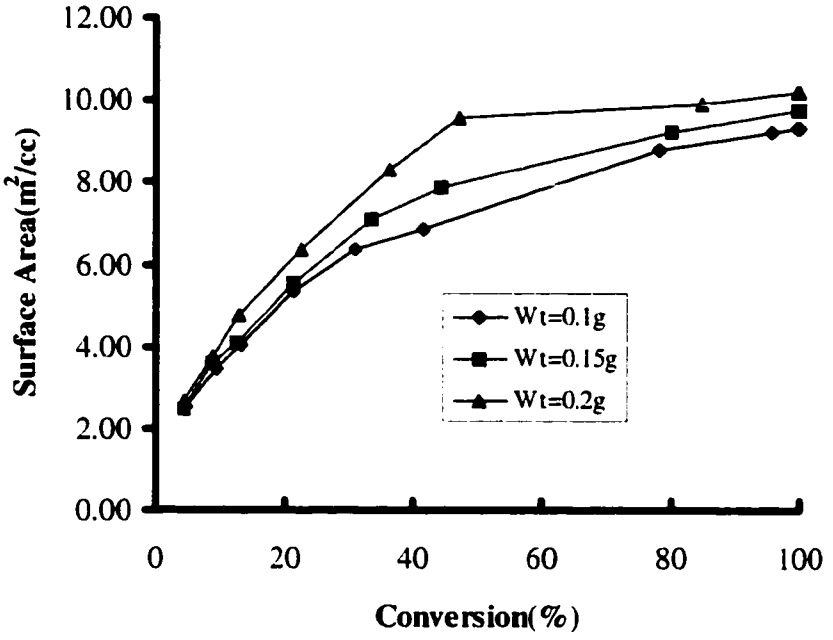
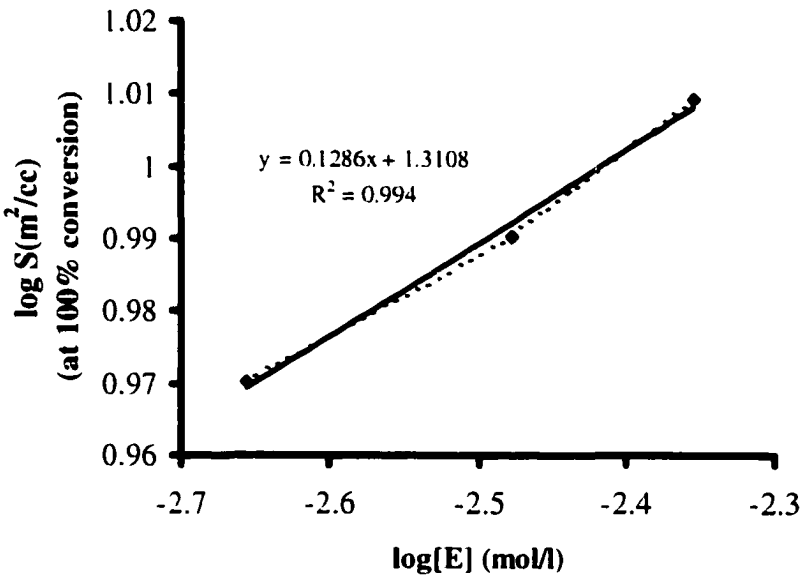
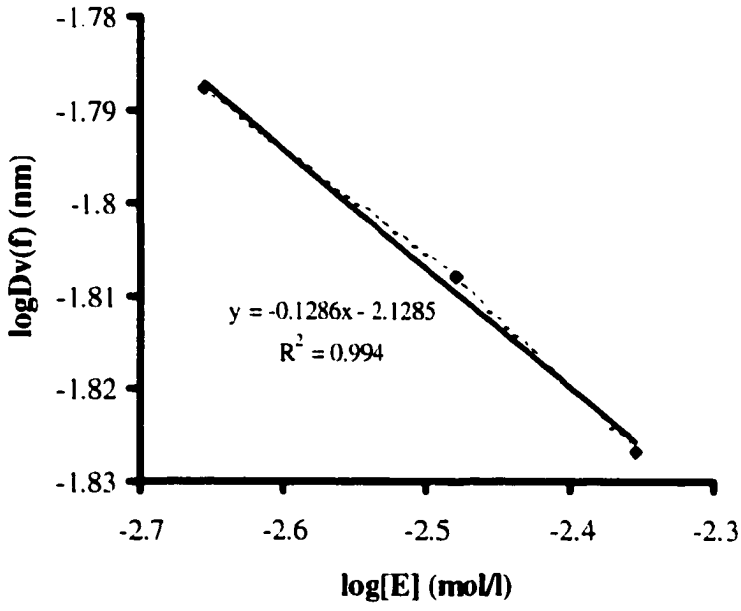


Figure 4.5: Total surface area *vs.* conversion curves for the model EMA/LMA non-aqueous emulsion polymerization system showing the effect of the variation in the concentration of PEO-PS-PEO triblock copolymer stabilizer at 60° C.



$$S\text{-}[E]^{0.13}$$

Figure 4.6: Dependence of the total surface area *vs.* the concentration of PEO-PS-PEO triblock copolymer stabilizer for the model EMA/LMA non-aqueous emulsion polymerization system at 60° C.



$$Dv\text{-}[E]^{-0.13}$$

Figure 4.7: Dependence of the particle size *vs.* the concentration of PEO-PS-PEO triblock copolymer stabilizer for the model EMA/LMA non-aqueous emulsion polymerization system at 60° C.

The effect of the concentration of PEO-PS-PEO triblock copolymer stabilizer on the total surface area is illustrated in Figure 4.5. From the particle diameter and particle density, the total surface area is determined. It can be expressed in the equation:

$S = \pi \times (Dv)^2 \times (N/cc)$

Where S is the total surface particle area;

Dv is the average volume diameter;

N/cc is the particle number density.

The experimental results indicate that the total particle surface area increases until it reaches total conversion, despite the decreasing particle number density. This is because the particle growth rate is faster than the limited rate of flocculation. Thus more stabilizer molecules are required to provide steric stabilization on the particles, while the separate monomer phase is present. Once the separated monomer phase disappears, the particles should shrink in volume and decrease in area. This should increase the adsorbed stabilizer concentration and hence increase particle stability. Higher stabilizer concentration yields slightly larger total surface area. The 0.13 power dependence of the total surface area on the concentration of PEO-PS-PEO triblock copolymer is suggested experimentally (see Figure 4.6).

As expected, the particle size decreases with high concentration of PEO-PS-PEO triblock copolymers. It indicates (-0.13) power dependence on the stabilizer concentration (shown in Figure 4.7).

In summary, as the solubility of monomers in propylene glycol is relatively high (5%), homogeneous nucleation is the dominant mechanism in the beginning. At high stabilizer concentration, more particles are stabilized at the start. This accelerates the

polymerization. As particles grow bigger, more stabilizer is required for each particle. However, the limited stabilizer amount is not enough to stabilize all the particles. Therefore, some will flocculate and surface coverage re-equilibrates in a dynamic sense. More surface coverage is achieved at the sacrifice of the particle number density. A faster polymerization rate and smaller particle size were obtained at higher stabilizer concentration. The particle number density was proportional to the 0.39 power of the stabilizer concentration. The particle surface coverage area was proportional to the 0.13 power of the stabilizer concentration. The final particle size was inversely proportional to the 0.13 power of the stabilizer concentration. The kinetic dependence on stabilizer concentration, which was obtained in this study, is in the range of the reported value [25] for emulsion polymerization of water-soluble monomers in aqueous medium. This implies the similarity between this model system with aqueous emulsion polymerization for water-soluble monomers.

4.3.2 Effect of initiator concentration

The emulsion copolymerizations of ethyl methacrylate / laury methacrylate were carried out based on the recipe described in Table 4.2. The amount of initiator was varied as follows: 0.04g (1.35wt%), 0.055g (1.36wt%), and 0.07g (1.38wt%), respectively. Figure 4.8 shows the effect of initiator on conversion. The rate of polymerization increases with increasing initiator concentration at low conversion. It is independent of the initiator concentration at high conversion. The initial rate of polymerization is proportional to the 0.5 power of the initiator concentration (see Figure 4.9). Particle number density increases with increasing initiator concentration in the beginning of the polymerization.

However, it is independent of the initiator concentration towards high conversion of polymerization. This is illustrated in Figure 4.10. Accordingly, the total surface area increases with rising initiator concentration at low conversion. The total surface area reaches the same value regardless of the initiator concentration used. Figure 4.11 reflects the effect of initiator concentration on the total surface area during the entire polymerization. The effect of initiator concentration on final particle size and distribution is shown in Table 4.7. As expected, the final particle size is independent of initiator concentration (see Figure 4.12).

The influence of initiator concentration on the kinetics of ethyl methacrylate / lauryl methacrylate emulsion polymerization in the non-aqueous propylene glycol medium can be explained by the general equation (1) for heterogeneous polymerization kinetics (Smith-Ewart case I kinetics):

$$Rp = kp[Mp]\{(\rho_A \times Vp)/2\ kt\}^{0.5} \qquad (1)$$

Where Rp is the rate of polymerization;

Mp is the monomer concentration in particle;

ρ_A is the rate of adsorption of oligomeric radicals by polymer particles;

Vp is the volume fraction of polymer particles in the system;

kp is the rate constant for propagation;

kt is the rate constant for termination.

