

Synthesis of poly(methacrylic acid) core/ polystyrene shell type polymer microspheres

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Poly(styrene-*b*-methacrylic acid) block copolymers were synthesized by hydrolysis of poly(styrene-*b*-*tert*-butyl methacrylate) block copolymers. The microphase separated structures of these block copolymers were poly(methacrylic acid) spheres in polystyrene matrices. Upon crosslinking the poly(methacrylic acid) spheres with hexanediisocyanate in the solid film, the poly(methacrylic acid) core/polystyrene shell type polymer microspheres were obtained. The packing structures of the microspheres were hexagonal and face centred cubic in two and three dimensions, respectively. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

We have reported that the core shell type polymer microspheres can be synthesized upon crosslinking the spherical microdomains of the sphere-matrix type microphase separated films composed with AB type diblock copolymers¹. The poly(4-vinyl pyridine) (P4VP) core/polystyrene (PS) shell type polymer microsphere synthesized on the basis of the above method consisted of a P4VP core with many PS hairy shell chains². This structure is very similar to that of the star polymers proposed by Daoud and Cotton³. For the star polymers with many arms, de la Cruz and Sanchez predicted a macrolattice formation⁴. The macrolattice formation of star polymers was confirmed in the solid state and in the solution above overlap concentration (c^*)^{5,6}. Similar to the star polymers, the P4VP core/PS shell type microspheres formed a macrolattice structure in the solid and in the solution above their $c^{*7,8}$. Moreover, it was found that the superlattice structure was hierarchically transformed from a body centred cubic (BCC) to a face centred cubic (FCC) by increasing with the polymer concentration⁸. However, the lattice formation was only examined for P4VP core-PS microspheres. The main purpose of this study is to investigate the superlattice formation of the core/shell type microspheres with different chemical species from P4VP core/PS shell type polymer microspheres.

In the previous work, we reported the synthesis of the poly(methacrylic acid) (PMAA) core/PS shell type polymer microspheres from the poly(styrene-*b*-methacrylic acid) [P(S-*b*-MAA)]⁹. However, the previous synthesis method for the microspheres required very strict control of the evaporating rate of the solvent during casting of the solution. As a result, it was difficult to produce the core/shell type polymer microspheres in large quantities. Thus, the new method of synthesis of the

PMAA core/PS shell type polymer microspheres was also investigated in this work.

The precursor block copolymers, P(S-*b*-MAA), for synthesis of the core/shell type polymer microspheres were synthesized by hydrolysis of the poly(styrene-*b*-*tert*-butyl methacrylate) [P(S-*b*-BuMA)], which was polymerized by an anionic additional living polymerization. Hexamethylene diisocyanate (HDI) was chosen as the crosslinking reagent for the PMAA sequences. The morphologies of the block copolymers and the core/shell type polymer microgels were observed by transmission electron microscopy (TEM). The three-dimensional packing structures of the microspheres were investigated by small angle X-ray scattering (SAXS).

EXPERIMENTAL

*Synthesis and characteristics of the P(S-*b*-MAA) block copolymers*

Well-defined P(S-*b*-BuMA) diblock copolymers were prepared by the usual anionic additional polymerization using *n*-butyl lithium as initiator at -78°C ¹⁰. Number-average molecular weight (M_n) and distribution of molecular weight (M_w/M_n) of the PS were determined with a Tosoh HLC-8020 g.p.c. with tetrahydrofuran (THF) as eluent at 38°C . A TSK-gel GMXL column was used and the flow rate was 1.0 ml min^{-1} . The PS content in the block copolymer was determined with a ¹H n.m.r. (JEOL, GSX500) and FTi.r. (Shimadzu, FTIR-8010 spectrophotometer). The M_n of the block copolymer was determined by g.p.c. combined with the PS content of the block copolymer.

Poly(S-*b*-MAA) was synthesized by hydrolysis of the P(S-*b*-BuMA). The hydrolysis was carried out as by Bugner¹¹. The degree of hydrolysis was measured by acid/base titration with sodium methoxide in dimethylformamide.

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Crosslinking of P(S-b-MAA)

The polymer (0.05 g) was dissolved in 0.5 ml THF. The polymer solution was then cast on a Teflon sheet and dried gradually. The polymer film obtained was soaked in a HDI hexane mixture for 48 h at room temperature. The feed values for the isocyanate group were varied from 20 to 100 mol% for the carboxyl group in the AB block copolymers ($[-NCO]/[-COOH]$).

