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ESR Studies of the Adsorption Behavior of Styrene-Methyl Methacrylate Copolymer at the Solid-Liquid Interface

Kazutoshi Kobayashi,* Kazuo Araki, Yoshio Imamura, and Ryuichi Endo
Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162
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The conformation of the copolymer of styrene and spin-labeled methyl methacrylate adsorbed on nonporous silica from solution was investigated by the use of the ESR method. The attached segment fraction of methyl methacrylate, P_{MMA}, in the copolymer was evaluated experimentally. The attached segment fraction of styrene, P_{ST}, and the total attached segment fraction, P_{TOT}, in the copolymer were estimated by means of numerical calculations from the value of P_{MMA}. The amounts of saturated adsorption, A_{S}, were obtained as a function of the mole fraction of styrene in the copolymer. The A_{S} values of the copolymers through the mole fractions of styrene of 0.8 increased slightly with the mole fraction of styrene. The A_{S} values of the copolymers at the mole fractions of styrene in excess of 0.8 decreased steeply to that of the styrene homopolymer. The change in the A_{S} values of the copolymers was explicable in terms of the changes in the values of the surface coverage and the values of P_{TOT}. The adsorbed methyl methacrylate homopolymer had a flat conformation, whereas the adsorbed styrene homopolymer had a loopy conformation. When the styrene content in the copolymer increased, the adsorbed conformations of the copolymers varied gradually from the conformation of the methyl methacrylate homopolymer to that of the styrene homopolymer.

A number of techniques have recently been applied to the study of the conformation of the polymers adsorbed at the solid-liquid interface; FT-IR,[1–6] ESR,[7–14] NMR,[15–17] ellipsometry,[18,19] and so on. Fontana and Thomas first developed a technique for the quantitative estimation of the segment fraction attached to the surface sites, using infrared spectroscopy.[1] Sakai and Imamura reported a procedure for estimating the three components of adsorbed polymer segments (train, short loop, and long loop or tail) from the ESR spectra of spin labeled polymers.[11] In the same series of investigations,[14] the dependence of the adsorption of the methyl methacrylate homopolymer on the molecular weight over a wide range with reference to the molecular conformation was reported.

Several papers studying the segment fractions of the adsorbed copolymers have been published recently.[20,21] Kawaguchi et al. reported on the adsorption of styrene-butadiene copolymers on the silica surface using IR spectroscopy.[20] They estimated the bound fractions for the two monomer components as a function of the surface coverage (the fraction of surface silanol groups occupied), θ_{IR}, and of the compositions of the copolymers. Herd et al., also using the IR method, studied the adsorption of styrene-methyl methacrylate copolymers and discussed the effect of the addition of a different solvent on the equilibrium adsorption.[21] However, they stressed the amount of adsorption of the adsorbed copolymer and made a slight reference to the conformation of the adsorbed copolymer. Therefore, we will discuss in detail the conformation of the adsorbed styrene-methyl methacrylate copolymer (PMCS) using the ESR method, based on the estimation of the values of P_{MMA} and P_{ST}. At the present stage, it is impossible to deal with a system with both copolymer components labeled or to analyze the ESR spectrum for the dynamic behavior of methyl methacrylate and the styrene segment individually.

Experimental

Materials and Measurements. The copolymers of styrene and methacryloyl chloride were prepared by radical polymerizations, using α,α'-azobisisobutyronitrile as an initiator and benzene as the solvent. The copolymers were spin-labeled by the reaction of the acid chloride moieties with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxyl in a benzene solution in the presence of pyridine. The labeled copolymers were precipitated by pouring the solution into methanol; then, the unreacted chloride atoms in the copolymers were replaced by methoxyl groups. The spin-labeled methyl methacrylate homopolymer was prepared by the procedure described in a previous paper.[11] A styrene homopolymer with a narrow molecular weight distribution was purchased from the Pressure Chemical Co. The polymer samples are characterized in Table 1.