The rate of adsorption of oligomeric radicals by the particles ρ_A can be given by diffusion theory. It determines the average number of radicals per particle.

$$\rho_A = 4\ \pi\ r\ Np \sum_{j=1}^{jcr-1} DjPj^* \qquad (2)$$

Table 4.7: Effect of Initiator Concentration on Particle Size and Distribution

Initiator Concentration (g)	Dn (nm)	Dw (nm)	Polydispersity
0.07	**163**	**171**	**1.05**
0.055	**163**	**173**	**1.06**
0.04	**163**	**171**	**1.05**

*Dn: number average particle size

*Dw: weight average particle size

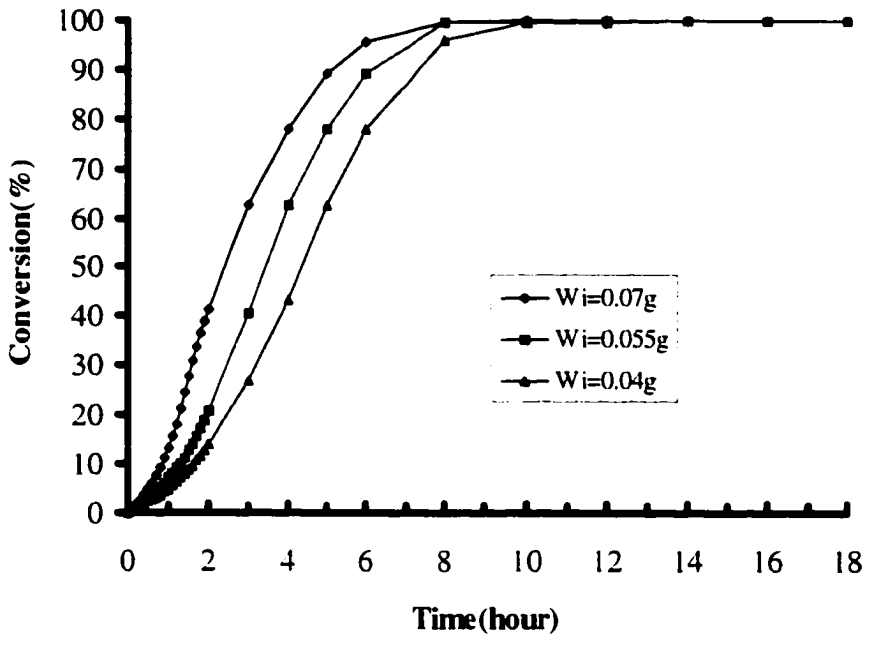
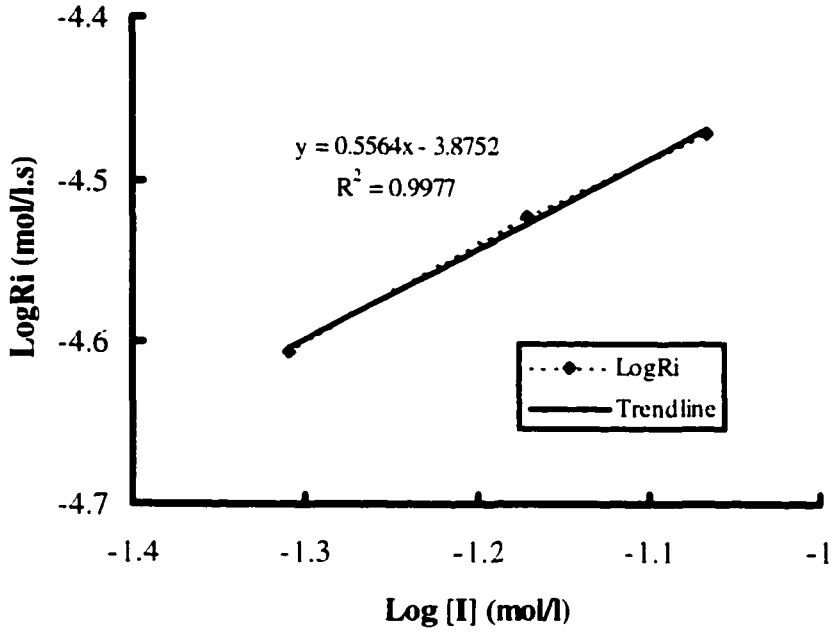


Figure 4.8: Conversion *vs.* time curves for the model EMA/LMA non-aqueous emulsion polymerization system showing the effect of the variation in the concentration of initiator (AIBN) at 60° C.



$$Ri \text{ -}[I]^{0.5}$$

Figure 4.9: Dependence of the initial rate of polymerization *vs.* the concentration of initiator (AIBN) for the model EMA/LMA non-aqueous emulsion polymerization system at 60°C.

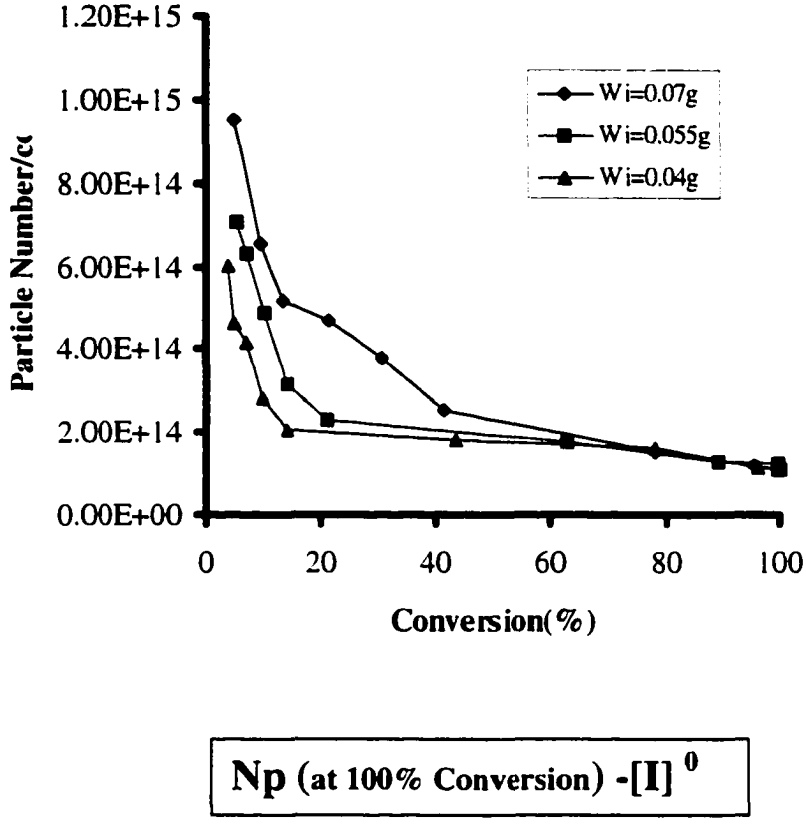
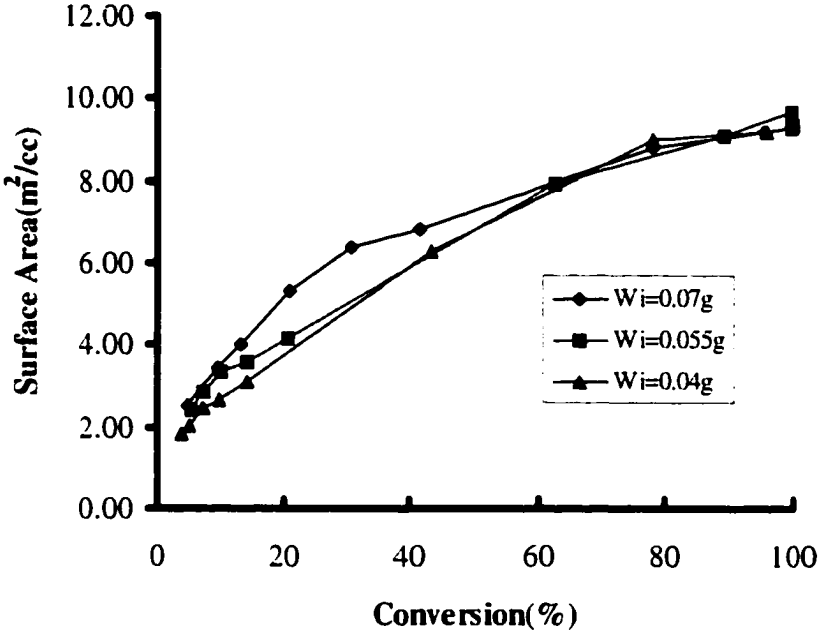


Figure 4.10: Particle density *vs.* conversion curves for the model EMA/LMA non-aqueous emulsion polymerization system showing the effect of the variation in the concentration of initiator (AIBN) at 60° C.



$$S \text{ (at 100\% Conversion)} - [I]^{0}$$

Figure 4.11: Total surface area *vs.* conversion curves for the model EMA/LMA non-aqueous emulsion polymerization system showing the effect of the variation in the concentration of initiator (AIBN) at 60° C.