Morphological observation

The ultra-thin film specimens of the starting diblock copolymers or crosslinked products were prepared for TEM by placing one drop of polymer solution with a certain polymer concentration on a copper grid coated with carbon film and then evaporating as gradually as possible at room temperature. In order to obtain contrast for the film, the PS sequences were stained with OsO_4 by placing the specimen in OsO_4 gas for 72 h at room temperature. The morphological results were obtained with a transmission electron microscope (Hitachi, H-500) at 75 kV.

Dynamic light scattering (DLS) measurement

The diameter and the distribution of the micelle and microgel were measured by DLS (Photal, DLS-7000) for the solutions at an angle of 90° at 1 and 0.005 wt%, respectively.

SAXS measurement

The SAXS intensity distribution of the polymer film 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 to $Cu K\alpha$ ($\lambda = 1.54 \text{ \AA}$) radiation. The SAXS patterns were recorded with a fine-focused X-ray source using a flat-plate camera (Rigaku Denki, RU-100).

RESULTS AND DISCUSSION

P(S-b-MAA) diblock copolymers

The properties of the P(S-*b*-BuMA) AB type diblock copolymers and the results of hydrolysis of P(S-*b*-BuMA), i.e. the properties of P(S-*b*-MAA) block copolymers, are shown in Table 1. Since the microphase separated structure of the block copolymer in the solid state was used as the template of the core/shell type polymer microsphere, the morphology of the microphase separation of the films should be PMAA spheres in a PS matrix. The morphology of microphase separation of AB diblock copolymers is governed by Molau's law¹². Thus, the contents of PS were set larger than 70 mol%. The

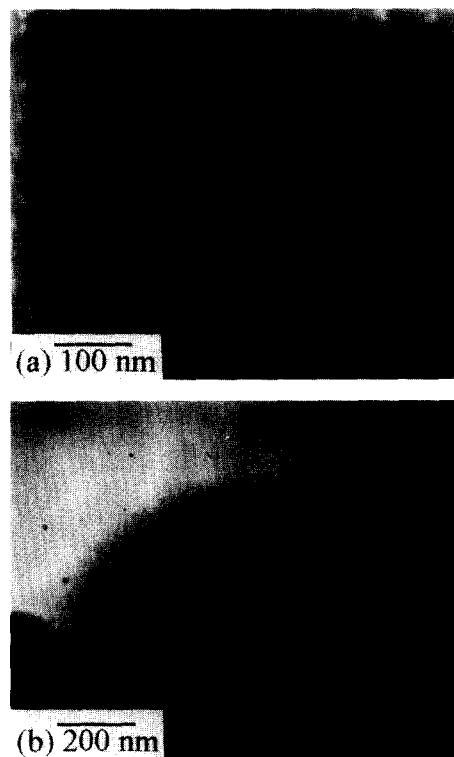


Figure 1 TEM micrographs of the block copolymers cast from THF at 1 w/v%: (a) SA1; (b) SA2

P(S-*b*-MAA) block copolymers were not dissolved in benzene, but in THF or 1,4-dioxane.

Figure 1 depicts the TEM micrographs of the block copolymers SA1 and SA2 cast from THF. The dark regions in both micrographs are PS stained with OsO_4 . For the block copolymer SA1, the spherical domains of PMAA (white regions) are observed in the PS matrix. The number-average diameter (D_n) of PMAA spherical microdomains was 22.0 nm, and its distribution (D_w/D_n) was 1.02. It was found that the PMAA spherical microdomains have a narrow size distribution for the synthesis of monodispersed microspheres. On the other hand, the TEM micrograph of SA2 shows not only the spherical microdomains, but also cylindrical microdomains of PMAA. The fraction of cylindrical microdomains in PMAA microdomain was increased by changing the cast solvent from THF to 1,4-dioxane. The reason for the appearance of cylindrical microdomains is due to the high PMAA content in SA2. Based on the purpose of this study, the SA1 was used for the synthesis of the microspheres.

Table 1 Characteristics of P(S-*b*-MAA) diblock copolymers

Sample name	$M_{n,PS}^a$ $\times 10^{-4}$	$M_{n,block}^b$ $\times 10^{-5}$	Degree of hydrolysis (%) ^c	PS content ^d (mol %)	D_n (core) (nm) ^e	D_w/D_n^e
SA1	8.3	1.0	73.1	82.4	22.0	1.02
SA2	5.3	0.7	67.4	76.1	13.9	—

^a M_n of precursor PS determined by g.p.c.

