

Crosslinking of the inner poly(methyl methacrylate) core of poly(α -methylstyrene-*b*-methyl methacrylate) micelles in selective solvent: 2. Effect of polymer concentration

R. Saito, K. Ishizu and T. Fukutomi

Tokyo Institute of Technology, Department of Polymer Science, 2-12 Ookayama, Meguro-ku, Tokyo 152, Japan

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Core–corona type microgels composed of poly(methyl methacrylate) core and poly(α -methylstyrene) corona were synthesized from poly(α -methylstyrene-*b*-methyl methacrylate) in benzene/cyclohexane mixtures with varying polymer concentration. It was possible to synthesize soluble core–corona type microgels from the block copolymer with a small degree of polymerization (*DP*) in concentrated solution, when the micelle system turned from ‘open associated’ (stepwise associated) to ‘closed associated’ (mass action type) with increase of the polymer concentration. In the ‘open associated’ systems, the increase of the polymer concentration was the cause of inter-micelle crosslinking due to macrogelation and anomalization of the shape of the products.

(Keywords: core–corona type microgel; polymer concentration; open association; closed association; polymer micelle)

INTRODUCTION

In the previous paper¹, crosslinking of poly(α -methylstyrene-*b*-methyl methacrylate) (P(MeSt-*b*-MMA)) micelles in solvents was carried out, and the effects of solvent composition and polymer composition on the diameter of the crosslinked products (microgels) were investigated. Soluble spherical core–corona type microgels could be synthesized from P(MeSt-*b*-MMA) with high degree of polymerization (*DP*) in a narrow region of solvent composition. However, it was impossible to synthesize soluble products from P(MeSt-*b*-MMA) with low *DP*.

These results were explained by assuming that the polymer micelles from block copolymer with low *DP* broke up and re-formed during the crosslinking reaction of the core; therefore, macrogelation of the system occurred.

For synthesis of soluble microgels, the polymer micelles must be stabilized during the crosslinking reaction. The increase of the polymer concentration and the decrease of the reaction temperature can be proposed to increase the stabilizing time of the polymer micelles.

In this study, polymer concentration was chosen as the factor to stabilize the micelles, because the mean value of the size of the micelle does not change drastically on increasing the polymer concentration between the critical micelle concentration and the second critical micelle concentration^{2,3}.

Five block copolymers (assigned Nos. 2, 4, 6, 7 and 11 in the previous paper¹) with various *DP* and two solvents 4/6 and 2/8 (benzene/cyclohexane, v/v) were chosen. The diameters and external forms of the crosslinked products were investigated with transmission and scanning electron microscopes (TEM and SEM), and the stabilities of the polymer micelles were also investigated by the concentration jump method.

EXPERIMENTAL

Crosslinking of the block copolymers

The modified block copolymers were dissolved in benzene (good solvent for poly(methyl methacrylate) (PMMA) and poly(α -methylstyrene) (PMeSt)). Then, cyclohexane (non-solvent for PMMA) was added to these benzene solutions. The polymer concentrations and compositions of the solvents are shown in Table 2. The crosslinking reaction was carried out with azo-initiator (2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile)) (V-70, Wako Pure Chemical Industries Ltd) at 40°C. The methods for the termination of the crosslinking reaction and the purification of these products were the same as in the previous paper¹. The preparation of the samples for the transmission electron microscope (TEM) and the scanning electron microscope (SEM) was carried out as in the previous paper¹. The particles were shadowed with platinum at an angle of 60°.

Annealing of the crosslinked products

First, 0.05 g of the crosslinked product of block copolymer No. 7 (crosslinked at 4 wt% in solvent 4/6) was dissolved in 5 ml *o*-xylene. The solution was refluxed at 120°C for 4 h. After cooling, the solution was sprayed on the glass to observe the shape of the product with the SEM.

Measurement of the viscosity after rapid dilution of the solution

The concentration jump method and the viscosity measurement were combined to evaluate the stability of the micelle solution. Briefly, the solution was diluted rapidly to one-tenth concentration, and then the viscosity of the solution at 40°C was measured with an Ubbelohde

viscometer. The raw block copolymers were dissolved in solvent 2/8 (benzene/cyclohexane, 2/8 (v/v)) and solvent 4/6 (benzene/cyclohexane, 4/6 (v/v)). The polymer concentration for this measurement was set 10 times higher than the polymer concentration for the crosslinking.

