Crosslinking of the inner poly(methyl methacrylate) core of poly(α-methylstyrene-*b*-methyl methacrylate) micelles in a selective solvent: 4. Reaction rate effects

Reiko Saito, Koji Ishizu and Takashi Fukutomi
Tokyo Institute of Technology, Department of Polymer Chemistry,
2-12 O-okayama, Meguro-ku, Tokyo 152, Japan
(Received 27 September 1990; revised 7 March 1991; accepted 25 March 1991)

A poly(α-methylstyrene-*b*-methyl methacrylate) with styryl groups on the poly(methyl methacrylate) (PMMA) sequence was prepared and dissolved in a mixed solvent, benzene/cyclohexane (30/70 v/v), to make micelles with a PMMA core. The dissociation time of a polymer chain from a polymer micelle was determined as 46.3 min from viscometric measurements by the concentration jump method. The PMMA core of the polymer micelles was crosslinked via the styryl groups with a radical initiator (2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile), V-70) or a redox initiator (dimethylaniline plus benzoyl peroxide) at 40°C. With the redox initiator, 96% of the crosslinking groups reacted after 46.3 min and monodisperse microgels were obtained. With V-70, 2% of the crosslinking groups reacted after 46.3 min and inter-micelle crosslinking was not prevented.

(Keywords: core–corona type microgel; polymer micelle; reaction rate; inter-micelle crosslinking)

INTRODUCTION

It is well known that an AB diblock copolymer forms polymer micelles in a so-called selective solvent that is a good solvent for one sequence and a non-solvent for the other sequence. When the core part is crosslinked, polymer microspheres with crosslinked core and soluble corona can be obtained.

Based on this supposition, we have investigated the synthesis of core–corona microgels in selective solvents[1–5]. On crosslinking of the poly(allylamine) core of poly(allylamine-*g*-vinyl acetate) with 1,3-dibromopentan-2-ol in an acetone/water system[1], polymer microspheres with a poly(allylamine) core and poly(vinyl acetate) corona were obtained. However, it was difficult to control the size of the microspheres by changing the crosslinking conditions, because the crosslinking was very slow.

For the poly(α-methylstyrene-*b*-methyl methacrylate) (P(MeSt-*b*-MMA)) system[2–5], micelle formation of P(MeSt-*b*-MMA) with PMMA core and PMeSt shell in a benzene/cyclohexane mixture, which was a good solvent for PMeSt and a non-solvent for PMMA, was confirmed. Styryl groups were introduced on the PMMA sequences of the P(MeSt-*b*-MMA) by a Grignard reaction. The PMMA core containing styryl groups was formed with P(MeSt-*b*-MMA) with styryl groups in benzene/cyclohexane mixture, and microgels with crosslinked PMMA core and PMeSt corona were synthesized by the radical reaction of the styryl groups in the PMMA core with a radical initiator.

In those studies[2–4], it was concluded that the reaction rate of intra-micelle crosslinking and the lifetime of the polymer micelle were important for the crosslinking of the polymer micelle. When intra-micelle crosslinking occurred before the break-up of the micelle, a microgel with a core–corona morphology could be synthesized. Therefore, in order to synthesize the core–corona type microgel, the lifetime of the micelle must be increased, when the reaction rate of intra-micelle crosslinking is constant. Based on this consideration, the polymer micelle with long lifetime was crosslinked, and it was possible to control the size of the microgel by changing the temperature and the polymer concentration.

From these considerations, it was also suggested that macrogelation would be hindered by the rapid crosslinking reaction, even though the lifetime of the polymer micelle was constant. The purpose of this study is to synthesize core–corona type microgels by protection of inter-micelle crosslinking on increasing the reaction rate.

As in the previous studies[2–5], the well defined P(MeSt-*b*-MMA) diblock copolymer No. 6 ($\bar{M}_n = 6.3 \times 10^4$, MeSt = 68 mol%, 10 mol% styryl groups in PMMA chain) and a 30/70 v/v benzene/cyclohexane mixture were chosen as the block copolymer and the selective solvent, respectively. The radical initiator, 2,2′-azobis-(4-methoxy-2,4-dimethylvaleronitrile) (V-70), and the redox initiator, dimethylaniline plus benzoyl peroxide (DMA + BPO), were used for normal crosslinking and rapid crosslinking, respectively. The diameters of the crosslinked polymer micelles were measured in solution and in the solid state with a submicrometre particle size analyser and a transmission electron microscope (TEM), respectively.

