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Synthesis and dilute solution properties of poly(diblock macromonomer)s

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Poly[(styrene-b-isoprene) diblock macromonomer]s were prepared by free radical polymerization of corresponding vinylbenzyl-terminated diblock macromonomers (polyisoprene blocks = 21~26 wt%). Poly (diblock macromonomer)s consisting of side chains ($\overline{M}_n = 3600\ \mathrm{g\ mol^{-1}}$) exhibited degrees of polymerization in the range 54~200. The radius of gyration (R_g) and the cross-sectional radius of gyration ($R_{g,c}$) were determined by small-angle X-ray scattering. We studied the structural characterization of such poly(diblock macromonomer)s in a dilute solution. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(diblock macromonomer); solution property; SAXS)

INTRODUCTION

Topological structures of multi-component polymers have a strong effect on the solution and solid properties. We have prepared the $(AB)_n$ type stars by free radical microgelation in micelles formed by crosslinking poly[styrene(S)-b-isoprene(I)] diblock macromonomers[1,2] or diblock mono-anions with divinyl benzene (DVB)[3]. It was found from the small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) measurements that these stars [arm number n = 16~42, polyisoprene (PI) blocks = 16~19 wt%] formed the lattice with a face-centred cubic (FCC) structure in the bulk film[3] and were packed in the lattice with a body-centred cubic (BCC) structure near the overlap threshold (C^*)[4]. Thus, multibranched star copolymers formed a unimolecular micelle in solution due to a very high arm density, and led to hierarchical transformation of cubic lattices.

On the other hand, polymerizations of macromonomers provide regular multibranched polymers with a branch density. Since both the degree of polymerization (P_w) and the length of branches are varied, poly(macromonomer)s are interesting models for the study of branched polymers[5–8]. Recent structure characterization of such long-chain poly (macromonomer)s revealed that the main chain exhibits an almost rodlike conformation as measured by the Kuhn statistical segment length of $l_K > 1000$ A[9,10]. Investigations on such poly(macromonomer)s by X-ray scattering and polarized light microscopy showed the formation of lyotropic phases[11,12]. This phenomenon is based on the overcrowding of bulky side chains which forces the otherwise flexible main chains into a stretched conformation with significantly reduced degrees of freedom. Thus, solution properties of poly(macromonomer)s are very similar to those of $(AB)_n$ stars.

In this article, poly(diblock macromonomer)s were prepared by free radical homopolymerization of end-functionalized poly[styrene(S)-b-isoprene(I)] macromonomers. We studied the dilute solution properties of poly(diblock macromonomer)s with different degrees of polymerization.

EXPERIMENTAL

Synthesis and characterization of diblock macromonomers

Vinylbenzyl-terminated poly(S-b-I) diblock macromonomers were synthesized by the living anionic polymerization technique. The details concerning the synthesis and characterization of such diblock macromonomers have been given elsewhere[1]. The microstructure of PI blocks from this method (benzene solvent) contained 50% 3,4- and 50% 1,4-structures (60% *cis*, 40% *trans*)[13]. *Table 1* lists the characteristics of monodisperse diblock macromonomers.

Radical polymerization of diblock macromonomers

Free radical polymerization of diblock macromonomers was carried out in benzene at 60°C initiated by 2,2′-azobisisobutyro-nitrile (AIBN) in a sealed glass ampoule under high vacuum. In order to study the solution properties of poly(diblock macromonomer)s, we also carried out large-scale polymerization. Poly(diblock macromonomer) was removed from the diblock macromonomer precursor by precipitation fractionation (benzene–methanol system). Subsequently, the poly(diblock macromonomer) obtained was fractionated stepwise by precipitation fractionation to perform narrow molecular weight distribution.

