Ordered lattice formation of $(AB)_n$ type star copolymers

Koji Ishizu* and Satoshi Uchida
Department of Polymer Science, Tokyo Institute of Technology, 2-12 Okayama, Meguro-ku, Tokyo 152, Japan
(Received 28 March 1994)

$(AB)_n$ star copolymers were prepared by crosslinking poly(styrene-*b*-isoprene) diblock anions with divinylbenzene. The microphase-separated structures of $(AB)_n$ star copolymers (arm number, $n=16$, 16–19 wt% polyisoprene blocks) were formed with the dimensions of a unimolecular micelle in strong segregation. We carried out small-angle X-ray scattering measurements for $(AB)_n$ star copolymers in the form of dry film. These star copolymers formed the superlattice with a face-centred cubic structure in the bulk film.

(Keywords: star copolymer; microphase separation; face-centred cubic lattice)

INTRODUCTION

Theoretical studies of the microphase separation of block copolymers are classified into two types, namely, strong segregation theories[1-3] and weak segregation theories[4-8]. de la Cruz and Sanchez[9] have calculated the phase stability criteria and static structure factors in the weak segregation regime for *n*-arm star diblock copolymers [$(AB)_n$ star]. According to their results, 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. In recent studies[10,11], $(AB)_n$ star copolymers were synthesized by free-radical microgelation in micelles (organized polymerization) formed by diblock macromonomer with ethylene glycol dimethacrylate as a linking agent, and we studied the self-micellization of $(AB)_n$ star copolymers as a parameter of n. As a result, the microphase-separated structures of these star copolymers ($n=14$–30, 18.7 wt% B blocks) were formed with the dimensions of a unimolecular micelle in strong segregation. In this microphase-separation process, the packing structure of the $(AB)_n$ star copolymers in solution and in the solid state is not yet clear.

At present, the most rigorous way to prepare $(AB)_n$ star copolymers possessing more than 10 arms is to crosslink AB diblock monocarbanions with divinylbenzene (DVB)[12-14].

In this article, $(AB)_n$ star copolymers were prepared by crosslinking poly(styrene-*b*-isoprene) [poly(S-*b*-I)] diblock anions with DVB. We studied the self-micellization of $(AB)_n$ star copolymers as a parameter of n by transmission electron microscopy (TEM) observation of microphase-separated structure in the strong segregation regime. We also clarified the packing structure of $(AB)_n$ star copolymers in the bulk film by small-angle X-ray scattering (SAXS) measurements.

EXPERIMENTAL

Synthesis and characterization of $(AB)_n$ star copolymers

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[15]. In brief, poly(S-*b*-I) diblock anions were prepared by the usual sequential anionic addition using n-butyllithium (n-BuLi) as an initiator in benzene in a sealed glass apparatus under a pressure of 10^{-6} mmHg. Next, isoprene monomer was added to this solution with vapour.

The number-average molecular weight ($\bar{M}_n$) of polystyrene (PS) precursors was determined by gel permeation chromatography (g.p.c.; Tosoh high-speed liquid chromatograph HLC-8020), with tetrahydrofuran (THF) as eluent at 38°C, using a TSK gel GMH_{XL} column and a flow rate of $1.0\,\mathrm{ml\,min^{-1}}$. The $\bar{M}_n$ of poly(S-*b*-I) diblock copolymer precursor was also determined by universal calibration[16] ($\log[\eta]M$ *versus* elution volume) by g.p.c. The intrinsic viscosity $[\eta]$ of diblock copolymers was measured in THF at 38°C with an Ubbelohde viscometer. The content of polyisoprene (PI) blocks was determined by ^{1}H n.m.r. spectrometry in $CDCl_3$. The polydispersity ($\bar{M}_w/\bar{M}_n$) was determined from g.p.c. distribution functions improved by the reshaping method[17] with a personal computer.

$(AB)_n$ star copolymers were prepared by crosslinking poly(S-*b*-I) diblock anions with a small amount of DVB (Tokyo Kasei; ~55%, *m*-/*p*-isomer = 2) in benzene. The resulting solution was stirred at 20°C for 48 h and the temperature was subsequently raised to 50°C. Polymerization was stopped by introducing the viscous solution into an excess of methanol.