EXPERIMENTAL

Crosslinking of the polymer micelle

The crosslinking of the polymer micelles of the block copolymer No. 6 was carried out at 40°C as in the

0032-3861/92/081712-05

Table 1 The crosslinking conditions of the poly(α-methylstyrene-*b*-methyl methacrylate) micelles

	Polymer concn. (wt%)	Temperature (°C)	Initiator	
			Type[a]	[I] (mol l^{-1})
1	1.0	40.0	V-70	3.24×10^{-3}
2	1.0	40.0	DMA + BPO	3.24×10^{-3}

[a] V-70: 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile); DMA + BPO: dimethylaniline + benzoyl peroxide

previous paper[2]. The crosslinking conditions of the polymer micelles are listed in *Table 1*.

Sampling was carried out at regular intervals of 0.5 h. For each sampled solution, the diameter of the microgel was measured in solution and in the solid state with a submicrometre particle size analyser and a TEM, respectively.

Measurement of the diameter of the product in the solid state

The preparation of the sample for TEM observation was carried out as in the previous paper[2]. The PMeSt sequences were stained with RuO_4. The sample was observed with a TEM (Hitachi, H-600) at 75 kV.

Measurement of the diameter of the products in solution

First, 0.3 ml of the sample solution was diluted with the solvent to 30 ml. The diluted sample solution was then filtered through a Teflon membrane (pore size 3000 nm) to remove dust. The particle diameter was measured with a submicrometre particle size analyser (Courler Electrics Inc., Sub-micron Particle Analyzer Model N4) at 40°C.

Measurement of the styryl group concentration in the microgel

Styryl groups remaining in the crosslinked microgels were determined by using a gel permeation chromatograph (Tosoh, 801A type instrument; column GM-6, solvent tetrahydrofuran (THF), 38°C, flow rate 1.0 ml min^{-1}) equipped with both refractive index (r.i.) and ultra-violet (u.v., 292 nm) detectors (Tosoh, UV-8 model II spectrophotometer), *p*-methylstyrene being the standard material[6].

RESULTS AND DISCUSSION

The characteristics of the polymer micelles

Figure 1 shows the size of the polymer micelles of the block copolymer No. 6 measured in the mixed solvent at 40°C. No polymer micelles were observed at a polymer concentration of 0.001%, and monodispersed polymer micelles with number-average radius of 32 nm were observed at a polymer concentration of 1%. It was expected that polymer micelles with PMMA core and PMeSt corona were formed at a polymer concentration of 1 wt%.

Next, the kinetic behaviour of the polymer micelles was investigated. It is well known that block copolymer micelles break up and the block copolymer chains aggregate again in solution. As described in the 'Introduction', the lifetime of the polymer micelles was one of the most important factors for the crosslinking of the polymer micelles, because the break-up of the polymer micelles during crosslinking results in inter-micelle crosslinking (macrogelation).

The equilibrium of micelle formation is given by the following equations[7–9]:

$$(s+1)\mathrm{A} \underset{k_D}{\overset{k_F}{\rightleftharpoons}} \mathrm{A}_s + \mathrm{A} \underset{k_-}{\overset{k_+}{\rightleftharpoons}} \mathrm{A}_{s+1} \qquad (1)$$

where A is a block copolymer chain, A_s is a polymer micelle with an aggregation number s, k_F and k_+ are the aggregation rate constants, and k_D and k_- are the dissociation rate constants. When the polymer concentration is changed suddenly, the polymer micelle system reaches a new equilibrium very fast. The relation between k_+, k_- and the relaxation time τ of the solution after rapid dilution are given as follows[10–12]:

$$\tau^{-1} = k_+ c - k_- \qquad (2)$$

where c is the concentration of the block copolymer chain. The τ values were found by viscometric measurements and are listed in *Table 2*; k_+ and k_- are calculated

Table 2 The relaxation time τ of the solution viscosity after rapid dilution[a]

Polymer concn. (wt%)	$\tau^{-1} \times 10^4$ (s^{-1})
8.0	0.33
4.0	1.11
2.0	9.14
1.0	3.19

