Self-micellization of $(AB)_n$ type star-block copolymers

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Vinylbenzyl-terminated poly(styrene-*b*-isoprene) AB type diblock macromonomers were prepared by the direct coupling of corresponding living diblock anions with a large excess of *p*-chloromethylstyrene. $(AB)_n$ type star-block copolymers were synthesized by microgelation in micelles formed by diblock macromonomer with ethylene glycol dimethacrylate as a linking agent. We studied the self-micellization of $(AB)_n$ type star-block copolymers as a parameter of arm number (n) from electron microscopy observations.

(Keywords: star-block copolymer; microgelation; self-micellization)

Introduction

On the basis of compositional variations in domains and thickness of the interface between domains, theoretical treatments of the phase separation of block copolymers are classified into two types, namely, strong segregation theories[1–3] and weak segregation theories[4–9]. de la Cruz and Sanchez[4] have calculated the phase stability criteria and static structure factors in the weak segregation regime for a simple AB graft copolymer, for star copolymers with equal numbers of A and B arms, and for *n*-arm star diblock copolymers. They have predicted that it is easier to phase separate star copolymers than corresponding graft and block copolymers. As the arm number (n) increases, the core of the $(AB)_n$ type star will naturally become richer in A monomers and the monomers deep in the core will be effectively screened from interacting with B monomers. While the order–disorder transitions for $(AB)_n$ star copolymers have been studied in the weak segregation regime[10,11], the quantitative nature of predictions has not yet been examined in detail for neat copolymers.

At present, the most rigorous way to prepare $(AB)_n$ type star copolymers is the coupling of narrow-molecular-weight-distribution diblock anions with multifunctional chlorosilane compounds[10–13]. Fetters and co-workers[14,15] have reported another synthetic approach to $(AB)_n$ star copolymers by means of crosslinking AB diblock monocarbanions with divinylbenzene. More recently, we have reported the formation of $(AB)_n$ star copolymers by microgelation in micelles between diblock macromonomers and ethylene glycol dimethacrylate (EGDM)[16]. We could obtain relatively 'monodisperse' $(AB)_n$ star copolymers with an arbitrary number of arms ($n = 5$–30) using this 'organized polymerization'.

In this communication, $(AB)_n$ star-block copolymers were synthesized by microgelation in micelles (organized polymerization) formed by diblock macromonomer with EGDM as a linking agent. We studied the self-micellization of $(AB)_n$ star-block copolymers as a parameter of arm number (n) from the observation of microphase-separated structures in the strong segregation regime.

Experimental

Synthesis and characterization of diblock macromonomers. Diblock copolymer anions were prepared by living anionic polymerization techniques using the break–seal method. Details concerning the synthesis and purification of such diblock anions have been given elsewhere[16,17]. The characteristics of the poly(styrene-*b*-isoprene) (poly(S-*b*-I)) diblock macromonomer, SIM-3, used in this work are as follows: number-average molecular weight ($\bar{M}_n$) = 1.06×10^4; molecular weight distribution ($\bar{M}_w/\bar{M}_n$) = 1.04; polyisoprene (PI) blocks = 18.7 wt%; functionality of terminal vinylbenzyl groups = 0.95 per molecule.

Synthesis and characterization of $(AB)_n$ star-block copolymers. Details concerning the synthesis of $(AB)_n$ star copolymers have been given elsewhere[16]. The organized polymerization was carried out in micelles (benzene solvent) formed by diblock macromonomers with addition of a small amount of EGDM at 60°C initiated by 2,2′-azobisisobutyronitrile (AIBN) in a sealed glass ampoule under high vacuum. Polymerization was stopped by introducing the viscous solution into an excess of methanol.

In order to separate the unreacted diblock macromonomers from the polymerization product, the precipitation fractionations were carried out in the benzene–methanol system at 20°C, where the turbidity of SIM-3 was measured beforehand at a wavelength of 500 nm (Hitachi Perkin–Elmer 139 u.v.–vis. spectrometer).

The weight-average molecular weight ($\bar{M}_w$) of $(AB)_n$ star copolymers was determined by gel permeation chromatography (g.p.c.; Tosoh high-speed liquid chromatograph HLC-802A), with a low-angle laser light scattering (LS) detector (LS-8; He–Ne laser with detection angle of 5°) and refractive index (RI) detector, which was operated with a TSK gel GMH column with tetrahydrofuran as eluent at a flow rate of $1.0\,\mathrm{ml\,min^{-1}}$. The concentration of the sample injected was kept small, typically less than 0.1 wt%, to minimize the concentration

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effect in the scattered light intensity. Details of the calculation method for $\bar{M}_w$ for $(AB)_n$ star copolymers have been given elsewhere[18]. The polydispersity ($\bar{M}_w/\bar{M}_n$) was determined from g.p.c. distribution functions improved by the reshaping method[19] with a personal computer.

