

Nonaqueous Emulsion Copolymerization of Ethyl Methacrylate/Lauryl Methacrylate in Propylene Glycol. II. Adsorption of Poly(ethylene oxide)–Polystyrene–Poly(ethylene oxide) Triblock Copolymer on Latex Particles

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ABSTRACT: The adsorption behavior of various poly(ethylene oxide)–polystyrene–poly(ethylene oxide) (PEO-PS-PEO) triblock copolymer (TBC) s on acrylic latex particles in propylene glycol was studied. The composition of the PEO-PS-PEO triblock polymers varied from 41 to 106 in each PEO block length and from 18 to 41 in the PS block length. The location of the PEO-PS-PEO TBC was determined by analyzing for the physically adsorbed amount on the latex surface, the anchored amount on the surface, the entrapped amount inside the particle, and the “free” PEO-PS-PEO TBCs in the propylene glycol. A contour graph technique was applied to analyze the experimental data, which showed that a minimum existed for the physically adsorbed portion at a PS block length of about 30 units. When the PS block length was less than 30 units, the adsorption decreased with increasing PS block length, indicating rearrangement of mixed PEO brush and adsorbed PS block. When the PS block was greater than 30 units, the adsorption increased with increasing block length because of the poor solvency of the PS block in the propylene glycol medium, resulting in a collapse of the PS chain. Considering the binding energy between the PS block and the latex particle surface, which governs adsorption, it was 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 fraction of the block copolymer increased continuously with increasing PS block length in the entire region investigated. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1963–1975, 2001

Key words: poly(ethylene oxide)–polystyrene–poly(ethylene oxide) triblock copolymer; adsorption; ethyl methacrylate; lauryl methacrylate; propylene glycol

INTRODUCTION

Poly(ethylene oxide)–polystyrene–poly(ethylene oxide) (PEO-PS-PEO) triblock copolymer (TBC) coils at the solid–liquid interface are of technolog-

ical interest for many reasons. When PEO-PS-PEO TBCs 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. Thus, adsorption is a vital pa-

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Table I Characteristics of PEO-PS-PEO Triblock Copolymers

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

^a GPC data.^b Calculated data.

parameter for determining the stabilizing efficiency of PEO-PS-PEO TBCs.

Many studies investigated PEO-PS diblock copolymers or PEO-PS-PEO TBCs adsorption behavior at the solid-liquid interface.¹⁻²⁰ 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. The scaling laws and self-consistent field theory were both applied to develop these theoretical models for adsorption. This adsorption mechanism was supported not only by experimental evidence but also by theoretical modeling.

Sixteen well-defined and narrowly distributed PEO-PS-PEO TBCs were synthesized via an anionic polymerization process described elsewhere.²¹ Their compositions are listed in Table I. These PEO-PS-PEO TBCs were used as stabilizers in a model nonaqueous system, which contained ethyl methacrylate/lauryl methacrylate (EMA/LMA) as monomers, 2,2'-azobis(isobutyronitrile) (AIBN) as the free-radical initiator, and propylene glycol as the continuous phase in the nonaqueous emulsion polymerization. The stabilizing efficiency of these 16 PEO-PS-PEO TBCs was examined in this system. The experimental results demonstrated that among the 16 PEO-PS-PEO TBCs, only six of them could give a stable latex in a narrow window of composition.

The adsorption of PEO-PS-PEO TBCs on latex particles was studied in order to fully understand the stabilizing mechanism of PEO-PS-PEO TBCs in a propylene glycol medium. The latexes were cleaned via a serum replacement cell to determine the adsorbed and anchored fraction of different PEO-PS-PEO TBCs. The contour graphing technique was used to analyze the partitioning and variation of the adsorbed and anchored PEO-PS-PEO TBCs on the latex particles.

EXPERIMENTAL

Materials

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

All other materials were used as received, including propylene glycol (99.5+%, ACS reagent, Aldrich), AIBN (98%, Aldrich), hydroquinone (99%, Aldrich), iodine (99.8+%, ACS reagent, Aldrich), and potassium iodide (99+%, ACS reagent, Aldrich). The PEO-PS-PEO TBCs were synthesized as described elsewhere.²¹

Determination of Amount of Adsorbed PEO-PS-PEO TBC on Latex Particles

After emulsion polymerization the PEO-PS-PEO stabilizer is located in one of the following places:

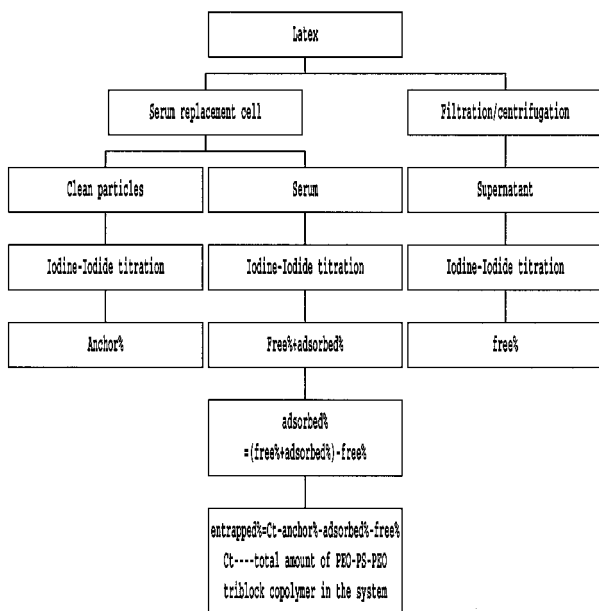


Figure 1 The procedure for measuring the partitioning of the PEO-PS-PEO triblock copolymer stabilizer.

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 TBC in the latex system is given schematically in Figure 1. The latex synthesis was done by batch polymerization and is fully described elsewhere.²¹ A serum replacement cell was used to clean the latex and collect all of the free and adsorbed PEO-PS-PEO TBC. 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^{22,23} was used to determine the concentration of the PEO-PS-PEO TBC in the serum according to the following procedures that are represented schematically in Figure 2.

