Free-Radical Cross-Linking Polymerization of Diallyl Terephthalate in the Presence of Microgel-like Poly(allyl methacrylate) Microspheres

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ABSTRACT: The cross-linking polymerization of diallyl terephthalate (DAT) was explored in detail in the presence of microgel-like poly(allyl methacrylate) (PAMA microsphere) as an extension of our continuing studies concerned with the elucidation of cross-linking reaction mechanism and the control of network formation in the free-radical cross-linking polymerization of multivinyl compounds. Thus, PAMA microspheres were prepared by the emulsion polymerization of AMA as reactive cross-linked polymer microspheres having abundant pendant allyl groups. The polymerization of DAT in the presence of microsphere was conducted in bulk using BPO as initiator at 80 °C. The gel-point conversion became higher with an increase in the feed amount of microsphere. No gel effect was observed. Variation of RI-monitored SEC curves with conversion suggested the copolymerization of the pendant allyl groups present on the surface of microsphere with DAT; this was also supported by light scattering and ^{1}H NMR spectroscopy. The swelling ratios of the gels in the presence of microsphere were not high even just beyond the gel points, suggesting a preferential incorporation of microsphere into the gel. These are discussed mechanistically.

Introduction

For a long time, the network formation mechanism and the fine structure of cured resins have been controversial problems because of the complexity of the reactions involved and the insolubility of the products. In particular, the free-radical cross-linking polymerization and copolymerization of multivinyl compounds are the problem cases. Since the pioneering theoretical and experimental works of Flory and Stockmayer[1,2] and Walling,[3] many papers have been published, especially on ethylene dimethacrylate,[3−18] divinylbenzene,[19−28] and diallyl dicarboxylates[18,29−34] as typical divinyl compounds. Dusek[35] reviewed the network formation by chain cross-linking (co)polymerization, especially emphasizing the importance of cyclization leading to the formation of microgel-like particles. Recently, Dotson et al.[17,36] tested the predictions of classical Flory−Stockmayer's theory for the establishment of a network by free-radical cross-linking polymerization, and Zhu et al.[37] summarized their studies on the elucidation of the cross-linking mechanism and kinetics, the characterization of network microstructures, and the development of kinetic gelation models; both research groups have dealt with the copolymerization of methyl methacrylate with ethylene dimethacrylate, a historical copolymerization system which was first investigated in 1945 by Walling.[3] Styrene−divinylbenzene copolymers have also been under investigation for more than 50 years because of their commercial importance as the resins for SEC and ion exchangers. Apparently, the interpretation of studies of the free-radical cross-linking polymerization and copolymerization of multivinyl compounds have been complicated by the great number of research groups and gelling systems, frequently providing scattered data, although several factors, including cyclization, reduced reactivity of pendant vinyl groups of the prepolymer, intramolecular cross-linking, microgelation, and thermodynamic excluded-volume effect, have been proposed in order to interpret the observed discrepancy from theory for each polymerization system.[38]

In this article, we will discuss further the cross-linking polymerization mechanism of multivinyl compounds in order to explore the significance of microgelation in more detail as one of the most important factors for a full understanding of network formation processes. In 1935, Staudinger et al.[39] reported the formation of styrene−divinylbenzene microgel as the first example of microgelation. Thereafter, numerous reports on microgel formation were published in the homopolymerizations of multivinyl compounds and their copolymerizations with monovinyl monomers.[6−8,11,24] On the contrary, in the bulk polymerization of diallyl phthalate no microgelation was observed[40] although in the polymerization of multiallyl compounds the primary chain length was quite short compared to common vinyl polymerizations. In addition, no microgelation occurred in the monovinyl−divinyl copolymerizations with only a small amount of divinyl monomer.[26] Thus, a detailed study on microgelation, especially up to the actual gel-point conversion, is required because microgelation leads not only to delayed gelation but also to the inhomogeneity of network structures of three-dimensional polymers as closely related to their properties. In this connection, we pursued a critical condition under which microgelation could occur up to the gel-point conversion in the monovinyl−divinyl copolymerizations by investigating the conversion dependencies of the solution properties of resulting prepolymers by light scattering and viscosity measurements.[41,42] In addition, the process of microgel formation was followed directly by performing a light scattering measurement of the polymerization solution without isolating the resulting prepolymer.[43,44] Certainly, the microgelation in free-radical monovinyl−divinyl copolymerizations depended on the polymerization conditions, including primary chain length, divinyl content, dilution, solvent employed, and so on.