[a] Solvent: 30/70 benzene/cyclohexane (v/v); temperature: 40.0°C

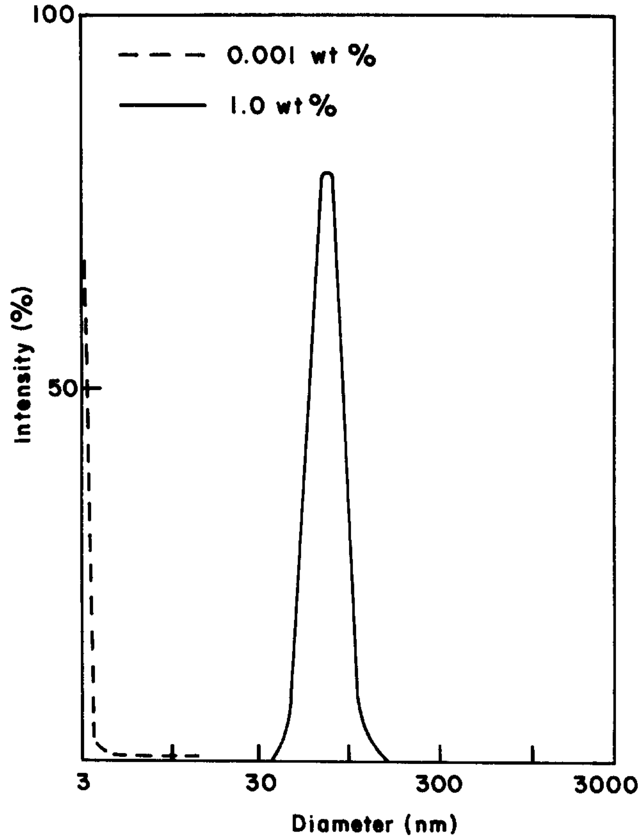

Figure 1 The diameter of block copolymer No. 6 micelles in the solvent 30/70 benzene/cyclohexane (v/v) at 40°C: (– – – –) polymer concentration 0.001 wt%; (——) polymer concentration 1.0 wt%

from equation (2) as $k_+ = 4.08 \times 10^{-4}\,\mathrm{wt\%^{-1}\,s^{-1}} = 4.57 \times 10^{-3}\,\mathrm{l\,mol^{-1}\,s^{-1}}$ and $k_- = 3.6 \times 10^{-4}\,\mathrm{s^{-1}}$. The dissociation time of a block copolymer chain from a polymer micelle was calculated from the k_- value as 46.3 min in this micelle system.

The critical micelle concentration (*CMC*) was 0.88 wt%, as $CMC = k_-/k_+$ (ref. 13). Above the *CMC*, the distribution of aggregation number of the block copolymers in a micelle increases with increase of the polymer concentration[14,15]. In order to neglect the polymer concentration effect, the polymer concentration was set at 1 wt%, which was slightly larger than the *CMC*.

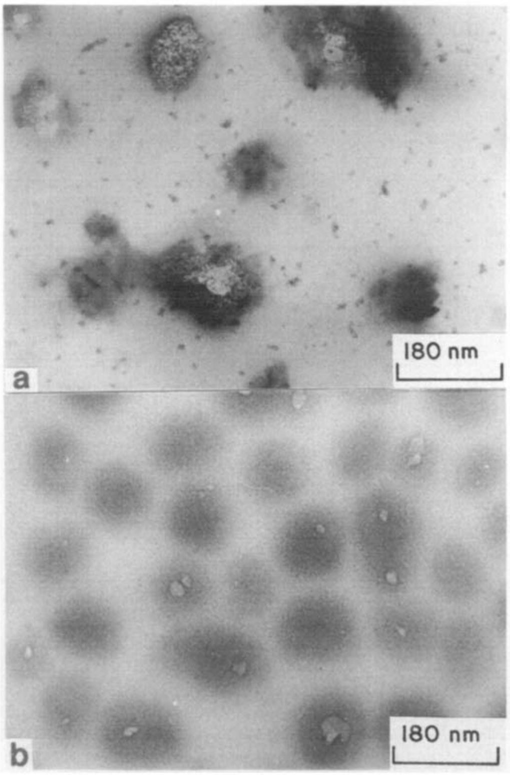

Figure 2 TEM micrographs of microgels showing PMeSt stained with RuO_4: (a) crosslinked with V-70; (b) crosslinked with BPO + DMA

Crosslinking of the polymer micelle

The characterized polymer micelles were crosslinked with V-70 and DMA + BPO initiators at 40°C. The crosslinking conditions are listed in *Table 1*.

