

# Nonaqueous Emulsion Copolymerization of Ethyl Methacrylate/Lauryl Methacrylate in Propylene Glycol. I. Evaluation of Stabilizing Efficiency for PEO-PS-PEO Triblock Copolymers

XIAORONG YOU, VICTORIA L. DIMONIE, ANDREW KLEIN

Emulsion Polymers Institute, Center for Polymer Science and Engineering Lehigh University, 111 Research Drive, Bethlehem, Pennsylvania 18015

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**ABSTRACT:** Sixteen poly(ethylene oxide)–polystyrene–poly(ethylene oxide) (PEO-PS-PEO) triblock copolymers were synthesized by anionic polymerization. They were characterized by gel permeation chromatography and proton NMR. The molecular weight of these 16 PEO-PS-PEO triblock copolymers ranged from 5100 to 13,300. The polystyrene (PS) block length was between 13 and 41. The PEO block length was between 41 and 106. The polydispersity index for these PEO-PS-PEO triblock copolymers were  $1.05 \pm 0.02$ . When using these stabilizers in the emulsion copolymerization of ethyl methacrylate and lauryl methacrylate in propylene glycol, only a narrow window of stability was observed. Stable latexes were formed only when the molecular weights of the PEO blocks were within the range of 5300–7700 and the molecular weights of the PS blocks were 2000–4000. The stabilizer ability for these triblock copolymers was correlated with their molecular weight and conformation in propylene glycol. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1951–1962, 2001

**Key words:** PEO-PS-PEO triblock copolymer; stabilizer; ethyl methacrylate; lauryl methacrylate; propylene glycol; anionic polymerization

## INTRODUCTION

Nonaqueous emulsion polymerization systems have a number of advantages, despite the fact that these systems are not environmentally friendly in comparison to aqueous systems. A nonaqueous system has several advantages. First, most organic liquids have small latent heats of evaporation, corresponding to a smaller heat input for its evaporation during film formation. Second, because 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, because the freezing points of most organic liquids are very low, any problems in the storage and transport of nonaqueous 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.

Because of these advantages, nonaqueous emulsion polymerization systems can be industri-

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Correspondence to: A. Klein (E-mail: ak04@lehigh.edu).

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ally important when the environmental issues can be controlled.

The terms "stabilizers" and "stabilization" are defined to mean a method for producing colloidal polymer dispersions that are stable toward 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, 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.<sup>1,2</sup>

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

Block copolymers offer a simple and versatile method for steric stabilization of colloidal particles suspended in a dispersion medium.<sup>1-20</sup> Block copolymers have gained considerable attention during 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).<sup>21-24</sup>

The best steric stabilizers are the amphiphathic 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 surface such that the anchoring part will not be easily 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 because of the marked difference in the properties and behavior of their individual components. Whereas PEO is crystallizable, polar, and hydrophilic, PS is glassy, nonpolar, 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.<sup>25</sup>

Many investigators<sup>26-50</sup> have investigated the colloidal behavior of PEO-PS-PEO triblock copolymers in aqueous and nonaqueous 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 nonaqueous media.

Piirma and colleagues<sup>49</sup> 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 examined, the diblock copolymers that had a 75-90% weight ratio of PEO/PS were effective stabilizers for styrene emulsion polymerization in water.

Riess and colleagues<sup>50</sup> investigated PS-PEO diblock and PEO-PS-PEO triblock copolymers as the stabilizers for the dispersion polymerization of styrene in methanol. The effect of the molecular weight of stabilizer, PS/PEO ratio, and stabilizer concentration on the particle size and polydispersity were examined. The results showed that large (2- $\mu\text{m}$ ) 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 and Mura<sup>51</sup> 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.

During the course of our current study of a latex system composed of ethyl methacrylate and lauryl methacrylate in propylene glycol medium, it was found that a stable and small particle size

(150 nm) latex at 30% solids content could only be made with a narrow range of molecular weights and compositions of PEO-PS-PEO triblock copolymers. Diblock copolymer PEO-PS with the same composition did not generate stable latex.<sup>25</sup>

