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Synthesis and solution properties of gradient-modulus star copolymers

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Gradient-modulus star copolymers were prepared by crosslinking poly[isoprene(I)-b-I/styrene (S)-b-S] tapered block monoanions with divinylbenzene (DVB) in benzene. The dilute-solution properties of these stars were characterised by static and dynamic light scatterings (SLS and DLS). The ratio of radius of gyration over the Stokes radius (R_G/R_H) in benzene decreased gradually and approached unity as the arm number became large. Even gradient-modulus stars with multiarms behave not as neat hard spheres but as soft spheres which were penetrable near the edge in a good solvent. It was found from the results of DLS that gradient-modulus stars formed unimolecular micelles even in selective solvent. © 1997 Elsevier Science Ltd.

(Keywords: gradient-modulus star; tapered block copolymer; unimolecular micelle)

INTRODUCTION

The preparation of gradient-modulus polymeric materials in which the composition gradually changes gradually along the copolymer chain from predominantly one comonomer to the other, is based on a general idea which allows wide variations in mechanical, optical and other properties. These preparation techniques can be applied to a wide range of polymers, such as polyisocyanurate elastomers, polyurethanes, and epoxy resins.

About 20 years ago, Asai and coworkers[1,2] developed styrene–butadiene tapered block copolymer resins with a gradient-modulus in the middle block and indicated the utilities as a transparent high impact resin. Similar tapered block copolymers were generally prepared using living anionic polymerisations[3–5]. There have also been a few reports claiming synthesis of gradient-modulus copolymers using iniferters[6,7].

The anionic copolymerisation of the two dienes, butadiene and isoprene, with styrene has been studied most extensively in the homogeneous organolithium systems[8–15]. The most striking feature of these systems is the effect of polar solvents. In the case of nonpolar media, there is an overwhelming preference for the diene, and the styrene monomer is almost excluded. However, the addition of a polar solvent has a marked effect in reversing this behaviour, favouring the inclusion of styrene in the copolymer. The effect of polar solvents on the organolithium copolymerisation of styrene and 1,3-dienes has been generally explained on the basis of the changes in the carbon–lithium bond structure caused by such solvents. So, the tapered block copolymers can be produced when a mixture of two monomers is added to the living end, changing their mixing ratios.

More recently, Greszta and Matyjazewski[16] have reported the new approaches towards the gradient-modulus copolymers through controlled radical polymerisation, such as atom transfer radical polymerisation (ATRP). In copolymerisations with a controlled changes in comonomers (styrene and methylacrylate), the second monomer was added using a high performance liquid chromatograph (h.p.l.c.) pump.

On the other hand, de la Cruz and Sanchez[17] have calculated the phase stability criteria and static structure factors in the weak segregation regime for n-arm diblock copolymers [$(AB)_n$ star]. According to their results, as the arm number (n) becomes large, the $(AB)_n$ star begins to develop a 'core and shell' type structure. This self-segregation or self-micellisation tends to create significant concentration fluctuations at the core–shell interface. We prepared the $(AB)_n$ stars by free radical microgelation in micelles formed by poly[styrene(S)-b-isoprene(I)] diblock macromonomers[18,19] or crosslinking poly(S-b-I) diblock monoanions with divinylbenzene (DVB)[20]. Subsequently, we studied the self-micellisation of $(AB)_n$ stars, varying the arm numbers. As a result, the microphase-separated structures of these star copolymers [n = 14~30, polyisoprene (PI) blocks = 16~19 wt%] were formed with the dimension of a unimolecular micelle even in the strong segregation regime. It was found also from small-angled X-ray scattering (SAXS) measurements that these stars formed a lattice with a face-centred cubic (FCC) structure in the bulk film[20] and were packed in the lattice with a body-centred cubic (BCC) structure near the overlap threshold (C^*)[21].