Determination of the critical micelle concentration of block copolymers by viscosity measurements

The raw block copolymer solutions were dissolved in the solvents to give a 10 wt% polymer concentration. These solutions were gradually diluted with solvent till the polymer concentration of the solution became 0.01 wt%, and the viscosity of the solution was measured at each step with the Ubbelohde viscometer at 40°C.

RESULTS AND DISCUSSION

Crosslinking of the block copolymers

The crosslinking reaction must be carried out between the critical micelle concentration (c.m.c.) and second critical micelle concentration (c.m.c.*), because the size of the polymer micelles should be constant on changing the polymer concentration. So, the c.m.c. and c.m.c.* of the block copolymers in solvents 4/6 and 2/8 were determined by viscometric measurements of the block copolymer solutions and are shown in Table 1. The range of polymer concentration was determined from 1 to 8 wt%. Then, all crosslinking reactions of this study were carried out between the c.m.c. and c.m.c.*. The reaction conditions of the crosslinking and the solubility of the crosslinked products are shown in Table 2.

Crosslinking in solvent 4/6

Soluble crosslinked products could not be obtained from poly(α -methylstyrene-*b*-methyl methacrylate) (P(MeSt-*b*-MMA)) copolymer No. 2 ($M_n = 2.2 \times 10^4$, MeSt = 49 mol%) with low degree of polymerization (*DP*) by crosslinking in any solvents (benzene fraction, 10–50 vol%; crosslinking conditions, polymer concentration 1 wt% at 40°C)¹. In solvent 4/6, all crosslinked products of block copolymer No. 2 became insoluble at any polymer concentration (from 1 to 8 wt%). There was no effect of increasing the polymer concentration on the synthesis of soluble crosslinked products from the block copolymer with low *DP* in solvent 4/6.

Contrary to this result, from block copolymers No. 6 ($M_n = 6.3 \times 10^4$, MeSt = 68 mol%), No. 7 ($M_n = 8.2 \times 10^4$, MeSt = 49 mol%) and No. 11 ($M_n = 2.8 \times 10^4$, MeSt = 55 mol%) with high *DP*, soluble crosslinked products were obtained in a wide region of polymer concentrations in solvent 4/6.

The shapes and sizes of the soluble products were

Table 1 The critical concentration of block copolymers in selective solvents (estimated by viscometric measurement at 40°C)

Polymer	Solvent ^a	Polymer concentration (wt%)	
		Critical	Second critical
No. 2	4/6	1.0	–
No. 4	4/6	0.8	6.0
No. 7	2/8	0.6	4.5
No. 7	4/6	0.8	–

^aSolvent 4/6: benzene/cyclohexane (4 vol/6 vol)

Table 2 The conditions and results of crosslinking of block copolymer micelles in selective solvents (initiator, V-70; temperature, 40°C)

Block copolymer	Polym. concn. (wt%)	Diameter of products (nm) ^a	
		Solvent 4/6 ^b	Solvent 2/8
No. 2 ($M_n = 2.2 \times 10^4$, MeSt = 49 mol%)	1.0	× ^c	×
	2.0	×	21–70
	4.1	×	21–42
	8.2	×	106–280
No. 4 ($M_n = 3.2 \times 10^4$, MeSt = 48 mol%)	1.1	×	×
	2.4	28–84	28–37
	4.2	70–590 ^{*d}	36–250
	8.0	×	×
No. 6 ($M_n = 6.3 \times 10^4$, MeSt = 68 mol%)	1.0	100–150	370
	2.0	30–2000*	30–60
	4.2	30–2000*	50–155
	8.0	×	×
No. 7 ($M_n = 8.2 \times 10^4$, MeSt = 49 mol%)	1.0	40	700
	2.0	28–98	25–65
	4.0	42–630*	200–300
	8.0	35–424*	×
No. 11 ($M_n = 2.8 \times 10^5$, MeSt = 55 mol%)	2.0	70–500*	–
	3.8	35–500*	–
	6.0	120–530*	–

^aEstimated with TEM observation under the dry state

^bSolvent 4/6 = benzene/cyclohexane (4 vol/6 vol)

^c× = insoluble product

^d* = 'void' particle

investigated with the TEM and SEM. As all samples for TEM observation were prepared with dilute polymer solution and PMeSt parts were stained with RuO₄, the products were separated from each other and the dark parts of the micrographs were PMeSt^{4,5}.