Morphological observations. $(AB)_n$ star copolymer film (40 μm thick) was cast from a 0.03 g ml^{-1} benzene solution onto a Teflon sheet (0.11 ml cm^{-2}) as substrate. The casting solvent was evaporated as slowly as possible under saturated vapour. The films were annealed at 80°C for 2 days. Next, the films were embedded in an epoxy resin and cut perpendicularly to the film interfaces into ultrathin sections (~700–1000 Å thick) using an ultramicrotome (Reichert–Nissei Co., Ultracut N). This specimen was exposed to osmium tetroxide (OsO_4) vapour for 24 h. Morphological results were obtained with a transmission electron microscope (TEM, Hitachi H-500 at 75 kV).

Results and discussion

In previous work[16] on $(AB)_n$ star copolymers with an arbitrary number of arms (n = 5–30), the number of arms depended strongly on the feed macromonomer concentration, [M], and the feed mole ratio of EGDM concentration, [EGDM], to [M]. The microgelation proceeded effectively in PI micellar domains formed by diblock macromonomers. The EGDM is compatible with PI but not so compatible with polystyrene (PS) segments. So, the feed EGDM may be present in PI micellar domains formed by diblock macromonomers (the terminal vinylbenzyl group is connected to the PI block end).

In this work, we have prepared $(AB)_n$ star copolymers with various arm numbers, varying the feed SIM-3 concentration. *Table 1* shows microgelation conditions and results for SIM-3 diblock macromonomer. Macrogelation has never been observed for all experimental series. This suggests that the copolymerization of SIM-3 diblock macromonomer with EGDM leads to microgelation in PI domains of micelles formed by diblock macromonomers. *Figure 1* shows typical g.p.c. profiles of S34 and SIM-3 taken with RI and LS detectors. The g.p.c. distribution of S34 is bimodal. The first peak at lower elution volume in an RI chart corresponds to $(AB)_n$ star copolymer.

It was found from the turbidity curve that the SIM-3 macromonomer was precipitated at a value of 0.48 (methanol fraction) for the precipitant fraction. The precipitation fractionation was carried out three times in this solvent composition for each product S31 to S36. A typical g.p.c. profile of fraction S34F is shown in *Figure 1*. The g.p.c. profile shows that this fraction has a single molecular weight distribution. *Table 1* also lists the characteristics ($\bar{M}_w$, $\bar{M}_w/\bar{M}_n$, arm number) of the fractionated $(AB)_n$ star copolymers.

We observed the microphase-separated structure of $(AB)_n$ star copolymers in the solid state. Therefore the information obtained corresponded to the microphase separation in the strong segregation regime. Typical TEM micrographs of S33F and S35F are shown in *Figures 2a* and *b*, respectively, and *Figure 2c* shows the TEM micrograph of SIM-3 diblock prepolymer. The dark portions indicate PI blocks selectively stained with OsO_4. Both morphologies of $(AB)_n$ star copolymers show the texture of very small PI spheres dispersed in a PS matrix.

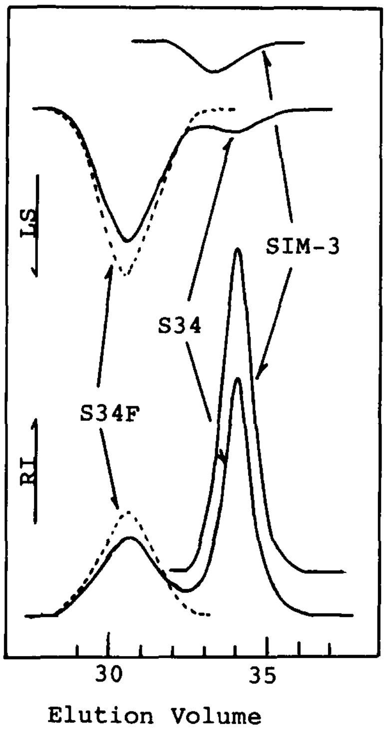

Figure 1 G.p.c. profiles of S34, S34F and SIM-3 diblock macromonomer

Table 1 Microgelation conditions and results of SIM-3 diblock macromonomer[a]

