Crosslinking of the inner poly(methyl methacrylate) core of poly(α-methylstyrene-*b*-methyl methacrylate) micelles in selective solvent: 3. Temperature effects

R. Saito, K. Ishizu and T. Fukutomi
Department of Polymer Chemistry, Tokyo Institute of Technology, 2-12, Oookayama, Meguro-ku, Tokyo 152, Japan

(Received 8 March 1990; revised 13 June 1990; accepted 22 August 1990)

The crosslinking of the core of the poly(α-methylstyrene-*b*-methyl methacrylate) micelle was carried out while varying the temperature of the system from 0 to 60°C, and microgels were obtained. Below 40°C it became possible to control the diameter of the spherical microgel from 20 to 100 nm by changing the temperature. At 60°C, on the other hand, the microgel had a random mixing morphology due to intermicelle crosslinking.

(Keywords: core–corona type microgel; polymer micelle; reaction temperature; stability of micelle; turbidimetric titration)

INTRODUCTION

In previous papers[1,2], the effects of the selectivity of the solvent and polymer concentration on the crosslinking of polymer micelles were investigated. Monodispersed spherical soluble microgels with core–corona morphology [core, poly(methyl methacrylate) (PMMA); corona, poly(α-methylstyrene) (PMeSt)] were synthesized from poly(α-methylstyrene-*b*-methyl methacrylate)s [P(MeSt-*b*-MMA)s] under specific conditions. It was suggested that the monodispersed spherical microgels could be synthesized when the lifetime of the polymer micelle was long.

It is well known that the lifetime of the polymer micelle increases with increase in polymer concentration and/or decrease in temperature of the system[3–5]. The size of the micelle is independent of polymer concentration, and the size increases with decrease in temperature. The purpose of this study was to control the diameter of a crosslinked polymer micelle (a microgel) by changing the temperature. The crosslinking temperature was varied from 0 to 60°C.

Two types of P(MeSt-*b*-MMA)s and *o*-xylene were chosen as the block copolymers and the selective solvent, respectively. The polymer micelles were crosslinked with the redox initiator benzoyl peroxide (BPO) and dimethylaniline (DMA) which could initiate above 0°C. The lifetime of the polymer micelle was studied by the 'concentration-jump' method. The sizes and shapes of the crosslinked products were estimated using a transmission electron microscope and a submicron particle size analyser. The solubilities of the products were measured by turbidimetric titrations.

EXPERIMENTAL

Polymers

The original P(MeSt-*b*-MMA)s, their modified block copolymers (no. 3 and no. 6) used for crosslinking and their parent PMMAs have been synthesized and characterized previously[1]. The molecular weight ($\bar{M}_n$) and composition of the block copolymers were: for the modified block copolymer no. 3, $\bar{M}_n = 2.1 \times 10^4$ and α-methylstyrene (MeSt) = 69 mol%; and for block copolymer no. 6, $\bar{M}_n = 6.3 \times 10^4$ and MeSt = 68 mol%. The styryl group content (the reaction groups for crosslinking) in the PMMA sequence of the block copolymers was ~10 mol% per MMA unit.

The poly(methyl methacrylate-*co*-divinylbenzene) macrogel (molecular weight between crosslinking points = 486) and the random mixing microgel (diameter < 100 nm in the solid state, MeSt = 68 mol%, MMA = 32 mol%) have been synthesized and characterized previously[6].

Measurement of the degree of swelling of the polymers

The parent PMMA of block copolymer no. 6 and the PMMA macrogel were swollen in *o*-xylene at 0, 20, 40 and 60°C for 3 days. The weights of the polymers before and after swelling were measured.

Viscometric measurement of the solution after rapid dilution

The preparation and measurement of a sample were carried out as described previously[2] at 0, 20, 40 and 60°C.

Crosslinking of the block copolymer

Modified block copolymer (0.5 g) was dissolved in 45 g *o*-xylene at 60°C. The polymer concentration was 1 w/v% at 25°C. Then the temperature of the solution was adjusted to 0, 20, 40 and 60°C. Then 2.5×10^{-5} mol BPO and 2.5×10^{-5} mol DMA were added and crosslinking was carried out for 4 h.

The termination methods for the crosslinking and the purification of the products were the same as described previously[1]. The shape and size of the products were

0032–3861/91/122258–05

estimated using a transmission electron microscope as in a previous paper[1].