Figure 1 shows the TEM and SEM micrographs of these soluble products. The polymer concentration of block copolymer No. 6 increased from 1% (a) to 4% (d). The most distinct feature of these micrographs was for that crosslinked in a low concentration system. The products had very narrow size distribution (average diameter was 180 nm) at low concentration. The platinum shadowing showed that these particles were hard and the highest value was 185 nm. Consequently, these particles were not flattened on the carbon substrate (Figure 1b). However, as the concentration increased, the size distribution became wide (40 to 2000 nm) and the shape of the large particles became anomalous (so-called 'void structure')^{6–9}. A similar tendency of change of the size and shape of the products was observed for the block copolymer No. 7 series. The narrow size distribution (diameter was 40 nm) of the products at 1% (e) became wider and 'void particles' were observed (f) on increase of the polymer concentration.

In conclusion, in solvent 4/6, it was impossible to synthesize soluble products from the block copolymer with low *DP* by increasing the polymer concentration. Not only spherical products with polydispersion but also 'void' particles were obtained from the block copolymer with high *DP* at high polymer concentration in solvent 4/6.

Annealing of the 'void' particles

To investigate whether the structure of these 'void' particles was temporary or not, annealing of these products was carried out at 120°C for 4 h. The external

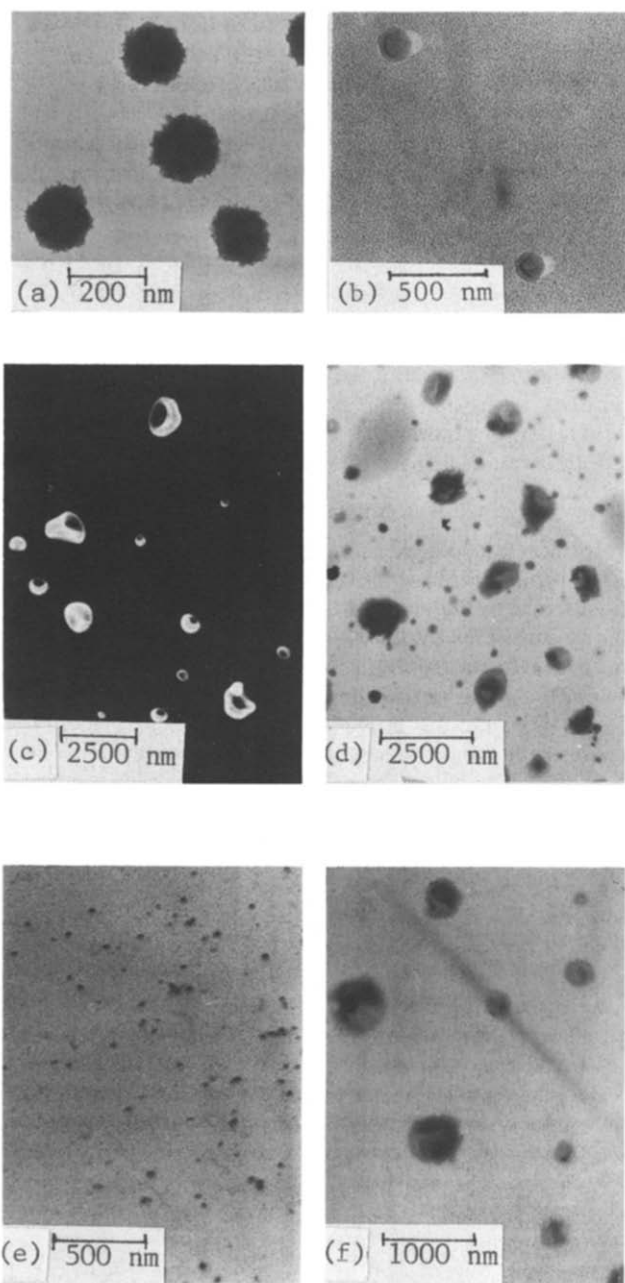


Figure 1 Electron micrographs of the products of block copolymers No. 6 and No. 7 crosslinked in solvent 4/6 at 40°C: (a) No. 6 at 1 wt% with TEM; (b) No. 6 at 1 wt% shadowed with platinum at an angle of 60° with TEM; (c) No. 6 at 2 wt% with SEM; (d) No. 6 at 4 wt% with TEM; (e) No. 7 at 1 wt% with TEM; (f) No. 7 at 4 wt% with TEM. The products for TEM observation were stained with RuO₄.