## EXPERIMENTAL

### Synthesis of PEO-PS-PEO Triblock Copolymers

#### Materials

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

Styrene (99%, Aldrich) and ethylene oxide (99.5+%, Aldrich) were used as monomers to prepare PEO-PS-PEO triblock copolymers. Anhydrous toluene (99.8%, Aldrich) was used as a solvent for the anionic polymerization. Calcium hydride (powder, -40 mesh, 90–95%, Aldrich) was used as drying agent. Acetic acid (99.8%, Aldrich) was used to terminate the polymerization. Cyclohexane (99.9+%, HPLC grade, Aldrich) 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) was used as an eluant for the gel permeation chromatography measurements. Carbon tetrachloride (99.9+%, HPLC grade, Aldrich) was used as the solvent for proton nuclear magnetic resonance (NMR) measurements. Tetramethylsilane (99.9+%, NMR grade, Aldrich) was used as an internal standard. Propylene glycol (99.5+%, Aldrich) was used as a solvent to study the temperature dependence of the intrinsic viscosity for different PEO-PS-PEO triblock copolymers as well as of two PEO homopolymers.

Ultrapurity 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.

#### Preparation of Initiator

The Atmosbag (Aldrich) was attached to the vacuum line via flexible vacuum tubing and kept under vacuum overnight. The vacuum line was then filled with ultrahigh purity nitrogen, and the procedure was repeated twice. This operational procedure was used for handling all the air and moisture sensitive chemicals during the course of anionic polymerization. A small rod of potassium was taken out from the storage container by forceps and was wrapped thoroughly with filter paper for removing the mineral oil. Soon afterward, 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 upon completing the addition of reagents, and removed from the Atmosbag.

The reaction mixture was stirred for 2 h at room temperature. The color of the 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 gas-tight syringe under nitrogen blanket (transferred in the Atmosbag). Then, it was mixed with 5 mL distilled water and 20 mL methanol. Standardized hydrochloric acid solution (0.1*N*) was used to titrate the mixture. This procedure was repeated three times to eliminate the experimental error.

#### Preparation of PEO-PS-PEO Triblock Copolymers

A 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 h before carrying out the polymerization and then filled with ultrapure 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 1-mL 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 drop-

wise to the flask until a ruby red color appeared and persisted for 5 min. Immediately afterward, the desired amount of initiator solution was injected into the flask. The mixture was stirred in an ice bath for 2 h. The color of the solution was dark red.

Ethylene oxide was recondensed twice over calcium hydride. It was then 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 4 days. The color of the resulting mixture was amber. When the polymerization was nearly complete (after 96 h), 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 in the form of white granules. The crude product was dispersed in cyclohexane solvent at the room temperature with stirring for 24 h. The mixture was vacuum filtered and the filtrate was clear. The white granules that were left on the filter were redispersed into cyclohexane solvent at the room temperature with stirring for 8 h. 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%.

### Characterization

Gel permeation chromatography (Waters GPC model: 570; Column: 1 × 60 cm PLgel 5 μm 10<sup>3</sup> Å; Solvent: Chloroform; Flowrate: 1 mL/min; Detector: Ultraviolet; 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 min. 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 (20–30 mg) were dissolved in carbon tetrachloride using tetramethylsilane (TMS) as the internal standard. Proton NMR spectra were used to confirm the block formation and determine the ratio of the PS/PEO blocks.

**Table I** Nonaqueous 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 methacrylate	0.41–0.85
AIBN (g)	0.04–0.07

AIBN, 2,2'-azobis(isobutyronitrile).

### 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  $[\eta]$  at several temperatures ( $T$ ) within the range of 20–70°C were measured with a conventional Ubbelohde viscometer. The PEO-PS-PEO triblock copolymers and two PEO homopolymers ( $M_n = 5000$  and  $M_n = 18,500$ ) were dissolved in propylene glycol with the measurement being made at a constant temperature.

### Emulsion Copolymerization

#### Materials

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

All other materials were used as received, including propylene glycol (99.5+%, ACS reagent, Aldrich), 2,2'-azobis(isobutyronitrile) (AIBN) (98%, Aldrich), and hydroquinone (99%, Aldrich). PEO-PS-PEO triblock copolymers were used as stabilizers.

#### Emulsion Copolymerization

The emulsion polymerization of ethyl methacrylate/lauryl methacrylate was carried out in propylene glycol at 60°C for a period of 24 h. The recipe is given in Table I. 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 methacrylate and lauryl methacrylate were mixed well in a separate beaker and poured into the small glass vial containing the

**Table II 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

mixture of propylene glycol, 2,2'-azobis(isobutyronitrile) (AIBN), PEO-PS-PEO triblock copolymers and the 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).

## RESULTS AND DISCUSSION

Four series of PEO-PS-PEO triblock copolymers were designed for this research program. They are summarized in Table II. 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 a 20-unit 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 lengths are 40, 60, 80,

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 evaluate systematically and fully 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 to 100 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 actual experimental recipe is shown in Table III.