A combination of gel permeation chromatography (g.p.c.) with light scattering (LS) detector is very useful for measuring the weight-average molecular weight ($\overline{M}_w$) and molecular weight distribution ($\overline{M}_w/\overline{M}_n$) of branched polymers such as poly(macromonomer)s, since one does not need any isolation procedures to remove unreacted diblock macromonomers. Gel permeation chromatography measurements were carried out with a Tosoh HLC-802A equipped with a low-angle laser LS detector, LS-8 (He–Ne laser with a detection angle of 5°) and refractive index (r.i.), which was operated with TSK gel GMH column on tetrahydrofuran (THF) as eluent. The conversion on poly(diblock

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Table 1 Characteristics of poly(S-b-I) diblock macromonomers

Code	$\overline{M}_n^a$	$\overline{M}_w/\overline{M}_n^b$	PS block^c (wt%)	Functionality^d (number/molecule)
M36	3600	1·06	79	0·96
M50	5000	1·08	74	1·01

[a] Determined by vapor pressure osmometer in benzene
[b] Determined by g.p.c.
[c] Determined by ^{1}H n.m.r. in $CDCl_3$
[d] Determined by g.p.c. equipped with r.i. and u.v. double detectors

macromonomer)s was determined by the change in the ratio of the peak area of the poly(diblock macromonomer) produced to the total peak area of the polymerization product in g.p.c. charts. The details concerning the calculation method have been given elsewhere[14].

Dilute solution properties

Both $\overline{M}_w$ and the second virial coefficient (A_2) were determined by static light scattering (SLS) in benzene at 20°C, on a Photal TMLS-6000HL (Otsuka Electronics Ltd) with a He–Ne laser (λ_0 = 632.8 nm) in the Zimm mode[15]. The refractive index increment d*n*/d*c* of each macromonomer was measured with a differential refractomer. Samples were filtered through membrane filters with nominal pore of 0.2 μm before measurement. Solutions were measured in the concentration range 0.6~6.2 g l^{-1}.

The radius of gyration (R_g) of poly(diblock macromonomer)s prepared by this work was very small. It was impossible to evaluate R_g from SLS. Then R_g was determined by SAXS. The SAXS intensity distribution $I(q)$ was measured with a rotating-anode X-ray generator (Rigaku Denki Rotaflex RTP 300 RC) operated at 40 kV and 100 mA. The X-ray source was monochromatized CuK_α (λ = 1.54 Å) radiation. In the measurement of a benzene solution (1 wt%) of the sample, we used the cell sandwiched between mica plates as a holder vessel. The background correction was carried out using polyethylene film. The value of R_g is estimated by Guinier's method from the following equation[15]

$$\ln I(q) = \text{const} - (1/3)(R_g^2)q^2 \qquad (1)$$

where q is the scattering vector.

The value of cross-sectional radius of gyration ($R_{g,c}$) is estimated from the following equation[16]

$$\ln [I(q)q] = \text{const} - (1/2)(R_{g,c}^2)q^2 \qquad (2)$$

RESULTS AND DISCUSSION

Radical polymerization of diblock macromonomers

In a previous work[1], we investigated the radical polymerization behaviour of poly(S-b-I) diblock macromonomers. It was made clear that the $\overline{M}_w$ of poly(diblock macromonomer)s formed was very small at a feed macromonomer concentration $[M]_0$ less than *ca.* 2 × 10^{-2} mol l^{-1}. So we carried out free radical polymerization of diblock macromonomers in the range of $[M]_0$ more than *ca.* 0.1 mol l^{-1}. The polydispersity of polymerization products was very narrow, because polymerization proceeded in PI spherical micelles formed by diblock copolymer macromonomers. It seemed, therefore, that the 50% pendant vinyl groups of PI chains were inert during free radical polymerization. Moreover, we prepared the core-shell type polymer microspheres by crosslinking reaction of PI spherical domains of poly(S-b-I) diblock copolymers with sulfur monochloride[17]. In a preliminary experiment, we tried the domain fixing by radical coupling in the presence of AIBN or benzoylperoxide. But PI microgels were not obtained from this method. In general, poly(S-b-butadiene-b-S) triblock copolymer micelles with a core of poly(butadiene) blocks were stabilized by crosslinking of PI chains using fast electrons[18].