We suggest a novel architecture of gradient-modulus star copolymers by means of anionic copolymerisation of tapered block copolymer monoanions with DVB in uniform micelles. When each arm is composed of gradient-modulus concerning the molecular structure and composition, it can be expected that the gradient-modulus stars with multiarms will form the unimolecular micelle in solution. Moreover,

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these spherical particles will essentially possess a gradient-modulus in direction from the central core to outermost shell region.

In this article, gradient-modulus star copolymers were prepared by crosslinking poly (I-b-I/S-b-S) tapered block anions with DVB in benzene. We investigated the solution properties [radius of gyration (R_G), hydrodynamic radius (R_H)] of these stars and the behaviour for the micelle formation in selective solvent by dynamic light scattering measurements.

EXPERIMENTAL

Synthesis of gradient-modulus star copolymers

Tapered block copolymer anions were prepared by living anionic polymerisation techniques using the break-seal method. Anionic polymerisation was carried out by the three-stage addition of isoprene (I), I/styrene (S) mixture, and styrene at 4°C, using *n*-butyllithium (*n*-BuLi) as the initiator under a pressure of 10^{-6} mmHg.

The gradient-modulus star copolymers were prepared by crosslinking poly (I-b-I/S-b-S) tapered block anions with a small amount of DVB (Tokyo Kasei; ≈ 55%, *m*-/*p*-isomer = 2) in benzene. Details concerning the synthesis and purification of such star copolymers have been given elsewhere[20].

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

Characterisation of gradient-modulus star copolymers

The number-average molecular weights ($\bar{M}_n$) of the polyisoprene (PI) precursors were determined by gel permeation chromatography (g.p.c.; Tosoh high-speed liquid chromatograph HLC-8020) using PI standard samples with tetrahydrofuran (THF) as the eluent at 38°C, using a TSK gel GMH$_{XL}$ column and a flow rate of 1.0 ml min^{-1}. The $\bar{M}_n$ of poly (I-b-I/S) and poly (I-b-I/S-b-S) precursors was also determined by universal calibration[22] (log[η]M versus elution volume) by g.p.c. The polydispersity ($\bar{M}_w/\bar{M}_n$) was determined by the reshaping method[23] with a personal computer.

The composition of star copolymers was determined by ^{1}H nuclear magnetic resonance (n.m.r.; 500 Hz, JEOL GSX-500 n.m.r. spectrometer) in $CDCl_3$.

The weight-average molecular weights ($\bar{M}_w$), the radii of gyration (R_G) and the second virial coefficients (A_2) of the star copolymers were determined in benzene, by static light scattering (SLS) on Photal TMLS-6000HL (Otsuka Electronics) with an He–Ne laser (λ_0 = 632.8 nm) in the Berry mode[24]. The scattering angles were in the range 30–150°. Samples were filtered through membrane filters with nominal pore of 0.2 μm before measurement. Solutions were measured in the concentration range 2–10 mg ml^{-1}.

The hydrodynamic radii (R_H) of the star copolymers were determined using dynamic light scattering (DLS; scattering angles 60 and 90°, Otsuka Electronic) in 0.1 wt% benzene (η = 0.654 cp, n_D = 1.501) solution at 23°C.

To check the formation of unimolecular micelles for gradient-modulus stars, DLS measurements were carried out in cyclohexane that dissolved PI but precipitated PS.

RESULTS AND DISCUSSION

Synthesis of gradient-modulus star copolymers

In the anionic copolymerisation of styrene (M_1) with isoprene (M_2), the reactivity ratios were: $r_1 = 0.14$ and $r_2 = 7.0$ (initiated by *n*-BuLi in benzene)[11]. This means that the living end with non-solvated lithium counter ion consumes isoprene monomer preferably to styrene monomer. Therefore, the synthesis of the tapered block copolymers with gradient-modulus can be achieved by the three-stage anionic addition of isoprene, isoprene/styrene mixture, and styrene.