1. The free and desorbed PEO-PS-PEO TBCs 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 and centrifugation (C_f).
3. The difference between the results of step 1 and step 2 represented the amount of adsorbed copolymer (C_{ads}).

4. The cleaned latex was titrated with iodine-iodide to determine the amount of anchored (grafted) copolymer at the particle interface (C_{anc}).
5. The amount of entrapped (buried) copolymer inside the particles (C_{ent}) was calculated by mass balance using the following equation:

$$C_{ent} = C_t - C_f - C_{ads} - C_{anc} \quad (1)$$

where C_{ent} is the entrapped amount of copolymer in the latex particles, C_t is the total amount of PEO-PS-PEO TBC 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, and C_{anc} is the amount of anchored copolymer on the particle surface.

6. Control experiments were carried out in which a known amount of PEO-PS-PEO TBC was used with no latex present to determine if any TBC remained adsorbed on the serum replacement membrane.

Iodine (1 wt %) and potassium iodide (2 wt %) in propylene glycol were mixed together. The serum sample (19 mL) containing PEO-PS-PEO TBC 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 of propylene glycol and 1 mL of iodine-iodide reagent (yellow). The concentration of the PEO-PS-PEO TBC was deter-

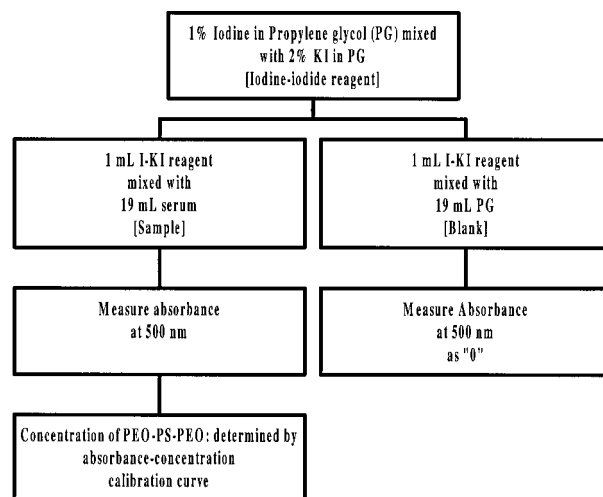


Figure 2 A schematic representation of the I_2 titration procedure.

Table II Partitioning Behavior of Different PEO-PS-PEO Triblock Copolymers (TBC) on Latex Particles

	Sample Identification					
	<i>xyd33</i>	<i>xyd34</i>	<i>xyd38</i>	<i>xyd37</i>	<i>xyd43</i>	<i>xyd42</i>
Composition of PEO-PS-PEO	69-29-69	85-28-85	88-19-88	62-19-62	82-40-82	62-39-62
No. PS units	29	28	19	19	40	39
No. PEO units	138	170	176	124	164	124
Molecular weight of TBC	9,100	10,400	9,700	7,400	11,400	9,500
Total no. 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 soln 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	3,235	3,629	5,852	5,529	4,829	5,660
Anchored on each particle	3,213	3,003	2,378	2,957	4,250	5,062
Entrapped in each particle	1,130	918	1,117	2,005	273	429
Free TBC molecules in medium	4,320	2,769	1,716	4,142	61	146
Total TBC adsorbed (phys. + anchored) on each particle	6,448	6,632	8,230	8,486	9,090	10,722

The values are for the systems in which 0.1 g of TBC was used in nonaqueous propylene glycol in the emulsion copolymerization of EMA-LMA at 30% solids.

mined from a previously measured absorbance-concentration calibration curve.

A UV-vis spectrophotometer (Bausch & 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 TBC were determined to generate a calibration curve (a plot of absorbance vs. concentration) from which the concentration of an unknown solution could be determined.

The total number of molecules of PEO-PS-PEO TBC in the reactor for a given polymerization was calculated using the following equation:

total molecules of TBC in reactor

$$= (W_{\text{TBC}}/M_{\text{TBC}})N_A \quad (2)$$

where W_{TBC} is the total amount of PEO-PS-PEO TBC added to the reactor, M_{TBC} is the molecular

weight of PEO-PS-PEO TBC added to the reactor, and N_A is Avogadro's number (6.023×10^{23}).

All the latexes listed in Table II had 30% solids content and 0.1 g of PEO-PS-PEO TBC as stabilizer. Every latex listed in Table III contained 30% solids content and 0.2 g of PEO-PS-PEO TBC as stabilizer. In the latexes included in Table IV the solids content of each latex was 40% and the amount of PEO-PS-PEO TBC was 0.2 g. Because different PEO-PS-PEO TBCs had different molecular weights, the total number of molecules of PEO-PS-PEO TBCs in the reactor was different in each case. This led to the different TBC molar concentrations because the total solution volume was constant for all six latexes in each table.

The particle density, which was the number of particles per milliliter (N/mL), was calculated using eqs. (3) and (4):

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

Table III Partitioning Behavior of Different PEO-PS-PEO Triblock Copolymers (TBC) on Latex Particles

	Sample Identification					
	<i>xyd33</i>	<i>xyd34</i>	<i>xyd38</i>	<i>xyd37</i>	<i>xyd43</i>	<i>xyd42</i>
Composition of PEO-PS-PEO	69-29-69	85-28-85	88-19-88	62-19-62	82-40-82	62-39-62
No. PS units	29	28	19	19	40	39
No. PEO units	138	170	176	124	164	124
Molecular weight of TBC	9,100	10,400	9,700	7,400	11,400	9,500
Total no. 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 soln 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	3,193	3,508	5,256	4,868	4,622	4,880
Anchored on each particle	3,080	2,884	2,313	2,901	4,241	4,727
Entrapped in each particle	1,855	1,529	2,245	3,455	757	1,025
Free TBC molecules in medium	9,869	7,837	7,195	10,922	4,669	6,736
Total TBC adsorbed (phys. + anchored) on each particle	6,273	6,392	7,569	7,769	8,863	9,607

The values are for the systems in which 0.2 g of TBC was used in nonaqueous propylene glycol in the emulsion copolymerization of EMA-LMA at 30% solids.