Here we deal with the free-radical cross-linking polymerization of diallyl terephthalate (DAT) in the presence of microgel-like poly(allyl methacrylate) microsphere (PAMA microsphere) because in the polym-

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erization of DAT no microgelation occurred up to the gel point[45] and PAMA microspheres obtained as reactive cross-linked polymer microspheres or microgel-like polymers with abundant pendant allyl groups[46] would be models of microgels or pseudo-microgels. In addition, our research interest is in clarifying the reactivity of cross-linked polymer microspheres, especially in connection with our continuing studies aimed at the elucidation of the cross-linking reaction mechanism and the control of network formation in order to molecular design vinyl-type network polymers with high performance and high functionality.

Experimental Section

DAT and allyl benzoate (ABz), supplied by Daiso Co., Ltd., as monomers were purified by vacuum distillation under nitrogen. Benzoyl peroxide (BPO) as initiator was purified by conventional methods.

Polymerization was carried out as described previously.[47] After a predetermined time of reaction, the polymer was precipitated by pouring the reaction mixture into a large excess of chilled methanol containing a small amount of hydroquinone as inhibitor. The purification of the polymer was done by reprecipitation from a tetrahydrofuran (THF)−precipitant system. The gel fraction of polymer at conversions beyond the gel point was separated by extracting the sol fraction with THF.

Fractionation of the copolymer was carried out by using THF−methanol system; thus, methanol was added dropwise into ca. 2% (w/v) of THF solution of the polymer sample until the solution became turbid. The turbid solution was then warmed to dissolve the precipitated polymer, and subsequently, the solution was gradually cooled to obtain a high-molecular-weight fraction of the polymer. These processes were repeated for a supernatant solution to obtain another fraction containing a lower-molecular-weight polymer.

The weight-average molecular weight, $\bar{M}_w$, and molecular-weight distribution (MWD) were measured by size-exclusion chromatography (SEC) using a dual-detector system, set in the direction of flow, consisting of a multiangle laser light scattering (MALLS) device and a differential refractometer in sequence. SEC-MALLS measurements were carried out at 40 °C in THF using a Shodex GPC KF-806L × 5 columns, at polymer concentrations 0.1−0.5% (w/v) and flow rate 1 mL/min. The MALLS device was a DAWN model F (Wyatt Technology Corp.) where the laser beam, of wavelength 632.8 nm, was focused on a 67 μL flow cell. The resulting polymers were also subjected to light scattering measurement in order to estimate $\bar{M}_w$, rms radii of gyration $\langle S^2\rangle_z^{1/2}$, and second virial coefficients A_2. The measurements were carried out in THF at 30 °C with an Otsuka Electronics DLS-700 dynamic light scattering spectrophotometer over the angular range between 30° and 150°, using unpolarized light of wavelength 632.8 nm.

Results and Discussion

Preparation of PAMA Microspheres. Two types of microgel-like PAMA microspheres, **I** and **II**, were prepared according to our previous work[46] as follows: Emulsion polymerizations of AMA were carried out in an ampule at 50 °C according to the following recipe: AMA, 10 g; water, 90 g; sodium dodecyl sulfate, 1.3 g; and potassium peroxodisulfate, 0.03 g. Ultrasonification was applied to provide the fine monomer emulsion. After a predetermined time of reaction, the polymer obtained was precipitated by pouring into a large amount of methanol. The purification of the polymer obtained was done by repeated reprecipitation from a THF−methanol system. Thus, PAMA microspheres, **I** and **II**, were prepared as the polymers obtained at ca. 80 and 15% conversions, respectively, and characterized as shown in Table 1.

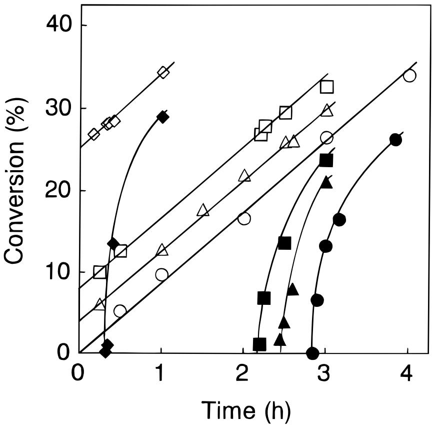

Figure 1. Conversion−time curves for the bulk copolymerizations of DAT in the absence (○, ●) and presence of (△, ▲) 4.7, (□, ■) 9.1, and (◇, ◆) 25.1 wt % of **I** using 0.05 mol dm^{-3} of BPO at 80 °C. Open and full symbols correspond to total and gel polymers, respectively.