Measurement of the size of the products in solution

Polymer (0.3 g) was dissolved in 27 g *o*-xylene. The solution was filtrated through a Teflon filter (pore size 3000 nm). Dynamic light scattering (DLS) was carried out with a submicron particle size analyser DLS-700 (Otsuka Electronics Co., Ltd).

Turbidimetric titration

Polymer (0.05 g) was dissolved in 20 ml toluene (or benzene), and then n-hexane (or n-butanol) was added stepwise under vigorous stirring in a cell (cylindrical Pyrex cell, 200 ml) at 20°C. At each step, the turbidity of the solution was measured with a single beam ultraviolet-visible (u.v.-vis.) spectrophotometer (Hitachi, u.v.-vis. spectrophotometer 139) at 600 nm.

RESULTS AND DISCUSSION

Micelle formation of the block copolymers

o-Xylene (a good solvent for PMeSt above 0°C) was chosen as the selective solvent for this study. The benzene–cyclohexane mixture used in the previous studies[1,2] was not suitable since the solubility of the PMeSt in cyclohexane changed drastically with temperature.

The micelle formation of P(MeSt-*b*-MMA) in *o*-xylene was examined. Flory's interaction parameters[7] between *o*-xylene and PMMA were 0.508–0.502 in the temperature range 0–60°C. The critical interaction parameters, χ, of PMMA sequences of the block copolymers were calculated as $\chi_{\mathrm{no.3}} = 0.566$ and $\chi_{\mathrm{no.6}} = 0.537$. From these values, it was suspected that PMMA was soluble in *o*-xylene above 0°C. Consequently, the solubilities of the parent PMMAs and the PMMA macrogel in *o*-xylene were measured, and the degrees of swelling are listed in *Table 1*. The degrees of swelling of these polymers were ~1. The PMMA was not soluble in *o*-xylene. Thus, *o*-xylene was a selective solvent for P(MeSt-*b*-MMA) above 0°C.

It was impossible to measure the diameter of the polymer micelle in *o*-xylene by DLS because the scattering intensity of the sample solution was too weak for measurement. However, it was confirmed that polymer micelles of P(MeSt-*b*-MMA) (core, PMMA; corona, PMeSt) existed in *o*-xylene from 0 to 60°C. The bluish tint indicating the presence of polymer micelles was observed for all samples.

Crosslinking of the micelle

In *Figure 1* the diameters of the microgels estimated using transmission electron microscope in the solid state are shown. For any temperature from 0 to 60°C macrogelation did not occur, and spherical microgels were obtained. The diameter of the microgel was 20–300 nm, and the size dispersions were narrow when the diameters were below 100 nm. The microgel with the minimum diameter (20 nm) was obtained from block copolymer no. 3 at 20°C.

Generally from thermodynamic theories[8–12], the diameter of the polymer micelle (D) is given as follows:

$$D \propto M^{2/3}T^{-1/3} \qquad (1)$$

where M is the degree of polymerization (DP) of the core sequence, and T is the temperature of the system.

For block copolymer no. 6 with large DP, except for crosslinking at 60°C, the diameter of the microgel

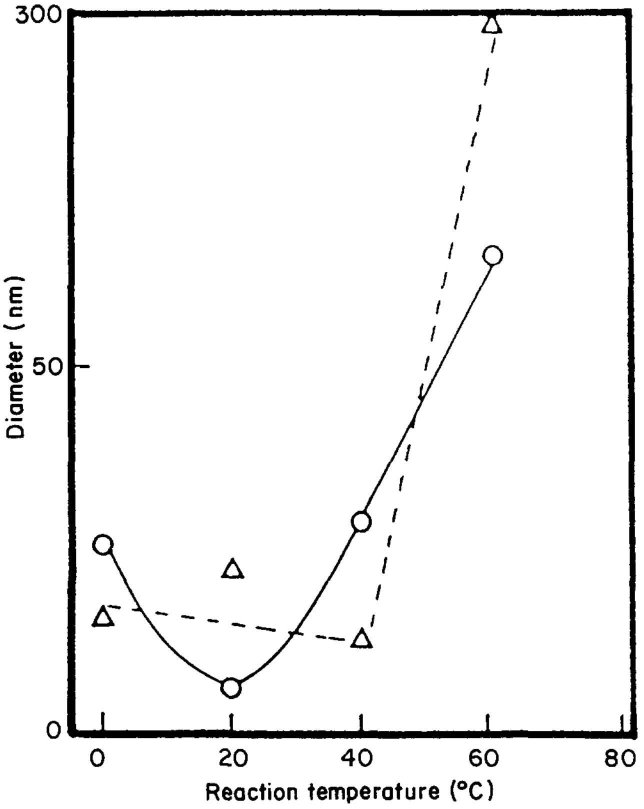

Figure 1 Diameter of the microgel determined using TEM. Block copolymers 3 (○) and 6 (△)