Thus,

$$N/\text{mL} = [(W_{\text{EMA}} + W_{\text{LMA}})x]/[(\pi/6)D^3d] \quad (4)$$

where W_{EMA} is the amount of monomer (EMA) in 1 mL of latex (g/mL), W_{LMA} is the amount of monomer (LMA) in 1 mL of latex (g/mL), D is the particle diameter (cm), d is the latex density (1.19 g/mL), and x is the percentage of monomer converted to polymer.

RESULTS AND DISCUSSION

The experimental results are listed separately in Tables II–IV, respectively. No residual block polymer was retained on the serum replacement membrane for all of the six PEO-PS-PEO TBCs investigated. Only six PEO-PS-PEO TBCs produced stable latexes in propylene glycol. The sta-

ble latexes were used to determine the partitioning behavior for these PEO-PS-PEO TBCs on latex particles. The compositions of these PEO-PS-PEO TBCs 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 number-average molecular weights ranged from 7,400 to 11,400 g/mol. Sample *xyd37* had the lowest molecular weight, and *xyd43* had the highest molecular weight.

Adsorption of PEO-PS-PEO TBC on Latex Particles

The PEO-PS-PEO TBC stabilizer in the latex system could possibly be found at four locations: entrapped within the latex copolymer particles, anchored (grafted) on the surface of the copolymer particles, physically adsorbed on the copolymer particles, and as free TBC in the propylene glycol solution. Among these four locations, only the

Table IV Partitioning Behavior of Different PEO-PS-PEO Triblock Copolymers (TBC) on Latex Particles

	Sample Identification					
	<i>xyd33</i>	<i>xyd34</i>	<i>xyd38</i>	<i>xyd37</i>	<i>xyd43</i>	<i>xyd42</i>
Composition of PEO-PS-PEO	69-29-69	85-28-85	88-19-88	62-19-62	82-40-82	62-39-62
No. PS units	29	28	19	19	40	39
No. of PEO units	138	170	176	124	164	124
Molecular weight of TBC	9,100	10,400	9,700	7,400	11,400	9,500
Total no. 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 soln 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	3,864	4,393	6,778	6,191	7,200	7,930
Anchored on each particle	3,569	3,389	3,039	3,705	4,970	5,535
Entrapped in each particle	3,999	3,211	4,227	6,101	1,859	2,496
Free TBC molecules in medium	13,871	11,154	9,701	15,130	6,223	8,750
Total TBC adsorbed (phys. + anchored) on each particle	7,433	7,782	9,818	9,896	12,170	13,465

The values are for the systems in which 0.2 g of TBC was used in nonaqueous propylene glycol in the emulsion copolymerization of EMA-LMA at 40% solids.

anchored and adsorbed PEO-PS-PEO TBCs 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 TBCs.

A contour plotting technique²⁴ was used to analyze the partitioning in 3 dimensions with respect to PS and PEO block lengths. The variation of the adsorbed and anchored PEO-PS-PEO TBC on the latex particles, for instance, is shown in Figures 3 and 4. The procedure used to construct the contour plot is described in the next two paragraphs.

On a normal 2-dimensional coordinate, assign the corresponding number of adsorbed TBC molecules (or anchored molecules) to the corresponding PEO-PS-PEO TBC. For example, in the case of sample *xyd33* there were 3235 TBC molecules adsorbed on each latex particle, which corresponded to the point where there were 29 PS

units and 138 PEO (69 units on each side of the chain) units present in the TBC molecule. This is shown as the middle point in Figure 5. The same approach was utilized for the other five TBC samples. The assumption was then made that linear extrapolation can be used between experimental points to obtain intermediate values, and those similar values can be connected to yield isocontour lines.

The data were thus interpolated with an increment of 500 TBC molecules. The small diamond symbols given in Figure 5 between two experimental data points are the interpolated values. All the points were used to obtain the contour plots.

Contour plots showing the number of PEO-PS-PEO TBC molecules physically adsorbed on the latex particles are given in Figures 3, 4, and 6. Contour plots displaying the number of PEO-PS-PEO TBC molecules anchored (grafted) on the latex particles are presented in Figures 7–9.

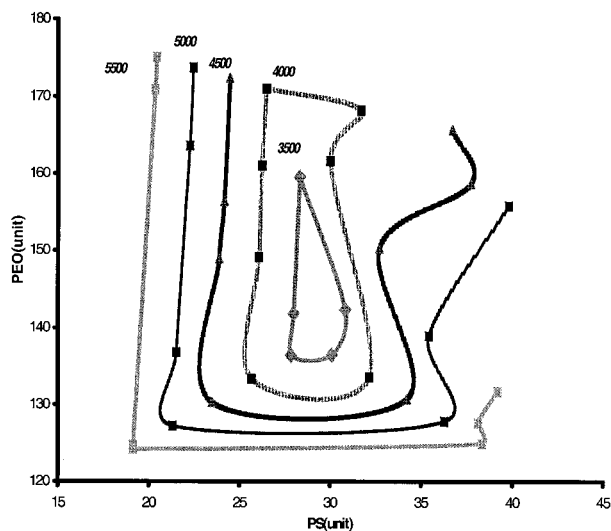


Figure 3 A contour plot showing the number of PEO-PS-PEO triblock copolymer (TBC) chains adsorbed on each latex particle. The numbers on the plot represent the number of TBC molecules adsorbed on a latex particle based on connecting the interpolated data, which have the same value (from Fig. 3; 30% solids latex prepared with 0.1 g of TBC).