In order to analyze the synthesized triblock copolymer 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 1. The proton NMR spectrum was used to verify the copolymer composition. A typical pro-

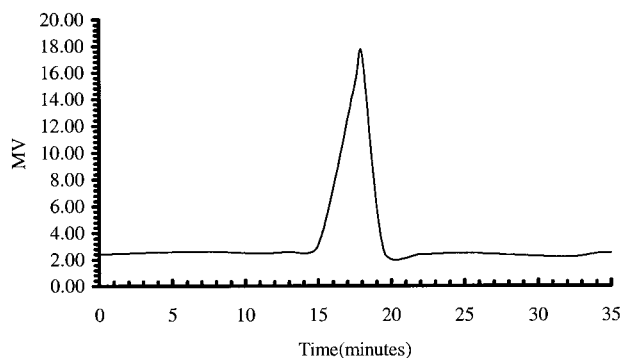
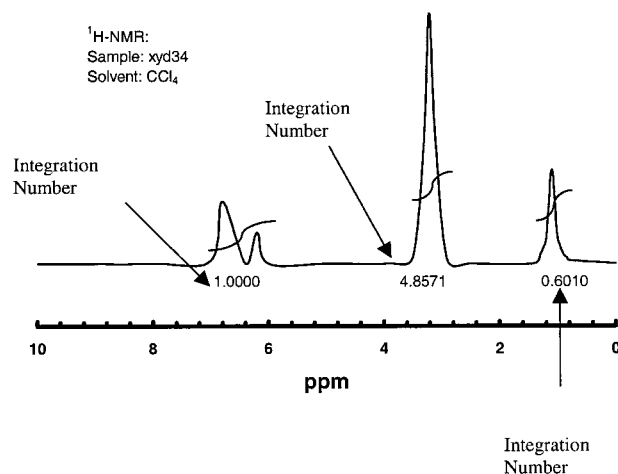
**Table III** Recipe for Synthesis of PEO-PS-PEO Triblock Copolymers

Ingredient	Amount
Toluene	100 mL
Potassium naphthalene (0.4738 mol/L)	8 mL
Styrene	7.90–15.79 g (variable)
Ethylene oxide	13.7–3.39 g (variable)
Cyclohexane	300 mL
Acetic acid (10% toluene solution)	2.28 mL

ton NMR spectrum is shown in Figure 2. The chemical shift for the protons in the  $-\text{CH}_2-\text{CH}_2-$  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 nonaromatic protons in the  $\text{Ar}-\text{CH}_2-\text{CH}_2-$  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. The measured characteristics of all 16 PEO-PS-PEO triblock copolymers are listed in Table IV. The polydispersity of all these PEO-PS-PEO triblock copolymers was 1.03–1.07 as determined by gel permeation chromatography.

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

Among 16 PEO-PS-PEO triblock copolymers that were tested, only six gave stable latex. The compositions of these six PEO-PS-PEO triblock copol-

**Figure 1** A typical GPC curve for a synthesized PEO-PS-PEO triblock copolymer.**Figure 2** A typical proton NMR spectrum for synthesized PEO-PS-PEO triblock copolymer.

ymers 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 ( $M_n = 9100$ ), xyd34 ( $M_n = 10400$ ), xyd37 ( $M_n = 7400$ ), xyd38 ( $M_n = 9700$ ), xyd42 ( $M_n = 9500$ ), and xyd43 ( $M_n = 11400$ ). It seems that the minimum polystyrene block (PS) length for providing latex stability is 19 Styrene units ( $M_n = 2000$  g/mol) and the maximum PS block length for imparting stabilization is 40 Styrene units ( $M_n = 4000$  g/mol). Similarly, the minimum poly(ethylene oxide) (PEO) block length for offering efficient steric hindrance is 124 units (62 units on each side) ( $M_n = 5300$ ) 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.

It appears 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.<sup>52</sup> 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.

It is hypothesized that for triblock copolymers xyd32 (41PEO-30PS-41PEO) and xyd41 (41PEO-41PS-41PEO), the soluble PEO block is very short

**Table IV** Characteristics of Synthesized PEO-PS-PEO Triblock Copolymers

Sample	MW (Total) <sup>a</sup>	MW (PS) <sup>b</sup>	PS Block	MW (PEO) <sup>b</sup>	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

<sup>a</sup> GPC data.<sup>b</sup> Calculated data.