Young and Fetters[25] studied the formation of PI stars by the reaction of PI monoanions with DVB. They found that *m*-DVB was more effective than the para form in linking the dienyllithium chains into the star-branched architecture. In the anionic polymerisation the reactivity of the double bond in DVB is ten times greater than that of the pendant double bond[26]. So, essentially the tapered block chains possessing terminal vinylbenzyl groups must be formed in the initial stage of reaction of tapered block monoanions with DVB. If such primary copolymer anions form polymeric micelles in benzene, microgelation can be expected to proceed within micelles.

Tapered block copolymer was prepared by the three-stage

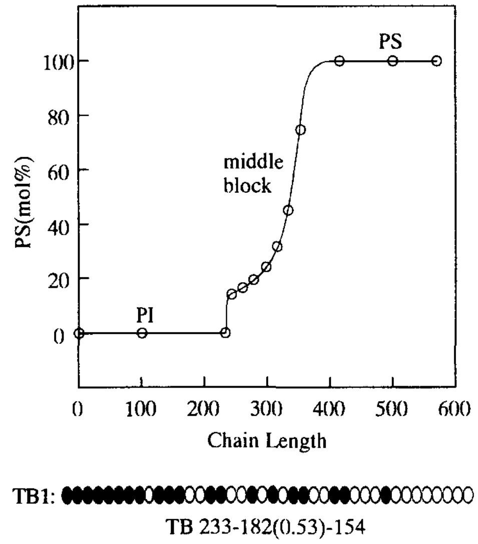

Figure 1 Relationship between chemical composition and chain length for tapered block copolymer TB1

Table 1 Characteristics of tapered block copolymer

	$10^{-4}\bar{M}_n$ [a]		PS of[b] middle block	Tapered block copolymer		
Code	PI	Poly(I-b-I/S)	(mol%)	$10^{-4}\bar{M}_n$ [a]	$\bar{M}_w/\bar{M}_n$ [a]	PS (mol%)[b]
TB1	1.6	3.2	53.3	4.8	1.08	44.1

[a] Determined by g.p.c. using universal calibration.
[b] Determined by ^{1}H n.m.r. in $CDCl_3$.

anionic addition of I, I/S, and S monomers. *Table 1* lists the characteristics of tapered block copolymer TB1. Monomer conversion at each stage was almost 100% within experimental error. Polymer specimens at each stage exhibited a very sharp and single g.p.c. peak. *Figure 1* shows the relationship between chain length and chemical composition for TB1. The chemical composition of the middle block was evaluated from the reactivity ratio in Ref. 11. Tapered block copolymer TB1 is composed of the chain length (degree of polymerisation) of PI: 233, P(I/S): 182, PS: 154. The PS composition (mole fraction) of the middle block is 0.53.

We have prepared gradient-modulus stars with various arm numbers, varying the initial concentration of tapered block anion. *Table 2* lists the reaction conditions and results for gradient-modulus stars. A typical g.p.c. profile of GS1-2 is shown in *Figure 2*. The g.p.c. distribution is bimodal in RI monitor [RI and u.v. at 292 nm (characteristic absorption of vinylbenzyl groups of DVB) double detectors]. The low molecular weight fraction is in agreement with the elution pattern of the TB1 precursor. Therefore, the polymerisation product is the mixture of the gradient-modulus star and TB1 precursor. Unreacted TB1 precursor has no absorption at 292 nm. This fact indicates that all of the feed DVB were consumed in the core formation of star polymers. Moreover, macrogelation was never observed during polymerisation for all experiments. It seems, therefore, that TB1 block anions bind to the linear macromonomers possessing terminal pendant double bonds at the initial stage of reaction. These macromonomers may form uniform micelles in benzene. As a result, core formation by crosslinking proceeds within such micelles.

After the precipitative fractionation, we performed the characterisation of the fractionated stars. G.p.c. profiles of high molecular weight fraction GS1-2F is shown in *Figure 2*. *Table 2* also lists the characteristics of gradient-modulus stars. The values of $\bar{M}_w$ were derived from Berry plots in benzene. The yield of stars was estimated by g.p.c. distributions. The arm number (n) of stars increased with increasing initial concentration [TB] of tapered block monoanions. All stars had apparently narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 1.08~1.10) from g.p.c. calibration. The absolute $\bar{M}_n$ of stars could not be determined by osmometry because their molecular weights were too high. It should be noticed of course that the $\bar{M}_w/\bar{M}_n$ ratio determined by g.p.c. is overestimated from the absolute value due to highly branched structures.