From the contour plots of the number of adsorbed PEO-PS-PEO TBC molecules on a latex particle (Figs. 3, 4, 6), 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 TBCs where the PS block length was less than 30 units, the PEO chains most likely ad-

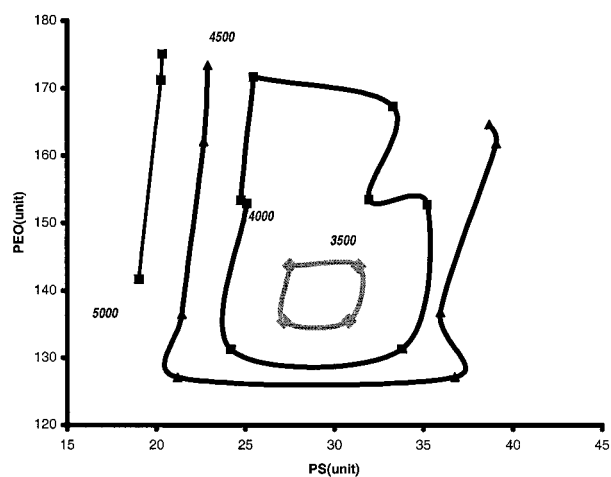


Figure 4 A contour plot showing the number of PEO-PS-PEO triblock copolymer (TBC) chains adsorbed on each latex particle (30% solids latex prepared with 0.2 g of TBC).

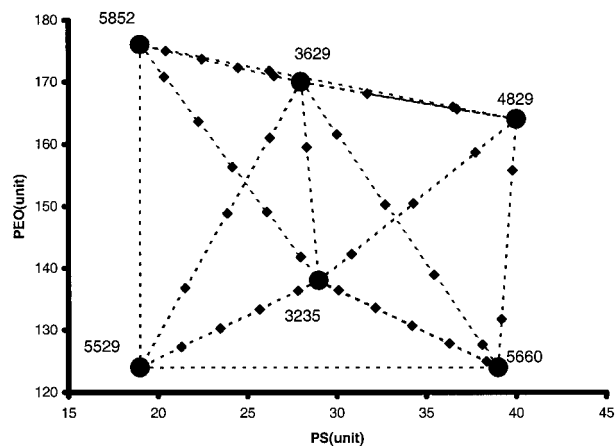


Figure 5 The construction of a contour plot showing the number of PEO-PS-PEO triblock copolymer (TBC) molecules adsorbed on each latex particle. The six numbers on the plot represent the actual number of TBC molecules adsorbed on the copolymer particles as shown in Table II.

sorbed on the surface of the particles to form a loose brush-type layer that conferred stability to the particles. As the PS block length increased, the binding energy between the PS block and the particle increased. Thus, anchoring of more segments of the PS block to the particle surface increased. The PEO brush on the particle surface must be rearranged to make space for the PS block to attach on the particle surface. Conse-

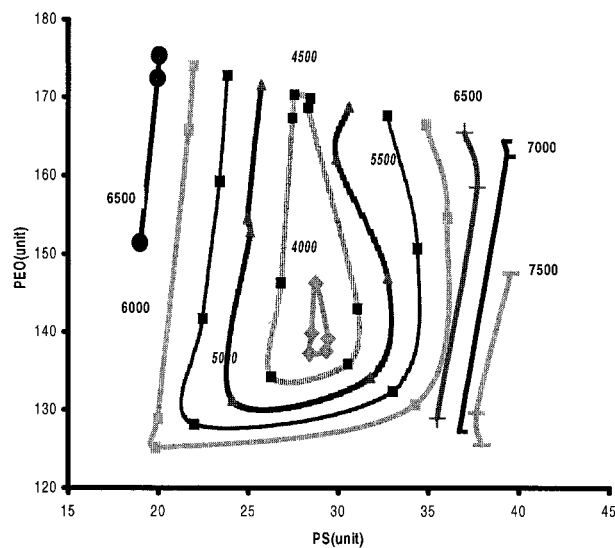


Figure 6 A contour plot showing the number of PEO-PS-PEO triblock copolymer (TBC) chains adsorbed on each latex particle (40% solids latex prepared with 0.2 g of TBC).

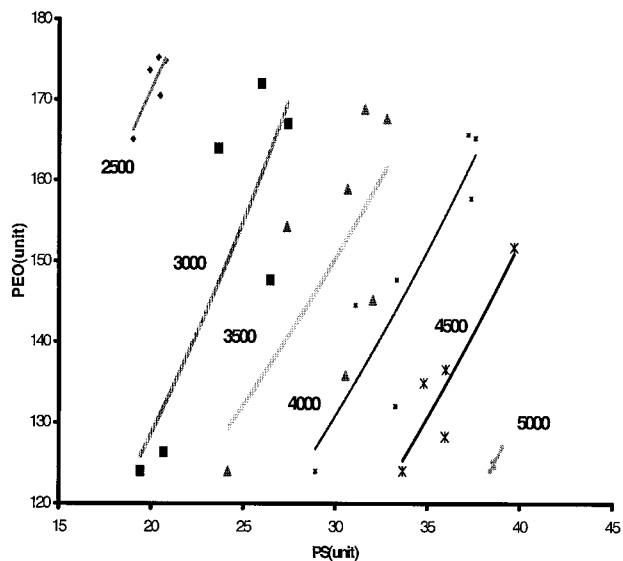


Figure 7 A contour plot showing the number of PEO-PS-PEO triblock copolymer (TBC) chains anchored on each latex particle (30% solids latex prepared with 0.1 g of TBC).

quently, the overall number of adsorbed PEO-PS-PEO TBC molecules on the latex particle decreased.