Table 2 lists free radical polymerization conditions and results of M50 and M36 diblock macromonomers. *Figure 1* shows typical g.p.c. profiles of PM36-66 taken with r.i. and LS detectors. The g.p.c. distribution of PM36-66 is bimodal. The first peak at lower elution volume corresponds to poly(diblock macromonomer). The values of $\overline{M}_w$ (2.36 × 10^5) and conversion (35.7%) are estimated from the g.p.c. chart. It is found from these profiles that the fraction PM36-66F is removed from the macromonomer precursor by this fractionation and has a single and broad molecular weight distribution ($\overline{M}_w/\overline{M}_n$ = 1.64). The polydispersity for PM50 series was very narrow ($\overline{M}_w/\overline{M}_n$ = 1.07 1.08) due to low P_w. On the other hand, the polydispersity for the PM36 series was broad ($\overline{M}_w/\overline{M}_n$ = 1.43~1.64). Microgels were not formed from these polymerization products. It seemed that PM36 series proceeded with usual radical polymerization mechanism.

Figure 2 shows the plots of the degree of polymerization (P_w) or conversion against the polymerization time (PM50 series; $\overline{M}_n$ = 5000, $[M]_0$ = 0.1 mol l^{-1}). The conversion increases gradually with an increase in polymerization time. However, P_w does not show a large variation (P_w = 3~10). Therefore, we set *ca.* 150 h as the polymerization time in the following experiments.

Table 2 Free radical polymerization conditions and results of M50 and M36 diblock macromonomers^a

Expt	Macromonomer $[M]_0$(mol l^{-1})	Time(h)	Poly(diblock macromonomer)			
			$10^{-5}\,\overline{M}_w^b$	$\overline{M}_w/\overline{M}_n^c$	Conversion^c(%)	P_w^d
PM50-3	0·1	48	0·17	1·08	18·5	3
PM50-7	0·1	96	0·33	1·07	26·4	7
PM50-10	0·1	150	0·48	1·07	40·3	10
PM36-42	0·5	155	1·50	1·43	30·1	42
PM36-55	0·6	155	1·97	1·56	31·8	55
PM36-66	0·7	155	2·36	1·64	35·7	66

[a] Polymerized in benzene at 60°C initiated by AIBN (1.6 × 10^{-2} mol l^{-1})
[b] Determined by g.p.c. equipped with LS and r.i. detectors
[c] Determined by g.p.c. profiles
[d] Degree of polymerization was calculated from g.p.c.-LS

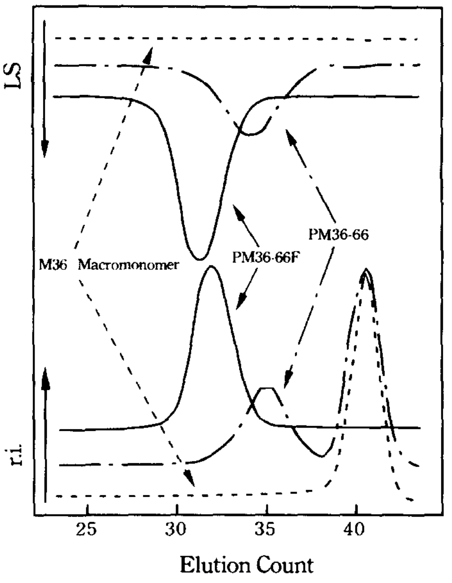

Figure 1 Gel permeation chromatography profiles of PM36-66, PM36-66F and M36 macromonomer

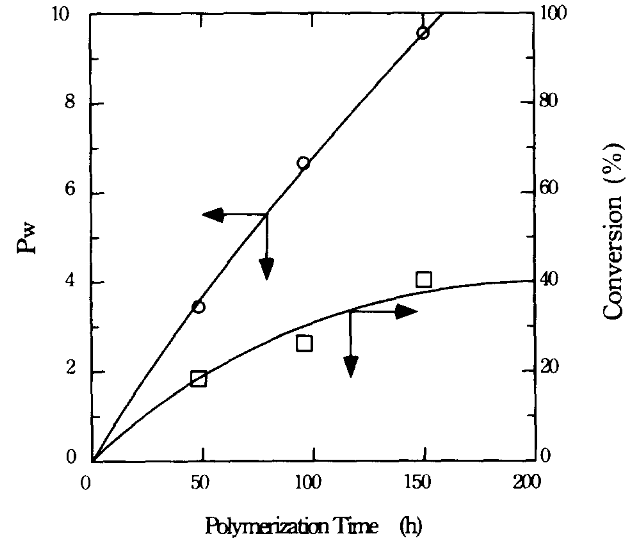

Figure 2 Plots of degree of polymerization (P_w) or conversion against polymerization time for the PM50 series (side chain $\overline{M}_n = 5000$, $[M]_0 = 0.1$ mol l^{-1})