^b Determined by combining g.p.c. data, FTi.r. data and degree of hydrolysis

^c Determined by titration with sodium methoxide

^d Determined by FTi.r.

^e D_n and D_w are number-average and weight-average diameters of PMAA spherical domains determined by TEM

Table 2 Conditions and results of crosslinking of PMAA core of SA1 series

Sample name	Conditions		Results		
	$[-\text{NCO}]/$ $[-\text{COOH}]^a$	HDI/hexane (v/v)	Introduced HDI (mol %) ^b	$D_{n\text{DLS}}$ (nm) ^c	$D_w/D_{n\text{DLS}}$ ^c
SA1M-20	0.20	0.001	32	105.7	1.01
SA1M-50	0.47	0.002	—	108.8	1.01
SA1M-100	0.98	0.005	—	93.5	1.05

^a $[-\text{NCO}]$; isocyanate groups in hexane, $[-\text{COOH}]$; carboxyl groups in PMAA

^b Introduced HDI ratio in P(S-*b*-MAA) film to feed HDI determined by g.c.

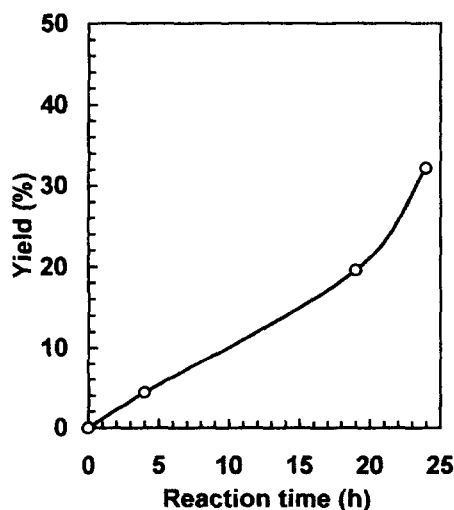
^c $D_{n\text{DLS}}$ and D_w/D_n (DLS) are the number-average diameter and its distribution of the microspheres in 0.01 wt% of 1,4-dioxane determined by DLS

Microsphere synthesis

Next, the PMAA sequences in the microphase separated film were crosslinked with HDI. For crosslinking, the SA1 film was soaked in hexane/HDI mixture at room temperature. Here, hexane is a non-solvent for both PMAA and PS, and HDI is a good solvent for both. Therefore, the selective permeation of HDI into the film was expected. However, as the HDI is a good solvent for the film, too large an amount of HDI in the film would be due to the microscopic dissolution of the film even in the hexane matrix. This dissolution of the film leads to the macrogelation of the film. The crosslinking conditions are listed in *Table 2*. In order to make clear the effect of HDI on the crosslinking density of the microspheres, the feed values for HDI for PMAA were varied from 20 to 100 mol%.

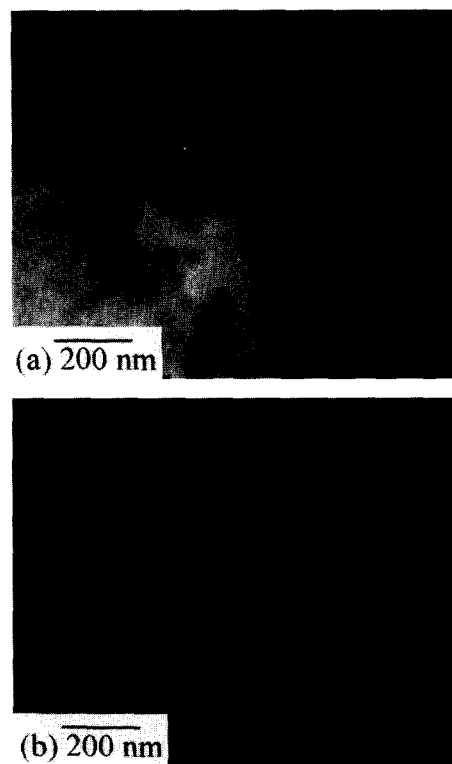
In order to investigate the amount of HDI introduced into hexane, the content of HDI in the hexane was measured by g.c. (*Figure 2*). It was found that 32 mol% of HDI was introduced into the film after 24 h. In styrene, the reaction of carboxylic acid and isocyanate groups was completed within 24 h¹³. Therefore, a reaction time of 24 h was sufficient to crosslink the PMAA sequences.