For those PEO-PS-PEO TBCs where the PS block length was longer than 30 units, the PS block collapsed and was only swollen in the propylene glycol medium as the PS block length increased. The large swollen PS core created a free volume for the PEO block. Therefore, the PEO

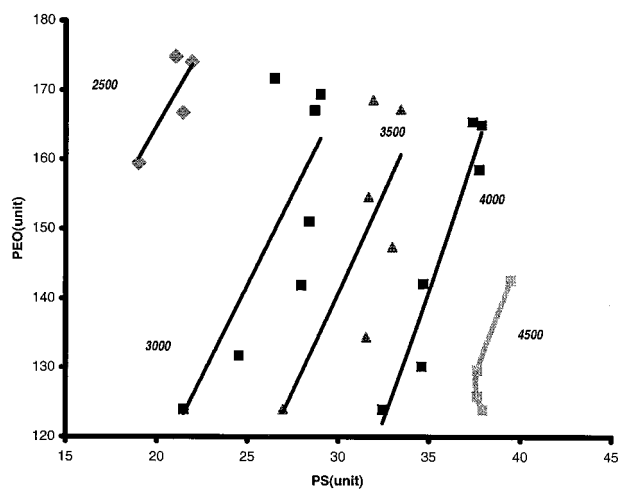


Figure 8 A contour plot showing the number of PEO-PS-PEO triblock copolymer (TBC) chains anchored on each latex particle (30% solids latex prepared with 0.2 g of TBC).

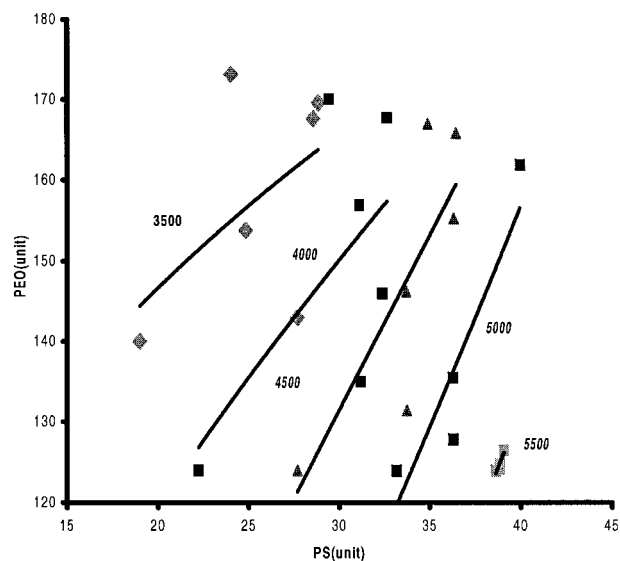


Figure 9 A contour plot showing the number of PEO-PS-PEO triblock copolymer (TBC) chains anchored on each latex particle (40% solids latex prepared with 0.2 g of TBC).

chains could reside inside the PS core. Because propylene glycol is a poor solvent for the PS block, the PEO-PS-PEO TBC chains preferred to remain anchored on the particle surface rather than desorbing into the medium because of the unfavorable environment (poor solvency) for the PS block. This could be confirmed from the concentration of the free PEO-PS-PEO TBC in the continuous phase, which was found to be close to zero for the two PEO-PS-PEO TBCs that had 40 PS units (0.7 and 1.3%, see Table II). However, the anchored and adsorbed PEO-PS-PEO TBC molecules saturated the particle surface. The copolymer molecules were in a dynamic equilibrium between adsorbed and desorbed TBC molecules on the particle surface.

As the PS block chain length increased, the area occupied by each TBC increased and the number of chains packed decreased to a minimum of around 30 PS block units. After this point, the PS block collapsed and therefore larger number of TBC chains could be packed on the same particle. The data on intrinsic viscosity²¹ also support the proposed mechanism of TBC adsorption. For similar values of total (PS + PEO) molecular weights (TBCs *xyd39* and *xyd43*) but with different PS block chain lengths of 20 and 40 PS units, respectively, the intrinsic viscosity was lower for the TBC with a larger PS block. This demonstrated that the polymer chain was in a collapsed config-

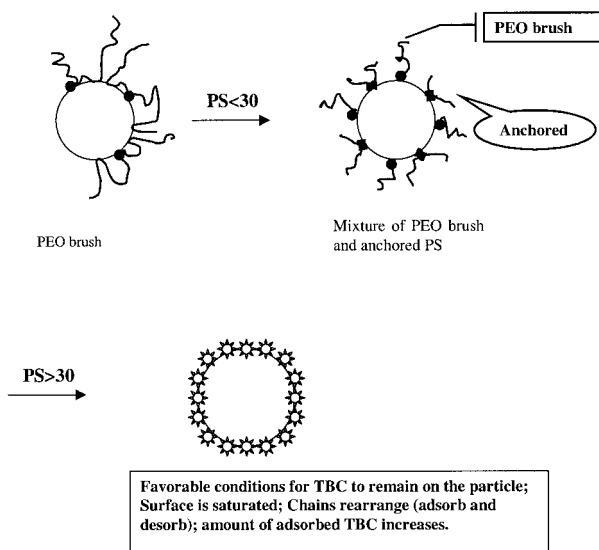


Figure 10 A schematic representation of the adsorbed PEO-PS-PEO triblock copolymer on latex particles.

uration and therefore had reduced hydrodynamic volume of the random coil. Thus, the number of adsorbed PEO-PS-PEO TBC molecules increased as the PS block length increased. A schematic representation of the scenario described above is shown in Figure 10.