Table 1 Degree of swelling of PMMA and the PMMA macrogel

Polymer	Temperature (°C)	Weight of polymer (g)		Degree of swelling
		Before	After	
Parent PMMA of no. 6	0	2.8	2.8	1.0
	20		2.8	1.0
	60		2.9	1.0
PMMA macrogel	0	3.4	3.3	1.0
	20		3.5	1.0
	60		3.5	1.0

Conditions: swollen in *o*-xylene for 3 days decreased from 50 to 40 nm with increase in temperature from 0 to 40°C.

The ratio of the diameters of the microgels synthesized at 40 and 0°C, D_{40}/D_0, was calculated using equation (1) ($D_{40}/D_0 = 0.87$). This calculated value was in fair agreement with the experimental value ($40/50 = 0.8$).

Next, the diameters of the microgels synthesized from block copolymers no. 3 and 6 at 20°C were compared. The ratio of the diameters of the microgels of block copolymers no. 3 and 6 was $40/70 = 0.57$. The calculated ratio using equation (1) was $D_{\mathrm{no.3}}/D_{\mathrm{no.6}} = 0.5$. The experimental and calculated values were in close agreement. These results suggested that the diameter of the microgel could be controlled by changing the temperature. However, the microgels synthesized from block copolymer no. 6 at 60°C and block copolymer no. 3 above 40°C were larger than expectation. It was reported by Roe and co-workers that the diameter of the micelle increased drastically when the temperature of the system was near the critical micelle temperature[13,14]. At such time, the micelle swelled with the solvent and the micelle system was referred to as 'open-associated'. As reported previously[2], when crosslinking was carried out in an 'open-associated' system, intermicelle crosslinking occurred, and large microgels with a wide dispersion of diameters were obtained. Then, the lifetime of the polymer micelles of block copolymer no. 3 was investigated by the 'concentration-jump' method.

The viscosity of the solution of block copolymer no. 3 was measured after rapid dilution. The stabilizing time of the solution, t (the time taken to reach a new constant value after dilution) is shown in *Figure 2*. The lifetime of the polymer micelle was longest at 20°C because t showed a minimum. The systems were regarded as 'closed-associated' below 20°C and 'open-associated' above 40°C.

From these results, the reason why microgels obtained at high temperature were larger than expected could be explained in terms of intercrosslinking occurring during the crosslinking of polymer micelles. Consequently, it was concluded that the diameter of the microgel could be controlled by changing the temperature of the system when the polymer micelle system was 'closed-associated'.