All films were not softened through soaking in the solution. All crosslinked films of SA1 freely dissolved in THF, and no macrogelation occurred for the synthesis of the microspheres by this method. Additionally, the films could be dissolved in benzene, which was a poor solvent for the block copolymer SA1. This indicates that the properties of PS reflected strongly on the crosslinked products.

**Figure 2** Yield of HDI introduced into the SA1 film (SA1M20)

Next, the structures of the crosslinked products were confirmed by TEM. *Figure 3* shows the TEM micrographs of crosslinked product SA1M20 cast from 0.01 and 1 wt% solution in THF. Similar to the TEM samples of the block copolymers, the PS sequences were stained grey with OsO₄. When the polymer concentration is 0.01 wt%, the block copolymer cannot segregate. Consequently, the microphase separated structure of the block copolymer cannot be observed by TEM. Contrary to the block copolymers, for the crosslinked samples, the spherical products are observed on the carbon substrate. It was found that each sphere had one PMAA core (white core) in a grey PS shell. This structure of the microsphere increases the solubility of the microspheres in benzene. By casting from condensed solution, the microspheres were segregated and formed a film with PMAA spheres in a PS matrix type structure.

The D_n values for the PMAA core at each polymer concentration were constant (21.8 nm) and agreed well with the D_n for PMAA spherical microdomains of

**Figure 3** TEM micrographs of SA1M20 cast from THF: (a) at 0.01 w/v%; (b) 1 w/v%

the block copolymer SA1 (22 nm). Moreover, the size distributions of the microspheres were narrow ($D_w/D_n = 1.01$).

In order to investigate the structure of the crosslinked products in the solvent, the DLS measurements were carried out for the block copolymer SA1 and the microspheres of SA1. The intensity distributions of the SA1 and SA1M20 at 0.01 wt% in 1,4-dioxane are shown in Figure 4. The hydrodynamic diameters ($D_{n,DLS}$) of the microspheres in the solutions are shown in Table 2. The values for $D_{n,DLS}$ of SA1M20 were larger than that of SA1 (31.1 nm) (Figure 4). It was concluded that PMAA microdomains in the film were fixed satisfactorily under these conditions; as a result, the PMAA core/PS shell type polymer microspheres with narrow size distribution were synthesized.

The $D_{n,DLS}$ of the microspheres slightly decreased with increasing of the feed value of HDI. 1,4-Dioxane is a good solvent for both the PMAA core and PS shell. The shell thickness of the microspheres could not be changed with the feed of HDI. Therefore, the decrease in the $D_{n,DLS}$ with increasing HDI feed suggests increase in the crosslink density of the core with the feed ratio of HDI. This also suggests that the PMAA cores were not crosslinked tightly and could be swollen in 1,4-dioxane.

As described in the Introduction, the self-micellization is expected for the core/shell type products with many arms in the solvent. Additionally, the superlattice formation is also expected for them above the c^* concentration. The arm-number of SA1M20 was calculated as 226.4, by combining the D_n value for the PMAA core, the density of PMAA and the degree of polymerization of the PMAA block. According to previous report⁸, the P(4VP) core/PS shell type microspheres, whose arm-number was larger than 70, could form the superlattice structure. Therefore, superlattice formation with the PMAA core/PS shell type microspheres was expected. In order to obtain the c^* concentration, the $D_{n,DLS}$ of the microsphere SA1M20 was measured in benzene. The $D_{n,DLS}$ was 96.5 nm and its distribution was 1.10. For SA1M20, the $D_{n,DLS}$ in benzene (96.5 nm) was smaller than in 1,4-dioxane (105.7 nm). This shows that

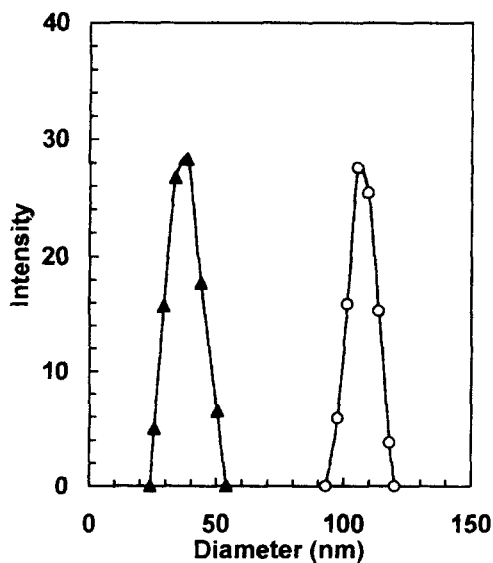


Figure 4 Intensity distribution of polymers at 0.01 w/v% in 1,4-dioxane: (▲) the block copolymer SA1; (○) the microsphere SA1M20