The spin concentrations of the polymers used were in the range of one label per 400 to 1000 monomeric residues. The molecular weights and the $\overline{M}_{\mathrm{w}}/\overline{M}_{\mathrm{n}}$ ratios were determined by

Table 1. Characterization of Polymer Samples Used

Polymer sample	Mole fraction of styrene[a]	$\overline{M}_{\mathrm{w}}$[b]	$\overline{M}_{\mathrm{w}}/\overline{M}_{\mathrm{n}}$[b]
PMMA	0	200000	1.5
PMCS-17	0.17	127000	2.0
PMCS-67	0.67	155000	1.8
PMCS-81	0.81	136000	2.5
PMCS-87	0.87	115000	2.0
PMCS-91	0.91	132000	2.4
PMCS-96	0.96	96900	1.6
PMCS-99	0.99	80200	1.4
PS	1	207000	1.1

a) The mole fraction of styrene was determined by means of FT-IR and ^{1}H NMR spectroscopy. b) $\overline{M}_{\mathrm{w}}$ and $\overline{M}_{\mathrm{w}}/\overline{M}_{\mathrm{n}}$ were determined by means of GPC in THF.

the use of the GPC method, calibrated with standard polystyrene. The mole fractions of the styrene in the copolymers were determined by means of FT-IR and ^{1}H NMR analysis.

Cabosil M5, with a specified surface area of 220 m^2 g^{-1} for nitrogen adsorption, was used as the adsorbent. The silica had a 2.2 nm^{-2} silanol density on its surface. The silica was essentially nonporous and had an average particle size of 14 nm.

Carbon tetrachloride was doubly distilled fractionally just before use as the solvent.

The experimental techniques for the adsorption of polymers on the silica adsorbents were basically the same as those described in previous papers.[14,22] The polymer solution was added to the silica adsorbent, and the mixture was stirred with a magnetic stirrer. The silica dispersions were separated by the use of a centrifuge. The amounts of adsorption, A (g m^{-2}), of the methyl methacrylate homopolymer and the styrene-methyl methacrylate copolymer were determined by means of ESR spectroscopy by measuring the difference in the polymer concentrations before and after the adsorption. C_e denotes the polymer concentration at the equilibrium state after the adsorption. The peak-to-peak signal amplitude for the polymer concentration in the ESR spectrum was calibrated by simultaneous measurement on an equal volume of the original solution. In the case of the adsorption of the styrene homopolymer, the amount of adsorption was determined by means of UV spectroscopy by measuring the decrease in the intensity at 262 nm after the adsorption. The amount of the saturated adsorption, A_s, was determined by taking the maximum values at $C_e > 1 \times 10^{-3}$ g cm^{-3} in Fig. 1.

The surface coverage (fraction of surface silanol groups occupied), θ_{IR}, was determined by the procedure of Kawaguchi et al. using infrared spectroscopy.[19] The differential IR spectra between the supernatant polymer solution and the silica on which the polymer was adsorbed show two characteristic bands: a band located at 3730 cm^{-1} due to the free silanol groups and another band located at 3520 cm^{-1} due to the interaction between the silanol groups and the polymer. From the mole extinction coefficients (L mol^{-1} cm^{-1}) at 3730 and 3520 cm^{-1}, both the number of the free silanol groups (S_{3730}) and the number of occupied silanol groups (S_{3520}) can be determined, while the surface coverage, θ_{IR}, can be calculated from this equation:

$$\theta_{IR} = S_{3520}/(S_{3520} + S_{3730}). \qquad (1)$$

In this experiment, we used 98.3 and 204 L mol^{-1} cm^{-1} as the mole extinction coefficients of 3730 and 3520 cm^{-1} respectively. All the IR spectra were recorded with a JASCO FT-IR 7000 spectrometer.

The ESR spectra of the adsorbed copolymer were measured in a quartz sample tube which contained ca. 0.5 cm^3 of a silica suspension after it has been sealed under nitrogen, using a JEOL JES FE-3X spectrometer with a X-band microwave, and 100 kHz field modulation.

Results and Discussion

The adsorption isotherms of the methyl methacrylate homopolymer, the styrene homopolymer, and the styrene-methyl methacrylate copolymers on Cabosil M5 against the equilibrium concentration, C_e, in the supernatant solution after the adsorption are illustrated in Figs. 1 (a) and (b). The appearance of the adsorption isotherms was of the high-affinity type. Initially, the isotherms rose steeply with the increase in the value of C_e before they reached a plateau region.