In order to separate unreacted diblock copolymers from the crosslinked product, the precipitation fractionations were carried out in the benzene–methanol system at 20°C, where the turbidity of diblock copolymer

---

* To whom correspondence should be addressed

0032-3861/94/22/4712-05

Table 1 Characteristics and domain size of poly(S-*b*-I) diblock copolymers[a]

Code	$\bar{M}_n$[b] $\times 10^{-4}$	$\bar{M}_w/\bar{M}_n$[c]	Content of PI block[d] (wt%)	Domain size, $\bar{R}_{PI}$[e] (nm)
SI1	5.37	1.07	16.0	7.6
SI2	3.79	1.07	19.1	5.8

[a] Polymerized in benzene
[b] Determined by g.p.c. using universal calibration
[c] Determined by g.p.c.
[d] Determined by ^{1}H n.m.r. in $CDCl_3$
[e] Average radius of PI spheres

precursor 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 g.p.c., with a low-angle laser light scattering (LS) detector (LS-8: He-Ne laser with detection angle of 5°) and refractive index (r.i.) detector. The concentration of the sample injected was kept small, typically less than 0.1 wt%, to minimize the concentration effect in the scattered light intensity. Details of the $\bar{M}_w$ calculation method for $(AB)_n$ star copolymers have been given elsewhere[18].

Morphological observation

Ultrathin film specimens of the starting diblock and $(AB)_n$ star copolymers for TEM observation were prepared by placing a drop of 1 wt% toluene solution on a microscope mesh coated with a carbon film, and then evaporating the solvent as slowly as possible at 25°C. This specimen was then exposed to osmium tetroxide (OsO_4) vapour for 24 h at room temperature.

For observation of the external shape of $(AB)_n$ star copolymers, a specimen cast from 0.1 wt% toluene solution was shadowed with chromium (Cr) at an angle of 20°. Morphological results were obtained on a Hitachi H-500 TEM at 75 kV.

SAXS measurement

The SAXS intensity distribution was measured with a rotating-angle X-ray generator (Rigaku Denki Rotaflex RTP 300RC) operated at 40 kV and 100 mA. The X-ray source was monochromatized to Cu Kα ($\lambda = 1.54$ Å) radiation.

RESULTS AND DISCUSSION

Generally, diblock copolymers form micelles above the critical micelle concentration. In order to obtain $(AB)_n$ copolymers with both narrow molecular weight distribution and high conversion, it is an advantage that crosslinking of diblock anions with DVB proceeds within micelles. Considering the compatibility of DVB with PS or PI blocks, it is preferable for molecular design that PS blocks form a core in solution and terminal anion ends are located in the PS core. We therefore carried out two preliminary studies: system 1 involved crosslinking poly(I-*b*-S) diblock anions (15 wt% PS blocks) with DVB; system 2 involved crosslinking poly(S-*b*-I) diblock anions (16 wt% PI blocks) with DVB in benzene. Neither system showed macrogelation and the polydispersity for both crosslinked products was very narrow ($\bar{M}_w/\bar{M}_n < 1.12$). However, partial macrogelation was observed when poly(S-*b*-I) diblock anions (16 wt% PI blocks) were crosslinked with *p*-DVB. In anionic polymerization the reactivity of the double bond (1-position) in *p*-DVB is 10 times greater than that of the pendent double bond (4-position)[19]. So, essentially the poly(S-*b*-I) block chains possessing terminal vinylbenzyl groups must be formed in the initiation reaction stage of the poly(S-*b*-I) diblock anion with *p*-DVB. The above experimental results cannot be explained by the reactivity of DVB; more experimental results are necessary to provide an explanation. In this work, we employed system 2 as a crosslinking method, because the film preparation is easy for the star sample having low PI content.

The characteristics and domain size of poly(S-*b*-I) diblock anions SI1 and SI2, used in this work are listed in *Table 1*. Both diblock copolymers have narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.07$) and the content of PI blocks is in the range 16–19 wt%. *Figure 1* shows a typical TEM micrograph of specimen SI2 cast from toluene. The dark portions indicate the selectively stained PI phases. The micrograph shows the texture of dispersed PI spheres in a PS matrix. The SI1 diblock copolymer showed the same morphology as specimen SI2. The average radii of PI spheres are also listed in *Table 1*.