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

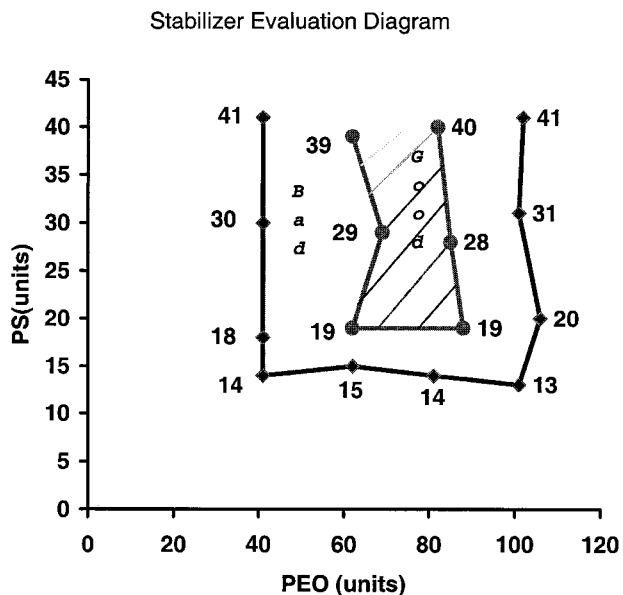
efficient protective layer around the polymer particles. Therefore, they are not good stabilizers.

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.

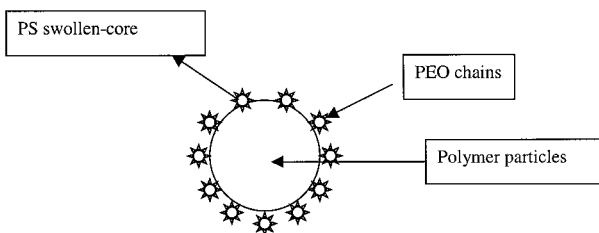
The PS blocks of the triblock copolymers xyd46 (62PEO-15PS-62PEO) and xyd47 (81PEO-14PS-81PEO) are very short and the volume of the swollen cores is relatively small. When these triblock copolymers are dissolved in the solvent (propylene glycol), PS block can not absorb or anchor strongly to the polymer 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-



**Figure 3** 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.



**Figure 4** Schematic representation of the no-overlap "island" conformation of PEO-PS-PEO triblock copolymers in propylene glycol.

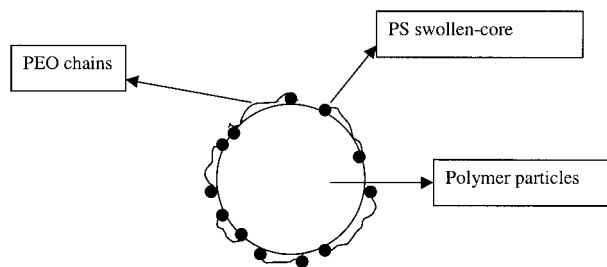
28PS-85PEO), xyd37 (62PEO-19PS-62PEO), xyd38 (88PEO-19PS-88PEO), xyd42 (62PEO-39PS-62PEO), and xyd43 (82PEO-40PS-82PEO)], have relatively moderate hydrodynamic size and a balance between hydrophilic/hydrophobic block lengths. The PS blocks are long enough to be strongly adsorbed or anchored to the particles, 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 are supported by experimental data in the next section. In brief, the conformation of these 16 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 nonoverlap "island" type conformation, which is caused by the short PEO chains. This can be schematically described as in Figure 4.

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. The adsorption energy is not sufficiently high to provide the copolymers with enough contact time on the particles surface and ensure full coverage which would prevent coagulation by collision of particles. This can be portrayed as in Figure 5.

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 could easily take place. This can be visualized in Figure 6.

It appears that the hydrodynamic volume of the PEO-PS-PEO triblock copolymer has to be



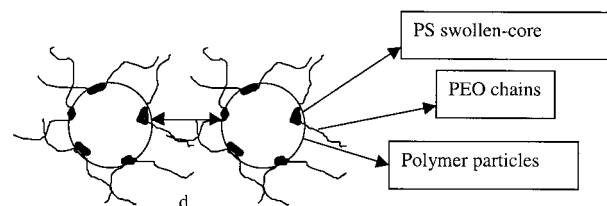
**Figure 5** Schematic representation of the "pancake" conformation of PEO-PS-PEO triblock copolymers in propylene glycol.

within a given range to be eligible as a good stabilizer. The ratio of PEO/PS block is proposed as one of the independent variables contributing to the hydrodynamic volume and hence colloidal stability.