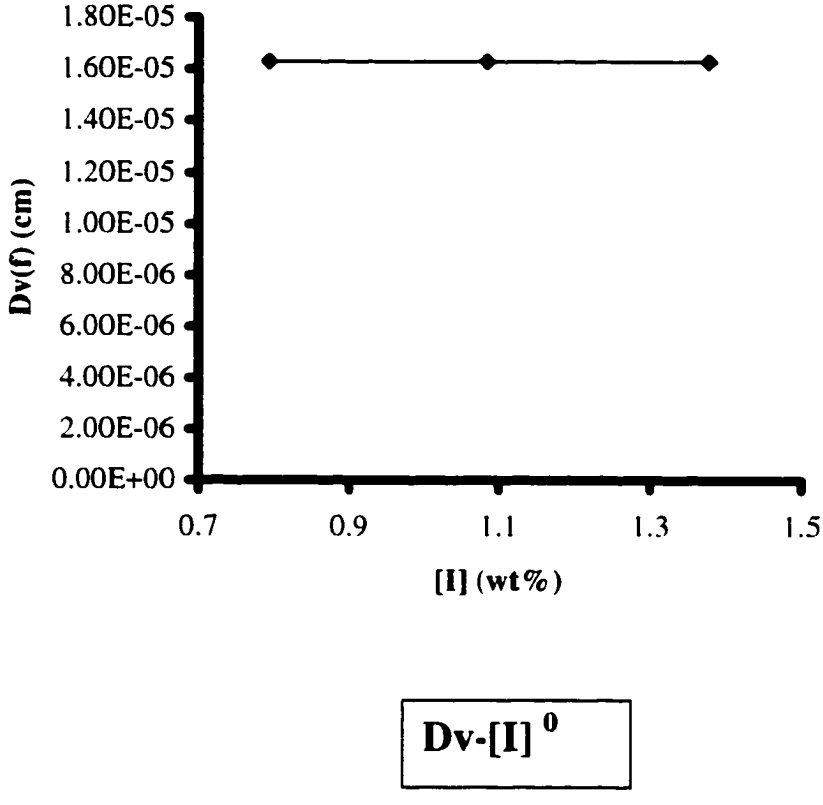


Figure 4.12: Dependence of the final particle size *vs.* the concentration of initiator (AIBN) for the model EMA/LMA non-aqueous emulsion polymerization system at 60°C.

Where r is the radius of monomer-swollen polymer particles;

Np is the particle number density;

Dj is the diffusion coefficient;

Pj* is concentration of oligomeric radicals of chain length j in the continuous phase.

Jcr is the critical length for oligomers to precipitate from the continuous phase.

At the same high conversion, the monomer concentrations in the polymer particles were identical when different initiator concentrations were used. The final particle size was independent of initiator concentration, thus, ρ_A is independent of initiator concentration. Consequently, the rate of polymerization is independent of initiator concentration at high conversion.

The particle number density and the final surface coverage were governed by limited coalescence, so they were independent of initiator concentration. Specifically, at low conversion, homogeneous nucleation dominates since monomers have high solubility in propylene glycol. The rate of polymerization, the particle density and the total surface area are dependent on initiator level. At high conversion, the heterogeneous polymerization mechanism becomes dominant. The rate of polymerization is the same due to the identical monomer concentration in each particle. The particle size, particle density and the total surface area are governed by the inherent nature of the PEO-PS-PEO triblock copolymers. Thus these factors are not affected by the initiator concentration. The kinetic dependence on initiator concentration, which was obtained in this study, is in the range of the reported value [25] for emulsion polymerization of water-soluble

monomers in aqueous medium. This further confirms the validity of the analogies between this model system with those of aqueous emulsion polymerization for water-soluble monomers.

4.3.3 Effect of Monomer Concentration

The same procedure was followed as before for the emulsion copolymerizations of ethyl methacrylate/laury methacrylate. The amount of ethyl methacrylate monomer concentration was varied as follows: 0.57g (11.59wt%), 0.87g (16.80wt%), and 1.15g (22.68 wt%) respectively. The corresponding changes in the amount of lauryl methacrylate monomer were: 0.41g (8.33 wt%), 0.63g (12.16wt%), and 0.85g (16.77 wt%). Figure 4.13 displays the effect of monomer concentration on conversion of emulsion copolymerization. The initial rate of polymerization is independent of monomer concentration. The rate of polymerization increases slightly with increasing monomer concentration in the high conversion region. The effect of monomer concentration on final particle size and distribution is shown in Table 4.8. The dependence of final particle size on monomer concentration is illustrated in Figure 4.14. Similarly, the particle number density decreases with increasing monomer concentration (see Figure 4.15) and is inversely proportional to the 2 power of the monomer concentration (see Figure 4.16). In the beginning of the polymerization, the total surface area decreases with increasing monomer concentration. At high conversion, it becomes independent of the monomer concentration. These facts are represented in Figures 4.17 and 4.18.

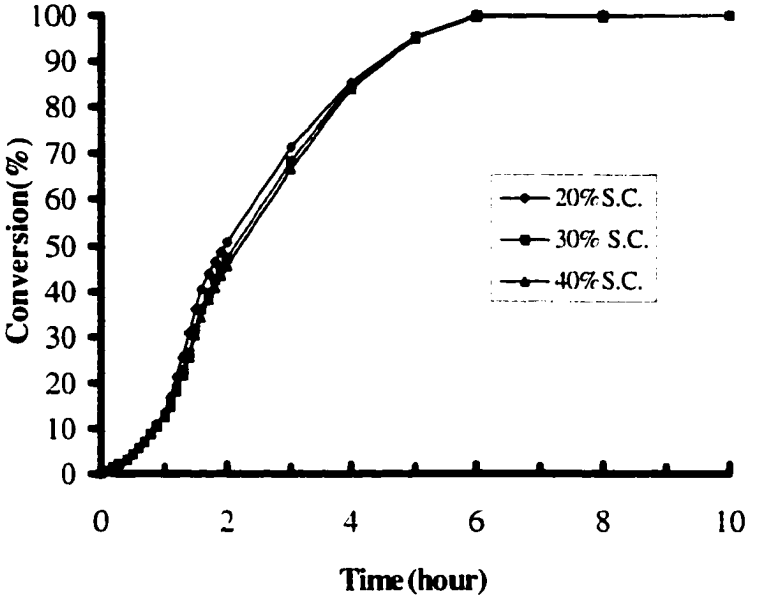
Since the nucleation starts in the propylene glycol medium, the initial rate of polymerization is determined by both the monomer concentration in the propylene glycol

Table 4.8: Effect of Monomer Concentration on Particle Size and Distribution

Monomer Concentration (%)	Dn* (nm)	Dw** (nm)	Polydispersity
20	**105**	**108**	**1.03**
30	**149**	**158**	**1.06**
40	**199**	**205**	**1.03**

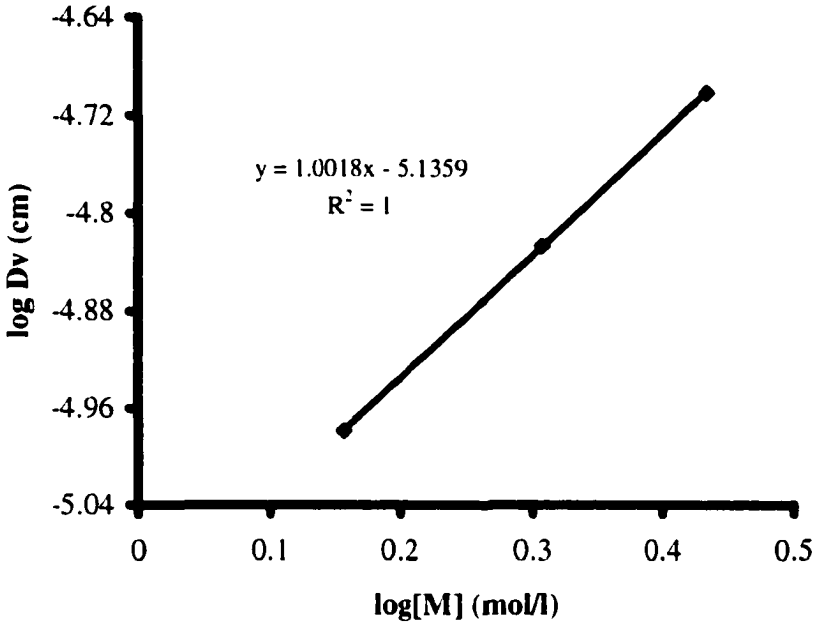
*Dn: number average particle size

**Dw: weight average particle size



Ri-$[M]^0$

Figure 4.13: Conversion *vs.* time curves for the model EMA/LMA non-aqueous emulsion polymerization system showing the effect of the variation in the monomers concentration at 60° C.



$$Dv \propto [M]$$

Figure 4.14: Dependence of the particle size *vs.* the monomers concentration for the model EMA/LMA non-aqueous emulsion polymerization system at 60° C.