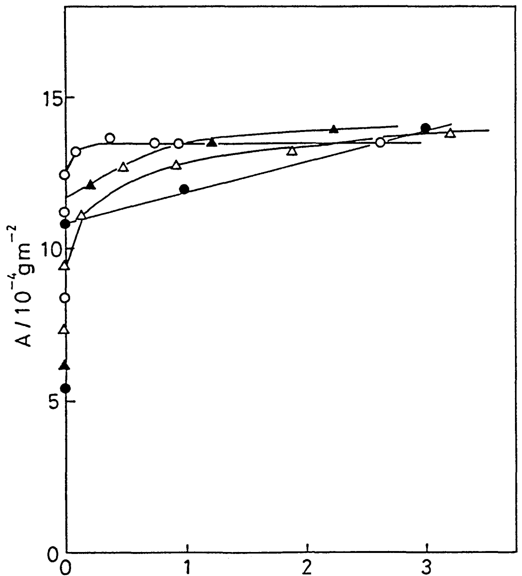

Fig. 1(a). Adsorption isotherms of PMMA and PMCS on Cabosil M5 from CCl$_4$.
○: PMMA, △: PMCS-17, ●: PMCS-67, ▲: PMCS-81.

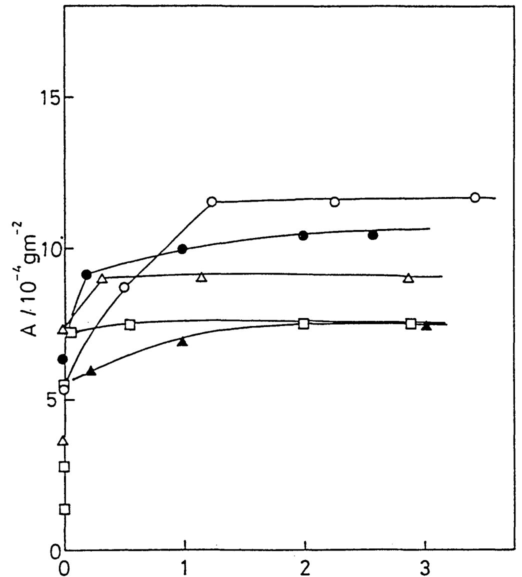

Fig. 1(b). Adsorption isotherms of PMCS and PS on Cabosil M5 from CCl$_4$.
○: PMCS-87, ●: PMCS-91, △: PMCS-96, ▲: PMCS-99, □: PS.

The amounts of saturated adsorption, A_s, are plotted as a function of the mole fraction of styrene in Fig. 2. The A_s values of the methyl methacrylate homopolymer and copolymers are larger than that of the styrene homopolymer. The A_s values of the copoly-

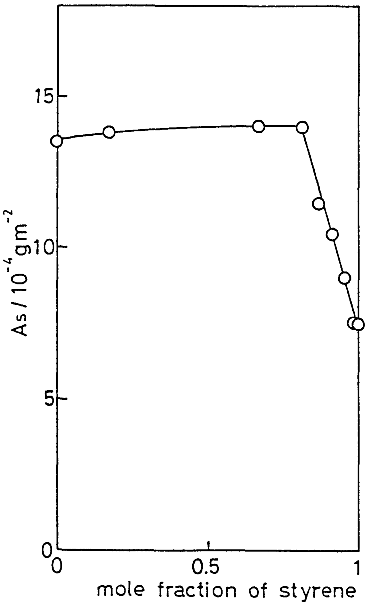

Fig. 2. The saturated adsorption, A_s, of PMMA, PMCS, and PS against the mole fractions of styrene on Cabosil M5 from CCl_4.

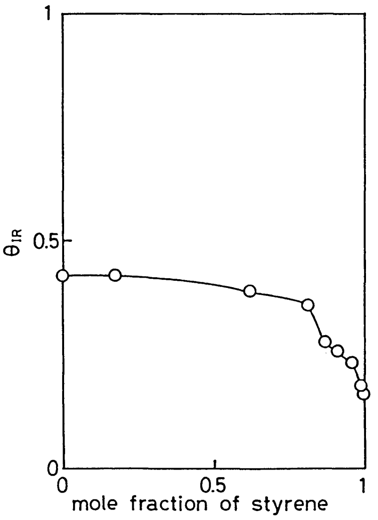

Fig. 3. Plots of the values of θ_{IR} against the mole fractions of styrene on Cabosil M5 from CCl_4.

mers through the mole fractions of styrene of 0.8 increased very slightly with the mole fraction of styrene. The A_s values at the mole fractions of styrene in excess of 0.8 decreased steeply to the level of the styrene homopolymer. This result is consistent with the result of Herd et al.,[21] who reported the amounts of styrene and methyl methacrylate copolymers adsorbed onto the silica surface from a trichloroethylene solution. However, this result has now been resolved in detail. Therefore, we tried to elucidate it on the bases of the surface coverage, θ_{IR}, and the fraction of the attached segment in the polymer, p.

