Flower shaped microgel 3: synthesis of poly(2-hydroxyethylmethacrylate) core–polystyrene shell type microgels

Reiko Saito*, Yoshihito Akiyama, Koji Ishizu

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

Abstract

Poly(2-hydroxyethyl methacrylate-b-styrene-b-2-hydroxyethyl methacrylate) triblock copolymer was synthesized by hydrolysis of poly(2[(trimethylsilyl)oxy]ethyl methacrylate-b-styrene-b-2[(trimethylsilyl)oxy]ethyl methacrylate) triblock copolymer polymerised with α-methylstyrene tetramer disodium as an initiator by an anionic living polymerisation technique. Micelle formation of the poly(2-hydroxyethyl methacrylate-b-styrene-b-2-hydroxyethyl methacrylate) triblock copolymer was investigated in dimethylformamide (DMF), toluene, cyclohexane and a toluene/n-hexane mixture by dynamic light scattering (DLS) method. Monodispersed polymer micelle with a poly(2-hydroxyethyl methacrylate) core and polystyrene shell chains was formed with the triblock copolymer in a toluene and n-hexane mixture when n-hexane was 62 vol%. The poly(2-hydroxylethyl methacrylate) core was crosslinked with 1,6-hexanediisocyanate. Crosslinked products were spherical and their diameters were measured in the toluene by the DLS method. Additionally, microgel with free end shell chains was synthesized as the reference of the microgels with loop shell chains by scission of the loop shell chains at their centre by exposure to ultraviolet light. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Loop chains; Polymer microsphere; Polymer micelle

1. Introduction

For the ABA triblock copolymer in the selective solvent that is a good solvent for middle block and a non-solvent for outer blocks, the polymer micelle with a solid core and swollen shell chains was formed. Especially, the shell chain forms a loop structure [1–3]. It is possible to synthesize core–shell microgels by crosslinking of spherical microdomains of the polymer micelle with the loop shell chains formed with ABA triblock copolymers [4–6]. The microgels synthesized from the polymer micelles with loop shell chains upon crosslinking the core part would have the crosslinked core and the loop shell chains (Fig. 1). Those microgels have interesting properties owing to their core–shell structure in solution [4,6].

The core–shell type microgels with the loop shell chains are topologically interesting. The core–shell type microgels with the loop shell chains can be assumed to have the microgel covered with ring polymers. In comparison with a linear polymer, the ring polymers show interesting features, such as lower solution viscosity at high polymer

concentration [7], lower glass transition temperature [8,9], a drastic increase of solution viscosity by blending with the linear polymers [10], etc. These features are due to the lower entanglement of the ring polymers in condensed solution. As well as the ring polymer, less entanglement between the microspheres is expected for the core–shell microgels with loop shell chains in condensed solution. Additionally, novel properties owing to the loop structure of the shell would be expected.

In previous work, the microgels with loop shell chains with poly(2-vinyl pyridine) (P2VP) core–polystyrene (PS) shell structure [4] and poly(vinyl alcohol) (PVA) core–PS shell structure [5] were synthesized. For both microgels, the viscosity of the microgel solutions in selective solvents used for micellization was clearly lower than that of the triblock copolymer solutions. However, effects of the 'loop' structure of the shell chains on the properties of the microgels were unclear since reference microgels for those microgels could not be obtained. In order to clarify the effect of loop shell chains, a reference microgel is required with the same properties to those of the core–shell microgels with loop shell chains except for the chain architecture of the shell chains. The best method for the synthesis of the

---

* Corresponding author.

reference microgel is to cut the loop shell chains of the microgel from their centre, because the characteristics of the original and reference microgels would be the same, except for the shell chain structure.