Figures 2a and *2b* are TEM micrographs of microgels crosslinked for 2.5 h with V-70 and BPO + DMA, respectively. The dark parts in the micrographs are segregated PMeSt chains selectively stained with RuO_4. In both micrographs, spherical microgels with PMMA core and PMeSt corona are observed on the carbon substrate. In *Figures 3a* and *3b*, the diameter distributions of the microgels crosslinked with V-70 and BPO + DMA are shown, respectively. The microgel synthesized with BPO + DMA had a narrow distribution. In contrast, the distribution was very wide for the microgel synthesized with V-70.

For the microgel crosslinked with V-70, the diameter of the microgel was measured in solution and in the solid state (*Figure 4*). The diameter of the microgel in solution (D_{dls}) was constant for 1.5 h. No macrogel was observed with the TEM until 1 h. This indicates that the crosslinking of the PMMA core was insufficient to keep the structure of the polymer micelles.

After 1 h, the presence of the microgel was confirmed with the TEM. The polymer micelles were crosslinked and did not break up during preparation for the TEM sample. The important thing is that the minimum time to obtain the microgel (1 h) was longer than the dissociation time of the block copolymer chain from a polymer micelle (46.3 min), because the polymer micelle can break up and the chains aggregate again before the crosslinking in such a system. In fact, after 1.5 h, the microgel solution could not be analysed with the submicrometre particle analyser; the diameter of the microgel in the solid state (D_{tem}) and the distribution of D_{tem} increased drastically with reaction time; and inter-micelle crosslinking could not be hindered in this system.

For the microgel crosslinked with BPO + DMA, the diameter of the microgel was measured in solution and in the solid state (*Figure 5*). For 0.5 h, the D_{tem} was observed (40 nm) and D_{dls} increased from 64 to 150 mm. This indicated that the microgel was present from the first stage of crosslinking. The D_{tem} increased from 40 to

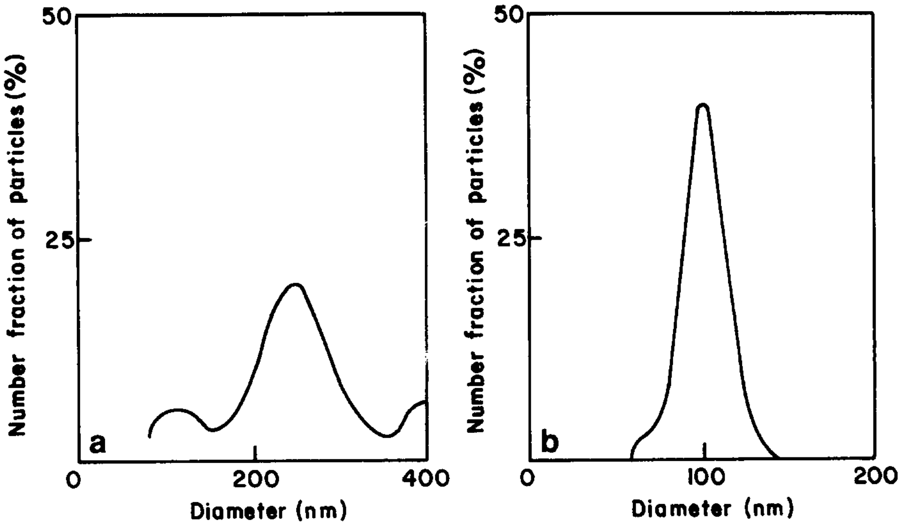

Figure 3 The diameter distribution of microgels estimated from TEM results: (a) crosslinked with V-70; (b) crosslinked with BPO + DMA