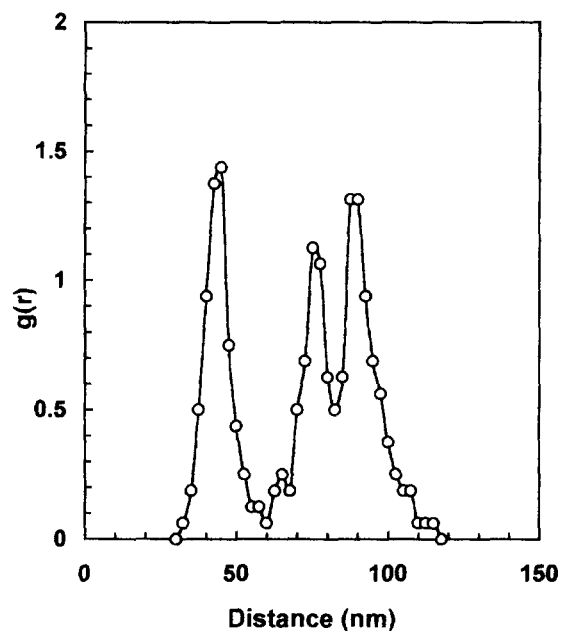


Figure 5 Distribution function of the distance between the centres of the cores for SA1M20

the microspheres shrink in benzene contrary to the case in 1,4-dioxane. The core part of the microspheres cannot be swollen in benzene, because benzene is a good solvent for the shell, but a non-solvent for the core, in contrast to 1,4-dioxane which is a good solvent for both sequences. Therefore, the diameter of the microsphere was decreased in benzene. By calculation with the $D_{n,DLS}$ in benzene and the arm-number of the microsphere, the c^* value was 8.1 w/v%.

Packing structure of microspheres

First, the two-dimensional packing behaviour of the microsphere SA1M20 was investigated with TEM micrograph. Figure 3b depicts the TEM micrograph of SA1M20 cast from condensed solution (at 1 wt%). The PMAA cores (white regions) seemed to be packed hexagonally. To investigate the degree of ordering of the microspheres, the distribution function of the PMAA core was measured and is shown in Figure 5. For the complete hexagonally packed film, the peaks should appear at distances $r, \sqrt{3}r$ and $2r$. In Figure 4, the clear three peaks appeared at 44.0, 76.0 and 88.3 nm. The ratios of the distance of the peaks are $r, 1.727r$ and $2.01r$, respectively. These values are in fair agreement with the theoretical values for the hexagonal packing. The packing structure of the microspheres was concluded to be a complete hexagonal in two dimensions.

Next, the three-dimensional packing behaviour of the microsphere SA1M20 in the solid state was investigated with SAXS. Figure 6 shows the SAXS intensity curve of SA1M20. The peaks of 2θ appeared at 0.27, 0.44, 0.51 and 0.62°. The d_1 is calculated as 36.4 nm from the first peak. The d_n values for the following peaks are 22.3, 19.2 and 15.8 nm at 0.44, 0.51 and 0.62 respectively. The packing structure is determined from the d_n/d_1 values. The d_1/d_n values for SA1M20 are 1, 1.63, 1.89 and 2.30. These values showed fair agreement with the d_1/d_n values for FCCs, i.e. 1, $\sqrt{(8/3)}$ (1.63), $\sqrt{(11/3)}$

