Crosslinking of the inner poly(methyl methacrylate) core of poly(α-methylstyrene-b-methyl methacrylate) micelles in selective solvent: 1. Effect of solvent selectivity

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The crosslinking reaction of poly(methyl methacrylate) cores in poly(α-methylstyrene-b-methyl methacrylate) micelles was carried out in mixed solvents of benzene and cyclohexane. In suitable solvent core–corona type particles were obtained for block copolymers with sufficiently high molecular weight and α-methylstyrene content >39%. The particle size became a minimum at a benzene/cyclohexane ratio of 3/7–4/6 (v/v) which depended on the nature of the block copolymers. The particle size increased drastically when the solvent compositions deviated from this region. When the molecular weight of the block copolymer was $<2 \times 10^4$, inter-micelle crosslinking took place under the experimental conditions of this study, even when the α-methylstyrene content was very high.

INTRODUCTION

It is well known that block copolymers form aggregates (or so-called polymer micelles) in a solvent which is good for one component but poor for the other. Many authors have treated this micelle formation theoretically[1-6]. According to these studies, the dimension of the micelle varies with the structure of the polymer, the segment–solvent interaction and the temperature.

We can expect to fix the micelle structure by a crosslinking reaction of the core segments, and to obtain similar microgels by seed polymerization. In the crosslinking reaction of micelles, the phase separation of the two segments is accomplished before the reaction. Therefore, particles with a well defined structure will be obtained easily.

Crosslinking of polymer micelles has been investigated previously by Tuzar and coworkers[7]. They showed the possibility of this reaction but did not mention the reaction conditions suitable for crosslinking of the polymer micelles and the properties of the products.

In a previous paper, we have reported the formation of a core–corona type polymer composed of poly(allyl amine) (core) and poly(vinyl acetate) (corona) by this crosslinking method[8]. It was confirmed by electron micrography that the products had a structure with distinctly separated core (crosslinked poly(allyl amine)) and corona (poly(vinyl acetate)). However, the diameter of the products was far larger (≈ 300–500 nm) than expected. Therefore, the crosslinking process of these particles was investigated in detail by electron micrography, viscosity and dynamic light scattering. From these results, it was concluded that large particles were formed by the aggregation of micelles and, as the reaction

proceeded, inter-micelle crosslinking and phase separation in the particles occurred simultaneously.

In the study described in this paper, we had two aims: first, to determine whether the process is always complicated; second, to find the conditions (polymer composition, length of segment, solvent composition) under which micelle structure is unaffected by the crosslinking reaction. If the conditions can be established, then the particle size and the thickness of the corona can be designed as desired before the crosslinking reaction. For this purpose, we prepared several poly(α-methylstyrene-b-methyl methacrylate)s (poly(MeSt-b-MMA)s) with pendent styryl groups in the PMMA sequence. The PMMA core was crosslinked in a mixed solvent of benzene (a good solvent for both sequences) and cyclohexane (non-solvent for PMMA sequence) by the radical polymerization of these pendent styryl groups.

Core–corona type polymers are regarded as stable micelles. Their fundamental structure does not change under any circumstances and is not fragile like normal micelles.

EXPERIMENTAL

Synthesis of block copolymer

Poly(MeSt-b-MMA)s were prepared by the usual anionic polymerization at $-78°C$ in vacuum[9]. Molecular weight was determined by the universal calibration method of gel permeation chromatography (g.p.c.) (TOSOH, 801A type instrument, column GM-6, solvent THF, 38°C, flow rate 1.0 ml min^{-1}). The MMA content was determined by ^1H nuclear magnetic resonance (n.m.r.) (Hitachi R-24B), from the relative intensity of

Table 1 Characteristics of poly(α-methylstyrene-b-methylmethacrylate) block copolymers and of the modified block copolymers

Specimen code	$10^{-4} \times \overline{M_n}$		PMeSt block[c] (mol%)	Styryl group[d] MMA unit (mol%)
	Block copolymer[a]	PMeSt sequence[b]		
1	2.8	0.7	37	15
2	2.2	1.2	49	8
3	2.1	1.5	69	35
4	3.2	1.7	48	17
5	4.8	3.9	80	11
6	6.3	4.4	68	14
7	8.2	4.4	49	13
8	10.4	4.4	39	13
9	9.3	6.7	68	42[f]
10	23.5	14.0	56	20
11	28.3	16.8	55	8
P1[e]	—	0.7	100	—

[a] Estimated by g.p.c. and viscometry in THF
[b] Estimated from the M_n data of block copolymers and [1]H n.m.r.
[c] Determined by [1]H n.m.r.
[d] Estimated by double-detection g.p.c. (r.i. and u.v.)
[e] The parent PMeSt of block copolymer no. 1, $M_w/M_n = 1.05$
[f] Macrogelation occurred during purification

the benzyl group signal (6.5 ppm) and the carboxyl group signal (3.8 ppm) in deuterated chloroform, or by ultraviolet (u.v.) absorbance at 254 nm using a Hitachi 124-type ultraviolet (u.v.) spectrophotometer[10].