We have prepared $(AB)_n$ star copolymers with various arm numbers, varying the concentration ratio of DVB to diblock anions ([DVB]/[LE]). *Table 2* shows the crosslinking conditions and results for diblock anions with DVB. Macrogelation has not been observed in any experimental series. *Figure 2* shows typical g.p.c. profiles of S2-2 and SI2 taken with r.i. and LS detectors. The g.p.c. distribution of S2-2 is bimodal. The first peak at lower elution volume in an r.i. chart corresponds to $(AB)_n$ star copolymer. It was found from the turbidity curve that the SI2 diblock copolymer was precipitated when the precipitant fraction (methanol fraction) was 0.51. The precipitation fractionation was carried out three times with this solvent composition. A typical g.p.c. profile shows that this fraction has a single molecular weight distribution. *Table 2* also lists the characteristics ($\bar{M}_w$, $\bar{M}_w/\bar{M}_n$, arm number) of the fractionated $(AB)_n$ star copolymers. The arm number of star copolymers increases with an increment of [DVB]/[LE]. $(AB)_n$ star copolymers obtained for both experimental series have narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.03$–$1.12$).

We observed the microphase-separated structure of $(AB)_n$ star copolymers in the solid state. Therefore the information obtained corresponds to the microphase separation in the strong segregation regime. A typical

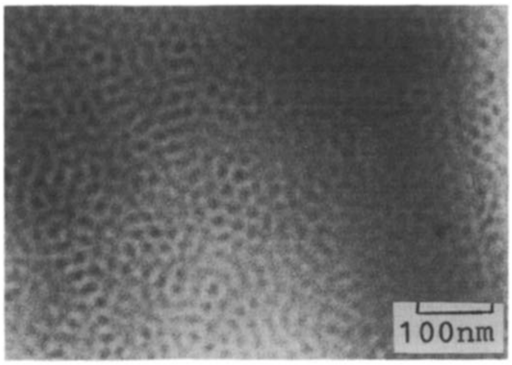

Figure 1 TEM micrograph of specimen SI2 cast from toluene

Table 2 Preparation conditions and results for $(AB)_n$ star copolymers[a]

No.	Feed concentration[b] [LE] × 10^3 ($mol\,l^{-1}$)	[DVB]/[LE] ($mol\,mol^{-1}$)	Star copolymer Conversion[c] (%)	$\bar{M}_w{}^d \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$	Arm number, n (number/polymer)
S1-1	1.97	5.6	11.4	13.0	1.06	24.3
S1-2	2.00	6.5	12.0	22.1	1.05	41.2
S1-3	1.98	15.4	19.6	49.1	1.12	91.5
S2-1	2.09	3.6	37.7	5.91	1.06	15.6
S2-2	2.07	7.2	48.5	7.92	1.04	20.9
S2-3	2.07	13.5	46.7	9.97	1.03	26.3

[a] Polymerized in benzene at 20–50°C. S1 and S2 series correspond to crosslinking using SI1 and SI2 as starting diblock copolymer, respectively
[b] [LE], concentration of diblock anion; [DVB], concentration of divinylbenzene
[c] Estimated by g.p.c. distributions
[d] Determined by g.p.c. with LS and r.i. double detectors