The intrinsic viscosity of these 16 PEO-PS-PEO triblock copolymers in propylene glycol were examined in an attempt to understand the relationship between intrinsic viscosity and the ratio of PS/PEO blocks.

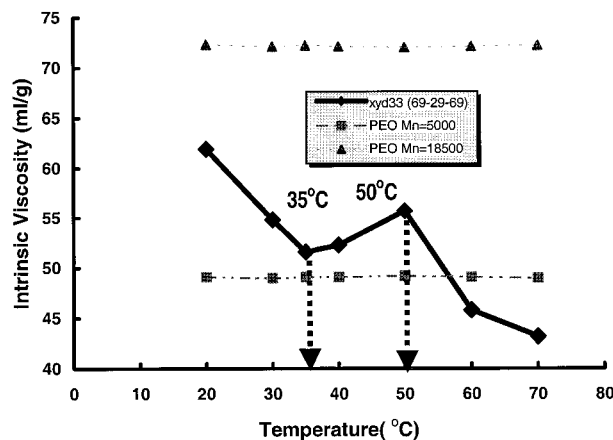
#### Relationship of Temperature Versus Intrinsic Viscosity in Propylene Glycol for Different PEO-PS-PEO Triblock Copolymers and Two PEO Homopolymers

The intrinsic viscosity of different PEO-PS-PEO triblock copolymers and of two PEO homopolymers was measured at 20–70°C to study the conformation of PEO-PS-PEO triblock copolymers in propylene glycol. All these triblock copolymers were found to behave similarly. Transition temperatures appear around 35°C and 50°C, as shown in Figure 7. Two PEO homopolymers with molecular weights of 5000 and 18,500 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.<sup>53</sup>



**Figure 6** Schematic representation of the "bridging" conformation of PEO-PS-PEO triblock copolymers in propylene glycol.





**Figure 7** Variation in the intrinsic viscosity of PEO-PS-PEO triblock copolymer and PEO homopolymers in propylene glycol.

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.

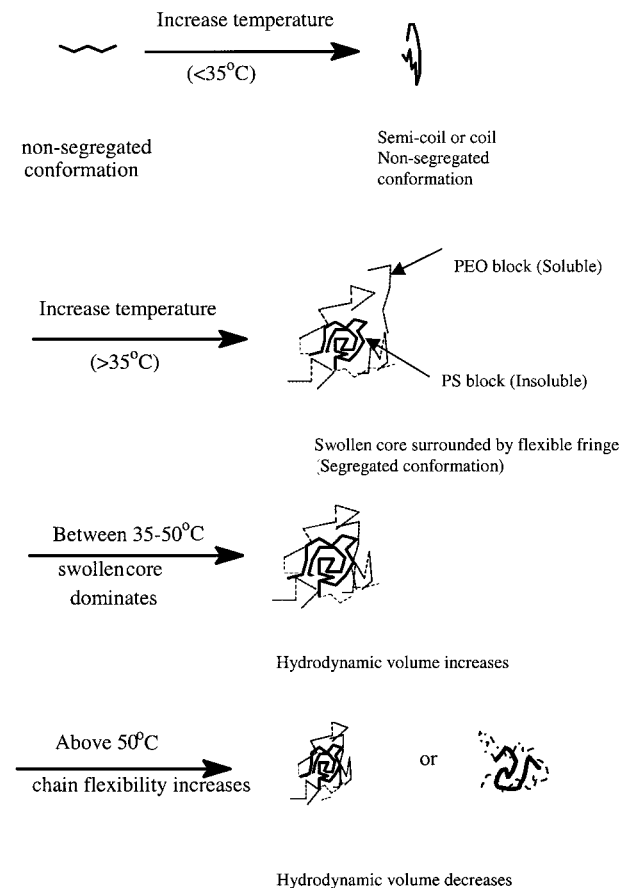
Since propylene glycol is a polar solvent, it is a good solvent for the PEO block regardless of the temperature range. Below 35°C, the PEO-PS-PEO block copolymer is in a nonsegregated conformation. The attractive force between the PEO blocks and propylene glycol molecules overcomes the nonpolar character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

As the temperature increases, the polymer chain becomes more flexible, (semicoil to coil), the intrinsic viscosity decreases. However, the nonpolar/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