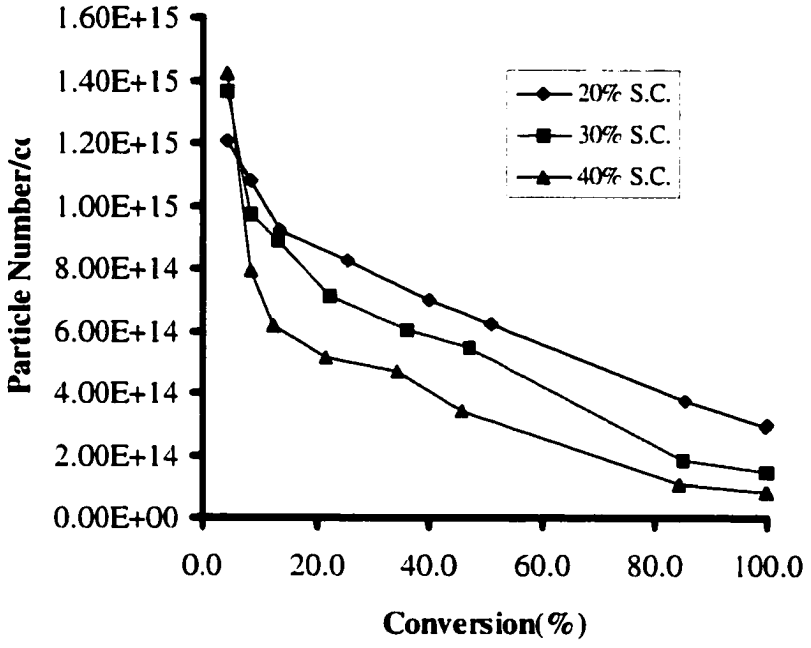


Figure 4.15: Particle number density *vs.* conversion curves for the model EMA/LMA non-aqueous emulsion polymerization system showing the effect of the variation in the monomers concentration at 60° C.

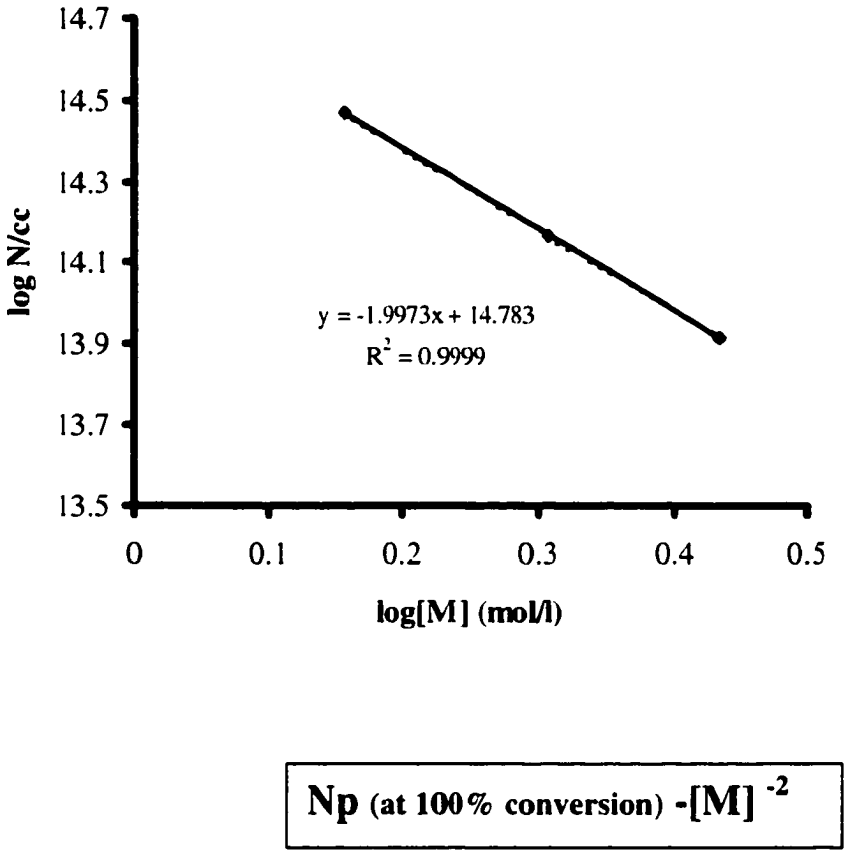


Figure 4.16: Dependence of the particle number density *vs.* the monomers concentration for the model EMA/LMA non-aqueous emulsion polymerization system at 60° C.

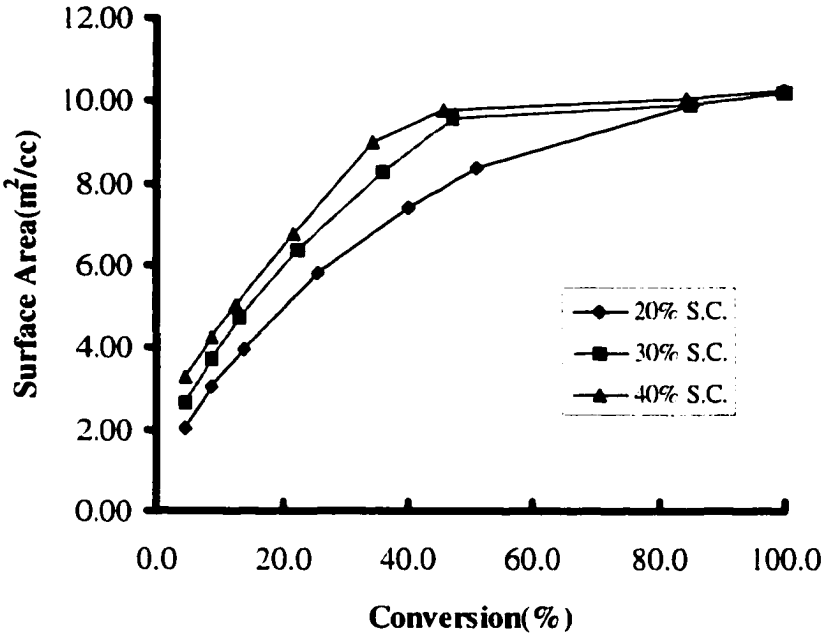
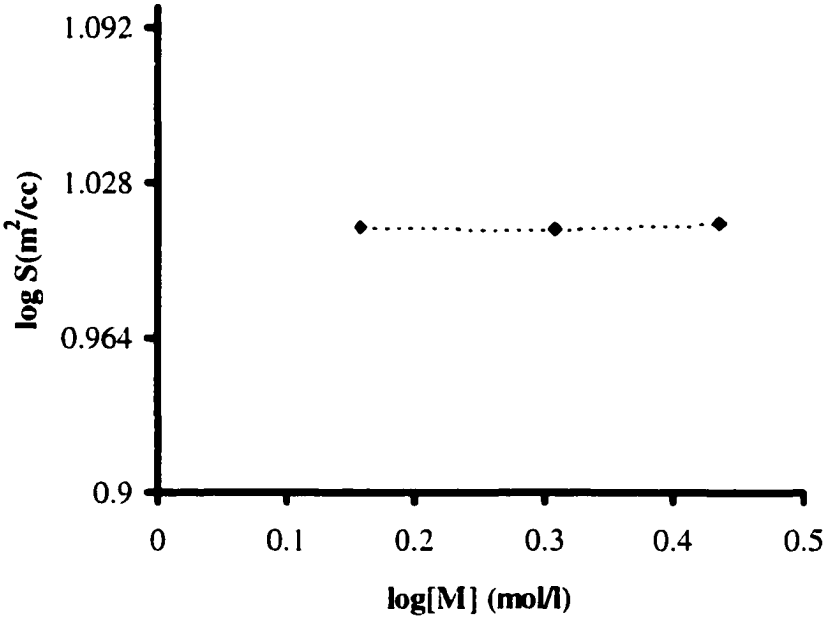


Figure 4.17: Total surface area *vs.* conversion curves for the model EMA/LMA non-aqueous emulsion polymerization system showing the effect of the variation in the monomers concentration at 60° C.



S (at 100% conversion) -$[M]^0$

Figure 4.18: Dependence of the total surface area *vs.* the monomers concentration for the model EMA/LMA non-aqueous emulsion polymerization system at 60° C.

and the initiator concentration in the medium. At the start of the polymerization, because the monomers (ethyl methacryiate and lauryl methacrylate) have limited solubility in propylene glycol, the actual monomer concentration in propylene glycol is the same regardless of the amount of monomers added to the reactor. The initial rate of polymerization would be the same if the same amount of initiator was in the reactor. As the polymerization proceeds, all the monomers are transported inside each particle. With higher monomer concentration, the particles are larger and the monomer concentration in each particle is greater. As a result, the rate of the polymerization is faster. This explains why the rate of polymerization is not affected by the monomer concentration at thc beginning, and increases slightly towards high conversion.

Due to the fixed amount of stabilizer in the reactor, the total surface area that can be stabilized in the system is restricted. As larger size particles have less surface area, lesser amount of the stabilizer is needed to provide steric stability. Since the particle density is inversely proportional to the 3 power of the particle diameter, the particle number density decreases with increasing monomer concentration. As the total surface area suggests 2 power dependency on particle diameter, it increases with monomer concentration in the early stage of the polymerization. However, the intrinsic properties of PEO-PS-PEO triblock copolymer determine the maximum surface area, which can be stabilized. Once the maximum surface area is reached, no more new particles can be stabilized. The PEO-PS-PEO triblock copolymers on the existing particles have to rearrange by means of reducing the particle number density and increasing particle diameter. Therefore, the total surface area is not controlled by monomer concentration at the end of the polymerization.