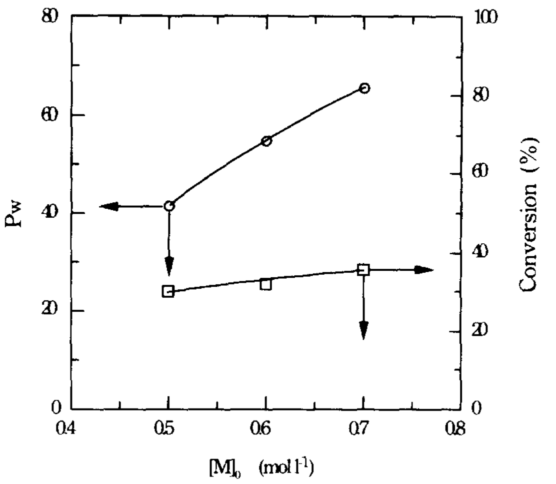

Figure 3 Plots of P_w or conversion against feed macromonomer concentration $[M]_0$ for PM36 series (side chain $\overline{M}_n = 3600$)

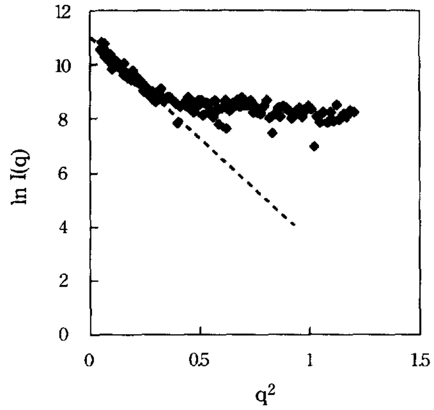

Figure 4 Typical Guinier's plot [ln $I(q)$ *versus* q^2] of PM50-29F

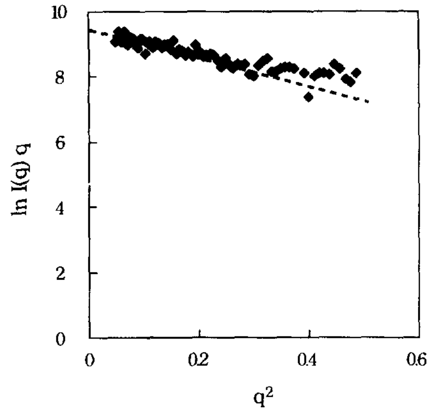

Figure 5 Typical plot of ln $I(q)q$ against q^2 for PM50-29F

Figure 3 shows the plots of P_w or conversion against the feed macromonomer concentration $[M]_0$ for the PM36 series ($\overline{M}_n = 3600$). The conversions are almost constant (30~36%), but P_w increases rapidly with an increase in $[M]_0$. This phenomenon seems to originate from the dead-end polymerization mechanism of vinylbenzyl groups of macromonomers. That is to say, the initiator was consumed at the final stage of polymerization and poly(diblock macromonomer) radicals were terminated with a combination process. It is indicated that P_w depends strongly on the feed concentration and the $\overline{M}_n$ of diblock macromonomers. However, such poly(diblock macromonomer)s have broad molecular weight distribution ($\overline{M}_w/\overline{M}_n = 1.4$~$1.6$).