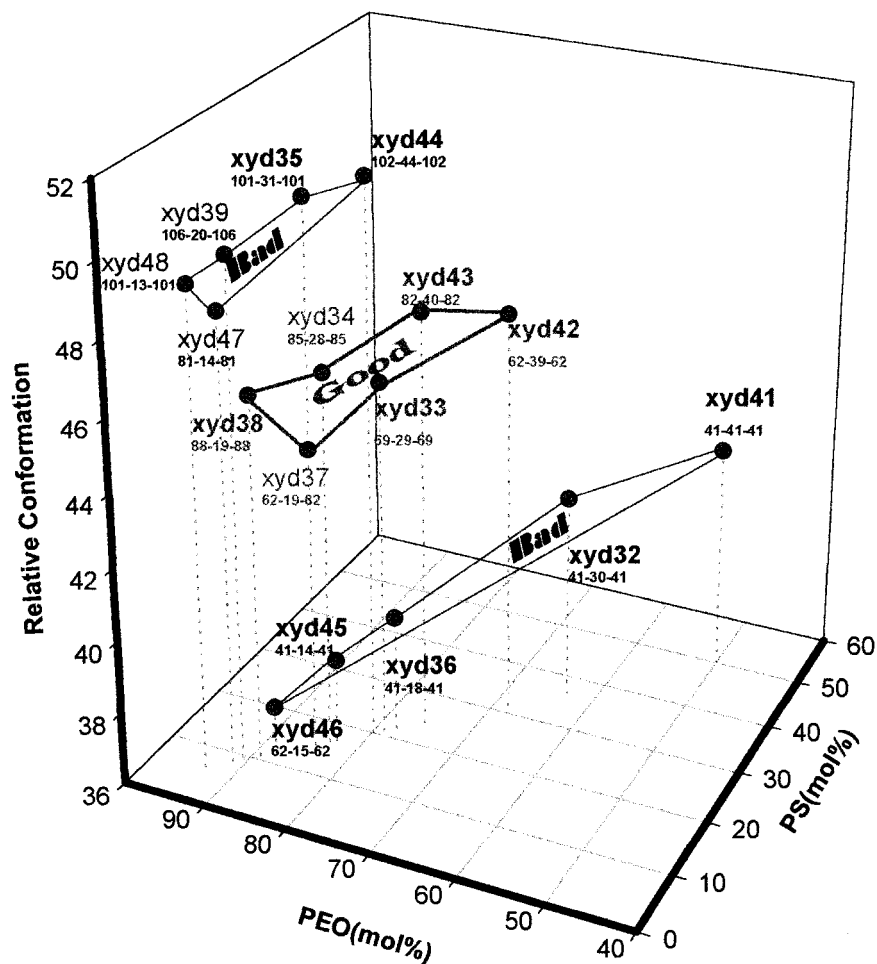
triblock copolymer and the block copolymer PEO-PS-PEO is in a segregated conformation. Consequently, the minimum in the plot of intrinsic viscosity vs. temperature is observed due to the transition in the conformation.

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 or the compatibility of PS with PEO chains increases with temperature and the PEO chain can penetrate the swollen PS core and entangle, decreasing the hydrodynamic volume. A schematic representation of the above model is illustrated in Figure 8.

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



**Figure 8** Schematic explanation for the conformation change of PEO-PS-PEO triblock copolymers in the propylene glycol within the temperature range of 20–70°C.



**Figure 9** Relative conformation vs. composition at 60°C for several PEO-PS-PEO triblock copolymers in propylene glycol.

intrinsic viscosity of these PEO homopolymers is independent of the temperature.

In order to account in stabilization efficiency for the effect of molecular conformation, as measured by intrinsic viscosity, a three-dimensional plot is shown in Figure 9. If the triblock composition falls in the low conformation region, the triblock copolymer either cannot 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. By contrast, 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.

To support the above statement, the distance between two particles was calculated to give feasibility to the bridging flocculation hypothesis. As the volume of a close-packed spherical particle 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 can be determined based on the value of the latex particle radius and latex particle density. For a particle radius of 81.5 nm, a protecting layer thickness of 116 nm was calculated. This then implies a distance between the particles in the close-packed situation 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 10, the hydrodynamic volume ( $V_e$ ) can be calculated according to the following equation:

$$V_e = (4\pi/3) \cdot Re^3 \quad (1)$$

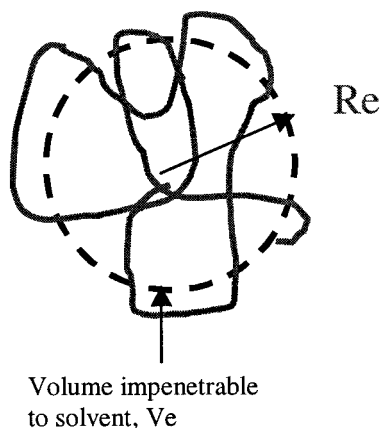
where  $Re$  is the radius of the equivalent hydrodynamic sphere of the PEO-PS-PEO triblock copolymer chain, and  $V_e$  is the volume of the equivalent hydrodynamic sphere of the PEO-PS-PEO triblock copolymer chain.