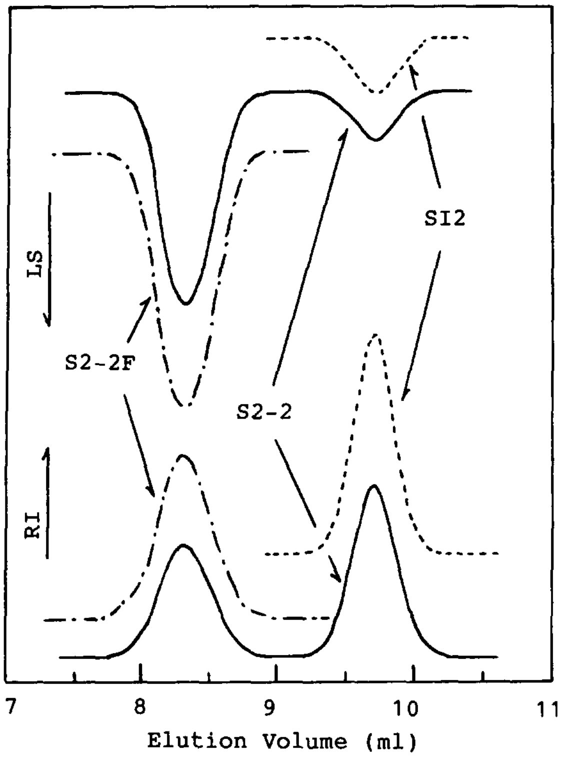

Figure 2 G.p.c. profiles of S2-2, S2-2F and SI2 diblock copolymer

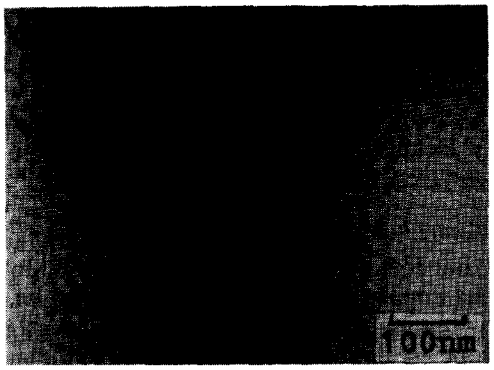

Figure 3 TEM micrograph of S2-1F specimen cast from 1.0 wt% toluene solution (stained with OsO_4)

Table 3 Domain sizes of $(AB)_n$ star copolymers[a]

No.	$(AB)_n$ star copolymer $\bar{M}_w \times 10^{-5}$ of PI blocks	Arm number	Domain size (nm) $\bar{R}_{PI}{}^b$	$R_0{}^c$	$\bar{D}^d$
S2-1F	1.06	15.6	6.0	3.6	20.6
S2-2F	1.42	20.9	7.1	3.9	23.8
S2-3F	1.79	26.3	7.5	4.2	26.0

[a] Composition of S2-F star copolymers, 19.1 wt% PI blocks
[b] Average radius of PI spheres
[c] Calculated radius of PI spheres, assuming that $(AB)_n$ star copolymer forms unimolecular micelle
[d] Average diameter of microsphere particles

TEM micrograph of S2-1F star copolymer is shown in *Figure 3*; the morphology is of dispersed PI spheres in a PS matrix. The TEM micrographs of other copolymer specimens showed similar morphology. *Table 3* lists the average radius of PI spheres ($\bar{R}_{PI}$) for star copolymers S2-1F–S2-3F 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:

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

where n is the arm number, ρ_{PI} is the density of PI ($1.36\times10^4\,mol\,m^{-3}$, from ref. 20), N_A is the Avogadro number ($6.023\times10^{23}\,mol^{-1}$) and P_{PI} represents the monomer units of PI blocks in an AB diblock copolymer. For the S2-F series, each observed value of $\bar{R}_{PI}$ is slightly larger than the calculated value of R_0. It seems that measuring errors on the TEM micrographs cause these differences.

In order to estimate both the shape and external size of star copolymers, TEM observations of the S2-F series, which had been stained with Cr, were carried out. *Figure 4* shows a typical TEM micrograph of S2-3F cast from 0.1 wt% toluene solution. It is found from this shadowed sample that the star copolymer is a microsphere particle, with diameter ($\bar{D}$) of 26.0 nm, dispersed on the carbon substrate. These $\bar{D}$ values are also listed in *Table 3*.

We have compared the domain sizes of $(AB)_n$ star copolymers with those of poly(S-*b*-I) diblock copolymers in the strong segregation regim. *Figure 5* shows the observed domain size $\bar{R}_{PI}$ of star copolymers with the

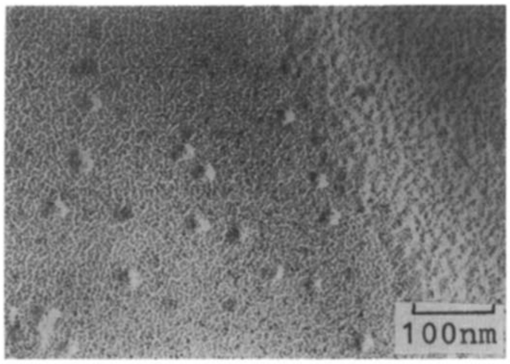

Figure 4 TEM micrograph of S2-1F specimen cast from 0.1 wt% toluene solution (shadowed with Cr)