From the contour plot of the anchored PEO-PS-PEO TBC on each particle (Figs. 7–9), it seems that the PS block length significantly affected the amount of anchored TBC chains on each particle. As the PS block length increased, the binding energy between the PS block and the polymer particle increased; therefore, the number of the anchored TBC chains increased continuously. With an increasing number of PS segments in contact with the particle surface during the polymerization reaction, the probability for grafting also increased. But the PS block length also affected the solubility of the TBC in the propylene glycol medium. In one extreme one may think that, when the length of the PS block exceeds a critical length, the TBC 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, the upper critical PS block length and the lower crit-

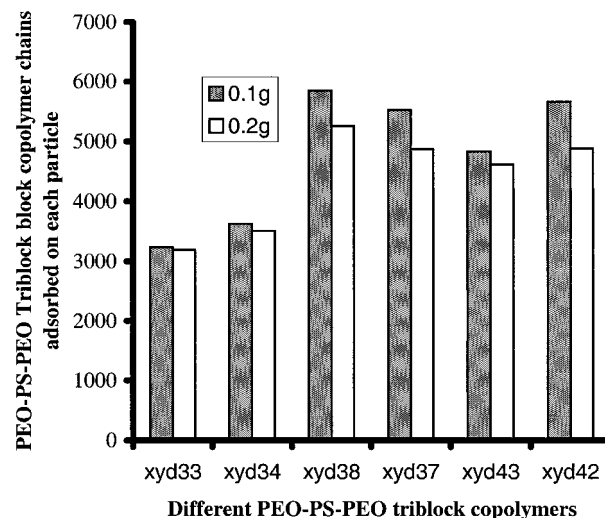


Figure 11 The effect of the stabilizer concentration on the adsorbed portion of PEO-PS-PEO triblock copolymer on each latex particle.

ical PS block length are both envisioned to be important parameters for a TBC to act as an efficient stabilizer.

Effect of Stabilizer Concentration on Partitioning Behavior of PEO-PS-PEO TBC on Each Latex Particle

As the amount of stabilizer increased from 0.1 to 0.2 g, the adsorbed or anchored PEO-PS-PEO TBC on each latex particle decreased consis-

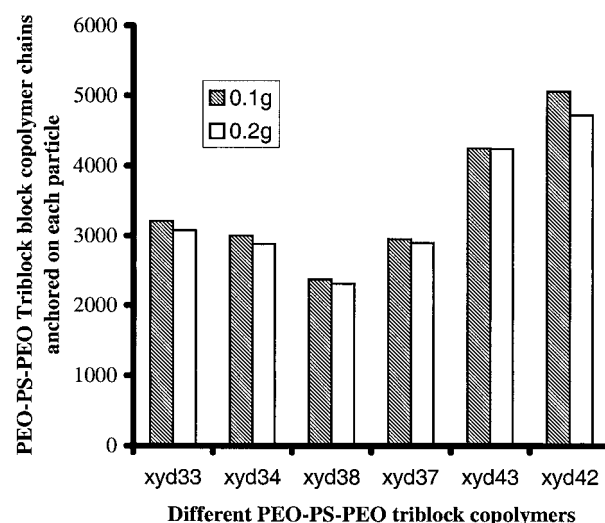


Figure 12 The effect of the stabilizer concentration on the anchored amount of PEO-PS-PEO triblock copolymer on each latex particle.

Table V Surface Area Occupied by Single PEO-PS-PEO Triblock Copolymer (TBC) Molecule

	Sample Identification					
	<i>xyd33</i>	<i>xyd34</i>	<i>xyd38</i>	<i>xyd37</i>	<i>xyd43</i>	<i>xyd42</i>
Composition of PEO-PS-PEO	69-29-69	85-28-85	88-19-88	62-19-62	82-40-82	62-39-62
No. PS units	29	28	19	19	40	39
No. PEO units	138	170	176	124	164	124
Molecular weight of TBC	9,100	10,400	9,700	7,400	11,400	9,500
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	3,235	3,629	5,852	5,529	4,829	5,660
Total surface area (m ² /mL)	9.34	9.34	9.34	9.34	9.34	9.34
Surface area (Å ² /TBC)	2,578	2,298	1,425	1,508	1,727	1,473

The values are for this system in which 0.1 g of TBC was used in nonaqueous propylene glycol in the emulsion copolymerization of EMA-LMA at 30% solids for the different TBC compositions.

tently. The effect of the stabilizer concentration on the adsorbed portion of PEO-PS-PEO TBC on each latex particle is shown in Figure 11. Figure 12 displays the influence of stabilizer concentration on the anchored portion of PEO-PS-PEO TBC 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 to 149 nm and the surface area of each particle decreased from $(8.34 \text{ to } 6.99) \times 10^{-14} \text{ m}^2$. The surface area occupied by a single PEO-PS-PEO TBC molecule in which 0.1 g of TBC was used in nonaqueous propylene glycol in the emulsion copolymerization of EMA-LMA at 30% solids for the different PEO-PS-PEO TBC compo-

sitions is shown in Table V. . Similarly, the surface area occupied by a single PEO-PS-PEO TBC molecule in which 0.2 g of TBC was used at 30% solids for the different PEO-PS-PEO TBC compositions is shown in Table VI.

As the amount of stabilizer increased from 0.1 to 0.2 g, the surface area occupied by a single TBC decreased from 15 to 3% for the different TBC compositions. This was most likely due to the particle curvature effect. Stutman²⁵ observed a similar trend in a monodispersed PS latex system using sodium lauryl sulfate as the surfactant.

Effect of Monomer Concentration on Partitioning Behavior of PEO-PS-PEO TBC on Each Latex Particle

When the monomer concentration was changed to yield 30–40% solid content, the adsorbed or an-

Table VI Surface Area Occupied by Single PEO-PS-PEO Triblock Copolymer (TBC) Molecule

	Sample Identification					
	<i>xyd33</i>	<i>xyd34</i>	<i>xyd38</i>	<i>xyd37</i>	<i>xyd43</i>	<i>xyd42</i>
Composition of PEO-PS-PEO	69-29-69	85-28-85	88-19-88	62-19-62	82-40-82	62-39-62
No. PS units	29	28	19	19	40	39
No. PEO units	138	170	176	124	164	124
Molecular weight of TBC	9,100	10,400	9,700	7,400	11,400	9,500
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	3,193	3,508	5,256	4,868	4,622	4,880
Total surface area (m ² /mL)	10.21	10.21	10.21	10.21	10.21	10.21
Surface area (Å ² /TBC)	2,132	1,940	1,295	1,398	1,473	1,395

The values are for this system in which 0.2 g of TBC was used in nonaqueous propylene glycol in the emulsion copolymerization of EMA-LMA at 30% solids for the different TBC compositions.