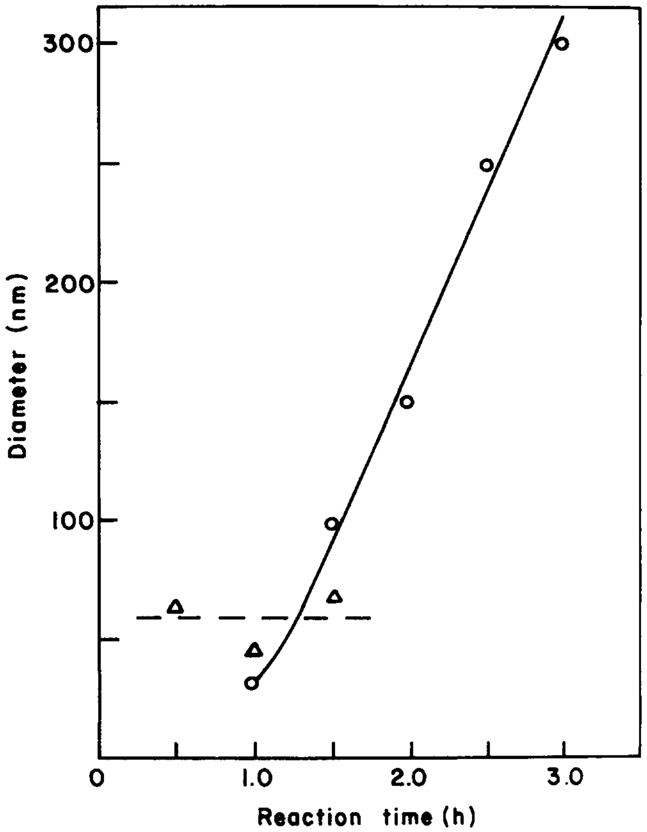

Figure 4 The diameter of block copolymer No. 6 micelles crosslinked with V-70 in the 30/70 benzene/cyclohexane mixture: (△) detected with the submicrometre particle analyser in solution; (○) detected with TEM in the solid state

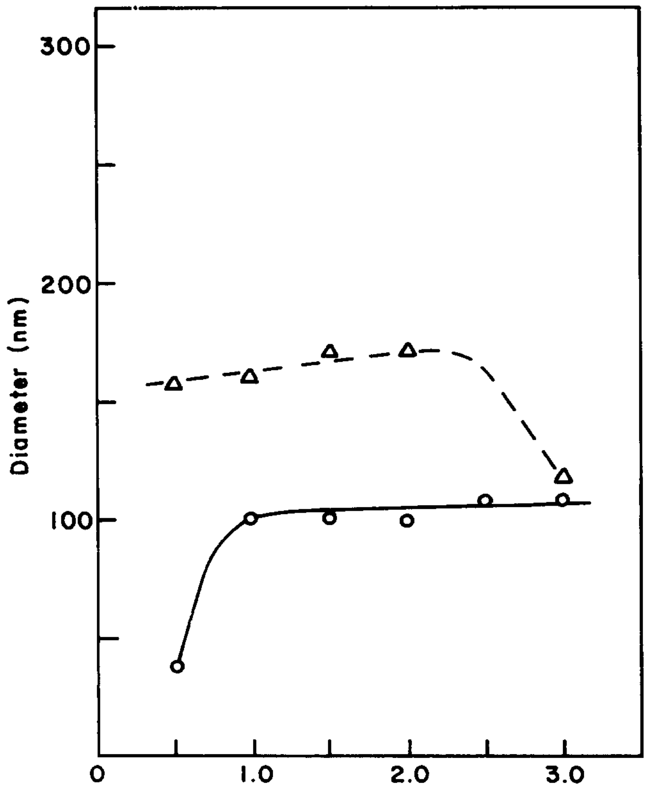

Figure 5 The diameter of block copolymer No. 6 micelles crosslinked with DMA + BPO in the 30/70 benzene/cyclohexane mixture: (△) detected with the submicrometre particle analyser in solution; (○) detected with TEM in the solid state