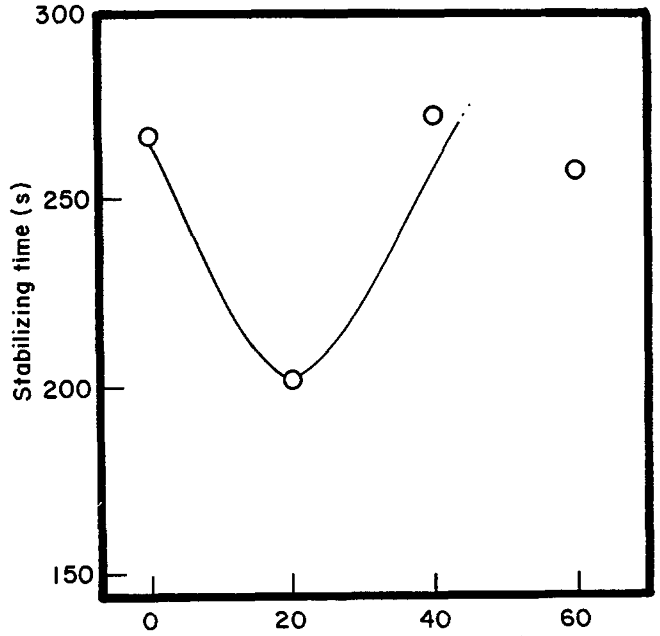

Figure 2 Stabilizing time of block copolymer no. 3 in *o*-xylene

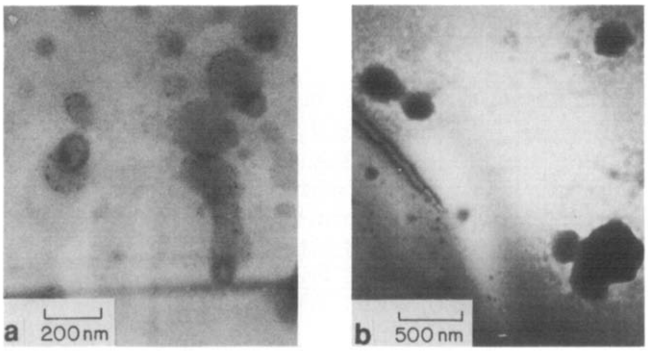

Figure 3 Transmission electron micrographs of the microgels stained with RuO_4: (a) microgel synthesized from block copolymer no. 3 at 0°C; (b) microgel synthesized from block copolymer no. 6 at 60°C

Table 2 Diameter and degree of swelling of the microgel

Block copolymer	Temperature (°C)	D_{TEM}[a] (nm)	D_{DLS}[b] (nm)	Q_m[c]	Q_c[d]
3	0	100	–	–	–
	20	20	35	5.8	0.9
	40	90	–	–	–
	60	200	413	9.3	8.7
6	0	50	313	140.0	1330.0
	20	70	159	24.3	15.6
	40	40	177	42.8	1090.0
	60	300	2300	439.0	572.0

[a] The diameter of the microgel was determined by TEM

[b] The diameter of the microgel was determined by DLS

[c] Degree of swelling of microgel: $(D_{DLS}/D_{TEM})^3$

[d] Degree of swelling of the core calculated using $(D_{DLS} - 2L_{DLS})^3/(D_{TEM} - 2L_{TEM})^3$. For block copolymer no. 3 $L_{DLS} = 15.6$ nm, $L_{TEM} = 7.9$ nm and for block copolymer no. 6 $L_{DLS} = 26.8$ nm, $L_{TEM} = 13.6$ nm

Properties of the microgels

The morphologies of the microgels were investigated by transmission electron microscopy (TEM). Typical TEM micrographs of the microgels are shown in *Figure 3*. (The grey and dark regions of the spherical microgel correspond to the core and corona, respectively.)

The microgel of block copolymer no. 3 crosslinked at 0°C (diameter 100 nm) showed clear core–corona morphology (*Figure 3a*). Moreover, the observed value of the corona thickness (10 nm) showed good agreement with the calculated value (8 nm). On the other hand, the inside morphology of the large microgel of block copolymer no. 6 crosslinked at 60°C (diameter 300 nm) was unclear, because it was stained homogeneously (*Figure 3b*).

Next, the properties of the microgels were measured. We expected that when the microgel had a core–corona morphology, the corona would behave as homo PMeSt and the core as crosslinked PMMA because crosslinking must occur in the core and the corona did not depend on crosslinking. Based on this consideration, the degree of swelling of the microgel at 20°C was investigated from the diameters of the microgels (D_{TEM} and D_{DLS}) in the dry state with TEM and in *o*-xylene with DLS, respectively. The D_{TEM}, D_{DLS} and degree of swelling of microgel, Q_m [$= (D_{DLS}/D_{TEM})^3$] are listed in *Table 2*.

All microgels swelled well in *o*-xylene. For the microgel, the PMeSt corona could dissolve in *o*-xylene. In order to estimate the true core state, the corona thickness of the microgel must be subtracted from the diameter of microgel. The corona thicknesses (L_{TEM} and L_{DLS}) in the solid state and in *o*-xylene at 20°C were calculated with the values of *DP* of the block copolymers as $L_{TEM} = 7.9$ nm, $L_{DLS} = 15.6$ nm for block copolymer no. 3 and $L_{TEM} = 13.6$ nm, $L_{DLS} = 26.8$ nm for block copolymer no. 6, respectively. The degrees of swelling of the core Q_c, $[(D_{DLS} - 2L_{DLS})^3/(D_{TEM} - 2L_{TEM})^3]$, were calculated from these values (*Table 2*).

The Q_c of the microgel synthesized from block copolymer no. 3 at 20°C which showed clear core–corona morphology was very close to 1. From the results in *Table 1*, the PMMA macrogel did not swell in *o*-xylene at 20°C. Then, the Q_c result also showed that the core of the microgel corresponded to PMMA gel.