α-Methylstyrene tetramer dianion is well known as an anionic initiator. Moreover, poly(α-methyl styrene) is a photodegradable polymer by exposure to ultraviolet (u.v.) light. If the microgel with loop shell chains is formed with the ABA triblock copolymer synthesized with a α-methylstyrene tetramer unit, the α-methylstyrene tetramer unit will be at the centre of the loop shell chains. Thus, by the exposure of the microgels with loop shell chains to the u.v. light, the reference microgel will be obtained (Fig. 1). Based on this concept, we synthesized a P(2VP) core–PS shell type microgel from P(2VP-b-S-b-2VP) triblock copolymer synthesized with α-methylstyrene tetramer, and exposed it to u.v. light. However, the microgel was degraded by u.v. irradiation because P2VP is a photodegradable polymer.

In order to obtain a microgel with the loop shell chains and its reference microgel, we have to chose photoresistable polymers for both A and B sequences. In contrast to P2VP, polymethacrylates are photoresistant polymers. Additionally, methacrylates can be polymerised with the α-methylstyrene tetramer disodium by an anionic living polymerisation technique [11]. Hirao et al. [12] reported that the synthesis of the poly(2-hydroxyethyl methacrylate-b-styrene-b-2-hydroxyethyl methacrylate) [P(HEMA-b-S-b-HEMA)] triblock copolymer. The PHEMA sequences can be crosslinked with diisocyanate under mild conditions.

Based on these considerations, in this paper, we aimed to synthesize PHEMA core–PS shell type microgels with the loop shell chains from the P(HEMA-b-S-b-HEMA) triblock copolymer and its reference microgel by cutting the loop shell chain from their centre.

2. Experimental

2.1. Synthesis of P(HEMA-b-S-b-HEMA) triblock copolymer

P(HEMA-b-S-b-HEMA) triblock copolymer was synthesized by hydrolysis of poly(2[(trimethylsilyl)oxy]ethyl methacrylate-b-S-b-2-[(trimethylsilyl)oxy]ethyl methacrylate) synthesized by the anionic living polymerisation with

α-methylstyrene tetramer disodium in THF at −78°C [12]. Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were measured with a Tosoh H-8020 GPC with THF as an eluent at 38°C, a TSK-gel GMHXL column and a flow rate of 1.0 ml min^{-1}. For g.p.c. measurement, the triblock copolymer was benzoylated with benzoic anhydride in THF. PHEMA content of the triblock copolymer was determined with FT-i.r. (Shimazu, FTIR-8500) using the peaks at 1500 and 1730 cm^{-1}, which were due to the styryl and carbonyl groups, respectively.

2.2. Turbidimetric titration of triblock copolymer in a toluene and n-hexane mixture

The triblock copolymer (0.001 g) was dissolved into 60 ml of toluene. Then n-hexane was added gradually. Turbidity of a solution was measured stepwise at 25°C.

2.3. Micelle formation of the triblock copolymer

P(HEMA-b-S-b-HEMA) triblock copolymer was dissolved in toluene. Then n-hexane was gradually added until the polymer concentration was 0.5 wt% and the n-hexane content was 62 vol%. The solution was stored at 25°C.

2.4. Crosslinking of the core part of micelles

A certain amount of 1,6-hexane diisocyanate was added to the micelle solution. The crosslinking of PHEMA was carried out for 2 days at 25°C.

2.5. Dynamic light scattering

The hydrodynamic diameter and distribution of the micelle and crosslinked products, for a solution of c = 0.005–1 wt% at an angle of 90°, were measured with a DLS (Photal, DLS-7000).

2.6. Morphological observation by transmission electron microscopy (TEM)

A solution of crosslinked products was cast on a copper microglid covered with carbon substrate. The solvent was evaporated quickly without heating. The sample specimen
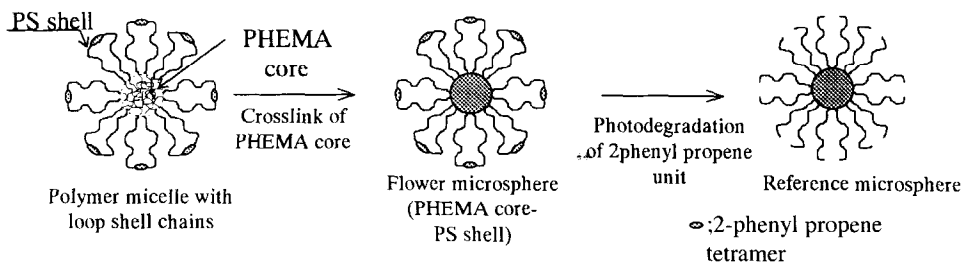