In summary, the pronounced effect of the monomer concentration on the polymerization is the influence on particle diameter. With high monomer concentration, larger particles are observed. Accordingly, the particle number density decreases with increasing monomer concentration. The total surface area is governed by the amount of PEO-PS-PEO triblock copolymers. Again, the kinetics dependence on monomer concentration, which was obtained in this study, is in range of the literature-reported data[25] for emulsion polymerization of water-soluble monomers in aqueous medium. This further suggests that this model system is similar to aqueous emulsion polymerization of water-soluble monomers.

4.3.4 Seeded Polymerization

This set of experiments was designed for providing experimental evidence to support the proposed homogeneous nucleation mechanism. The emulsion copolymerizations of ethyl methacrylate/laury methacrylate were carried out according to the recipe given in Table 4.4. The amount of PEO-PS-PEO triblock copolymers was varied as follows: 0g, 0.1g and 0.2g. The amount of seed was kept constant for all the experiments. The experimental results show that no stable latex can be generated without the participation of PEO-PS-PEO triblock copolymers. With the addition of a certain amount of the PEO-PS-PEO triblock copolymers, a stable latex can be made. The bimodal particle size distribution observed came from two possible sources: (1) existing seed particles; (2) new particles. Earlier the size of the newly generated particles is small when compared to the seed particles and two peaks are detected. This indicates that new particles are formed at the beginning. This demonstrates the effectiveness of

free radical capture of monomer molecules in solution. While monomer swollen particles will capture some of the radicals, new particles form by a homogeneous nucleation process.

4.3.5 Monomer Partitioning Behavior in the Latex

The monomer concentration in the polymer particles after swelling 1g of latex with 0.5 g of the monomer mixture is calculated as follows.

The amount of propylene glycol in 1g latex [W_{pg}] = (0.01) x 65.83 = 0.6583 g

The amount of solid polymer in 1 g latex [W_s] = 1- 0.6583 = 0.3417 g

Weight of the bottom layer after swelling [$W_{(bottom)}$] = 0.3892 g

Monomer concentration in polymer (wt %)

= ($W_{(bottom)}$ - W_s)/0.5 = (0.3892 - 0.3417)/0.5 = 9.5%

Weight of the top layer [$W_{(top)}$] = 1.1108 g

Monomer concentration in the propylene glycol continuous phase (wt%)

= ($W_{(top)}$ - $W_{(PG)}$)/0.5 = (1.1108 - 0.6583)/0.5 = 90.5 (%)

Based on the above data, it can be concluded that during the polymerization most of the monomers (90.5 wt%) reside in the propylene glycol continuous phase. This further implies that homogeneous nucleation occurs.

4.3.6 Mechanism of Particle Nucleation

The emulsion polymerization can be divided into three intervals, which include (1) particle formation; (2) particle growth in the presence of monomer droplets; and (3) polymerization of the monomer remaining in the monomer-swollen polymer particles.

In interval I, since ethyl methylacylate and lauryl methacylate have relatively high solubility (5%) in propylene glycol. free radicals react with the monomers to form oligomeric chains. When these oligomeric chains grow to the critical precipitation length, they will aggregate to form particles. PEO-PS-PEO triblock copolymers adsorbed on the surface of these particles impart steric stabilization (homogeneous nucleation). The location of nucleation is in propylene glycol solution instead of in the monomer-swollen micelles.

The second interval involves the growth of the polymer particles. As the particles grow, more PEO-PS-PEO triblock copolymers are required to offer stability. However, either a limited amount of PEO-PS-PEO triblock copolymers exist in the solution or the adsorption rate is slow with respect to the rate of surface area generation. Therefore, limited coalescence is unavoidable.

During interval III, the maximum surface coverage of PEO-PS-PEO triblock copolymers is reached. The polymer particles become more viscous as the monomer concentration falls. Therefore, the diffusion controlled termination and diffusion controlled propagation occur.

A mechanism based on the above discussions is proposed for particle nucleation and growth in this system. Schematic representations of these two processes are given in Figures 4.19 and 4.20, respectively.

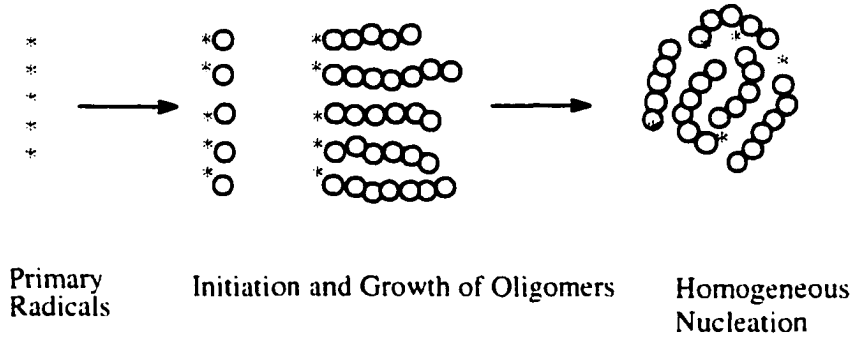


Figure 4.19: Schematic representation of the particle nucleation process [5].

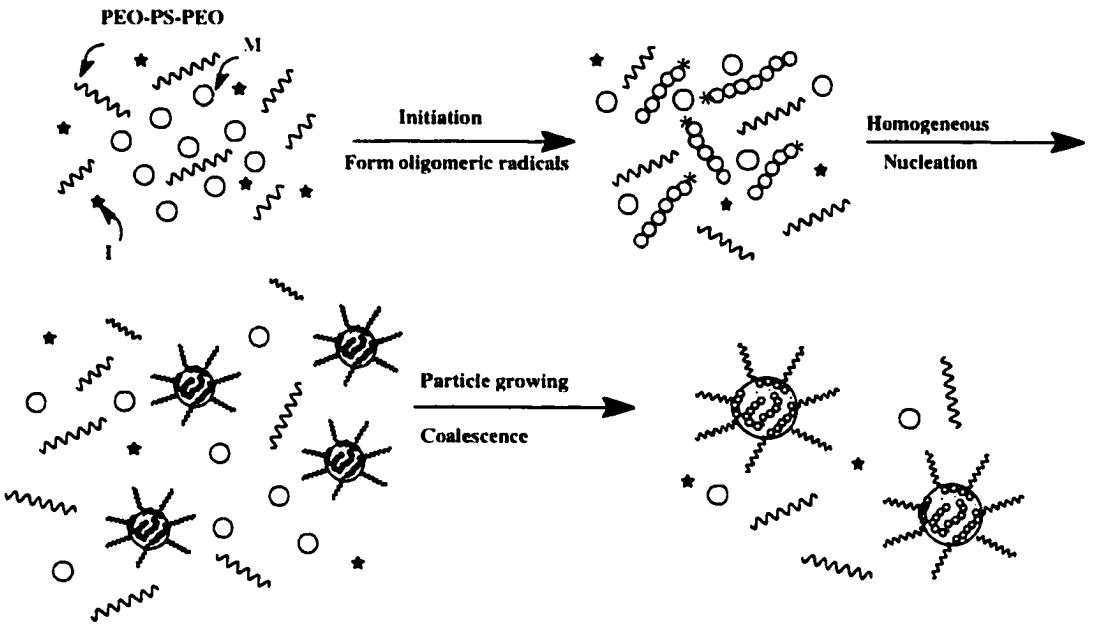


Figure 4.20: Schematic representation of the mechanism of the particle growth process (as well as particle formation).

4.3.7 Comparison of Kinetic Behavior of Different PEO-PS-PEO Triblock Copolymers

As mentioned before, only six synthesized PEO-PS-PEO tirblock copolymers could form stable latexes. The compositions of these six PEO-PS-PEO triblock copolymers are as follows: xyd33 (69PEO-29PS-69PEO), xyd34 (85PEO-28PS-85PEO), xyd37 (62PEO-19PS-62PEO), xyd38 (88PEO-19PS-88PEO), xyd42 (62PEO-39PS-62PEO), and xyd43 (82PEO-40PS-82PEO). All the latexes, which were stabilized with the above six PEO-PS-PEO triblock copolymers, gave similar particle diameters when the amount of stabilizer, initiator, and monomers were the same. Under the experimental conditions of 0.1 g of PEO-PS-PEO triblock copolymer, 0.07 g (or 0.04 g) initiator (AIBN), and 30% solid contents in the reactor, the particle diameter was about 163nm. The corresponding particle density was 1.12×10^{14} particles /cc, and the resulting total surface area was 9.34 m^2/g. When the reactor was charged with 0.2 g of PEO-PS-PEO triblock copolymer, 0.07g initiator (AIBN), and 30% solid contents, the particle size lowered to 149 nm, the particle density increased to 1.46×10^{14} particles/cc, and the total surface area increased to 10.21 m^2/g. While using 0.2 g of PEO-PS-PEO triblock copolymer, 0.07g initiator (AIBN) at 40% solid contents gave a particle size of 199 nm. The corresponding particle density reduced to 8.26×10^{13} particles /cc, and the total surface area was 10.27 m^2/g.