In Fig. 3, the values of θ_{IR} are plotted as a function of the mole fraction of styrene. As may be seen in this figure, the values of θ_{IR} remained constant through the mole fraction of styrene of 0.8 and then decreased steeply at the mole fractions of styrene in excess of 0.8. The A_s values of the copolymers at the mole fractions of styrene in excess of 0.8 decreased, as is shown in Fig. 2. This decrease is caused by the decrease in the values of θ_{IR}, as is shown in Fig. 3; that is, it is impossible for the copolymers at the mole fractions of styrene in excess of 0.8 to bind effectively to all of the silanol groups on the surface sites. As is shown in Fig. 2, the A_s values of the copolymers through the mole fractions of styrene of 0.8 increased very slightly. This phenomenon is due to the increase in the loop segments, because the θ_{IR} values of the copolymers through the mole fractions of styrene of 0.8 were held almost constant.

The analyses of the ESR spectra of the adsorbed copolymers were performed using the procedure described in a previous paper for the methyl methacrylate homopolymer.[14] The ESR line-shape observed from the adsorption system was simulated by the summation of three model spectra: a triplet line with a narrowed width showing high mobility, an intermediately broadened line showing a restricted segment motion, and a powder pattern showing rigid immobilization. The spectrum was normalized by the signal intensity obtained from a second integration of the first-derivative spectrum. The amplitude of each model spectrum was determined by a least-squares method on the multiple regression to fit the summation of the three spectra with the observed spectrum. The model spectra were selected to make the correlation coefficient close to unity between the observed spectrum and the summation of the three model spectra. In the three-component analysis, a close curve-fitting was found in every case.

Fontana and Thomas proposed the symbol "p" as the notation of the ratio of the segments attached on the solid surface to the total segments of the adsorbed polymer.[1] Since the nitroxide-spin radicals are present exclusively in the methyl methacrylate part, it is thought that this value of p expresses the ratio of the adsorbed segments in methyl methacrylate units in the copolymer. Therefore, this value of p will be symbolized by "P_{MMA}" hereafter. "P_{ST}" and "P_{TOT}" represent the values of p for the styrene parts and for the total segments respectively. It should be mentioned that the styrene segments are attached only through the hydrogen bond with the silanol groups on the silica surface. The values of P_{TOT} and P_{ST} can be evaluated by means of numerical calculation from the P_{MMA} value as follows.

From the experimental data of the amounts of the adsorption of the copolymers, A (g m^{-2}), and the compositions of the copolymers, f_{MMA} and f_{ST}, the numbers of adsorbed methyl methacrylate monomeric units per unit of area, n_{MMA}, and the numbers of adsorbed styrene monomeric units per unit of area, n_{ST}, are obtained by means of these equations;

$$n_{\mathrm{MMA}}=A\times f_{\mathrm{MMA}}\times N_{\mathrm{A}}/M_{\mathrm{MMA}}, \qquad (2)$$

$$n_{\mathrm{ST}}=A\times f_{\mathrm{ST}}\times N_{\mathrm{A}}/M_{\mathrm{ST}}, \qquad (3)$$

where N_{A} is Avogadro's number and where M_{MMA} and M_{ST} are the molecular weights of the monomeric units of methyl methacrylate and styrene respectively.

The number of methyl methacrylate units attached on the solid surface per unit of area, N_{MMA}, is given by this equation;

$$N_{\mathrm{MMA}}=n_{\mathrm{MMA}}\times P_{\mathrm{MMA}}. \qquad (4)$$

According to our previous studies,[22] the segments of the methyl methacrylate homopolymer adsorbed on the silica surface can be divided into two groups: one is the segments attached through the hydrogen bond between the carbonyl group of the polymer and the silanol group on the surface site, while the other is the segments attached except for the hydrogen bond. The value of the segment fractions attached through the hydrogen bond in the total train segments of the adsorbed polymer, f_{HB}, is almost constant for each copolymer. We used 0.34 as the value of f_{HB} in this experiment. Consequently, the number of N_{MMA} multiplied by the f_{HB} value is equal to the number of methyl methacrylate units attached through the hydrogen bond.

If we know the occupied area per adsorbed methyl methacrylate monomer on the solid surface, σ_{MMA}, we can calculate the surface area occupied by methyl methacrylate segments attached through the hydrogen bond per unit of surface area; S_{MMA} (m^2).