Fig. 1. Synthetic scheme of microgel with loop shell chains and its reference microgel.

was stained with OsO_4 overnight at room temperature. Inner texture of the crosslinked products was observed with a transmission electron microscope (Hitachi, H-500) at 75 kV.

2.7. Degradation of α-methylstyrene tetramer sequence

The polymer was dissolved in THF at a polymer concentration of 1 wt%. Polymer solution was exposed to u.v. light using a wolfram lamp (200 W, 100 V) without wavelength control. Then the polymer was precipitated with excess amount of water and dried under vacuum.

3. Results and discussion

3.1. Synthesis and scission of P(HEMA-b-S-b-HEMA)

The characteristics of P(HEMA-b-S-b-HEMA) triblock copolymer are listed in Table 1. For the required purpose, the P(HEMA-b-S-b-HEMA) triblock copolymer should have the α-methylstyrene tetramer unit at the centre of the polymer chain. Additionally, only the α-methylstyrene tetramer unit should be degraded by exposure to u.v. light. If the polymerisation rates of the sequences of both side of the initiator are the same, the α-methylstyrene tetramer unit would be present at the centre of the P(HEMA-b-S-b-HEMA) triblock copolymer. However, there is no evidence for this. Additionally, the PS polymer is photodegradable to u.v. light produced with a mercury lamp [13]. Thus, photodegradation of the PS homopolymer synthesized with the α-methylstyrene tetramer dianion was carried out.

Fig. 2 shows changes of M_n and M_w/M_n of the PS by exposure to u.v. light. The photodegradation was started at 4 h, since the M_n of the polymer decreased and the M_w/M_n increased after 4h. The increase of M_w/M_n was due to the fact that the solution was a mixture of the degraded and original polymers. After 13 h, the M_w/M_n was close to the initial value and the M_n became constant. The final M_n was almost half of the initial value. This indicates that the polymer was degraded from its centre. In this study further decreasing of the M_n was not observed. Here it should be noticed that only the α-methylstyrene tetramer unit was photodegraded. Consequently, the PS homopolymer could be separated into two parts from its centre by exposure to u.v. light over 13 h.

Table 1
Characteristics of poly(2-hydroxyethylmethacrylate-b-styrene-b-2-hydroxyethyl methacrylate) triblock copolymer

Polymer name	M_n of block ($\times$ 10^{-5} [a]	M_n/M_w^b	HEMA content[c] (mol%)
HSH1	1.18	1.14	9.0

[a]Determined by g.p.c. and HEMA content
[b]Distribution of molecular weight of the triblock copolymer determined by g.p.c.
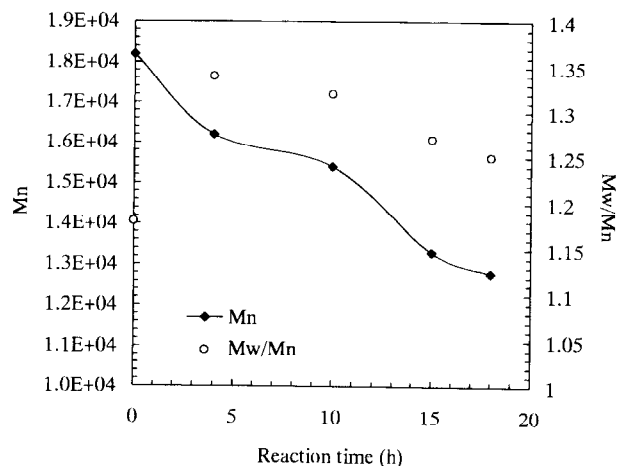[c]Determined by FT-i.r.