The difference between theses six PEO-PS-PEO triblock copolymers is the rate of the polymerization. For PEO-PS-PEO triblock copolymer xyd33 and xyd34, 40% of monomers were converted into polymer within 2 hours. In the case of PEO-PS-PEO triblock copolymer xyd37 and xyd38, only 20% conversion is reached at the two hour

interval. With PEO-PS-PEO triblock copolymers xyd42 and xyd43, approximately 10% of the monomers were reacted within 2 hours. Although all the latexes achieve 100% conversion over an 24-hour period, the rate of polymerization has significant differences at the early stage of the polymerization.

As discussed in Chapter 3, the adsorption behavior of these six PEO-PS-PEO triblock copolymers varies. Each PEO-PS-PEO triblock copolymer has its own partitions in the latex system. While xyd33 (or xyd34) is chosen as the stabilizer, the polymer particles require less amounts of PEO-PS-PEO triblock copolymers on the surface (including physically adsorbed on each particle and anchored on each particle). This is true regardless of the latexes that were made with different initiator concentrations, stabilizer concentrations and monomer concentrations. The amount of stabilizer needed increased when PEO-PS-PEO triblock copolymers xyd37 and xyd38 were substituted. Further increase in the amount needed for stability was observed for PEO-PS-PEO triblock copolymer xyd42 and xyd43. This implies that it takes longer for some molecules to achieve the same coverage. This represents the reduced stabilizing efficiency in the order of xyd33 (or xyd34), xyd37 (or xyd38), and xyd42 (or xyd43). As a result, more PEO-PS-PEO triblock copolymers are needed for stabilization, and slower rate of polymerization is obtained. This accounts for the difference in monomer conversion during polymerization.

4.4 Summary

The kinetics of emulsion copolymerization of ethyl methacrylate/lauryl methacrylate demonstrates many similarities when comparing it with counterpart water-

soluble monomers. The experimental results show the initial rate of polymerization is influenced by initiator concentration. However, it is independent of stabilizer concentration and monomer concentration. The rate of polymerization slightly increases with increasing stabilizer concentration and monomer concentration. Nonetheless, it is not affected by initiator concentration.

Particle number density increases with increasing stabilizer concentration, and decreases with increasing monomer concentration. Initiator concentration has no effect on particle number density towards the end of polymerization. Generally speaking, particle number density *vs.* conversion curve can be divided into three regions. Interval I corresponds to the particle nucleation stage, where the PEO-PS-PEO triblock copolymers adsorb on the particles without rearrangement. Interval II, particle number density is reduced gradually due to limited coalescence. The hallmark of this region is adsorption with rearrangement on primary particles. Interval III is characterized by saturation coverage of the PEO-PS-PEO triblock copolymer stabilizer. Dynamic equilibrium of PEO-PS-PEO triblock copolymer chains on the particle surface is established along with slow rearrangement.

Total surface coverage increases with increasing stabilizer concentration. Notwithstanding, it is independent of monomer concentration and initiator concentration.

Due to the high solubility of ethyl methacrylate/lauryl methacrylate in propylene glycol, particles are generated in the solution. Homogeneous nucleation is the dominant mechanism. This is supported by all the experimental kinetic data, seeded polymerization, and monomer partitioning behavior. Also, it has a good correlation with literature reported data for water-soluble monomers. It can be concluded that emulsion

copolymerization of ethyl methacrylate / lauryl methacrylate in non-aqueous (propylene glycol) medium behaves in a similar manner to the emulsion polymerization of water-soluble monomers.

The derivations in the kinetic profile between individual PEO-PS-PEO triblock copolymer results from their adsorption differences. Among the six PEO-PS-PEO triblock copolymers which were able to give stable latexes, the number of PEO-PS-PEO triblock copolymer chains needed for contributing to the stabilization increases in the sequence of xyd33 (69PEO-29PS-69PEO), xyd34 (85PEO-28PS-85PEO), xyd38 (88PEO-19PS-88PEO), xyd37 (62PEO-19PS-62PEO), xyd43 (82PEO-40PS-82PEO), and xyd42 (62PEO-39PS-62PEO). The rate of polymerization decreases in that order. This is because more time is demanded for establishing the dynamic equilibrium on the surface if more PEO-PS-PEO triblock copolymer chains are needed.

The above kinetic data offers a general guideline for controlling the emulsion polymerization of ethyl methacrylate / lauryl methacrylate in propylene glycol. It is valuable for modeling study.

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Chapter 5

Conclusions and Recommendations

5.1 Conclusions

The aim of this research program was to systematically study the PEO-PS-PEO triblock copolymers stabilizing efficiency in non-aqueous emulsion polymerization and focused on three specific areas: (1) synthesis and characterization of well defined PEO-PS-PEO triblock copolymers *via* anionic polymerization; (2) evaluation of the stabilizing efficiency of these PEO-PS-PEO triblock copolymers in a model non-aqueous emulsion copolymerization system; and (3) investigation of the kinetic behavior of emulsion polymerization by means of examining the important parameters such as initial polymerization rate, particle size, particle density, and total surface area. The following conclusions were deduced from each of these three aspects:

5.1.1 Preparation and Characterization of PEO-PS-PEO Triblock Copolymers with Desired Block Length *via* Anionic Polymerization

(1) PEO-PS-PEO triblock copolymers with proposed block lengths can be synthesized by means of anionic polymerization process. Four series (sixteen PEO-PS-PEO triblock copolymers) were prepared for this study.

(2) The success of anionic polymerization depends heavily on the experimental conditions. It requires an absolute air-free and moisture-free environment. A high vacuum line and ultra-pure nitrogen were essential for the success of the synthesis.

(3) These PEO-PS-PEO triblock copolymers were characterized by gel

permeation chromatography, Proton NMR and intrinsic viscosity methods. The data obtained from the different methods complement each other well.

(4) The dependence of intrinsic viscosity *vs.* temperature in propylene glycol displays two transitions over the temperature range of 20-70°C. The transition minimum at 35°C corresponds to the transformation from non-segregated conformation to segregated conformation. Propylene glycol is a good solvent for PEO-PS-PEO triblock copolymers below 35°C, and becomes a poor solvent for PEO-PS-PEO triblock copolymers above 35°C due to poor solvency for PS block. The transition maximum at 49°C is related to the hydrodynamic volume variation of the PS swollen core over the temperature range.

5.1.2 Assessment of The Stabilizing Efficiency of These PEO-PS-PEO Triblock Copolymers in A Model Non-Aqueous Emulsion Copolymerization System

(1) A non-aqueous polymerization model system, which consisted of ethyl methacrylate, lauryl methacrylate, 2,2'-azobis(isobutyronitrile) (AIBN), PEO-PS-PEO triblock copolymer, and propylene glycol, was examined for the stabilizing efficiency of synthesized PEO-PS-PEO triblock copolymers. Ethyl methacrylate and lauryl methacrylate were the monomers. 2,2'-azobis(isobutyronitrile) (AIBN) is a free-radical initiator. Propylene glycol was the continuous phase. PEO-PS-PEO triblock copolymer was the sole stabilizer.

(2) The influence of PEO block length as well as the PS block length was studied. To be eligible as a stabilizer for the emulsion copolymerization of ethyl methacrylate / lauryl methacrylate in propylene glycol, the PS block length should be between 19 units

and 40 units, which is equivalent to the molecular weight of PS block from 2000 to 4000. The PEO block length was in the range of 62 units to 88 units, which has comparable molecular weight from 5300 to 7700.

(3) The adsorption behavior of various PEO-PS-PEO triblock copolymers on latex particles was studied. Latex was cleaned using a serum replacement cell. The four locations of PEO-PS-PEO triblock copolymers in the latex were: physically adsorbed on the latex surface, anchored on the surface, entrapped inside the particle and as "free" PEO-PS-PEO triblock copolymers in the propylene glycol. A contour graph analysis was applied to reduce the experimental data. The experimental results showed that a minimum existed for the physically adsorbed portion at PS block length of about 30 units. When the PS units were less than 30 units, the adsorption decreased with increasing PS block length indicating rearrangement of mixed PEO brush and adsorbed PS block. While the PS units were greater than 30 units, the adsorption increased with increasing block length due to poor solvency of PS block in propylene glycol medium and collapse of PS block. Considering the binding energy between the PS block and the latex particle surface which governs adsorption, it is hypothesized that a lower block length limit exists, below which no adsorption takes place. The solubility of the PS block in propylene glycol guides the important upper block length limit. The anchored portion increases with increasing PS block length in the entire region investigated. The effect of stabilizer concentrations and monomer concentrations were also investigated. Both the physically adsorbed and anchored molecules decreased as increasing the stabilizer concentration. However, with increasing the monomer concentration, the amount of physically adsorbed as well as anchored molecules increased.

(4) Polynomial equations for predicting the total PEO-PS-PEO triblock copolymers needed for stabilization were obtained. These equations could be used as guidelines for the appraisal of the stabilizing efficiency.

5.1.3 Kinetics Studies for Emulsion Copolymerization

(1) The kinetics of emulsion copolymerization of ethyl methacrylate /lauryl methacrylate seems very similar to the water-soluble monomers due to the high solubility of ethyl methacrylate/lauryl methacrylate in propylene glycol.

(2) The initial rate of polymerization only depends on initiator concentration, and is not affected by monomer concentration and stabilizer concentration. The overall rate of polymerization slightly increased with higher monomer concentration and stabilizer concentration. However, it is independent of initiator concentration.