forms of these products before and after annealing are shown in *Figures 2a* and *2b*. From *Figure 2*, the products did not change their shapes on annealing. The 'void particles' synthesized from the seed polymerization changed their shape to spheres on annealing. The most obvious difference between our particles and those of others was that the block copolymer was used as the material in this study. In the 'void particles' synthesized by seed polymerization, the core could move in the corona part on annealing. But the corona chain (PMeSt) of this study was joined to the crosslinked core. This particle was surrounded by a PMeSt corona with constant thickness. Thus, if the shape of the core did not change on annealing, the external form of the product did not change. The core part of this particle was

crosslinked, and thus the core did not change its shape on annealing. This means that the shape of the core part of the 'void particles' of this study was very anomalous, and the structure of these 'void' particles was stable to change of temperature and solvent.

Crosslinking in solvent 2/8

From the results of the crosslinking, it was possible to synthesize soluble crosslinked products with block copolymer No. 2 by increasing the polymer concentration in solvent 2/8 at 40°C (*Table 2*).

The morphology of the crosslinked products of block copolymer with small *DP* (No. 2) in solvent 2/8 was investigated with TEM, and is shown in *Figure 3*. The diameter of the products showed a minimum (20 nm) from the middle concentrated solution, 4% (b). Then, the diameter of the products at 8 wt% increased and their shapes were no longer spherical (c).

The morphology of the crosslinked products of block copolymer with high *DP* (Nos. 6 and 7) in solvent 2/8 is shown in *Figure 4*. As reported in the previous paper, the diameter of the products crosslinked at 1 wt% was 700 nm. The polymer concentration of block copolymer No. 7 increased from 2% (a) to 4% (b). The shape (spherical) and size of the products did not change on increasing the polymer concentration, and the diameters of the products at 2 and 4 wt% were from 200 to 300 nm.

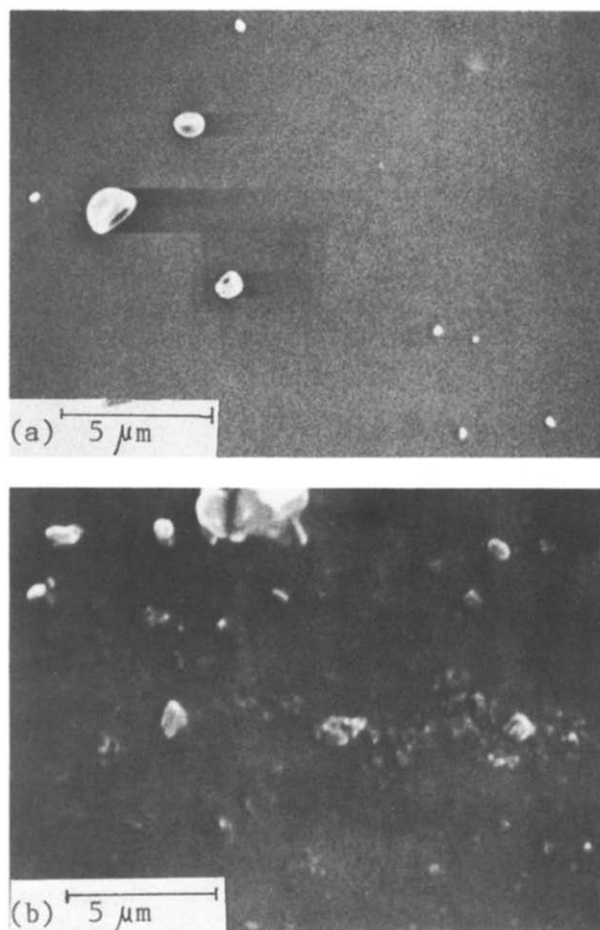


Figure 2 Scanning electron micrographs of the crosslinked products of No. 7 before and after annealing: (a) before; (b) after. Crosslinking conditions: at 4 wt% in solvent 4/6 at 40°C. Annealing conditions: at 120°C for 4 h in *o*-xylene