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

$$[\eta] = 2.5[(N \times V_e)/M] \quad (2)$$

where  $\eta$  is the intrinsic viscosity of PEO-PS-PEO triblock copolymer chain in propylene glycol at 60 °C,  $M$  is the molecular weight of PEO-PS-PEO triblock copolymer, and  $N$  is the Avogadro constant ( $6.023 \times 10^{23}$ ).

Consequently, the radius of the equivalent hydrodynamic sphere of the PEO-PS-PEO triblock copolymer chain ( $Re$ ) can be calculated according to eq. (1). The results are listed in Table V. 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.



**Figure 10** Schematic representation of the equivalent sphere model for PEO-PS-PEO triblock copolymer chains.

**Table V** Comparison of Radius of Equivalent Hydrodynamic Sphere of PEO-PS-PEO Triblock Copolymer Chain ( $Re$ ) for Three Different Levels in Figure 9

Sample	2Re (nm)	$D^*$ (nm)	$\Delta(2Re - D)$ (nm)	Result
Lower level	51	69	-18	No bridging
Middle level	64	69	-5	No bridging
Upper level	76	69	7	Bridging

$D^*$ , distance between the particles in the close packed situation.

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.

## CONCLUSIONS

The stabilizer effect of PEO-PS-PEO in the acrylic emulsion copolymerization in propylene glycol was systematically investigated. Only a narrow window in molecular weights and in PEO/PS ratio was found to be effective in stabilizing ethyl methacrylate/lauryl methacrylate emulsion copolymers in propylene glycol.

Both the influence of PEO block and the PS block length were studied as a function of structural variations. To be an effective stabilizing group, the molecular weight of the PEO blocks should be within 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. This narrow window of stability was explained in terms of the molecular conformation with changing molecular weight and PEO/PS ratio.

## REFERENCES

1. Chen, X.; Gardella, J. A., Jr.; Cohen, R. E. *Macromolecules* 1994, 27, 2206.
2. Napper, D. H. *Polymeric Stabilization of Colloidal Dispersion*; Academic Press: London, 1983.
3. Gast, A.; Leibler, L. *Macromolecules* 1986, 19, 686.
4. Goddard, E. D.; Vincent, B. *Polymer Adsorption and Dispersion Stability*; American Chemical Society: Washington, DC, 1984.