(3) The particle number density increased with increasing the amount of stabilizer, and decreased with increasing the monomer concentration.

(4) Total surface area increased with stabilizer concentration. It is not governed by initiator concentration and monomer concentration.

(5) Homogeneous nucleation was the dominant mechanism, and was supported by the kinetic data, seeded polymerization as well as monomer partition behavior.

(6) The different adsorption partitioning behavior on the surface accounts for the kinetic variance of PEO-PS-PEO triblock copolymers.

5.2 Recommendations

As a natural extension of this work, the following aspects should be investigated in the future:

(1) Study effect of agitation on stabilizing efficiency using PEO-PS-PEO triblock copolymer as stabilizer.

(2) Study the micelle formation and determine the critical micelle concentration *via* surface tension and light scattering technique.

(3) Study the adsorption behavior of PEO-PS-PEO tirblock copolymer with various molecular structures on cleaned latex particles.

(4) Investigate the stabilizing efficiency of PEO-PS-PEO triblock copolymers by exploring other monomers, other solvents, and feed ratio of monomers (ethyl methacrylate/lauryl methacrylate) on stabilizing efficiency as well as the kinetics behavior.

(5) Conduct a comprehensive kinetic study to gain a better understanding of emulsion copolymerization in a non-aqueous medium through mathematical modeling.

(6) Study the mechanical properties and optical gloss of the latex film which is made with PEO-PS-PEO triblock copolymer stabilizer.

(7) Study the particle curvature effect on adsorption to establish a mathematical model (empirical equation) to predict the entire adsorption behavior.

(8) Study the effect of monomers on the conformation of PEO-PS-PEO triblock copolymers.

Appendix I

Calculation of the Amount of Monomers for the Desired PEO-PS-PEO Triblock Copolymer

Example calculation is demonstrated as follows:

Assuming: Ci=0.4738 mol/L

If 8 mL initiator is injected into the reaction flask,

Moles of initiator = $0.4738 \times 8 \times 10^{-3} = 3.7904 \times 10^{-3}$ (mole)

★ For designed 20 units PS block length:

$MW_{PS} = 20 \times MW_S = 20 \times 104.15 = 2083$

Therefore,

The amount of styrene (W_S) = moles of initiator $\times$ MW_{PS}

$= 3.7904 \times 10^{-3} \times 2083 = 7.8954$ (g)

★For designed 60 units of PEO block length:

$MW_{PEO} = 60 \times MW_{PEO} = 20 \times 44.05 = 5286$

Thus,

The amount of ethylene oxide (W_{EO}) = moles of initiator $\times$ MW_{PEO}

$= 3.7904 \times 10^{-3} \times 5286 = 20.0361$ (g)

★For the amount of acetic acid (99.7%, Aldrich) in termination step:

Density of acetic acid = 1.049

Density of toluene = 0.865

Mole concentration of 10wt% acetic acid for stopping polymerization

$= [(10 \times 99.7\%) / 60.05] / \{[(10/1.049) + (90/0.865)] \times 10^{-3}\}$

=1.46 (mole/L)

So,

The volume of acetic acid

= Moles of initiator/ mole concentration of 10 wt% acetic acid in toluene

$=(3.7904 \times 10^{-3}) / 1.46 = 2.596 \times 10^{-3}$ (L) = 2.596 (mL)

The actual amount is 5 % excess,

$V_{HAc} = 2.596 \times 1.05 = 2.7$ (mL)

Where Ci---- concentration of the initiator;

MW_{PS}---- molecular weight of polystyrene block;

MW_{PEO} ---- molecular weight of PEO block;

W_S---- the amount of styrene;

W_{EO} ---- the amount of ethylene oxide;

V_{HAc} ---- volume of acetic acid.

Appendix II

Calculation of the PEO-PS-PEO Triblock Copolymer Composition

Example calculation is demonstrated as follows:

According to GPC analysis:

Molecular weight of sample xyd34 = 10400

According to proton NMR:

The ratio of aromatic protons to the protons in the oxyethylene repeats unit

= 1/ 4.8571 =0.3294

Assuming the PEO-PS-PEO composition is (PEO) n- (PS) m- (PEO) n:

MW_{PS} =104.15

MW_{PEO} = 44.05

$104.15\ m + 44.05 \times 2n = 10500$

There are 5 protons per PS unit, and 4 protons per PEO unit:

$(5 \times m) / (4 \times 2 \times n) = 0.2059$

Therefore, m=28, n=85

The sample composition is: 85 PEO-28PS-85PEO

Appendix III

Polynomial Equations

If PEO-PS-PEO triblock copolymer has Nps units of PS blocks, and Npeo units of PEO blocks, N represents the total PEO-PS-PEO triblock copolymer chains (anchored + adsorbed) on each latex particle which are required for stabilization. a, b, c, d, e, f, and g are constants.

(1) When 0.1g stabilizer is added, and the monomer concentration is 30% solid content:

(1.1) Assuming $N = aNps^3+bNps^2+cNps+eNpeo^2+fNpeo+g$

Based on the experimental data in Table 3.2:

xyd33 $6448=a(29)^3+b(29)^2+c(29)+e(138)^2+f(138)+g$ (1)

xyd34 $6632=a(28)^3+b(28)^2+c(28)+e(170)^2+f(170)+g$ (2)

xyd38 $8230=a(19)^3+b(19)^2+c(19)+e(176)^2+f(176)+g$ (3)

xyd37 $8486=a(19)^3+b(19)^2+c(19)+e(124)^2+f(124)+g$ (4)

xyd43 $9080=a(40)^3+b(40)^2+c(40)+e(164)^2+f(164)+g$ (5)

xyd42 $10722=a(39)^3+b(39)^2+c(39)+e(124)^2+f(124)+g$ (6)

So,

$N_{0130} = -2.6Nps^3+242.6Nps^2-7140.5Nps+2.7Npeo^2-818.5Npeo+134201.7$

(1.2) Assuming $N = aNpeo^3+bNpeo^2+cNpeo+eNps^2+fNps+g$

Based on the experimental data in Table 3.2:

xyd33 $6448=a(138)^3+b(138)^2+c(138)+e(29)^2+f(29)+g$ (7)

xyd34 $6632=a(170)^3+b(170)^2+c(170)+e(28)^2+f(28)+g$ (8)

xyd38 $8230=a(176)^3+b(176)^2+c(176)+e(19)^2+f(19)+g$ (9)

xyd37 $8486=a(124)^3+b(124)^2+c(124)+e(19)^2+f(19)+g$ (10)

xyd43 $9080=a(164)^3+b(164)^2+c(164)+e(40)^2+f(40)+g$ (11)

xyd42 $10722=a(124)^3+b(124)^2+c(124)+e(39)^2+f(39)+g$ (12)

Then,

$$\mathbf{N_{0130}=0.04Npeo^3-12.91Npeo^2+1397.93Npeo+15.11Nps^2-764.67Nps-26340.00}$$

(2) When 0.2g stabilizer is added, and the monomer concentration is 30% solid content:

(2.1) Assuming $N=aNps^3+bNps^2+cNps+eNpeo^2+fNpeo+g$

According to the experimental data in Table 3.3:

xyd33 $6273=a(29)^3+b(29)^2+c(29)+e(138)^2+f(138)+g$ (13)

xyd34 $6392=a(28)^3+b(28)^2+c(28)+e(170)^2+f(170)+g$ (14)

xyd38 $7942=a(19)^3+b(19)^2+c(19)+e(176)^2+f(176)+g$ (15)

xyd37 $8072=a(19)^3+b(19)^2+c(19)+e(124)^2+f(124)+g$ (16)

xyd43 $8863=a(40)^3+b(40)^2+c(40)+e(164)^2+f(164)+g$ (17)

xyd42 $9607=a(39)^3+b(39)^2+c(39)+e(124)^2+f(124)+g$ (18)

Thus,

$$\mathbf{N_{0230}=-1.4Nps^3+140.8Nps^2-4357.7Nps+1.6Npeo^2-470.8Npeo+84173.2}$$

(2.2) Assuming $N=aNpeo^3+bNpeo^2+cNpeo+eNps^2+fNps+g$

Based on the experimental data in Table 3.3:

xyd33 $6273=a(138)^3+b(138)^2+c(138)+e(29)^2+f(29)+g$ (19)

xyd34 $6392=a(170)^3+b(170)^2+c(170)+e(28)^2+f(28)+g$ (20)

xyd38 $7942=a(176)^3+b(176)^2+c(176)+e(19)^2+f(19)+g$ (21)

xyd37 $8072=a(124)^3+b(124)^2+c(124)+e(19)^2+f(19)+g$ (22)

xyd43 $8863=a(164)^3+b(164)^2+c(164)+e(40)^2+f(40)+g$ (23)

xyd42 $9607=a(124)^3+b(124)^2+c(124)+e(39)^2+f(39)+g$ (24)

Therefore,

$$\mathbf{N_{0230}=0.02Npeo^3-6.99Npeo^2+742.46Npeo+16.28Nps^2-867.57Nps-3706.55}$$

(3) When 0.2g stabilizer is added, and the monomer concentration is 40% solid content:

(3.1) Assuming $N=aNps^3+bNps^2+cNps+eNpeo^2+fNpeo+g$

According to the experimental data in Table 3.4:

xyd33 $7433=a(29)^3+b(29)^2+c(29)+e(138)^2+f(138)+g$ (25)

xyd34 $7782=a(28)^3+b(28)^2+c(28)+e(170)^2+f(170)+g$ (26)

xyd38 $9818=a(19)^3+b(19)^2+c(19)+e(176)^2+f(176)+g$ (27)

xyd37 $9896=a(19)^3+b(19)^2+c(19)+e(124)^2+f(124)+g$ (28)

xyd43 $12170=a(40)^3+b(40)^2+c(40)+e(164)^2+f(164)+g$ (29)

xyd42 $13465=a(39)^3+b(39)^2+c(39)+e(124)^2+f(124)+g$ (30)

Thus,

$$\mathbf{N_{0240}=-2.2Nps^3+221.4Nps^2-6778.9Nps+3.0Npeo^2-905.4Npeo+140093.8}$$

(3.2) Assuming $N=aNpeo^3+bNpeo^2+cNpeo+eNps^2+fNps+g$

Based on the experimental data in Table 3.4:

xyd33 $7433=a(138)^3+b(138)^2+c(138)+e(29)^2+f(29)+g$ (31)

xyd34 $7782=a(170)^3+b(170)^2+c(170)+e(28)^2+f(28)+g$ (32)

xyd38 $9818=a(176)^3+b(176)^2+c(176)+e(19)^2+f(19)+g$ (33)

xyd37 $9896=a(124)^3+b(124)^2+c(124)+e(19)^2+f(19)+g$ (34)

xyd43 $12170=a(164)^3+b(164)^2+c(164)+e(40)^2+f(40)+g$ (35)

xyd42 $13465=a(124)^3+b(124)^2+c(124)+e(39)^2+f(39)+g$ (36)

Thus,

$$\mathbf{N_{0240}=0.03Npeo^3-10.47Npeo^2+1007.39Npeo+25.09Nps^2-1276.59Nps+1546.74}$$

These equations can be used as general guidelines for evaluating the stabilizing efficiency of PEO-PS-PEO triblock copolymers as stabilizer in the non-aqueous propylene glycol system.

Appendix IV

Calculation of Conversion-Time in Dilatomery

The total fractional change in volume can be expressed as following equation (1):

$$\Delta V_{\text{total fract}} = (W_1/d_1 - W_1/d_2)/(W_1/d_1) \quad (1)$$

Where W_1 is the weight of monomers (g);

d_1 is the monomer density (g/ml);

d_2 is the polymer density (g/ml).

Above equation (1) can be simplified to equation (2):

$$\Delta V_{\text{total fract}} = (d_2 - d_1)/d_2 \quad (2)$$

The degree of monomer conversion is equal to equation (3):

$$\Delta[M]/[M] = (\Delta V/Vo)/[(d_2 - d_1)/d_2] \quad (3)$$

Where $\Delta[M]$ is the incremental change in monomer concentration;

[M] is monomer concentration;

ΔV is the change in volume from the initial volume Vo;

$(d_2 - d_1)/d_2$ is the fractional volume change which would occur at 100% conversion;

$(\Delta V/Vo)$ is the fractional volume change at any time Δt.

The ratio of these two quantities $\{[(\Delta V/Vo)]/[(d_2 - d_1)/d_2]\}$ should give the fraction of conversion.

Dividing Δt (incremental time) on both sides of equation (3), and rearranging the equation (3) derives Equation (4):

$$\Delta[M] = (\Delta V/\Delta t)([M]/Vo)/[(d_2 - d_1)/d_2]$$

$$=\{[[M]\, d_2]/[Vo(\, d_2-d_1)]\}(\Delta V/\Delta t) \qquad (4)$$

Thus, equation (5) is given as follows:

$$(\Delta[M]/\,\Delta t)_{\lim_{\Delta t\to 0}} = d[M]/dt \qquad (5)$$

-d[M]/dt is defined as the overall rate of polymerization, Rp.

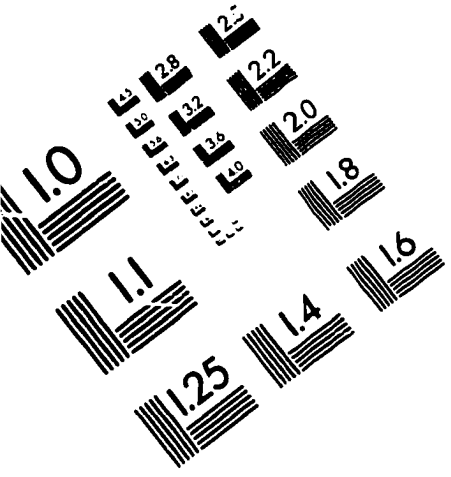
Vita

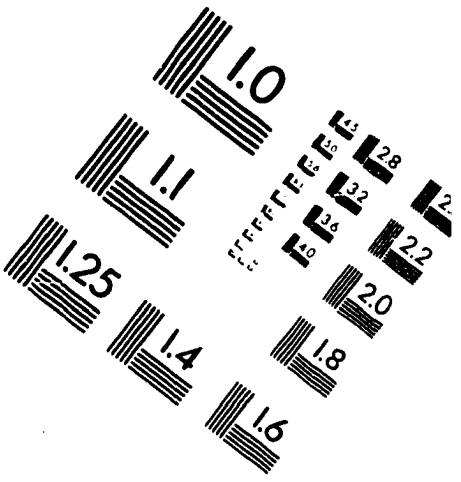
Xiaorong You, the oldest daughter of Zhi You and Jinmei Fan, was born on July 15, 1962 in Beijing, China. She received her B.S. degree in Polymer Science and Engineering from Tsinghua University, Beijing, China in 1985.

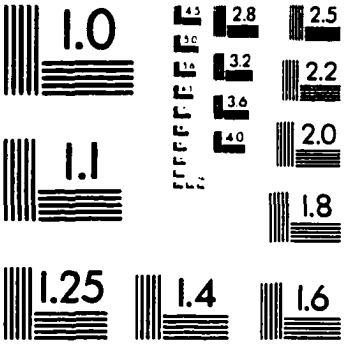
After she graduated from Tsinghua University, she worked at Beijing Chemical Industry Corp. as a chemical engineer for four and one-half years. She began her graduate study in the Chemistry Department, Kent State University, OH, U.S.A. in Jan. 1990, and received her M.S. in organic chemistry in Sept., 1992. Upon graduation, she worked as a development engineer for Gentex Optics, Inc., which is located in Carbondale, PA, U.S.A.

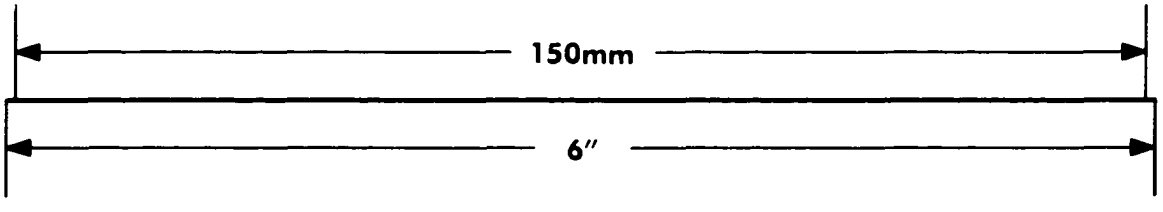
She joined the Emulsion Polymer Institute at Lehigh University in Jan., 1994, and started her research in the area of non-aqueous emulsion polymerization *via* PEO-PS-PEO triblock copolymers as stabilizers.

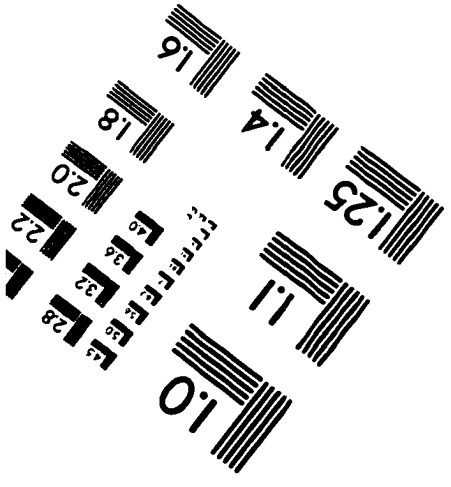
IMAGE EVALUATION
TEST TARGET (QA-3)

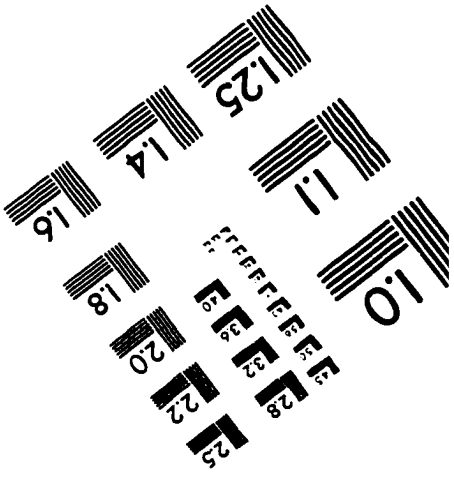












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