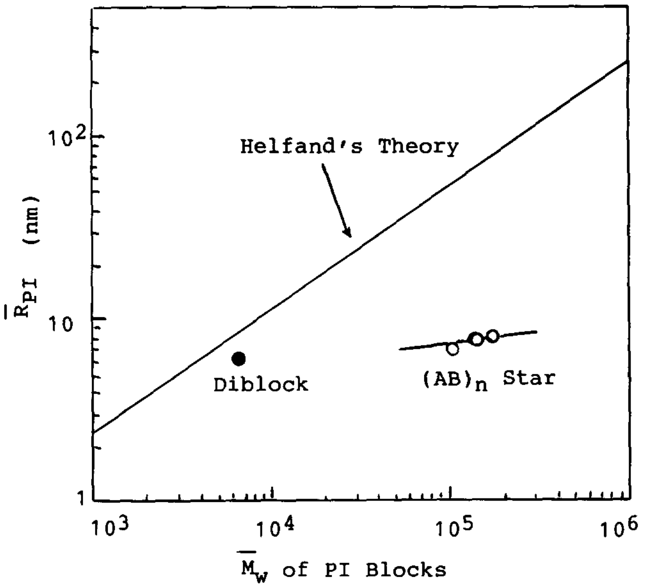

Figure 5 Plot of the average sphere size $\bar{R}_{PI}$ *versus* the molecular weight $\bar{M}_w$ of the PI blocks for $(AB)_n$ star copolymers and diblock copolymer

calculated domain sizes[21] 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. The domain size of the SI2 diblock copolymer specimen is almost identical to that predicted from the equilibrium theory of Helfand and Wassermann[21]. The absolute values of PI spheres for $(AB)_n$ star copolymers are far below the theoretical line for diblock copolymers, and the 2/3 power law is not consistent in star copolymers. These results agree well with those obtained in previous work[11]. As predicted by de la Cruz and Sanchez[9], the $(AB)_n$ star copolymers ($n > 10$) begin to develop a core–shell type structure in the weak segregation regime. During solvent evaporation, the PI cores cannot interpenetrate. The microphase-separated structure of star copolymers is formed with the dimension of a unimolecular micelle in the strong segregation regime.

We have also studied the structural arrangement of such star copolymers in the bulk film by means of SAXS measurements. *Figure 6* shows the SAXS intensity distributions in the small-angle region for S1-F3 ($\bar{M}_w = 4.9 \times 10^6$, $n = 91.5$, 16.0 wt% PI blocks) many-armed star copolymer film (the arrows show the scattering maxima). *Table 4* lists the cubic packing (d_1/d_i) at the scattering angles relative to the angle of the first maximum according to Bragg's equation: $2d\sin\theta = n\lambda$ (where θ is one-half the scattering angle, $\lambda = 1.5418$ Å). It is shown that the first four peaks appear close together at the relative angular positions of $1 : \sqrt{4/3} : \sqrt{8/3} : \sqrt{11/3}$. These values correspond to a packing pattern of (111), (200), (220) and (311) planes in a face-centred cubic (*FCC*) structure. Therefore, it is concluded that the S1-3F star copolymer is packed in a superlattice of *FCC* structure in the bulk film. This is the most efficient way of packing spheres.

In general, the spherical microdomains of diblock copolymers can be packed into one of the three cubic forms: simple cubic, *FCC* and body-centred cubic (*BCC*). According to Ohta and Kawasaki[3], a *BCC* arrangement is only slightly more favoured than the *FCC* arrangement. More recently, the superlattice structure in the film formation of core–shell type polymer microspheres has been reported[22]. These microspheres formed the superlattice with a *BCC* structure near the overlap concentration (C^*), while in the bulk of the film, this structure changed to an *FCC* lattice. On the other hand, Chevalier *et al.*[23] have investigated the coalescence of latex particles through small-angle neutron scattering and TEM. The latex particles were arranged as polyhedral cells in dispersion and these structures changed to colloidal crystals with an *FCC* lattice at the condensed solution (74 wt%). So, the transformation of a C^* solution into a continuous film for $(AB)_n$ star copolymers seems very similar to that for core–shell type microspheres and latex particles. We are investigating the structural arrangement of $(AB)_n$ star copolymers near the concentration C^*. The results obtained will be reported shortly.