Introduction of styryl groups to MMA sequence

Styryl groups were introduced to the MMA sequence by the following reaction:
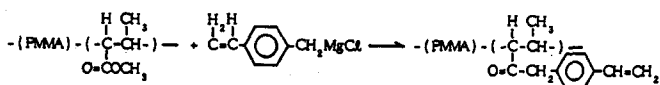
The Grignard reagent was prepared with 0.7 g Mg (Nakarai Chemicals Ltd) and 3 ml *p*-chloromethylstyrene (Seimi Chemical Ltd) in THF. This reagent was poured into the block copolymer solution (3 g/50 ml THF) at 0°C. The modified block copolymer was purified three times by reprecipitation from a benzene solution with methanol. Styryl groups contained in the modified block copolymer were determined by using g.p.c. with refractive index (r.i.) and u.v. absorbance double detectors at 292 nm (TOSOH UV-8 model II spectrophotometer), *p*-methylstyrene being the standard material[11].

Crosslinking reaction

The modified block copolymer was dissolved in the benzene/cyclohexane mixture (1/9, 2/8, 3/7, 4/6 and 5/5 v/v). The polymer concentration was kept at 1% w/v. The crosslinking reaction was initiated with 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) (Wako Pure Chemical Industries Ltd) and continued for 4 h at 40°C. The reaction was terminated by the addition of an iodine/THF solution. After crosslinking, the product was precipitated in hexane, washed with methanol and dried under vacuum.

Electron microscope observation

The crosslinking products were dissolved in THF to a polymer concentration of 0.5 wt%. For observation by transmission electron microscopy (TEM, JEOL JEM-

100CX), a polymer solution was dropped onto a copper grid covered with carbon, and a specimen was dried at room temperature. To stain the MeSt sequence, ruthenium tetroxide was used[12,13]. The double bonds remaining in the MMA sequence were stained selectively with iodine/THF solution before casting.

For observation with a scanning electron microscope (SEM, Hitachi S-510), a polymer solution was sprayed onto a cover glass, and Pt was spattered (Hitachi E-102) onto it.

RESULTS AND DISCUSSION

Synthesis and modification of block copolymers

The characters of the original and the modified block copolymers are summarized in *Table 1*. In *Figure 1*, the g.p.c.s of block copolymer no. 1 before and after Grignard reaction and of the parent homo-PMeSt are shown. The homo-PMeSt has a very narrow molecular weight distribution, and the half-width of other peaks is very close to that of homo-PMeSt. The peak at 292 nm results from the styryl groups in the modified block copolymer. Similar results are obtained from other block copolymers. This g.p.c. shows that the molecular weight and the molecular weight distribution of the block copolymer do not change during the Grignard reaction.

Crosslinking reaction

As shown in *Table 2*, macrogelation is suppressed except under the following three circumstances: when the molecular weight of the block copolymers is low (no. 1 $M_n = 2.8 \times 10^4$, MeSt 37 mol%; no. 2 $M_n = 2.2 \times 10^4$, MeSt 49 mol%; no. 3 $M_n = 2.1 \times 10^4$, MeSt 69 mol%); in a moderately good solvent for both sequences; and in the poorest solvent for the PMMA sequence.