	Feed concentration (mol l^{-1})		$(AB)_n$ star copolymers			
No.	[M] × 10^2	[AIBN] × 10	Conversion[b] (%)	$\bar{M}_w \times 10^{-5}$[c]	$\bar{M}_w/\bar{M}_n$	Arm number (number/polymer)
S31	3.35	1.35	26	1.65	1.31	15.0
S32	3.91	1.52	28	1.79	1.26	16.3
S33	4.67	1.87	29	1.51	1.39	13.7
S34	5.88	2.28	30	1.96	1.26	17.8
S35	7.81	3.19	31	3.30	1.31	30.0
S36	12.1	4.75	34	2.55	1.56	23.2

[a] Polymerized in benzene at 60°C. [EGDM]/[M] = 0.04 (mol/mol)
[b] Estimated by g.p.c. distributions
[c] Determined by g.p.c. with LS and RI double detectors

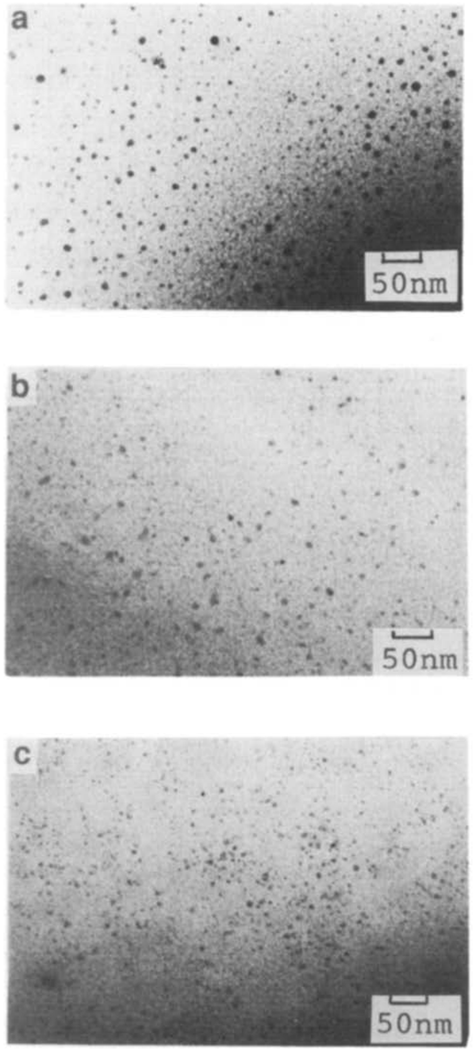

Figure 2 TEM micrographs of $(AB)_n$ star copolymers and SIM-3 diblock prepolymer: (a) S33F; (b) S35F; (c) SIM-3 diblock prepolymer

Table 2 Spherical domain sizes of $(AB)_n$ type star-block copolymers[a]

	$(AB)_n$ star copolymers		Domain size (nm)	
No.	$\bar{M}_w \times 10^{-4}$ of PI blocks	Arm number	$\bar{R}_{PI}$[b]	R_0[c]
S31F	3.08	15.0	3.5	2.4
S32F	3.34	16.3	4.0	2.5
S33F	2.81	13.7	3.0	2.3
S34F	3.65	17.8	3.0	2.5
S35F	6.15	30.0	4.0	3.0
S36F	4.76	23.2	3.3	2.8

[a] Composition of S31F–S36F star copolymers: PI blocks = 18.7 wt%
[b] Average radius of PI spheres
[c] Calculated radius of PI spheres, assuming that $(AB)_n$ star copolymer forms unimolecular micelle

Table 2 lists the average radius ($\bar{R}_{PI}$) of PI spheres for star copolymers S31F–S36F judged from TEM micrographs. In this table, R_0 is the radius of segregated PI spheres calculated from equation (1), assuming that $(AB)_n$ star copolymer forms unimolecular micelles:

$$n = (4\pi/3P_{PI})R_0^3\rho_{PI}N_A \qquad (1)$$

where n is the arm number, ρ_{PI} is the density of PI (1.36×10^4 mol m^{-3})[20], N_A is the Avogadro number (6.023×10^{23} mol^{-1}) and P_{PI} is the monomer units of PI blocks in an AB diblock copolymer. It is found from these results that each value of the observed $\bar{R}_{PI}$ is almost identical to the calculated R_0 for S31F to S36F.