S_{MMA} is given by this equation;

$$S_{\mathrm{MMA}}=N_{\mathrm{MMA}}\times\sigma_{\mathrm{MMA}}. \qquad (5)$$

Here, we adopted $3.62\times10^{-19}\,\mathrm{m}^2$ as the σ_{MMA} value; it was calculated from the data of the adsorption of the methyl methacrylate homopolymer in Fig. 1 (a).

At the saturated adsorption, the area of the train segments through the hydrogen bond with the surface silanol site should be equal to the value of unit of area multiplied by θ_{IR}. Therefore, the remaining surface area, $\theta_{\mathrm{IR}}-S_{\mathrm{MMA}}$ (m^2), should be equal to the area occupied by styrene units per unit of area, S_{ST}, because the styrene homopolymer adsorbs only through the hydrogen bond between the phenyl group of the polymer and the silanol group on the surface site. If we know the occupied area per adsorbed styrene monomer on the solid surface, σ_{ST}, we can calculate the number of styrene units attached on the solid surface, N_{ST}, by the use of this equation;

$$N_{\mathrm{ST}}=S_{\mathrm{ST}}/\sigma_{\mathrm{ST}}. \qquad (6)$$

Here, we adopted $2.30\times10^{-19}\,\mathrm{m}^2$ as the value of σ_{ST}; it was calculated from the data of the adsorption of the styrene homopolymer in Fig. 1 (b). Consequently, the fraction of the adsorbed units in styrene units in the copolymer, P_{ST}, is given by this equation;

$$P_{\mathrm{ST}}=N_{\mathrm{ST}}/n_{\mathrm{ST}}. \qquad (7)$$

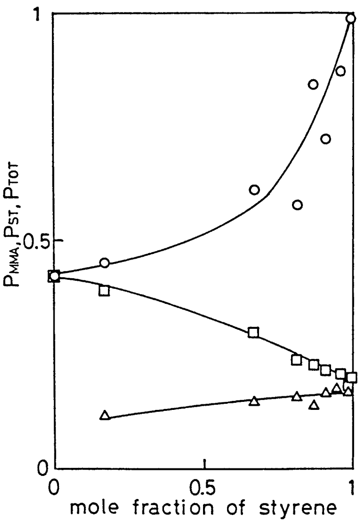

Fig. 4. Plots of the values of P_{MMA}, P_{ST}, and P_{TOT} against the mole fractions of styrene on Carbosil M5 from $\mathrm{CCl_4}$.
○: P_{MMA}, △: P_{ST}, □: P_{TOT}.

In the same way, P_{TOT} is expressed by this equation;

$$P_{\mathrm{TOT}}=(N_{\mathrm{MMA}}+N_{\mathrm{ST}})/(n_{\mathrm{MMA}}+n_{\mathrm{ST}}). \qquad (8)$$

In Fig. 4, the values of P_{MMA}, P_{ST}, and P_{TOT} are plotted as functions of the mole fraction of styrene. As may be seen in this figure, the values of P_{MMA} increased gradually with the increase in the mole fraction of styrene, because the silanol group on the surface interacts more strongly with the carbonyl group of methyl methacrylate than with the phenyl group of styrene. The values of P_{ST} increased gradually to the value of 0.2 with the increase in the mole fraction of styrene. When the styrene content in the copolymer increased, the values of P_{TOT} gradually decreased to the value of 0.2. This value of P_{TOT} for PMCS-99 (shown in Table 1) is almost equal to the value of p for the styrene homopolymer reported in the literature,[3] using the infrared spectroscopy. From the difference in adsorption ability between methyl methacrylate units and styrene units on the silica surface,[2] it can be understood why the values of P_{TOT} decreased with the increase in the mole fractions of styrene in the copolymer. Consequently, we can make the following statement on the basis of the θ_{IR} values in Fig. 3 and the P_{TOT} values in Fig. 4. It is possible for the methyl methacrylate homopolymer to bind the silanol groups on the surface sites more effectively than the styrene homopolymer; therefore, the adsorbed methyl methacrylate homopolymer has a flat conformation, however the adsorbed styrene homopolymer had a loopy conformation. When the styrene content in the copolymer increased, the adsorbed conformations of the copolymers varied gradually from the conformation of the methyl methacrylate homopolymer to that of the styrene homopolymer.