However, taking account of the thickness of the corona, it seemed that the cores of the other microgels swelled too much. The maximum diameters of the cores (D_{cores}) in the solid state were calculated as $D_{core} = 10.6$ and 18.7 nm for block copolymers 3 and 6, respectively, with the maximum expansion of PMMA sequences of the block copolymers. For the microgel of block copolymer no. 3 synthesized at 40°C, the diameter of the core (79.4 nm) was much larger than the maximum D_{core} (10.6 nm). This result indicated that the microgels did not have a microphase-separated morphology or PMeSt existed in the core. When the PMeSt sequences existed in the core, it was impossible to characterize the microgels with the results of swelling behaviour of the core in any solvent.

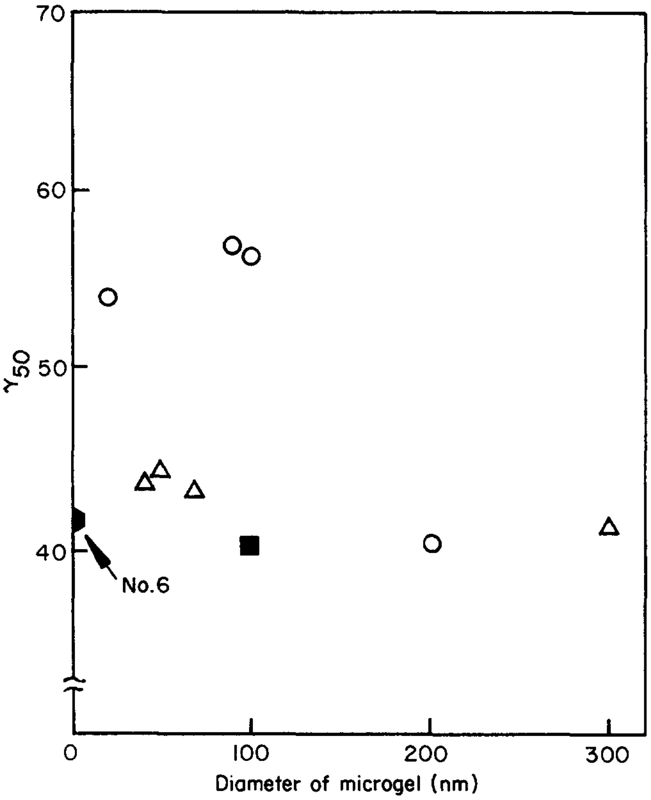

Figure 4 Composition of the precipitate in the solvent with 50% turbidity (γ_{50}) *versus* the diameter of microgel in the toluene-n-hexane system; (○) microgel of block copolymer no. 3; (△) microgel of block copolymer no. 6; (■) random mixing microgel

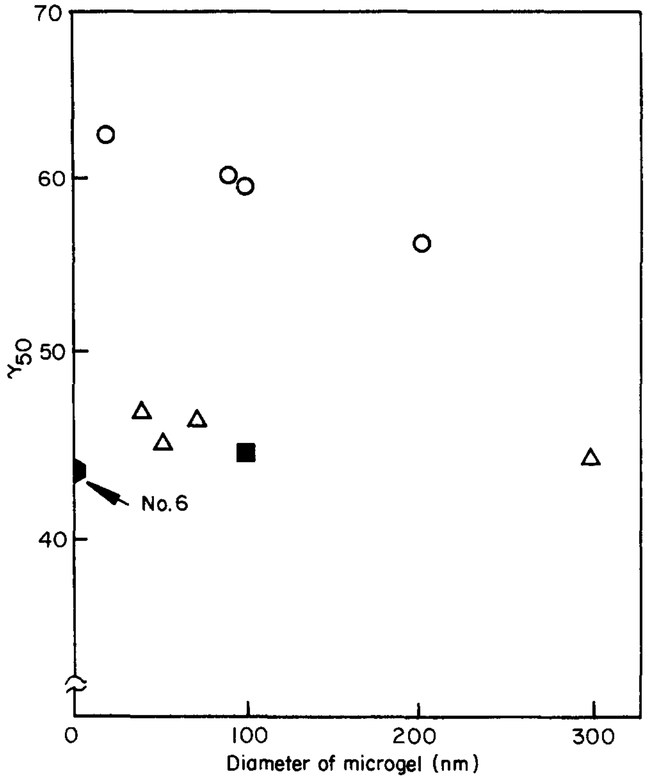

Figure 5 Composition of the precipitate in the solvent with 50% turbidity (γ_{50}) *versus* the diameter of microgel in the benzene–n-butanol system; (○) microgel of block copolymer no. 3; (△) microgel of block copolymer no. 6; (■) random mixing microgel

In order to check the presence of PMeSt in the core and the inside morphologies of the microgels, turbidimetric titrations in two solvent systems were carried out. The benzene–n-butanol system and the toluene–n-hexane system were chosen.