Fig. 2. Molecular weight and its distribution index of polystyrene homopolymer during photodegradation.

Next, the P(HEMA-b-S-b-HEMA) triblock copolymer was exposed to u.v. light. Fig. 3 shows the change of M_n and M_w/M_n of the P(HEMA-b-S-b-HEMA) triblock copolymer detected by g.p.c. during exposure. As with the PS homopolymer, the M_n of the polymer decreased and the M_w/M_n increased after 2 h. After 8 h, the M_n of the block copolymer became constant and the M_w/M_n was close to the initial value. Thus, The ABA triblock copolymer could be cut at the centre by exposure to u.v. light over 8 h. Faster photodegradation of the ABA triblock copolymer (8 h) than that of the PS (15 h) was the effect of PHEMA in the ABA triblock copolymer. PMMA is reported to accelerate the photodegradation of PS derivatives [14–17]. In order to prevent further degradation of PS, the exposure time of the microgel to u.v. light was determined to be 8 h.

3.2. Micellization of P(HEMA-b-S-b-HEMA)

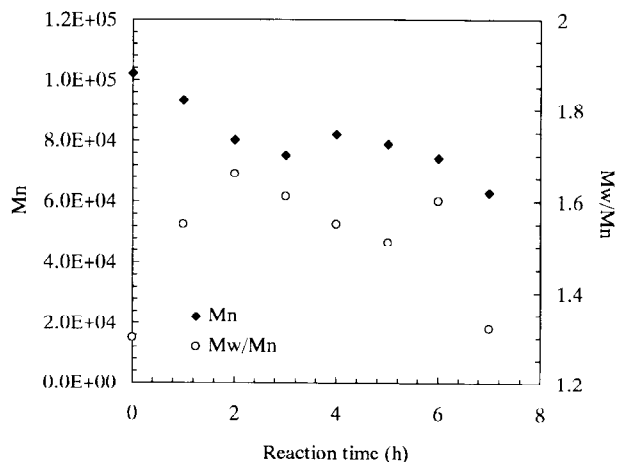In order to investigate the micelle formation of the P(HEMA-b-S-b-HEMA) triblock copolymer with the

Fig. 3. Molecular weight and its distribution index of poly(2-hydroxy-ethylmethacrylate-b-styrene-b-2-hydroxyethyl methacrylate) triblock copolymer during photodegradation.
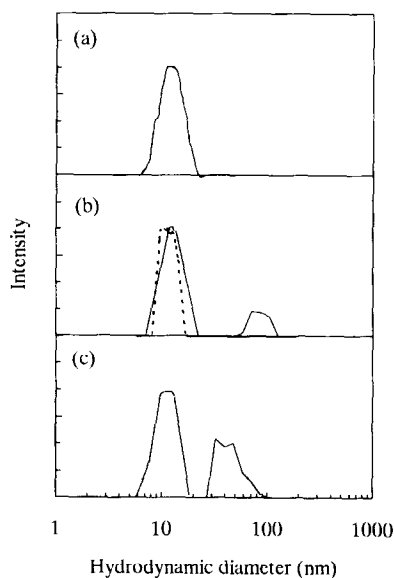
Fig. 4. Hydrodynamic diameter of aggregates of the HSH1 triblock copolymer in solvents, (a) HSH1 in DMF, (b) HSH1 (solid line) and modified HSH1 (dashed line) in toluene, (c) HSH1 in cyclohexane.

P(HEMA) core and PS loop shell, the hydrodynamic diameters (D_h) of the P(HEMA-b-S-b-HEMA) triblock copolymer in solvents were measured. Dimethylformamide (DMF), toluene and cyclohexane were used as solvents. Fig. 4 shows the particle diameter distribution of the P(HEMA-b-S-b-HEMA) in the solutions. DMF is a good solvent for both sequences, and toluene and cyclohexane are selectively good solvents for the PS and non-solvents for the P(HEMA). Thus, micelle formation with the P(HEMA) core–PS loop shell was expected in toluene and cyclohexane.