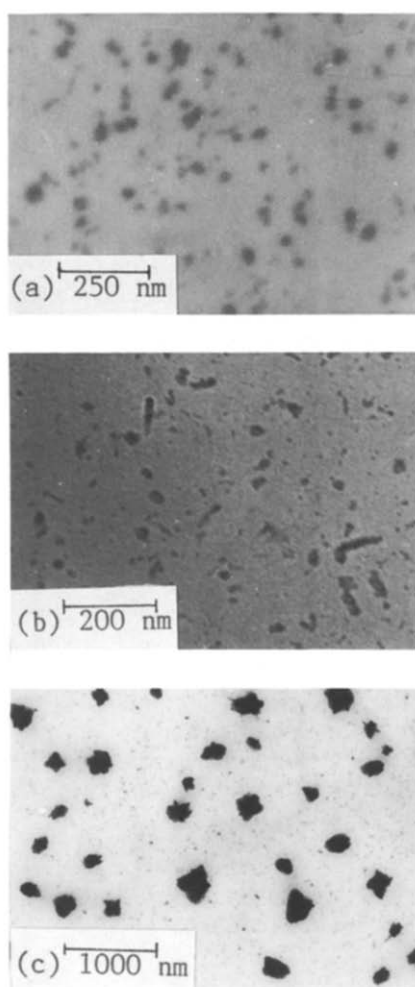


Figure 3 Transmission electron micrographs of the products of block copolymer No. 2 crosslinked in solvent 2/8 at 40°C: (a) at 2 wt%; (b) at 4 wt%; (c) at 8 wt%. The products were stained with RuO₄

Large products were synthesized at low polymer concentration; then the diameter of the products decreased slightly and became constant with increase of the polymer concentration in solvent 2/8. For block copolymer No. 6 with high *DP* and high MeSt content, the shapes of the products became anomalous (from (c) to (d)) with increase of the polymer concentration in solvent 2/8. However, in contrast with the anomalous products obtained in solvent 4/6, these anomalous particles were not 'void' particles.

In conclusion, the sizes of the products decreased or were constant and the size distribution was not changed with increase of the polymer concentration in solvent 2/8.

Stability of the polymer micelle

In many thermodynamic treatments of self-association, the diameter of the micelle is assumed to be constant between the c.m.c. and c.m.c.*^{2,3}. As described above, all products were crosslinked between the c.m.c. and c.m.c.*. However, the crosslinked products changed their shapes and sizes with increase of the polymer concentration. In fact, the distribution of micelle size increases with polymer concentration. However, the widest size distribution of the products was from 40 to 2000 nm. It is very hard to accept that the polymer micelle had such a wide distribution. Therefore, the possibility of inter-micelle crosslinking was assumed as the reason for the synthesis

of 'void particles'. So the stability of the polymer micelle in solution was investigated by the concentration jump method. The viscosity of the block copolymer solution was measured after rapid dilution. The most specific results of the viscometric measurements are shown in Figure 5. The stabilizing time *T* (time necessary to reach a new constant value after the dilution) is shown in Table 3.

In general, two kinetic systems have been used for the treatment of self-aggregation (micelle formation)¹⁰⁻¹². One system is 'open associated' and the other is 'closed associated'. In the 'open associated' system, the polymer chain (*A*) constructing the micelle (*A_i*) with aggregation number *i* dissolves to monomers stepwise and they subsequently reassociate; then the system reaches a new equilibrium state after dilution as follows:



It takes a long time to reach the new equilibrium state after rapid dilution. Thus the polymer chains tend to exist freely in the external area of the polymer micelle in the system. This causes the polydispersion of the polymer micelles. If crosslinking of the polymer micelle is carried out in such a system, inter-micelle crosslinking will easily occur, because the migration of a polymer chain from one micelle to another will occur frequently.