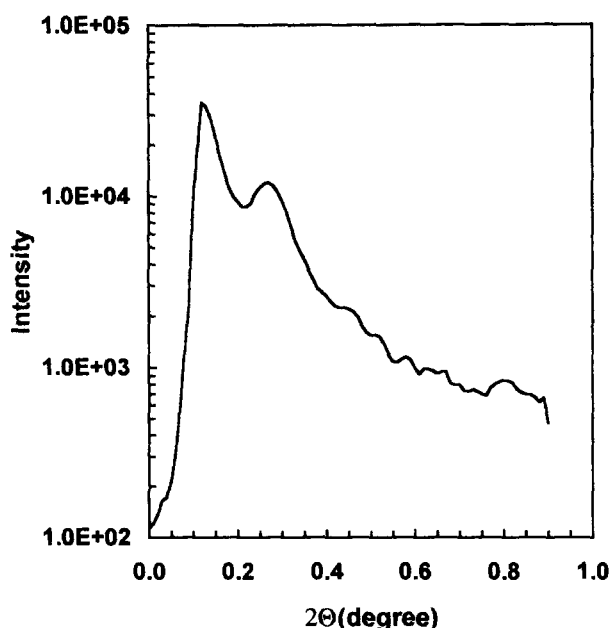


Figure 6 SAXS intensity curve of the SA1M20 film cast from benzene

(1.91) and $\sqrt{(16/3)}$ (2.30). Therefore, it was found that the microspheres of SA1M20 were packed in the FCC structure. In general, the BCC structures are reported for the AB type diblock copolymers¹⁴⁻¹⁸. In contrast to the block copolymers, the FCC was reported for the P4VP core/PS shell type polymer microspheres⁸. The change in the packing structures was due to the higher mobility of the microspheres in the condensed solution. In this work, the PMAA core/PS shell type microspheres were packed with FCC structures. Thus, it was concluded that the packing behaviour of the microspheres were not governed by the core but by the shell.

CONCLUSIONS

Two types of P(S-*b*-MAA) AB type diblock copolymers with PS contents larger than 76 mol% were obtained by hydrolysis of P(S-*b*-BuMA), which was polymerized by an additional anionic polymerization technique. The PMAA spheres in the microphase separated film of SA1

were crosslinked with HDI by soaking the film in a HDI/hexane solution. By DLS measurements and TEM observations of the crosslinked products, the synthesis of PMAA core/PS shell type polymer microspheres was confirmed. By increasing the feed of HDI, the swelling of the PMAA core in the good solvent was prevented.

The packing structures of the microspheres in two and three dimensions were investigated by TEM observation and SAXS measurements, respectively. From the distribution function of the PMAA core/PS shell type polymer microspheres, the packing structure was found to be hexagonal in two dimensions. The peaks of SAXS intensity showed fair agreement with the pattern of the FCC packing of the microspheres. Therefore, the packing structure of the PMAA core/PS shell type microspheres was FCC in three dimensions.

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REFERENCES

- 1 Ishizu, K. and Fukutomi, T. *J. Polym. Sci.: Polym. Phys. Edn.* 1988, **26**, 281
- 2 Ishizu, K. *Polymer* 1989, **30**, 793
- 3 Daoud, M. and Cotton, J. P. *J. Phys.* 1982, **43**, 531
- 4 de la Cruz, M. O. and Sanchez, I. C. *Macromolecules* 1986, **19**, 2501
- 5 Ishizu, K. and Uchida, S. *Polymer* 1994, **35**, 4712
- 6 Ishizu, K. and Uchida, S. *J. Colloid Interface Sci.* 1995, **175**, 293
- 7 Saito, R., Kotsubo, H. and Ishizu, K. *Polymer* 1994, **35**, 1747
- 8 Ishizu, K., Sugita, M., Kotsubo, H. and Saito, R. *J. Colloid Interface Sci.* 1995, **169**, 456
- 9 Saito, R., Kotsubo, H. and Ishizu, K. *Eur. Polym. Sci.* 1991, **27**, 1153
- 10 Kotaka, T., Tanaka, T. and Inagaki, H. *Polym. J.* 1972, **3**, 327
- 11 Burgner, D. E. *Am. Chem. Soc. Div. Polym. Prepr.* 1986, **27**, 57
- 12 Molau, G. E. in 'Block Polymers' (Ed. S. L. Aggarwal), Plenum Press, New York, 1970, p. 79
- 13 Saito, R., Chiu, Y.-Y. and Lee, L. J. *Polymer* 1996, **37**, 3567
- 14 Ohta, T. and Kawasaki, K. *Macromolecules* 1986, **19**, 2621
- 15 Thomas, E. L., Kinning, D. J., Alward, D. B. and Henke, C. S. *Macromolecules* 1987, **20**, 2934
- 16 Hashimoto, T., Fujiura, M. and Kawai, H. *Macromolecules* 1980, **13**, 1660
- 17 Roe, R. J., Kishkis, M. and Chang, V. C. *Macromolecules* 1981, **14**, 1091
- 18 Richard, R. W. and Thomason, J. L. *Polymer* 1981, **22**, 581