Dilute solution properties

Poly(diblock macromonomer)s obtained from the large-scale polymerization were fractionated by precipitation fractionation (benzene–methanol system). The $\overline{M}_w$ and A_2 were determined by SLS after purification. R_g and $R_{g,c}$ were determined by SAXS due to the small $\overline{M}_w$ of poly(diblock macromonomer)s. Typical Guinier's plot of PM50-29F is shown in *Figure 4*. *Figure 5* shows the plot of ln $I(q)q$ *versus* q^2 for PM50-29F. The values of R_g and $R_{g,c}$ were estimated from the corresponding slope of both plots, respectively. R_g is the observed value at the small angle region. In this measurement condition ($R_g q < 1$), R_g is independent of the segment density profile of monomolecular micelle. These characteristic values of poly(diblock macromonomer)s are

Table 3 Dilute solution properties of poly(diblock macromonomer)s

Code	$10^{-5}\overline{M}_w$		$\overline{M}_w/\overline{M}_n$ [b]	P_w [c]	10^4A_2 [d] (cm^3 mol g^{-2})	R_g [e] (nm)	$R_{g,c}$ [e] (nm)	g [f]	g_r [g]
	g.p.c.	SLS [a]							
PM50-29F	1.44	1.79	1.08	29	2.17	5.5	2.8	0.152	0.117
PM50-55F	2.74	2.94	1.14	55	0.94	6.0	2.8	0.085	0.072
PM50-71F	3.53	3.32	1.22	71	0.59	6.6	3.1	0.076	0.061
PM50-96F	4.75	4.17	1.26	96	0.48	7.2	3.1	0.063	0.050
PM36-54F	1.93	1.75	1.23	54	0.77	3.9	2.1	0.065	0.080
PM36-74F	2.65	2.61	1.34	74	0.57	5.2	2.1	0.066	0.066
PM36-103F	3.72	4.21	1.25	103	0.34	6.6	2.3	0.071	0.055
PM36-199F	7.18	7.35	1.20	199	0.21	17.0	4.6	0.214	0.042

[a] The refractive index increments d*n*/d*c* were 0.0822 (ml mg^{-1}) for M50 and 0.0906 (ml mg^{-1}) for M36 macromonomers

[b] Determined by g.p.c. profiles

[c] Degree of polymerization was calculated from g.p.c.-LS

[d] Determined by SLS

[e] Determined by SAXS

[f] $g = <R_g^2> / <R_g^2>_L$

[g] *g* factor for regular comb polymer with freely jointed chain

listed in *Table 3*. The values of $\overline{M}_w$ estimated from g.p.c. are almost identical to that obtained from SLS with experimental errors. The values of P_w are in the range 54~199 for the PM36 series. The A_2 shows gradually decreasing negative slope with increasing arm number and $\overline{M}_w$ in each poly(diblock macromonomer) series. This result indicates that the excluded-volume effect arising from intrachain or interchain segment–segment interactions decreases with increasing arm number for poly(diblock macromonomer)s.

The dependence of the branched polymer's dimensions of the functionality can be expressed by means of dimensionless parameters[19]

$$g = <R_g^2> / <R_g^2>_L \qquad (3)$$

where $<R_g^2>_L$ indicate the mean square radius of gyration of the linear polymer with identical molecular weight. In this work, we make the assumption that chemical structure of poly(S-b-I) diblock macromonomer can be approximated to the polystyrene macromonomer. For polystyrene in benzene, the empirical equations given by[20–23] were used

$$<R_g^2>_L^{1/2} = 1.17 \times 10^{-2} M_w^{0.597} \text{ (nm)} \qquad (4)$$

According to Orofino [24,25], the *g* factor (g_r) for regular comb polymers with freely jointed chain (random-walk) is given by

$$g_r = [p(r+1)+1]^{-3}[p(3p-2)r^3 + p(p+1)(p+2)r^2 + p(2p+1)(p+1)r + (p+1)^3] \qquad (5)$$

The regular comb polymers, each consisting of a linear backbone of chain of *y* units to which *p* linear chains of uniform length *y* units are attached at regular intervals to form the repeating unit (see *Figure 6*).

Values of *g* and g_r for poly(diblock macromonomer)s are also collected in *Table 3*. The values of *g* are larger than g_r except for the sample PM36-54F. This reflects the side chain stretching due to steric crowding of poly(diblock macromonomer)s.