Table 1. Preparation of PAMA Microspheres

PAMA microsphere	I	II
conversion (%)	80	15
noncyclic unit (%)	89	94
$\bar{M}_w \times 10^{-7}$	7.7	2.7
$\langle S^2\rangle_z^{1/2} \times 10^{-2}$ (Å)	2.5	2.6
$A_2 \times 10^7$ (mol cm^3 g^{-2})	2.2	14
$[\eta]$ (dL g^{-1})	0.10	0.41

Addition Effect of PAMA Microsphere on the Rate of Polymerization and Gelation in the Bulk Polymerization of DAT. Figure 1 shows the conversion−time curves for the polymerization of DAT in the absence and presence of 4.7, 9.1, and 25.1 wt % of **I** using 0.05 mol dm^{-3} of BPO at 80 °C. Here the conversion was calculated as follows:

$$\text{conversion (\%)} = \{(\text{PAMA} + \text{poly(DAT)})/(\text{PAMA} + \text{DAT})\} \times 100$$

where the PAMA microsphere is assumed to be a pseudo-microgel of poly(DAT).

No addition effect of **I** was observed on the rate of polymerization of DAT although the viscosities of the polymerization solutions increased with an increase in the feed amount of PAMA microsphere. Moreover, no Trommsdorff effect[48] was observed even beyond the gel point. This may be due to chain transfer from the growing polymer radical to the monomer (called degradative chain transfer[49]), which is very significant in the polymerization of allyl compounds; i.e., the allylic monomer radical plays an important role in the termination reaction.

The percentages of gel polymer were also plotted in Figure 1 along with the conversion−time curves. The gel point was determined by extrapolating the gel formation curve to zero percentage. Thus, the conversion at which gel starts to form, i.e., the gel point, was estimated to be 24.7, 26.5, 27.5, and 28.2% for the bulk polymerizations of DAT in the absence and presence of 4.7, 9.1, and 25.1 wt % of **I**, respectively. Apparently, gelation was delayed with an increase in the amount of **I**, in which the PAMA microsphere is assumed to act as a reactive, microgel-like prepolymer.

On the other hand, the corrected gel-point conversion [{poly(DAT)/DAT} × 100] is plotted against the amount of **I** in Figure 2, in which the PAMA microsphere is

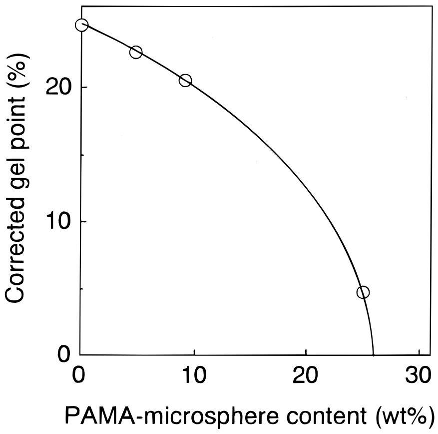

Figure 2. Dependence of corrected gel point on PAMA microsphere (**I**) content (see Figure 1). Corrected gel point is calculated as the PAMA microsphere is assumed to be an inactive polymer for the cross-linking polymerization of DAT.

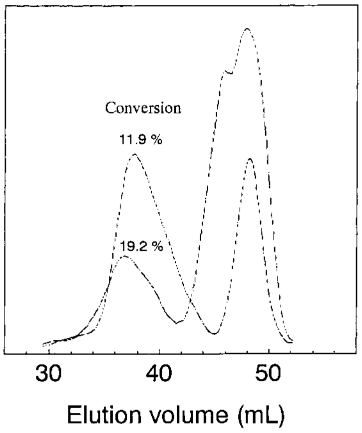

Figure 3. Variation of RI-monitored SEC curves with conversion for the polymerization of DAT in the presence of 9.1 wt % of **I** (see Figure 1).

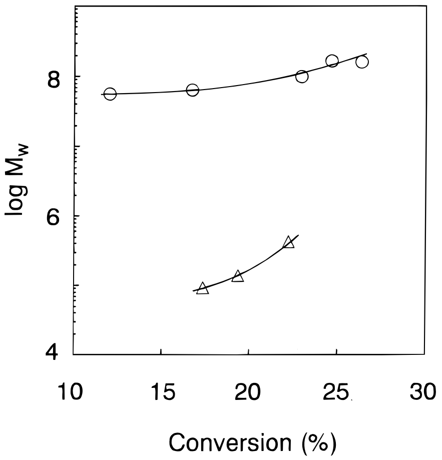

Figure 4. Dependence of $\bar{M}_\mathrm{w}$ on conversion for the polymerization of DAT in the absence (△) and presence of (○) 9.1 wt % of **I** (see Figure 1).