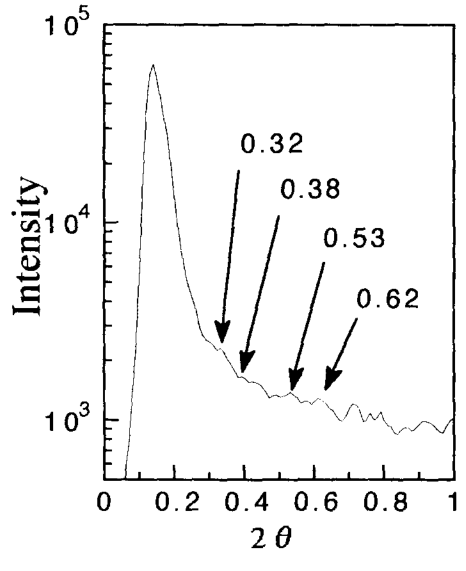

Figure 6 SAXS intensity distributions for S1-3F star copolymer film in the small-angle region: the arrows show the scattering maxima

Table 4 SAXS data for S1-3F film

n	2θ	d_i(nm)	d_1/d_i
1	0.32	27.6	1
2	0.38	23.2	$\sqrt{4/3}$
3	0.53	16.7	$\sqrt{8/3}$
4	0.62	14.2	$\sqrt{11/3}$

REFERENCES

1 Helfand, E. *Macromolecules* 1975, **8**, 552

2 Helfand, E. and Wasserman, Z. R. *Macromolecules* 1976, **9**, 879

3 Ohta, T. and Kawasaki, K. *Macromolecules* 1986, **19**, 2621

4 Leibler, L. *Macromolecules* 1980, **13**, 1602

5 Fredrickson, G. H. and Helfand, E. *J. Chem. Phys.* 1987, **87**, 697

6 Fredrickson, G. H. *Macromolecules* 1987, **20**, 2535

7 Green, P. F., Christensen, T. M., Russell, T. P. and Jerome, R. *J. Chem. Phys.* 1990, **92**, 1478

8 Green, P. F., Christensen, T. M. and Russell, T. P. *Macromolecules* 1991, **24**, 252

9 de la Cruz, M. O. and Sanchez, I. C. *Macromolecules* 1986, **19**, 2501

10 Ishizu, K., Yukimasa, S. and Saito, R. *J. Polym. Sci., Polym. Chem. Edn* 1993, **31**, 3073

11 Ishizu, K. and Yukimasa, S. *Polymer* 1993, **34**, 3753

12 Bi, L. K. and Fetters, L. J. *Macromolecules* 1975, **8**, 90

13 Bi, L. K. and Fetters, L. J. *Macromolecules* 1976, **9**, 732

14 Alward, D. B., Kinnings, D. J., Thomas, E. L. and Fetters, L. J. *Macromolecules* 1986, **19**, 215

15 Ishizu, K., Shimomura, K. and Fukutomi, T. *J. Polym. Sci., Polym. Chem. Edn* 1991, **29**, 923

16 Grubisic, Z., Rempp, P. and Benoit, H. *J. Polym. Sci., B* 1967, **5**, 753

17 Pierce, P. E. and Armonas, J. E. *J. Polym. Sci., C* 1968, **21**, 23

18 Ishizu, K., Shimomura, K., Saito, R. and Fukutomi, T. *J. Polym. Sci., Polym. Chem. Edn* 1991, **29**, 607

19 Worsfold, D. J. *Macromolecules* 1970, **3**, 514

20 Hashimoto, T., Fujimura, M. and Kawai, H. *Macromolecules* 1980, **13**, 1660

21 Helfand, E. and Wassermann, Z. R. *Macromolecules* 1978, **11**, 960

22 Ishizu, K., Sugita, M., Kotsubo, H. and Saito, R. *J. Colloid Interface Sci.* in press

23 Chevalier, Y., Pichot, C., Graillat, C., Joanicot, M., Wong, K., Maquet, J., Lindner, P. and Cabane, B. *Colloid Polym. Sci.* 1992, **270**, 806