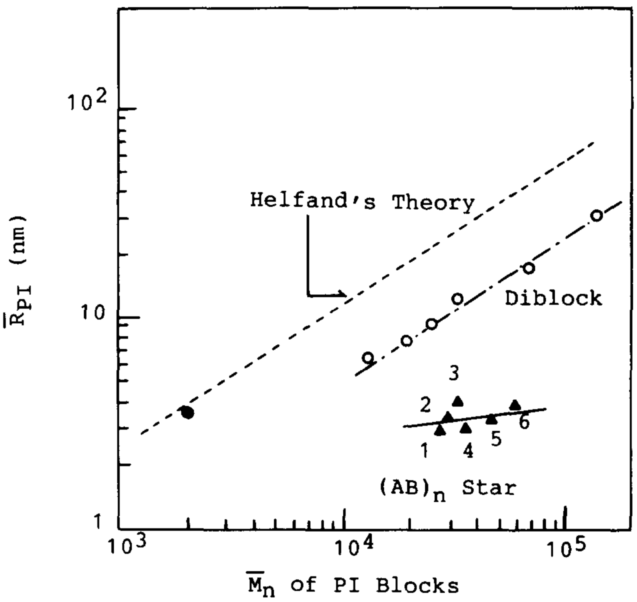

Figure 3 Plot of the average sphere size $\bar{R}_{PI}$ *versus* the molecular weight $\bar{M}_n$ of the PI blocks for $(AB)_n$ star copolymers and diblock copolymers. ---, Line with slope of 2/3 based on Helfand and Wassermann's results[21]; –·–·–, fit to the results (○) of Hashimoto *et al.*[20]; ●, indicates sphere size of SIM-3 diblock prepolymer. —, Best fit to values (▲) obtained in $(AB)_n$ star copolymers: 1, $n = 13.7$; 2, $n = 15.0$; 3, $n = 16.3$; 4, $n = 17.8$; 5, $n = 23.2$; 6, $n = 30.0$

We have compared the domain spacings of $(AB)_n$ star-block copolymers with those of poly(S-*b*-I) diblock copolymers in the strong segregation regime. *Figure 3* shows the observed domain size $\bar{R}_{PI}$ of star copolymers, with the calculated[21] and observed[20] domain sizes of diblock copolymers, as a function of the molecular weight of the PI blocks forming the spherical domains of poly(S-*b*-I) diblock copolymers. In diblock copolymers, the $\frac{2}{3}$ power law is consistent with the results predicted from the equilibrium theory of Helfand and Wassermann[21], but the absolute values of PI spheres reported by Hashimoto *et al.*[20] are far below the theoretical values (almost half of the theoretical values), due to a non-equilibrium effect encountered in the solvent evaporation process. On the other hand, Bates *et al.*[22] have found that the sphere radius is proportional to the 0.37 power of molecular weight. According to their results, the spherical domains are always smaller than predicted. The departure from theoretical prediction is exceedingly small at low molecular weights but increases at higher molecular weights. This result is intuitively satisfying since it is more likely that the equilibrium structures will be formed at the lower end of the molecular weight scale. In our work, the sphere radius for the SIM-3 diblock prepolymer specimen ($\bar{M}_n = 1.06 \times 10^4$; PI blocks = 18.7 wt%) was 3.5 nm (see *Figure 2c*). This domain size is identical to that predicted. So, the higher casting temperature and low molecular weight of SIM-3 diblock prepolymer both tend to favour the production of bulk equilibrium structures from solvent casting.

It is also found from *Figure 3* that the absolute values of PI spheres for $(AB)_n$ star copolymers ($n = 14$–30) are far below the observed values for diblock copolymers. These values are almost identical to the calculated R_0, as mentioned above. The speculated mechanism of microphase separation of $(AB)_n$ star copolymers is as follows. As predicted by de la Cruz and Sanchez[4], the $(AB)_n$ star copolymers ($n > 10$) begin to develop a 'core and shell' type structure in the weak segregation regime. This self-micellization tends to create significant concentration fluctuations at the core–shell interface. During solvent evaporation, the PI cores cannot interpenetrate with each other. As a result, the microphase-separated structures of $(AB)_n$ star copolymers ($n = 14$–30) are formed with the dimension of a unimolecular micelle in the strong segregation regime.

We are investigating the microphase separation of $(AB)_n$ star copolymers, varying the block compositions. These results will be reported in the near future.

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