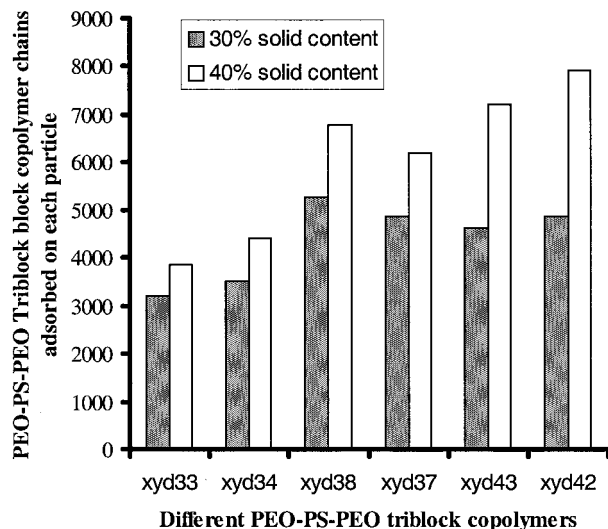


Figure 13 The effect of the monomer concentration on the adsorbed portion of PEO-PS-PEO triblock copolymer on each latex particle.

chored PEO-PS-PEO copolymer on each latex particle also increased. This was true for all six TBCs. Figure 13 demonstrates the influence of monomer concentration on the adsorbed portion of PEO-PS-PEO TBC on each latex particle. The efficacy of the monomer concentration on the anchored portion of PEO-PS-PEO TBC on each latex particle is illustrated in Figure 14. The above results can be understood by examining the effect of the monomer concentration on the particle surface area generated. The particle surface area

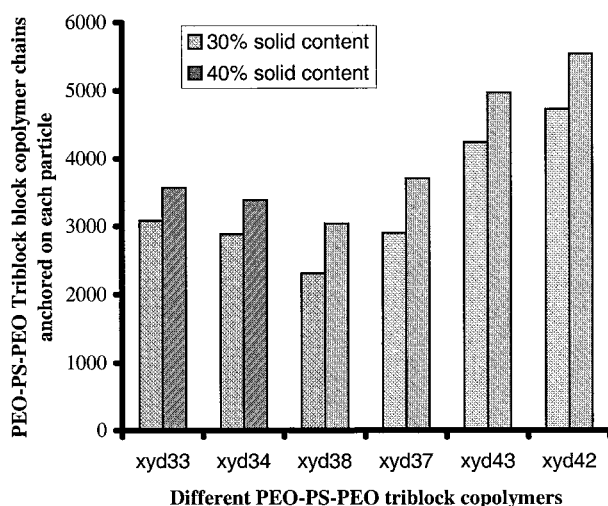


Figure 14 The effect of the monomer concentration on the anchored amount of PEO-PS-PEO triblock copolymer on each latex particle.

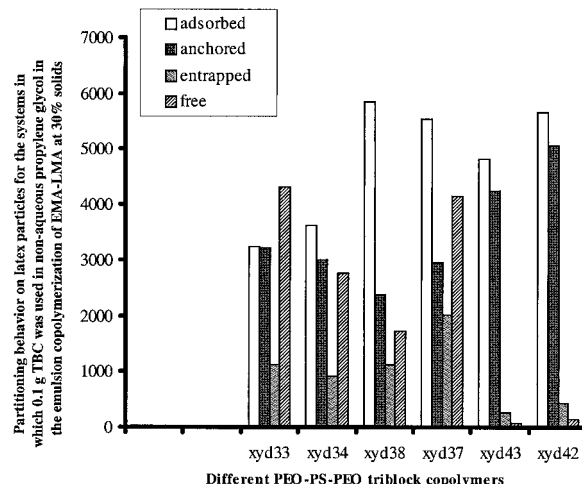


Figure 15 The partitioning behavior of different PEO-PS-PEO triblock copolymers (TBCs) on latex particles for the systems in which 0.1 g of TBC was used in nonaqueous propylene glycol in the emulsion copolymerization of EMA-LMA at 30% solids.

was determined based on the particle size data, which was measured by means of light scattering. When the amount of monomer increased, the particle size increased from 149 to 199 nm, the particle number density decreased from 1.46×10^{14} to 8.26×10^{13} , and the surface area of each particle increased from 6.99×10^{-14} to 1.24×10^{-13} m². Therefore, a larger surface area needs more PEO-PS-PEO TBCs to provide stabilization. This explains why the physically adsorbed and anchored PEO-PS-PEO TBC molecules both increased with increasing monomer concentration.

Entrapped and Free Partitions of Different PEO-PS-PEO TBCs on Latex Particles for Emulsion Copolymerization of EMA-LMA in Nonaqueous Propylene Glycol

As mentioned before, each PEO-PS-PEO TBC had four locations in a latex system, which were affected by the composition of PEO-PS-PEO TBC, the stabilizer concentration, and the monomer concentration. Figure 15 shows the partitioning behavior of different PEO-PS-PEO TBCs on latex particles for the systems in which 0.1 g of TBC was used in nonaqueous propylene glycol in the emulsion copolymerization of EMA-LMA at 30% solids. The PEO-PS-PEO TBCs *xyd43* (82-40-82) and *xyd42* (62-39-62) had a minimum amount of entrapped partitions due to the large volume of the PS swollen core. Similarly, the PEO-PS-PEO

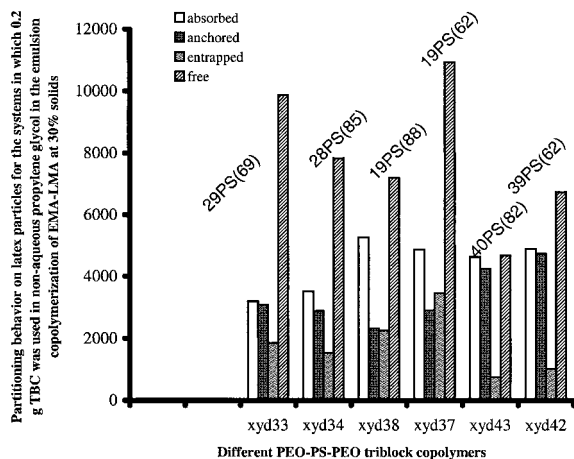


Figure 16 The partitioning behavior of different PEO-PS-PEO triblock copolymers (TBCs) on latex particles for the systems in which 0.2 g of TBC was used in nonaqueous propylene glycol in the emulsion copolymerization of EMA-LMA at 30% solids.