As explained earlier, all of the feed DVB were consumed in the core formation of stars. It is possible to estimate the core radius (R_c) of gradient-modulus stars, because the yield of star and the feed amounts of DVB are known. The R_c is calculated from the equation: $n = (4\pi/3P_E)R_c^3\rho N_A$, assuming that the core is spherical. n is the arm number, ρ is the density of the DVB core (1.01×10^4 mol m^{-3})[27], N_A is the Avogadro number and P_E is the number of monomer units (mixture of DVB and ethylstyrene) at the arm TB1 terminal end. The calculated R_c value is also listed in *Table 2*.

Dilute-solution properties

To discuss the hydrodynamic dimensions and shape of gradient-modulus stars in solution, we determined the Stokes radius (R_H: at 90° and 60° scattering angles), the radius of gyration (R_G) and the second virial coefficient (A_2) of the stars by DLS and SLS measurements in benzene. The observed values are presented in *Table 3*. The A_2 value indicates a gradually decreasing negative slope with increasing molecular weight and arm number n. The R_H values were measured by DLS at 60° and 90° scattering angles to judge the shape of gradient-modulus stars. It can

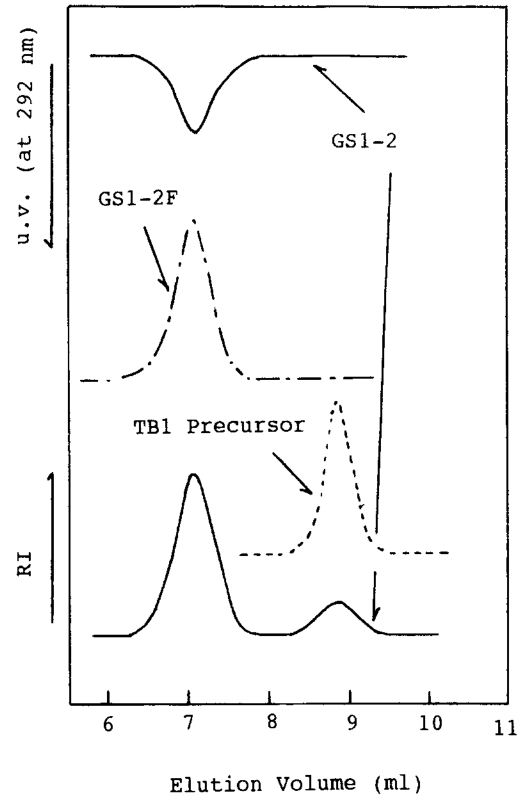

Figure 2 G.p.c. profiles of GS1-2, TB1 precursor and fractionated star GS1-2F

Table 2 Reaction conditions and characteristics of gradient-modulus stars[a]

	Feed		Gradient-modulus star			
Code	10^3 [TB][b] (mol l^{-1})	[DVB]/[TB] (mol mol^{-1})	Yield[c] (%)	$10^{-6}\,\bar{M}_w$[d]	n[e]	R_c[f] (nm)
GS1-1	1.5		80.3	1.05	19	2.0
GS1-2	3.2	8.0	80.0	3.63	67	3.0
GS1-3	5.2		81.8	15.7	289	4.8

[a] Polymerized in benzene.
[b] Initial concentration of tapered block anions.
[c] Determined by g.p.c.
[d] Determined by SLS.
[e] Arm number.
[f] Radius of core.