In DMF, a single peak was observed at 9 nm. Since DMF is a good solvent for the triblock copolymer, the D_h of the triblock copolymer chain was found to be 9 nm. In toluene and cyclohexane, the peaks were observed not only at 9 nm but also at 80 nm. Peaks appearing at larger D_h suggested the presence of aggregates in the systems. If the aggregates were formed due to the aggregation of the PHEMA sequences in the solution, the peak at 80 nm will vanish by increasing compatibility between PHEMA and the solvent. Thus, hydroxyl groups in PHEMA were reacted with phenyl isocyanate. After the modification, the peak at 80 nm vanished, while the peak at 9 nm remained. Therefore, it was concluded that the large aggregates in toluene and cyclohexane were the PHEMA core–PS shell type polymer micelles formed with the P(HEMA-b-S-b-HEMA) triblock copolymer.

However, in both systems, the P(HEMA-b-S-b-HEMA) triblock copolymer also existed as a unimer. This could be due to the high solubility of the PS into the solvents. In order to decrease the solubility of the PS in the solvent, n-hexane that was a non-solvent for both the PS and the PHEMA was added. Fig. 5 shows the turbidimetric titration curve of the P(HEMA-b-S-b-HEMA) triblock copolymer in a
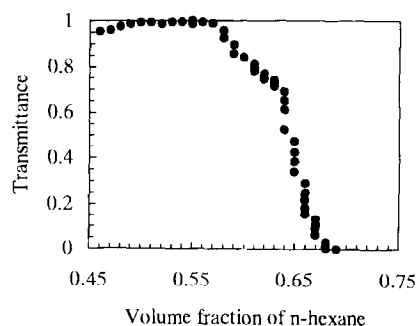

Fig. 5. Turbidimetric curve of HSH1 in the toluene/n-hexane mixture at 25°C.

toluene/n-hexane mixture. Transmittance of the solution decreased twice, at 56 and 65 vol% of n-hexane. Over 65 vol% of n-hexane, the polymer was precipitated. However, no precipitation of the polymer was observed in the solution in the range of n-hexane from 56 to 65 vol%. The decrease of the transmittance suggests the presence of the aggregates in the solutions. Thus, DLS measurements were carried out for these solutions.

Fig. 6 shows the D_h values detected by DLS. Below 58.5 vol% of n-hexane, two peaks of D_h were observed at 7 and 20 nm. As described above, these two peaks are the unimers and the aggregates. Over 60 vol%, only one peak was observed at 20 nm. This indicates that the triblock copolymer formed polymer micelles when the n-hexane content was larger than 58.5 vol%. For the crosslinking of the micelle, taking into account the effect of the 1,6-hexane diisocyanate, the n-hexane volume for the micelle formation was determined to be 62 vol%.

Next, in order to determine polymer concentration of polymer micelle solution for the crosslink, critical micelle concentration (cmc) was measured by DLS. Fig. 7 shows the D_h values of the aggregates in the toluene/n-hexane mixture at 62 vol% of n-hexane. Between 0.1 and 1 wt/vol% of the polymer concentration, the D_h values were constant (20 nm). On the other hand, when the polymer concentration was lower than 0.06 wt%, the intensity of
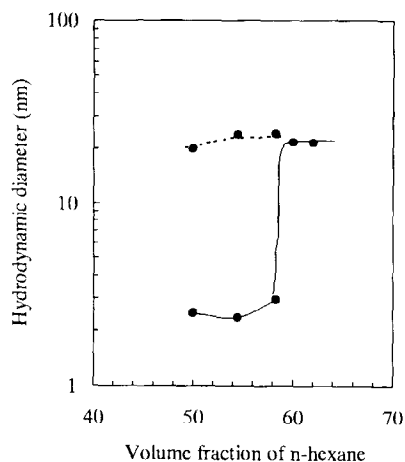