The theory predicts[3] that the size of the polymer micelle increases with increasing degree of polymerization (DP), because the solvent becomes poorer for the core sequence. The first and second cases described above are contrary
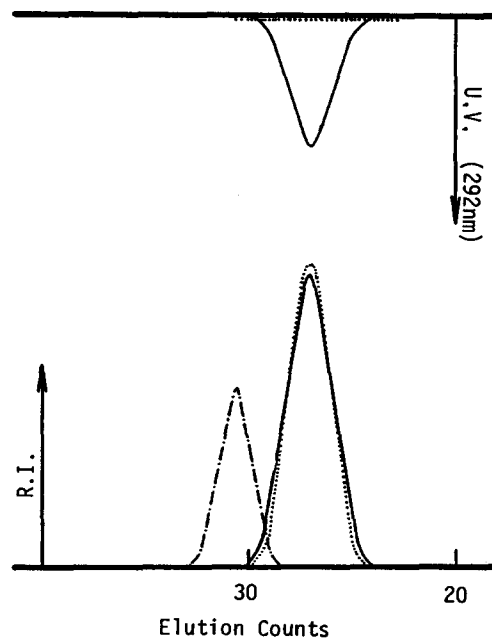

Figure 1 G.p.c. profiles of block copolymer no. 1 before (———) and after (······) Grignard reaction and of the parent PMeSt of the block copolymer (—·—·—). U.v. intensities were determined at 292 nm

Table 2 Results of the crosslinking reaction

Specimen code	Solvent composition (benzene/cyclohexane)[a]				
	1/9	2/8	3/7	4/6	5/5
1	×	×	×	×	×
2	×	×	×	△	×
3	×	×	×	△	△
4	△	△	○	○	△
5	○	△	○	○	○
6[b]	× (7.1)	× (8.0)	△ (9.9)	○ (18.3)	△ (12.4)
7[b]	△ (5.8)	△ (4.2)	○ (6.7)	○ (4.7)	△ (7.0)
8[b]	× (5.3)	△ (5.6)	○ (6.6)	△ (5.4)	× (5.9)
9	△	○	○	○	○
10	○	△	○	○	○
11	○	○	○	○	○

[a] ×, insoluble; △, a little cloudy; ○, soluble

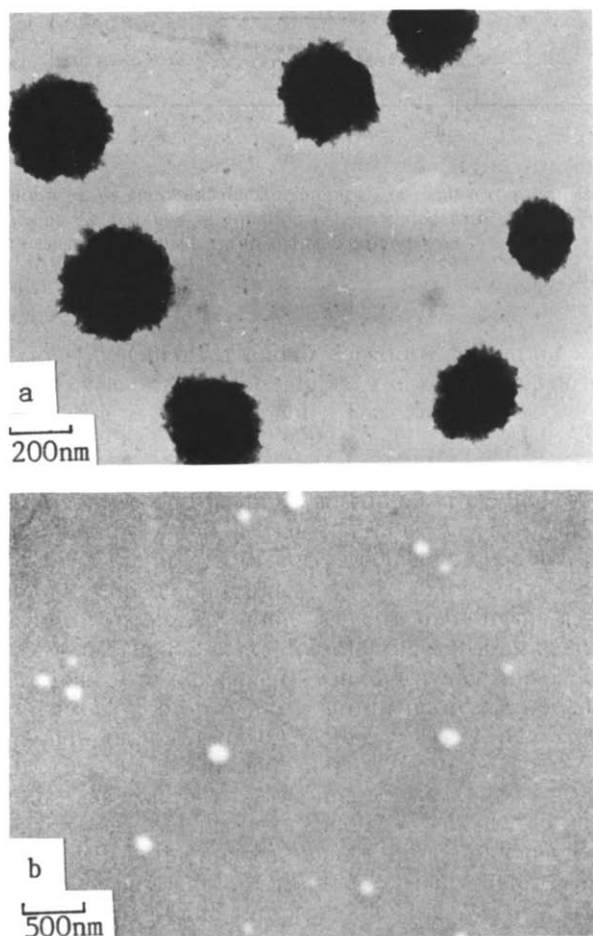[b] (η_{inh}) at 40°C, polymer concentration 1 g/100 ml

Figure 2 Electron micrographs of block copolymers nos 6 and 8. (a) Transmission electron micrograph of block copolymer no. 6 crosslinked in mixed solvent 3/7. The outer PMeSt corona is stained with RuO_4. (b) Scanning electron micrograph of block copolymer no. 8 crosslinked in solvent 2/8

to the prediction. Only the third case seems to agree with the theory. But even in this case, the diameter is much larger than the commonly expected value. Another interesting fact is that the solution in the 5/5 composition solvent of the crosslinked copolymer becomes very cloudy compared with the solutions in the 4/6 and 3/7 solvents. To elucidate these results, several properties of the crosslinked products were investigated.

First, the external forms of the crosslinked products were investigated by two types of electron microscopy.