Table 3 Dilute-solution properties of gradient-modulus stars

Code	Gradient-modulus star						
	$10^{-6}\,\bar{M}_w{}^a$	n	$\langle R_G^2\rangle^{1/2a}$ (nm)	$10^5\,A_2^a$ (ml mol^{-1} g^{-2})	$R_H(90°)^b$ (nm)	$R_G/R_H(90°)$	σ^c
GS1-1F	1.05	19	21.9	16.2	21.0	1.04	1.03
GS1-2F	3.63	67	39.2	1.25	39.4	0.99	1.05
GS1-3F	15.7	289	63.4	0.51	62.7	1.01	1.11

[a] Determined by SLS.
[b] Determined by DLS.
[c] $\sigma = R_H(60°)/R_H(90°)$

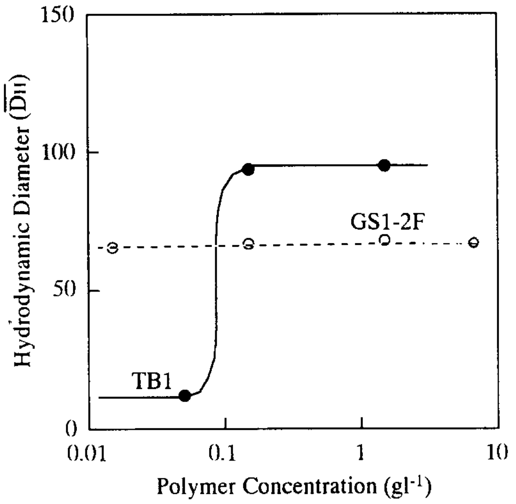

Figure 3 Relationship between hydrodynamic diameter D_H and polymer concentration for gradient-modulus star GS1-2F and tapered block copolymer TB1 in cyclohexane

be seen from *Table 3* that the ratio of the two hydodynamic sizes (σ) are close to each other: $\sigma = 1.07 \pm 0.04$. Then, gradient-modulus stars (GS1-1F to GS1-3F) take a spherical form in a good solvent.

The R_G/R_H ratio is a sensitive fingerprint of the inner density profile of star and polymeric micelle. It is close to unity in the range $n = 19$~289. It is well known that the R_G/R_H ratio ranges from 1.25–1.37 for linear unperturbed polymers[28] to 0.775 for the uniform-density hard sphere[29,30]. So, it seems that even gradient-modulus stars with multiarms behave not as neat hard spheres but as soft spheres which are penetrable near the edge. In fact, there are a few reports concerning the binary blends of core-shell type microsphere/homopolymer[31] or PS star/poly (vinyl methyl ether)[32] that each homopolymer was penetrable near the shell or star edge.

Figure 3 shows the relationship between the hydrodynamic diameter ($\bar{D}_H$) and polymer concentration for gradient-modulus star GS1-2F and tapered block copolymer TB1 in cyclohexane. Cyclohexane is a good solvent for PI but a poor one for PS. In TB1, $\bar{D}_H$ increases suddenly beyond 0.1 g l^{-1} polymer concentration. It indicates that TB1 forms polymeric micelles, such as PS core–PI corona structure. In GS1-2F, however, $\bar{D}_H$ shows a constant value in the range 0.02~8 g l^{-1} polymer concentration. This means that GS1-2F star forms unimolecular micelles even in selective solvent. Both GS1-1F and GS1-3F also showed unimolecular micelle formation in the range 0.02~8 g l^{-1}) of polymer concentration. The inner PS chains of gradient-modulus stars are bonded radially with crosslinked DVB core. But a strong repulsion force works between PS and PI chains due to incompatible segments. So, the inner PS parts of gradient-modulus stars may behave as hard cores in a selective solvent such as cyclohexane. Such behaviours are very similar to that of $(AB)_n$ type stars.

We are investigating the structural ordering of gradient-modulus stars in solution and the microphase separation in the solid state. These results will be reported in the near future.