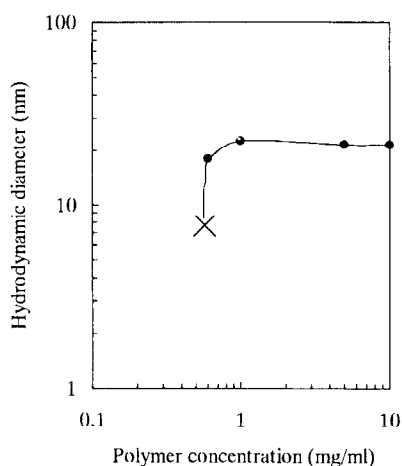Fig. 6. The effect of n-hexane content on the hydrodynamic diameter of HSH1.

Fig. 7. The effect of the polymer concentration on the hydrodynamic diameter of the HSH1.
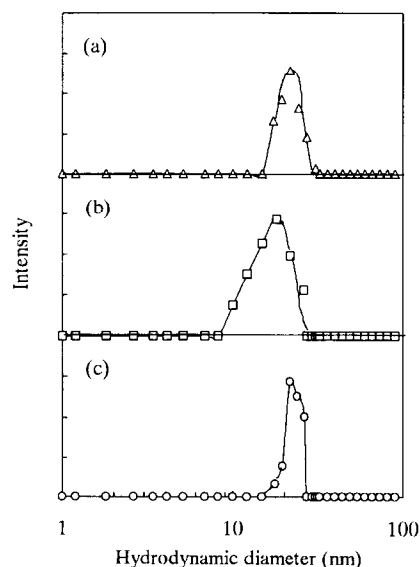

Fig. 8. The hydrodynamic diameter of aggregates of the HSH1 triblock copolymer. (a) Polymer micelle in the toluene/n-hexane mixture. (b) Cross-linked products in toluene. (c) Exposed products in toluene.

the solution was too low to be detected. The D_h values were not obtained. This indicates that the cmc was near 0.06 wt%. For the ABA triblock copolymer micelle system in the selective solvent for the B sequence, formation of mesogel (bridge) was reported at high polymer concentration [1–3,18–21]. Zhou et al. reported that a larger new peak due to the mesogel formation appeared at high polymer concentration [22]. In this study, however, only one peak was observed at 20 nm in this region of polymer concentration. The polymer concentration of the polymer micelle solution for crosslinking was determined to be 0.5 wt%.

3.3. Crosslink of the aggregates

Next, the P(HEMA) sequences in the aggregates were crosslinked with 1,6-hexane diisocyanate for 24 h. In general, catalysts are used to accelerate the crosslink with iso-cyanates. However, the catalyst would disturb the equilibrium of micelles. Thus, no catalyst was used in this study. It has been reported that the crosslink of hydroxyl groups with diisocyanate was finished by 24 h even without catalyst [23]. Thus, the crosslink time was determined to be 48 h.

After 48 h, no macrogelation of the system was observed. Fig. 8a and 8b show the D_h distributions of the polymer micelle and a crosslinked product measured in the toluene/n-hexane mixture and toluene, respectively. The D_h of both peaks are the same. It should be noticed that the peak due to the unimer was observed at 9 nm for the triblock copolymer in toluene (Fig. 4a). However, after crosslinking, no peak owing to unimer was observed at 9 nm, even in toluene. It was found that the polymer micelle was crosslinked and did not change size, even in the good solvent for the triblock copolymer.