In the 'closed associated' system, the kinetic equilibria between the polymer chain *A* and the polymer micelle

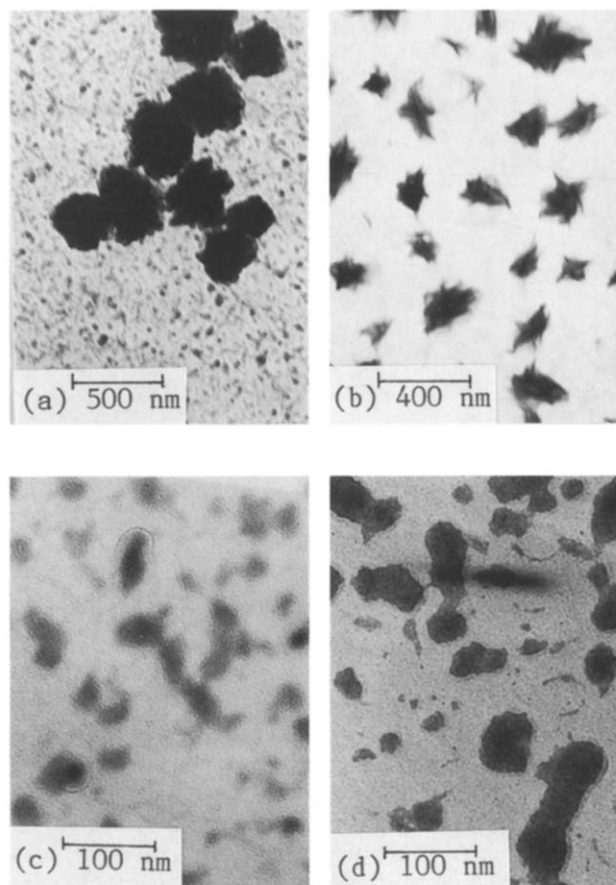


Figure 4 Transmission electron micrographs of the products of block copolymers No. 6 and No. 7 crosslinked in solvent 2/8 at 40°C: (a) No. 7 at 2 wt%; (b) No. 7 at 4 wt%; (c) No. 6 at 2 wt%; (d) No. 6 at 4 wt%. The products were stained with RuO₄

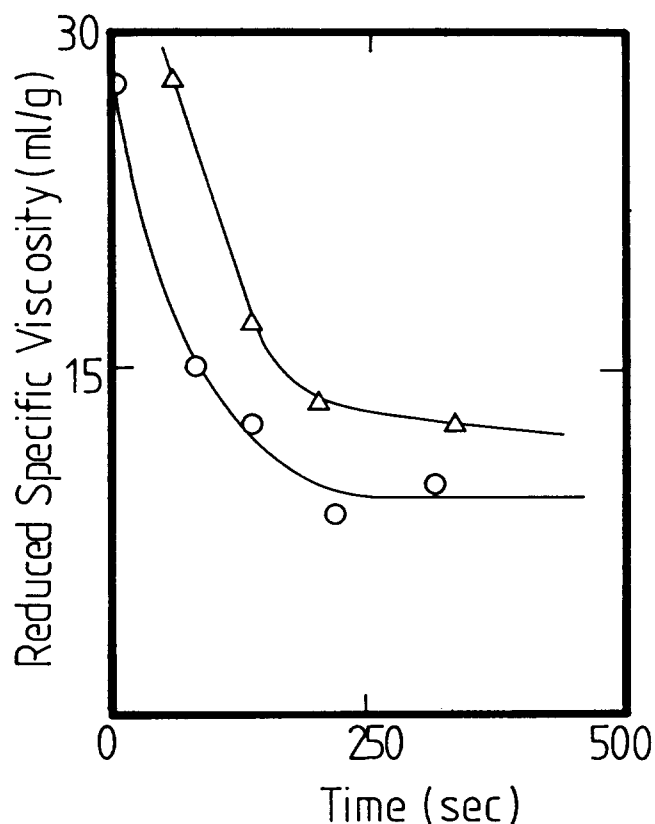


Figure 5 The viscosity change after rapid dilution by the concentration jump method: (O) block copolymer No. 2 at 4 wt% in solvent 2/8; (Δ) block copolymer No. 2 at 1 wt% in solvent 4/6

Table 3 The stabilizing time T of the solution viscosity after rapid dilution of micelle solution (measured at 40°C)

Polymer	Polym. concn (wt%)	Stabilizing time, T (s)	
		Solvent 2/8	Solvent 4/6
No. 2	1.0	295	397
	2.0	286	433
	4.0	205	574
	8.0	181	485
No. 6	1.0	—	41
	2.0	—	150
	4.0	—	169
	8.0	—	94
No. 11	1.0	78	218
	2.0	42	99
	4.0	55	598

A_n with aggregation number n are expressed as follows:



The polymer micelle system reaches a new equilibrium very fast when the concentration of polymer is changed suddenly (concentration jump) in such a system. Then, the stabilizing times T become very small. It is suggested that it is very difficult for the polymer chains to exist in solution without micelle formation. If crosslinking of the polymer micelle occurs, inter-micelle crosslinking will be hindered in the solutions as the polymer chains do not dissolve into the solution during the crosslinking reaction.