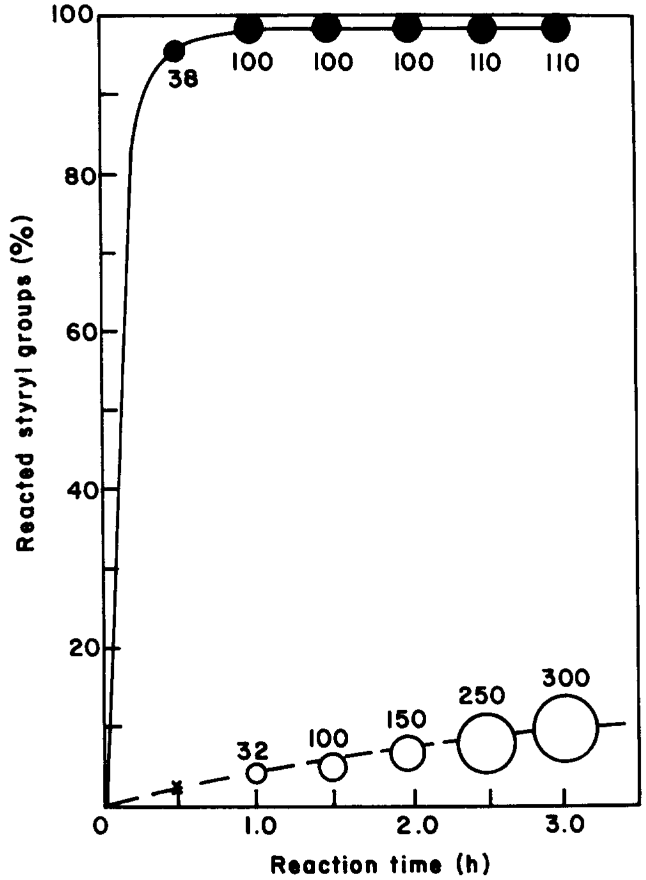

Figure 6 The molar fraction of the reacted styryl groups: (○) crosslinked with V-70; (●) crosslinked with DMA + BPO. The size of the circle and the number near the circle correspond to the diameter (nm) of the microgel determined with the TEM

100 nm for 1 h. The D_{tem} and D_{dls} did not change after that, and therefore inter-micelle crosslinking was hindered after 1 h.

From the results of *Figures 4* and *5*, it seemed that rapid crosslinking was effective for the crosslinking of the polymer micelle and the prevention of inter-micelle crosslinking.

In order to investigate the crosslinking state of the PMMA core of the microgel, the remaining styryl groups in the microgel were measured with the g.p.c. equipped with both r.i. and u.v. (292 nm) detectors. *Figure 6* shows the molar fraction of the reacted styryl groups of the microgels crosslinked with V-70 and BPO + DMA. The size of the circle corresponds to the D_{tem} of the microgels. The D_{tem} values are also shown near the circles in *Figure 6*.

The crosslinking in this study was the radical reaction of the styryl groups in the PMMA matrix. The rate constant of the initiation of V-70, k_i, the propagation rate constant of the styryl group, k_p, and the termination rate constant of the styryl radical, k_{tr}, used for the calculation are $k_i = 8.56 \times 10^{-5}\ \mathrm{s}^{-1}$ (ref. 16), $k_p = 89.8\ \mathrm{l\ mol}^{-1}\ \mathrm{s}^{-1}$ (ref. 14) and $k_{tr} = 44.2 \times 10^6\ \mathrm{l\ mol}^{-1}\ \mathrm{s}^{-1}$ (ref. 17), respectively. From these values, it is thought that crosslinking can occur effectively with coupling of the styryl radicals. Thus, the crosslink density can be calculated from the reacted styryl groups. When the amount of reacted styryl groups is k%, the crosslink density is slightly lower than $k \times 0.1$ mol%, because the molar fraction of the styryl groups per PMMA chain was 10 mol%.

For the V-70 series, 4% styryl groups had reacted after 1 h, and the crosslink density was less than 0.4%. In general, when the crosslink density is less than 1%, the polymer micelle can break up. For this system, it took more than 3.5 h for the crosslink density to reach 1%. It showed that the block copolymer micelle could break up and aggregate again until 3.5 h. It was impossible to hinder inter-micelle crosslinking in such a system. In fact, the increase of D_{tem} continued, and inter-micelle crosslinking could not be hindered.

For the DMA + BPO series, 96% styryl groups had reacted after 0.5 h, and the crosslink density reached more than 9%. This indicated that crosslinking had finished before the dissociation time (46.3 min) of the block copolymer chain from the polymer micelle. After 1 h, no styryl groups remained for crosslinking, so that the diameter of the microgel was not changed.