In *Figures 4* and *5*, the volume fractions[15,16] of the precipitate in the solvent at 50% turbidity, γ_{50}, are plotted against the diameter of the microgel in two solvent systems. In both solvent systems, the γ_{50}s of the microgels were larger than those of the block copolymers. This was explained by the PMeSt corona and PMMA core increasing the solubilities of the microgels in the toluene–n-hexane and benzene–n-butanol systems, respectively.

The microgels synthesized from block copolymer no. 6 at 60°C showed the lowest solubility in the microgels. In both systems, the values of γ_{50} for the microgel of block copolymer no. 6 synthesized at 60°C were very close to the values of γ_{50} for the random mixing microgels which had similar diameters to the microgel of block copolymer no. 6 at 60°C. This indicated that the microgel synthesized at 60°C did not have a microphase-separated morphology. In other words, this microgel was a random mixing microgel of PMeSt and PMMA.

For the other microgels, γ_{50} in the toluene–n-hexane system increased with the diameter of the microgel. In general, γ_{50} decreased with increase in particle size[15,16]. However, we previously reported that the turbidimetric behaviour was similar to PMeSt, when the corona was composed of PMeSt and PMMA was not included[17,18]. In this work, the γ_{50}s of the microgels were larger than the precursor block copolymers. Thus, it was concluded that these microgels were covered with PMeSt sequences.

Consequently, below 40°C it was possible to control the diameter of the microgel with clear core–corona morphology by changing the temperature. However, intermicelle crosslinking occurred at high temperature (at 60°C) and large microgels with a random mixing morphology were synthesized.

From TEM it was concluded that small microgels, with diameters below 100 nm, had core–corona morphology. The large microgel synthesized at 60°C was a random mixing microgel.

CONCLUSIONS

In order to control the diameter of the microgel, crosslinking of the core of the P(MeSt-*b*-MMA) micelle was carried out by changing the temperature of the system from 0 to 60°C.

Taking into account the temperature dependence of the properties of the block copolymers, *o*-xylene and the redox initiator (BPO + DMA) were chosen as a selective solvent and initiator, respectively.

Before crosslinking, the stability of the polymer micelle in solution and the solubility of the PMMA core were examined by the 'concentration-jump' method and by measuring the degree of swelling in *o*-xylene. From the results of these measurements, micelle formation of the block copolymer in *o*-xylene was confirmed.

By using the crosslinking of the micelles, soluble microgels with diameters from 20 to 300 nm were obtained. Especially below 40°C it was possible to control the diameter of the microgel by changing the temperature. However, the microgels synthesized at 60°C were very large, and the occurrence of intermicelle crosslinking at 60°C was proposed.

REFERENCES

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

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

3 Bug, A. L. R., Cates, M. E., Safran, S. A. and Whitte, T. A. *J. Chem. Phys.* 1987, **87**, 1824

4 Halperin, A. and Alexander, S. *Macromolecules* 1989, **22**, 2403

5 Price, C. *Pure Appl. Chem.* 1983, **55**, 1563

6 Saito, R., Ishizu, K. and Fukutomi, T. *J. Appl. Polym. Sci.* in press

7 Bristow, G. H. and Watson, W. F. *Trans. Faraday Soc.* 1952, **54**, 1567

8 Noolandi, J. and Hong, K. M. *Macromolecules* 1983, **16**, 1443

9 Leibler, L., Orland, H. and Wheeler, J. C. *J. Chem. Phys.* 1983, **79**, 3550

10 Zhulina, Ye. B. and Birshtein, T. M. *Vysok. Soyed.* 1985, **A27**, 511

11 Nagarajan, R. *J. Chem. Phys.* 1989, **90**, 1980

12 Nagarajan, R. and Ganesh, K. *J. Chem. Phys.* 1989, **90**, 5843

13 Rigby, D. and Roe, R. J. *Macromolecules* 1984, **17**, 1778

14 Roe, R. J. *Macromolecules* 1986, **19**, 728

15 Bischoff, J. and Desreux, V. *Bull. Soc. Chim. Belg.* 1951, **60**, 137

16 Oth, A. and Desreux, V. *Bull. Soc. Chim. Belg.* 1954, **63**, 261

17 Ishizu, K. *Polym. Commun.* 1989, **30**, 209

18 Ishizu, K. and Onen, A. *J. Polym. Chem., Polym. Lett. Edn* 1989, **27**, 3721