From the viewpoint of these kinetic models of polymer micelle systems, the T values of the block copolymer solutions listed in Table 3 were estimated. The T values of the solutions for the insoluble products were above 290 s. Especially, the T values of block copolymer No. 2 in solvent 4/6 were above 400 s. As described above, it is rational to suppose that the polymer micelle system with large T corresponds to the 'open associated' system and the polymer micelle system with small T to the 'closed associated' system. Crosslinking in the 'open associated' system tends to lead to inter-micelle crosslinking of the micelles. It was concluded that the products crosslinked in the solution whose T was above 290 s became insoluble in this study.

In solvent 2/8, the T values of block copolymers No. 2 and No. 11 decreased with increase of the polymer concentration. The T values of block copolymer No. 2 above 2 wt% were below 290 s. In Figure 5, the viscosity of block copolymer No. 2 in solvent 2/8 at 1 wt% falls rapidly and then decreases gradually. This viscosity behaviour was specific to the 'open associated' system. The viscosity of block copolymer No. 2 at 4 wt% falls drastically at first and then becomes constant suddenly. This behaviour was specific to the 'closed associated' system. These results show that the polymer micelles were stabilized by increasing the polymer concentration in solvent 2/8. Therefore, it became possible to synthesize soluble crosslinked products by increasing the polymer concentration even if the block copolymer with low DP was used.

In solvent 4/6, the products of block copolymers Nos. 6 and 11 crosslinked at any polymer concentration became soluble. In these cases all T values of block copolymers No. 6 and No. 11 solutions were below 290 s. However, in this solvent, the T values increased with polymer concentration. With the increase of T , the polymer micelle system became unstable and inter-micelle crosslinking occurred; that is to say, the micelle system turned from the 'closed associated' formation of the polymer micelle to the 'open associated' formation. This consideration showed good agreement with the synthesis of 'void' particles from No. 6 at high polymer concentration in solvent 4/6. According to Goodall *et al.* in the case of emulsion polymerization of styrene in soap-free systems, once the micelle has become a growing particle, the particles would coagulate together rapidly, when the surface charge density of these particles was low⁶. The same mechanism for formation of 'void' particles was suggested. Inter-micelle crosslinking was activated by the increase of the polymer concentration during crosslinking of the block copolymer micelle, and then the large 'void' products with wide distribution of their size were obtained in solvent 4/6.

CONCLUSIONS

To synthesize perfectly spherical microgels by crosslinking of the core part of the polymer micelle, inter-micelle crosslinking must be hindered by increasing the stability (lifetime) of the polymer micelle. One possible way to stabilize the polymer micelles was to increase the polymer concentration. Based on this supposition, crosslinking of the core part of the polymer micelle at various polymer concentrations was carried out, and the effect of polymer concentration on the synthesis of the microgels was examined.

The poly(α -methylstyrene-*b*-methyl methacrylate) micelle was crosslinked in the benzene/cyclohexane mixture (a selective solvent; good solvent for poly(α -methylstyrene) (PMeSt, corona), non-solvent for poly(methyl methacrylate) (PMMA, core)).

The stabilities of the solution systems were evaluated from the stabilizing time T of the solution viscosity after sudden dilution (T is the time to reach a new equilibrium after the dilution). The solution with large T corresponded to the 'open' associated system and that with small T to the 'closed' associated system.

From the measurements of T values, the polymer solution systems were divided into two types. One was the block copolymer system in which T increased with polymer concentration. Such a system was observed in solvent 4/6 (benzene/cyclohexane (v/v)), and the soluble products could not be synthesized at any polymer concentration from block copolymer with low DP . Moreover, the crosslinked products changed to large anomalous particles (so-called 'void' particles) with wide size distribution when the DP of the block copolymer increased in solvent 4/6.

The other one was the block copolymer system in which T decreased with increase of polymer concentration. Such a system was observed in solvent 2/8. In these

systems, soluble perfectly spherical small microspheres could be obtained by increasing the polymer concentration even in the case of the block copolymer with low DP . The maximum of T for the synthesis of the soluble products was 290 s in this study.

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