Consequently, it was concluded that hindrance of inter-micelle crosslinking succeeded with increase of the reaction rate, and monodisperse microspheres were synthesized.

CONCLUSIONS

For the crosslinking of the core part of the polymer micelle, it was suggested that inter-micelle crosslinking would be hindered by increasing the crosslinking rate, when the lifetime of the polymer micelle was constant.

Based on this suggestion, the poly(methyl methacrylate) parts of the poly(α-methylstyrene-*b*-methyl methacrylate) micelles in the 30/70 benzene/cyclohexane mixture were crosslinked with V-70 and DMA + BPO initiators with different crosslinking rate constants.

Before crosslinking, the characteristics of the polymer micelles were investigated as follows: diameter of the polymer micelles was 64 nm, aggregation rate constant $k_+ = 4.57 \times 10^{-3}\,\mathrm{l\,mol^{-1}\,s^{-1}}$, dissociation rate constant $k_- = 3.6 \times 10^{-4}\,\mathrm{s^{-1}}$, critical micelle concentration $CMC = 0.88$ wt%, and dissociation time of the block copolymer chain from the polymer micelle was 46.3 min.

After crosslinking, the diameters of the crosslinked products (the microgels) were measured in solution and in the solid state. The molar fraction of the reacted styryl groups was also measured with the g.p.c. equipped with both r.i. and u.v. (292 nm) detectors, and the crosslink density for each reaction time was calculated.

For the V-70 series, it took a long time to reach high crosslink density. The crosslink density of the microgel was too small to prevent the break-up of the block copolymer micelle. In fact, inter-micelle crosslinking occurred.

For the DMA + BPO series, before dissociation of the block copolymer chain from the polymer micelle (46.3 min), 96% of the styryl groups had reacted, and no styryl groups remained for inter-micelle crosslinking. Thus inter-micelle crosslinking was prevented totally.

Consequently, it was possible to synthesize microspheres with a narrow size dispersion by protection of inter-micelle crosslinking on increasing the reaction rate, even though the lifetime of the polymer micelles was constant.

REFERENCES

1 Saito, R., Ishizu, K. and Fukutomi, J. *J. Polym. Sci. (A) Polym. Chem. Edn.* 1990, **28**, 1793

2 Saito, R., Ishizu, K. and Fukutomi, T. *Polymer* 1990, **31**, 679

3 Saito, R., Ishizu, K. and Fukutomi, T. *Polymer* 1991, **32**, 531

4 Saito, R., Ishizu, K. and Fukutomi, T. *Polymer* 1991, **32**, 2258

5 Saito, R., Ishizu, K. and Fukutomi, T. *J. Appl. Polym. Sci.* 1991, **43**, 1103

6 Fukutomi, T. and Ishizu, K. *J. Polym. Sci. (C) Polym. Lett. Edn.* 1987, **25**, 175

7 Fendler, J. H. and Fendler, E. J. 'Catalysis in Micellar and Macromolecular Systems', Academic Press, New York, 1975

8 Muller, N. *J. Phys. Chem.* 1972, **76**, 3017

9 Muller, N. in 'Solution Chemistry of Surfactants' (Ed. K. L. Mittal), Plenum Press, New York, 1979

10 Sams, P. J., Wyn-Jones, E. and Rassing, J. *Chem. Phys. Lett.* 1972, **13**, 233

11 Sams, P. J., Wyn-Jones, E. and Rassing, J. *J. Chem. Soc., Faraday Trans. (II)* 1973, **69**, 180

12 Rassing, J. and Wyn-Jones, E. *Chem. Phys. Lett.* 1973, **21**, 93

13 Aniansson, E. A. G. and Wall, S. N. *J. Phys. Chem.* 1974, **78**, 1024

14 Mysels, K. J. 'Introduction to Colloid Chemistry', Wiley, New York, 1959

15 Shinoda, K., Nakagawa, T., Tamamushi, B. and Isemura, T. 'Colloidal Surfactants: Some Physio-chemical Properties', Academic Press, New York, 1963

16 Overberger, C. G., O'Shaughnessy, M. T. and Shalit, H. *J. Am. Chem. Soc.* 1949, **71**, 2661

17 Mahabadi, H. K. and O'Driscoll, K. F. *J. Macromol. Sci. (A)* 1977, **11**, 967