REFERENCES

1. Horiie, S., Kurematsu, S. and Asai, S., US Patent No. 3872068, 1975.
2. Horiie, S., Kurematsu, S., Asai, S. and Saito, C., US Patent No. 3853978, 1974.
3. Sardelis, K. M., Michaels, H. J. and Allen, G., *Polymer*, 1984, **25**, 1011.
4. Sardelis, K. M., Michaels, H. J. and Allen, G., *Polymer*, 1987, **28**, 244.
5. Tsukahara, Y., Nakamura, N., Hashimoto, T. and Kawai, H., *Polymer Journal*, 1980, **12**, 455.
6. Kuchanow, S. I. and Olenin, A. V., *Polymer Bulletin*, 1992, **28**, 449.
7. Zarembsky, M. V. and Olenin, A. V., *35th IUPAC International Symposium on Macromolecules*, 1994, p. 202.
8. Korotkov, A. A., *Angewandte Chemie*, 1958, **70**, 85.
9. Korotkov, A. A. and Chesonkova, N. N., *Vysokomolekulyarnye Soedineniya*, 1960, **2**, 365.
10. Korotkov, A. A., Mitsengendler, S. P. and Aleev, K. M., *Vysokomolekulyarnye Soedineniya*, 1960, **2**, 1811.
11. Rakova, G. A. and Korotkov, A. A., *Polymer Science USSR (Engl. transl.)*, 1962, **3**, 990.
12. Kuntz, I., *Journal of Polymer Science*, 1961, **54**, 569.
13. Spirin, Yu. L., Arest-Yakubovich, A. A., Polyakov, D. K., Gantmakher, A. G. and Medvedev, S. S., *Journal of Polymer Science*, 1962, **58**, 1181.
14. Morton, M. and Ells, F. R., *Journal of Polymer Science*, 1962, **61**, 25.
15. Spirin, Yu. L., Polyakov, D. K., Gantmakher, A. R. and Medvedev, S. S., *Journal of Polymer Science*, 1961, **53**, 233.
16. Greszta, D. and Matyjaszewski, M., *Polymer Preprints, American Chemical Society, Division of Polymer Chemistry*, 1996, **37**, 569.
17. de la Cruz, M. O. and Sanchez, I. C., *Macromolecules*, 1986, **19**, 2501.
18. Ishizu, K., Yukimasa, S. and Saito, R., *Journal of Polymer Science, Polymer Chemistry Edition*, 1993, **31**, 3073.
19. Ishizu, K. and Yukimasa, S., *Polymer Communications*, 1993, **34**, 3753.
20. Ishizu, K. and Uchida, S., *Polymer*, 1994, **35**, 4712.
21. Ishizu, K. and Uchida, S., *Journal of Colloid Interface Science*, 1995, **175**, 293.
22. Grubisic, Z., Rempp, P. and Benoit, H., *Journal of Polymer Science, Part B*, 1967, **5**, 753.
23. Pierce, P. E. and Armonas, J. E., *Journal of Polymer Science*, Part C, 1968, **21**, 23.
24. Katime, I. and Quintana, J. R., *Comprehensive Polymer Science*, Vol. 1, ed. C. Booth and C. Price. Pergamon Press, Oxford, 1986, Chapter 5.
25. Young, R. N. and Fetters, L. J., *Macromolecules*, 1978, **8**, 899.
26. Worsfold, D. J., *Macromolecules*, 1970, **3**, 514.

27. Hashimoto, T., Nakamura, N., Shibayama, M., Izumi, A. and Kawai, H., *Journal of Macromolecular Science, Physics*, 1980, **B17**, 389.
28. Roovers, J. and Martin, J. E., *Journal of Polymer Science, Polymer Physics Edition*, 1989, **27**, 2513.
29. Yamakawa, H., *Modern Theory of Polymer Solutions*, Harper & Row, New York, 1971, p. 321.
30. Antonietti, M., Bremser, W. and Schmidt, M., *Macromolecules*, 1990, **23**, 3796.
31. Sugita, M., Saito, R. and Ishizu, K., *Polymer Preprints, Japan*, 1996, **45**, 653.
32. Fanst, A. B., Sremcich, P. S., Gilmer, J. W. and Mays, J. W., *Macromolecules*, 1989, **22**, 1250.