Figure 2 shows the TEM of copolymer no. 6 crosslinked in solvent 3/7, and the SEM of copolymer no. 8 crosslinked in solvent 2/8. Casting from a very dilute solution enabled the observation of individual particles. The TEM (*Figure 2a*, the dark part corresponds to selectively stained PMeSt) and SEM (*Figure 2b*) images are both spherical. From these results, we conclude that the external forms of the crosslinked products are spherical with diameters of 180 (no. 6) and 100 nm (no. 8), respectively, and that the size distribution of these products is narrow. However, it is impossible to determine the inside forms of these products whether the sequences of PMMA and PMeSt are mixed homogeneously or are separated in these spheres.

Second, the inside forms of the crosslinked products were investigated by TEM with two different methods of polymer staining. *Figure 3* shows the TEM micrographs of block copolymer no. 8 crosslinked in solvent 3/7 and stained by two different methods. The dark round parts in *Figure 3a* correspond to the PMeSt domains, which were selectively stained with RuO_4 (average diameter $D \approx 40$ nm). The dark part in *Figure 3b* represents the PMMA domains (unreacted double bonds during the crosslinked reaction are stained with I_2). The average diameter of these spheres is 35 nm. Note that the molar ratio of PMMA/PMeSt is $\approx 6/4$. Then, provided that the PMMA core is surrounded by a PMeSt corona, the ratio of the diameters is calculated as $1.16/1.0$. This value is very close to the value observed by TEM. As a result, we conclude that the crosslinked products have spherical external forms and consist of a PMeSt core and a PMMA corona.

The diameters (*D*) of crosslinked polymers nos 6, 7 and 8 are summarized in *Figure 4*. The smallest diameters are obtained in solvent 4/6 or 3/7. *D* increased drastically when the solvent composition was outside this narrow region. For example, for copolymer no. 7, the diameter of the smallest particle is 40 nm (in solvent 4/6), but *D* increased to 125 nm (in 3/7) and then to 700 nm (in 2/8), and to 120 nm at the other extreme of solvent composition (5/5). Moreover, the distribution of *D* was wide in solvent 5/5. As mentioned above, there is a tendency to form macrogel at both extremes of solvent composition (*Table 2*, 5/5 and 1/9). This result corresponds well to the variation of *D* as a function of solvent composition shown in *Figure 4*.
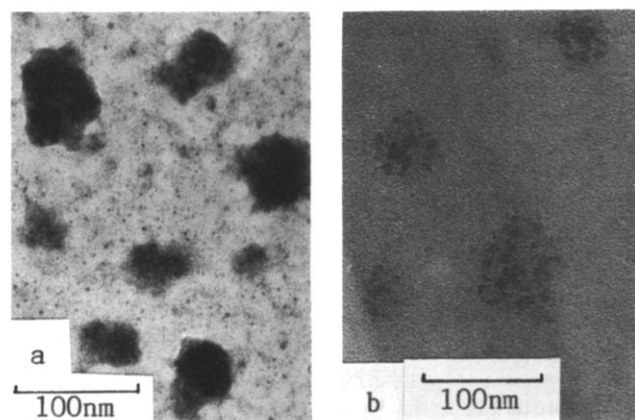

Figure 3 Electron micrograph of block copolymer no. 8 crosslinked in mixed solvent 3/7; dark parts correspond to: (a) outer corona stained with RuO_4; (b) inner core stained with I_2
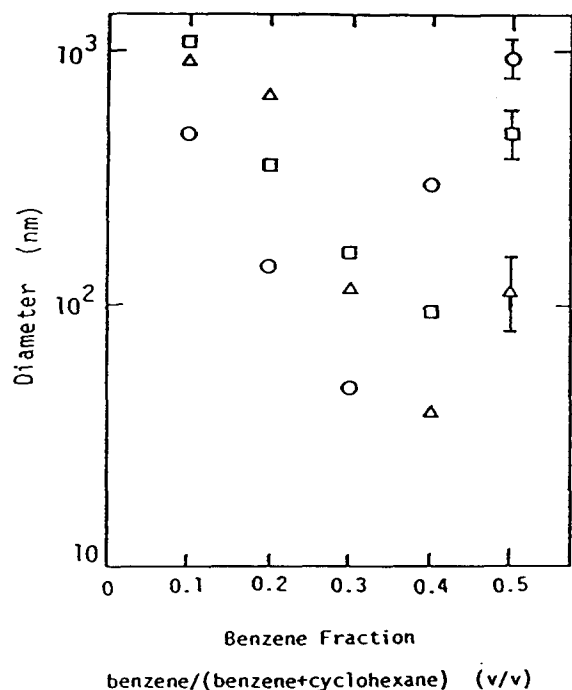
Figure 4 Diameter of core–corona type microgels determined by TEM: □, copolymer no. 6; △, copolymer no. 7; ○, copolymer no. 8