5. Tadros, Th.F.; Vincent, B. *J Phys Chem* 1980, 84, 1575.
6. Kayers, J. B.; Rawlins, D. A. *Colloid Polym Sci* 1979, 257, 622.
7. Dawkins, J. V.; Taylor, G. *J Chem Soc Faraday Trans* 1980, 76, 1263.
8. Hadziioannou, G.; Patel, S.; Granick, S.; Tirrell, M. *J Am Chem Soc* 1986, 108, 1869.
9. Patel, S.; Tirrell, M.; Hadziioannou, G. *Colloids Surf* 1988, 31, 157.
10. Taunton, H. J.; Toprakcioglu, C.; Klein, J. *Macromolecules* 1988, 21, 3333.
11. Baker, J. A.; Berg, J. C. *Langmuir* 1988, 4, 1055.
12. Ansarifar, M. A.; Luckham, P. F. *Polymer* 1988, 29, 329.
13. Marra, J.; Hair, M. L. *Colloids Surf* 1989, 34, 215.
14. Tadros, Th. F. *Adv. Colloid Interface Sci* 1980, 12, 141.
15. Tadros, Th. F. *The Effects of Polymer on Dispersions Properties*; Academic Press: London, 1982.
16. Napper, D. H. *J. Colloid Interface Sci* 1977, 58, 390.
17. Thyebault, H. Ph.D. Dissertation, Mulhouse, 1987.
18. Mura, J. L. Ph.D. Dissertation, Mulhouse, 1987.
19. Piirma, I. *Polymeric Surfactants, Surfactant Science Series 42*; Dekker: New York, 1992.
20. Kham, T. N.; Mobbs, R. H.; Price, C.; Quintana, J. R.; Stubbersfield, R. B. *Eur Polym J* 1987, 23, 191.
21. Riess, G.; Nervo, J.; Rogez, D. *Polym Prepr (Am Chem Soc, Div Polym Chem)* 1977, 181, 329.
22. Munch, M. R.; Gast, A. P. *Macromolecules* 1988, 21, 1366.
23. Marques, C. M.; Joanny, J. F.; Leibler, L. *Macromolecules* 1988, 21, 1051.
24. Evers, O. A. Ph.D Dissertation, Wageningen University, The Netherlands, 1990.
25. Klein, A.; Dimonie, V. *Emulsion Polymers* Institute, Lehigh University. 1994, unpublished results.
26. Evers, O. A.; Scheutjens, J. M. H. M.; Fleer, G. J. *J Chem Soc Faraday Trans* 1990, 9, 1333.
27. Riess, G.; Rogez, D. *Polym Prepr (Am Chem Soc, Div Polym Chem)* 1982, 23, 19.
28. Barker, M. C.; Vincent, B. *Colloids Surf* 1984, 8, 297.
29. Nakamura, K.; Endo, R.; Takeda, M. *J Polym Sci Polym Phys Ed* 1976, 14, 1287.
30. Khan, T. N.; Mobbs, R. H.; Price, C.; Quintana, J. R.; Stubbesfield, R. B. *Eur Polym J* 1987, 23, 191.
31. Zhao, C. L.; Winnik, M. A.; Riess, G.; Croucher, M. D. *Langmuir* 1990, 6, 514.
32. Wilhelm, M.; Zhao, C. L.; Wang, Y.; Xu, R.; Winnik, M. A.; Mura, J. L.; Riess, G.; Croucher, M. D. *Macromolecules* 1991, 24, 1033.
33. Xu, R.; Winnik, M. A.; Hallet, F. R.; Riess, G.; Croucher, M. D. *Macromolecules* 1991, 24, 87.
34. Rogez, D. Ph.D Dissertation, University of Haute Alsace, Mulhouse, France, 1987.
35. Riess, G.; Nervo, J.; Rogez, D. *Polym Eng Sci* 1977, 17, 634.
36. Tuzar, Z.; Knatochvil, P. *Adv Colloid Interface Sci* 1976, 6, 201.
37. Price, C. *Developments in Block Copolymers*; Goodman, I., Ed.; Applied Science: London, 1982; Vol. 1, p 39.
38. Riess, G.; Hurtrez, G.; Bahadur, P. *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Wiley: New York, 1985; Vol. 2, p 324.
39. Riess, G.; Rogez, D. *Polym Prepr (Am Chem Soc Div Polym Chem)*, 1982, 23, 19.
40. Leibler, L.; Orland, H.; Wheeler, J. C. *J Chem Phys* 1983, 79, 3550.
41. Nooland, J.; Hong, K. M. *Macromolecules* 1982, 15, 482.
42. Nooland, J.; Hong, K. M. *Macromolecules* 1983, 16, 1443.
43. Whitmore, M. D.; Nooland, J. *Macromolecules* 1985, 18, 657.
44. Munch, M. R.; Gast, A. P. *Macromolecules* 1988, 21, 1360.
45. Kalyanasundaram, K. *Photochemistry in Microheterogenous Systems*; Academic Press: Orlando, FL, 1987.
46. Turro, N. J.; Gratzel, M.; Braun, A. *Angew Chem Int Ed* 1980, 19, 675.
47. Xu, R.; Winnik, M. A.; Riess, G.; Chu, B.; Croucher, M. D. *Macromolecules* 1992, 25, 644.
48. Kogan, K. A.; Gast, A. P. *Macromolecules* 1990, 23, 745.
49. Jialanella, G. L.; Firer, E. M.; Piirma, I. *J Polym Sci Part A: Polym Chem* 1992, 30, 1925.
50. Winzor, C. L.; Mrazek, Z.; Winnik, M. A.; Croucher, M. D.; Riess, G. *Eur Polym J* 1994, 30, 121.
51. Mura, J. L.; Riess, G. *Polym Adv Technol* 1995, 6, 497.
52. Goddard, E. D.; Vincent, B. *Polymer Adsorption and Dispersion Stability*; American Chemical Society: Washington, DC, 1984.
53. Dondos, A.; Papanagopoulos, D. *J Polym Sci Part B: Polym Phys* 1996, 34, 1281.