The P_{TOT} values obtained by the present work throughout the range of the mole fraction of styrene are somewhat higher than those reported by Herd et al., who used infrared spectroscopy.[21] Especially, our adsorption data at a high content of methyl methacrylate in the copolymer are remarkably larger than those of Herd et al. However, at a low content of methyl methacrylate, the difference is smaller. This behavior results in the attached methyl methacrylate segments consisting of both the segments attaches through the hydrogen bond and the segments attaches except for the hydrogen bond. The IR method evaluates only the train segments adsorbed through the hydrogen bond by utilizing the frequency shift. The values of p proposed by Herd et al. underestimated because they did not take into account the segments of methyl methacrylate attached except for the hydrogen bond in the copolymer.

The amounts of the saturated adsorption of the copolymers were not proportional to the composition of the monomers, but they began to decrease abruptly at a content of less than 0.2 monomer fraction of the styrene. This behavior is interpreted as being accompanied by changes in the values of θ_{IR} and P_{TOT}. As is shown in Fig. 2, the A_s values of the copolymers through the mole fractions of styrene of 0.8 increased very slightly. This phenomenon is due to the decrease in the value of P_{TOT} (i.e., the increase in the loop segments), because the θ_{IR} values of the copolymers through the mole fractions of styrene of 0.8 held almost constant. The A_s values of the copolymers at the mole fractions of styrene in excess of 0.8 decreased, as is shown in Fig. 2. This was caused by the decrease in the values of θ_{IR}; that is, it is impossible for the copolymers at the mole fractions of styrene in excess of 0.8 to bind effectively to all of the silanol groups on the surface sites.

References

1) B. J. Fontana and J. R. Thomas, *J. Phys. Chem.*, **65**, 480 (1961).
2) C. Thies, *J. Phys. Chem.*, **70**, 3783 (1966).
3) C. V. Linden and R. V. Leemput, *J. Colloid Interface Sci.*, **67**, 48 (1978).
4) M. Kawaguchi, K. Hayakawa, and A. Takahashi, *Polym. J.*, **12**, 265 (1980).
5) K. I. Brebner, R. S. Chahal, and L. E. St-Pierre, *Polymer*, **21**, 533 (1980).
6) K. K. Kalnin'sh, A. N. Krasovskii, B. G. Belen'kii, and G. A. Andreyeva, *Vysokomol. Soedin., Ser. A*, **18**, 2304 (1976).
7) K. K. Fox, I. D. Robb, and R. Smith, *J. Chem. Soc., Faraday Trans. 1*, **70**, 1186 (1974).
8) A. T. Clark, I. D. Robb, and R. Smith, *J. Chem. Soc., Faraday Trans. 1*, **72**, 1489 (1976).
9) I. D. Robb and R. Smith, *Eur. Polym. J.*, **10**, 1005 (1974).
10) I. D. Robb and R. Smith, *Polymer*, **18**, 500 (1977).
11) H. Sakai, T. Fujimori, and Y. Imamura, *Bull. Chem. Soc. Jpn.*, **53**, 3457 (1980).
12) H. Sakai and Y. Imamura, *Bull. Chem. Soc. Jpn.*, **53**, 1749 (1980).
13) H. Sakai, T. Asakura, K. Suzuki, K. Horie, Y. Maeshima, and Y. Imamura, *Bull. Chem. Soc. Jpn.*, **54**, 2180 (1981).
14) H. Sakai and Y. Imamura, *Bull. Chem. Soc. Jpn.*, **60**, 1261 (1987).
15) T. Miyamoto and H. J. Cantow, *Makromol. Chem.*, **162**, 43, (1972).
16) K. G. Barnett, T. Cosgrove, B. Vincent, D. S. Sissons, and M. Cohen-Stuart, *Macromolecules*, **14**, 1018 (1981).
17) T. Cosgrove and K. G. Barnett, *J. Magn. Reson.*, **43**, 15 (1981).
18) M. Kawaguchi and A. Takahashi, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 2069 (1980).
19) M. Kawaguchi, K. Maeda, T. Kato, and A. Takahashi, *Macromolecules*, **17**, 1666 (1984).
20) M. kawaguchi, M. Aoki, and A. Takahashi, *Macromolecules*, **16**, 635 (1983).
21) J. M.Herd, A. J. Hopkins, and G. J. Howard, *J. Polym. Sci., Part C*, **34**, 211 (1971).
22) K. Kobayashi, K. Araki, and Y. Imamura, *Bull. Chem. Soc. Jpn.*, **62**, 3421 (1989).