We studied the geometrical structures of poly(diblock macromonomer)s in a dilute solution. Wintermantel and coworkers[10,26] reported that the conformation of poly(macromonomer)s changed from ellipsoid to cylinder shapes in a dilute solution with increasing degree of polymerization (P_w). The radii of gyration for ellipsoid and cylinder models can be approximated by the following equations[27], respectively

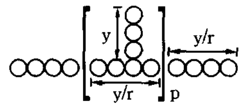

Figure 6 Representation of regular comb polymer model

$$R_g = R_{g,c}[(2+\omega_2)/5]_{1/2} \text{ for ellipsoid} \qquad (6)$$

where ω is the aspect ratio. The length of major axis is equal to $\omega R_{g,c}$.

$$R_g = (R_{g,c}^2/2 + H^2/3)^{1/2} \text{ for cylinder} \qquad (7)$$

where $2H$ is the height of cylinder. The aspect ratio of cylinder (γ) is equal to $H/R_{g,c}$.

As mentioned in the Introduction, poly(macromonomer)s exhibiting relatively short P_w of the backbone behaved as ellipsoid in a dilute solution. So, the physical values for PM50 and PM36 series were evaluated by equation (3), assuming an ellipsoid model. The aspect ratio (ω) and the length of major axis ($\omega R_{g,c}$) are collected in *Table 4*. *Figure 7* shows the plot of the aspect ratio (ω) against P_w. In the PM50 series (side chain $\overline{M}_n = 5000$, $P_w = 29$~96), the values of ω are the range 4~5. Therefore, poly(diblock macromonomer)s for PM50 series seem to take conformation of ellipsoid in a dilute solution.

On the other hand, the values of ω for the PM36 series (side chain $\overline{M}_n = 3600$, $P_w = 54$~199) increase rapidly with increasing P_w. Especially in the sample PM36-199F, both R_g (17.0 nm) and $R_{g,c}$ (4.6 nm) show far larger values than those of other poly(diblock macromonomer)s. If we assume the conformation of this copolymer to a cylinder model, characteristic values of aspect ratio (γ) and *H* are estimated to be 6.3 and 28.9 nm from equation (4), respectively. Therefore, the sample PM36-199F shows relatively higher geometrical anisotropy in a dilute solution.

In this work, we could not determine the type of conformations from experimental data for poly(diblock macromonomer)s. It is necessary to determine such conformations from the curve fitting of scattering functions

Table 4 Geometrical structures of poly(diblock macromonomer)s in dilute solution

Code	R_g (nm)	$R_{g,c}$ (nm)	Ellipsoid ω^a	Ellipsoid $\omega R^b_{g,c}$ (nm)
PM50-29F	5·5	2·8	4·2	11·7
PM50-55F	6·0	2·8	4·6	12·9
PM50-71F	6·6	3·1	4·5	14·1
PM50-96F	7·2	3·1	4·9	15·2
PM36-54F	3·9	2·1	3·9	8·1
PM36-74F	5·2	2·1	5·2	10·9
PM36-103F	6·6	2·3	6·2	14·2
PM36-199F	17·0	4·6	8·2	37·8

[a] Aspect ratio of ellipsoid
[b] Major axis

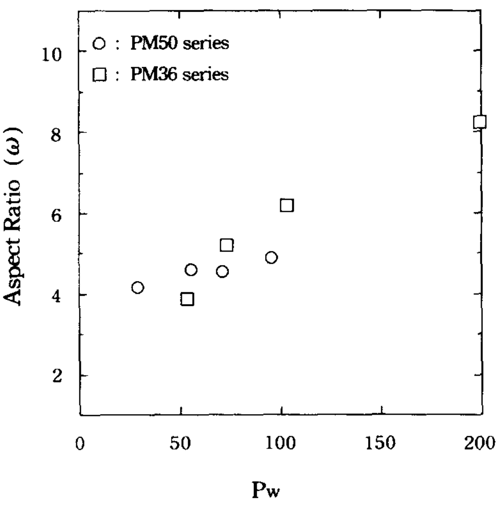

Figure 7 Relationship between aspect ratio (ω) and degree of polymerization (P_w) under assumption of ellipsoid model

approximated by various models. It is interesting to study the possibility of unimolecular micelle formation of poly(diblock macromonomer)s in solution. The results obtained will be reported in the near future.

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