3.4. Synthesis of reference microgel

The photodegradation of the α-methylstyrene tetramer in the shell chain was carried out by exposure of the microgels

to u.v. light. Fig. 8c shows the D_h distribution of the microgel after the exposure. If the α-methylstyrene sequence in the dangling chain was photodegraded, a new peak should appear at a small diameter. Additionally, if the microgels with loop shell chains composed of several PHEMA cores, in other words, if the bridge structure connected some PHEMA cores, the peak should shift to a smaller level since the PHEMA cores lose the connection between PHEMA cores after the photodegradation. However, the size of the microgel was not changed after exposure to u.v. irradiation. This indicates that no dangling chain existed in the microgel, and each microgel with the loop shell chains was composed of a PHEMA core. Consequently, it was found that the PHEMA core–PS shell type microgel was not broken by degradation of the α-methylstyrene sequences in the microgels. The slight changes of the size of the microgel would be due to the conformational change of the shell chains. In this stage, the cellular evidence of the complete scission of the loop shell chains could not obtained because the phenyl groups of the PS shell sequence screened the disappearance of the phenyl group of the 1,4-diphenylstyrene tetramer sequence. For further investigations, mass production of the microgels is required.

4. Conclusions

The P(HEMA-b-S-b-HEMA) triblock copolymer was synthesized by the anionic living polymerisation and hydrolysis of the P(2[trimethylsilyl]oxy methacrylate-b-S-b-2[trimethylsilyl]oxy methacrylate) triblock copolymer. The P(HEMA-b-S-b-HEMA) triblock copolymer was converted to P(S-b-HEMA) by the photodegradation of

the α-methylstyrene tetramer by exposure to u.v. light. Monodispersed polymer micelles with PHEMA cores and PS loop shell chains were formed with the P(HEMA-b-S-b-HEMA) triblock copolymer in a toluene/n-hexane mixture of 62% n-hexane. The micelle was successfully fixed by cross-linking of the PHEMA core with 1,6-hexane diisocyanate. The crosslinked products were the PHEMA core–PS shell type spherical microgels. By the expose of the the microgel to u.v. light, a reference microgel with the same size as the original microgel with loop shell chains was obtained.

Acknowledgements

References

[1] Krause SJ. Phys Chem 1964;68:1948.
[2] Tang WT, Hadziioannou G, Cotts PM, Smith BA, Frank CW. Polym Prep 1986;27:107.
[3] Balsara NP, Tirrell M, Lodge TP. Macromolecules 1991;24:1975.
[4] Saito R, Ishizu K. Polymer 1997;38:225.
[5] Saito R, Yoshida S, Ishizu K. J Appl Polym Sci 1997;63:849.
[6] Saito R, Tanaka M, Akiyama Y, Ishizu K. J Appl Polym Sci, submitted.
[7] Semlyen JA et al. Polymer 1988;29:1452.
[8] Clarson SJ, Semlyen JA, Dodgson K. Polymer 1991;32:2823.
[9] Lin X, Chen D, He Z, Zhang H, Hu H. Polym Commun 1991;32:123.
[10] Patel A, Cosgrove T, Semlyen JA. Polymer 1991;32:1313.
[11] Mita I, Watabe Y, Akatsu T, Camble H. Polymer J 1973;4:271.
[12] Hirao A, Kato H, Yamaguchi K, Nakahama S. Macromolecules 1986;19:1294.
[13] Itagaki H, Mita I. In: Jellinek HH, editors. Degradation and stabilization of polymers, 2. New York: Elsevier, 1989.
[14] Torikai A, Sekigawa Y, Fukui K. Polym Degr Stab 1988;21:43.
[15] Torikai A, Hiraga S, Fueki K. Polym Degr Stab 1992;37:73.
[16] Kaminski A, Kaczmarek H, Sanyal S. Polym Networks Blends 1991;1:171.
[17] Kaczmarek H, Decker C. Polym Networks Blends 1995;5:1.
[18] Tuzar Z, Kratochivil P. Adv Colloid, Interface Sci 1976;6:201.
[19] Price C. In: Goodman I, editor. Development of block copolymers, vol. 1. London: Applied Science, 1982:39.
[20] Tanaka T, Kotoka T, Inagaki H. Polym J 1972;3:327.
[21] Smenov AN, Joanny J-F, Khokholov AR. Macromolecules 1995;28:1066.
[22] Zhou Z, Chu B, Yang YW, Booth C. Macromolecules 1996;29:3663.
[23] Saito R, Kan WMJ, Lee LJ. Polymer 1996;37:3567.