The inherent viscosities η_{inh} of the polymers before the crosslinking reaction are also shown in *Table 2* (in parentheses). The values vary in the usual manner. The η_{inh} first rise and then fall as the cyclohexane content increases (with the exception of copolymer no. 7). According to Mandema *et al.*[14], η_{inh} is approximately proportional to the hydrodynamic volume of the polymer or its aggregate. The copolymer starts to aggregate at solvent composition 5/5 and forms a micelle with the bluish tint characteristic of micelle formation with an increase in η_{inh}. The diameter of the products after the crosslinking reaction varied inversely with η_{inh} in this region of solvent composition. For solvent composition 5/5, the polymers are considered to be loosely fixed in the micelle. In other words, the micelle is similar to the so-called 'open associate' system. The polymer molecules can move in the micelles easily. Occasionally, inter-micelle crosslinking, which results in a wide distribution of *D* and in the macrogelation of the system, occurs during the crosslinking reaction.

The above supposition is supported by the results obtained from the crosslinking of small polymer molecules. As Noolandi predicted[3], the dimension of the micelles increased with the molecular weight of the pre-polymer. But macrogelation (or increase of the particle size and extension of its distribution) was observed for small polymer molecules $(M_n < 2.8 \times 10^4)$. The small polymer molecules will escape easily from a micelle and recombine with another micelle because of their mobility.

In the solvent which is least compatible with PMMA, the diameters of the crosslinked products increase, while η_{inh} becomes small. It is very difficult to explain this result in terms of the mobility of the chain. Possible explanations are as follows. First, PMeSt chains shrink in solvent 1/9 ($[\eta] = 1.85 \times 10^{-2} M^{0.675}$ ml g^{-1} in solvent 3/7, $[\eta] = 3.71 \times 10^{-1} M^{0.545}$ ml g^{-1} in solvent 1/9 at 40°C) and inter-micelle contact will then occur

frequently. Second, the solubility of the polymer is very sensitive to the DP in this region of solvent composition. It is supposed that the polymer micelles are in the non-equilibrium state during the crosslinking reaction, as the DP and structure of the polymer chain are changing. So the dramatic difference between the particle diameters before and after crosslinking appears.

In general, block copolymers with a long insoluble sequence form a stable micelle in a solvent with moderate miscibility with the core component. As can be seen in *Figure 4*, of the block copolymers nos 6, 7 and 8, which have the same DP of the PMeSt sequence, block copolymer no. 8 with the longest PMMA sequence formed the smallest particles in solvent 4/6. This result suggests that the core is somewhat swollen and has a soft structure. For copolymer no. 8, the corona thickness relative to the core size is smallest. This corona may be too soft and too thin to prevent inter-micelle crosslinking in solvent 4/6. A poorer solvent (3/7) would then be required for block copolymer no. 8.

CONCLUSION

The crosslinking reaction of PMMA cores of poly(MeSt-b-MMA) block copolymer micelles was carried out in mixed solvents of benzene and cyclohexane. When the molecular weight of PMeSt was $< 1.2 \times 10^4$, it was impossible to hinder the inter-micelle crosslinking reaction, and macrogelation of the system occurred.

On the other hand, we obtained small spherical particles (core–corona type microgel) in some cases. The smallest diameter of these particles was achieved in a very narrow region of solvent composition (benzene fraction 0.3–0.4), and the particle size increased when the composition of the solvent deviated from this region. This was explained as follows for each solvent.

In the poorest solvent for PMMA (benzene/cyclohexane = 1/9 v/v) the solubility of PMeSt (corona) decreased simultaneously. Aggregation of micelles occurred easily and larger particles were obtained with the crosslinking reaction.

In the intermediate solvent compositions (3/7 or 4/6, depending on the block copolymer composition), the original micelle form was fixed and the inter-micelle crosslinking reaction was hindered perfectly during the crosslinking reaction. Small particles with narrow size distributions were obtained.

In solvent 5/5 (moderately good for PMMA), the core was swollen, i.e. its diameter increased, and the aggregated chains could move easily. The diameter of the particles increased and the diameter distribution was wide. Macrogelation sometimes occurred during the crosslinking reaction.

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