TBCs *xyd38* (88-19-88) and *xyd37* (62-19-62) had a maximum amount of entrapped partitions because of the small volume of the PS swollen core. The “free” partitions of the PEO-PS-PEO TBCs *xyd43* (82-40-82) and *xyd42* (62-39-62) were near zero because the large PS swollen core preferred to stay on the particle surface. For the rest of the PEO-PS-PEO TBCs [*xyd33* (69-29-69), *xyd34* (85-28-85), *xyd38* (88-19-88), and *xyd37* (62-19-62)] a significant amount of TBCs existed in the continuous phase.

Figure 16 illustrates the partitioning behavior of different PEO-PS-PEO TBCs on latex particles for the systems in which 0.2 g of TBC was used in nonaqueous propylene glycol in the emulsion copolymerization of EMA-LMA at 30% solids. Figure 17 depicts the partitioning behavior of different PEO-PS-PEO TBCs on latex particles for the systems in which 0.2 g of TBC was used in nonaqueous propylene glycol in the emulsion copolymerization of EMA-LMA at 40% solids. Correspondingly, the PEO-PS-PEO TBCs *xyd43* (82-40-82) and *xyd42* (62-39-62) had a minimum amount of entrapped partitions, despite the stabilizer concentration and monomer concentration. With increasing monomer and stabilizer concentrations a large amount of TBC was free in the medium, regardless of the composition of the TBCs.

In summary, the entrapped partition was mainly determined by the composition of the PEO-PS-PEO TBCs and was slightly affected by the monomer and stabilizer concentrations. The free partition was decided by the monomer con-

centration, the stabilizer concentration, and the composition of the PEO-PS-PEO TBC.

CONCLUSION

In order to understand the mechanism of PEO-PS-PEO TBC as a stabilizer in a model nonaqueous emulsion polymerization system consisting of EMA and LMA comonomers, a method was developed to measure the adsorption of PEO-PS-PEO TBC on latex particles. The PEO-PS-PEO TBC could be found at four different locations in the latex system: entrapped inside the copolymer particles, anchored to the surface of the copolymer particles, physically adsorbed onto the particles, and as free TBC in the propylene glycol continuous phase. The location of the TBCs 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 TBC that was physically adsorbed on the latex particles for a PS block length of about 30 units. When the PS block size was increased to 30 units, adsorption was decreased because of the rearrangement of the mixed PEO brush and adsorbed PS block. When the PS block length was greater than 30 units, adsorption increased again because the PS swollen core preferred to remain on the particle surface as op-

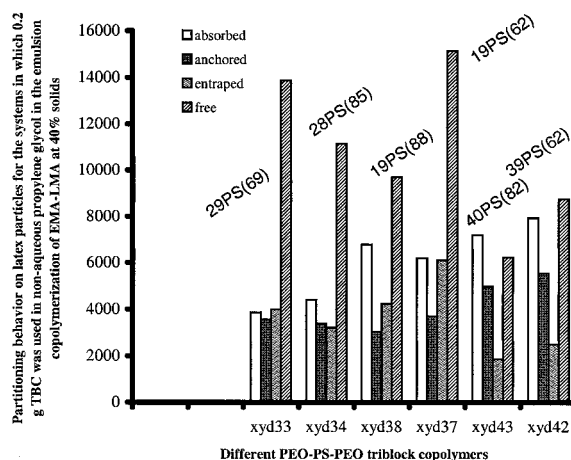


Figure 17 The partitioning behavior of different PEO-PS-PEO triblock copolymers (TBCs) on latex particles for the systems in which 0.2 g of TBC was used in nonaqueous propylene glycol in the emulsion copolymerization of EMA-LMA at 40% solids.

posed to desorbing into the propylene glycol medium. Also, the lower limit for the PS unit length was controlled by the binding energy between the PS block and the latex surface. The upper limit of the PS block length was governed by the solubility of the PS block in propylene glycol.

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

We found that the physically adsorbed and anchored molecules both decreased with increasing stabilizer concentration. On the other hand, when the monomer concentration was increased, the physically adsorbed molecules and the anchored molecules increased.

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: 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, T. 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, 1, 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, T. F. *Adv Colloid Interface Sci* 1980, 12, 141.
15. Tadros, T. F. *The Effects of Polymer on Dispersions Properties*; Academic: London, 1982.
16. Napper, D. H. *J Colloid Interface Sci* 1977, 58, 390.
17. Thyebault, H. Ph.D. Thesis, Ecole Nationale Supérieure de Chimie de Mulhouse, France, 1987.
18. Mura, J. L. Ph.D. Thesis, Ecole Nationale Supérieure de Chimie de Mulhouse, France, 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. You, X.; Dimonie, V. L.; Klein, A. *J Appl Polym Sci*, submitted.
22. Ross, S.; Oliver, J. P. *J Phys Chem* 1959, 63, 1671.
23. El-Aasser, M. S.; Ahmed, S. M.; Poehlein, G. W.; Vanderhoff, J. W. In *Polymer Colloids II*; Fitch, R. M., Ed.; Plenum: New York, 1980; p 361.
24. Otterloo, P. J. *A Contour-Oriented Approach to Shape Analysis*; Prentice-Hall: New York, 1991.
25. Stutman, D. R. Ph.D. Thesis, Lehigh University, 1984.