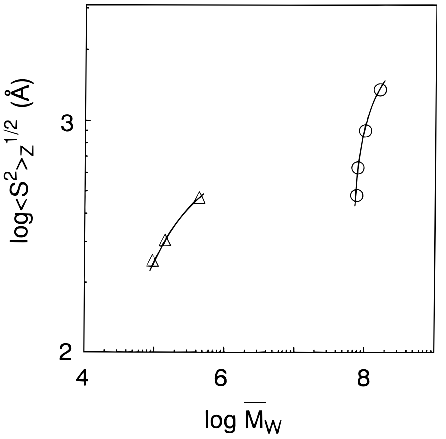

Figure 5. Double-logarithmic plots of $\langle S^2\rangle_z^{1/2}$ versus $\bar{M}_\mathrm{w}$ (see Figure 4).

supposed to be an inactive or dead polymer for the cross-linking polymerization of DAT. Clearly, gelation appeared to be promoted. Then, the correlation curve would be extrapolated to ca. 26% conversion, suggesting that in the presence of 26 wt % of **I** gelation would occur simultaneously at the start of polymerization. These results clearly demonstrate that the PAMA microsphere is active for promoting gelation in the polymerization of DAT, although the copolymerizability of the pendant allyl groups belonging to the PAMA microsphere with DAT may be quite reduced since only the allyl groups present on the surface of the microsphere are responsible for the cross-linking reaction. Moreover, the molecular structure of the PAMA microsphere is not always similar to that of DAT, probably reducing the compatibility of the microsphere with growing DAT radical.

SEC-MALLS Measurement of Resulting Polymers. Figure 3 shows the variation of RI-monitored SEC curves of resulting polymers with conversion for the bulk polymerization of DAT in the presence of 9.1 wt % of **I**. Clearly, two peaks were observed at 11.9% conversion, which corresponds to an early stage of polymerization; this suggests that the polymerization of DAT proceeded mainly in the free space among microspheres. Then, at 19.2% conversion, the peak of the SEC curve at a low elution volume, corresponding to the PAMA microsphere, shifted toward a lower elution volume or higher-molecular-weight side; this would be ascribed to the copolymerization of microsphere with DAT. Concurrently, the homopolymerization of DAT in the free space accompanied by an enhanced cross-linking reaction with conversion results in the broadened SEC curve toward a higher-molecular-weight side.

Characterization of Resulting Polymers by Light Scattering. The resulting polymers obtained in the polymerization of DAT in the presence of 9.1 wt % of **I** were characterized by light scattering: Figure 4 shows the dependence of $\bar{M}_\mathrm{w}$ on conversion; the molecular weight of resulting polymers increased slightly with an increase in conversion. Figure 5 shows the double-logarithmic plots of $\langle S^2\rangle_z^{1/2}$ versus $\bar{M}_\mathrm{w}$. The higher radius of gyration was observed with conversion; the increased $\langle S^2\rangle_z^{1/2}$ value suggests the growth of the PAMA microsphere through the copolymerization of the allyl groups present on the surface of microsphere with DAT. Here it should be noted that the number of allyl groups present on the surface of the microsphere would be increased remarkably by the copolymerization with DAT since the cyclopolymerizability of DAT is quite low.[50] Thus, the molecular size of the highly shrunken, original PAMA-microsphere (**I**) in THF would be increased remarkably by the copolymerization with DAT at the surface of the microsphere as the DAT polymer chains incorporated onto the microsphere surface would constitute the shell part of the microsphere swollen by THF.

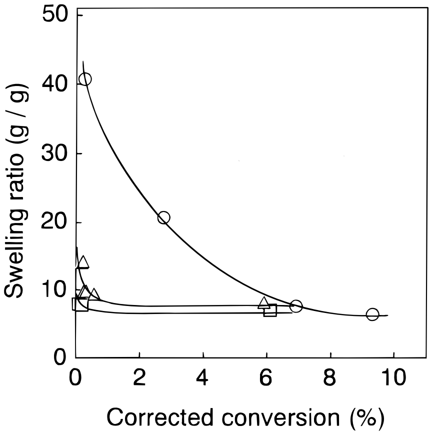

Figure 6. Decrease in swelling ratio of resulting gel in THF with the progress of polymerization beyond the gel point for the polymerizations of DAT in the absence (○) and presence of (△) 9.1 and (□) 25.1 wt % of **I** (see Figure 1). Conversion in the abscissa is corrected such as the corresponding gel point is 0% of conversion.

Swelling Ratio of Resulting Gels. The swelling ratios of resulting gels for the polymerization of DAT in the absence and presence of 9.1 and 25.1 wt % of **I** were plotted against conversion as shown in Figure 6; although the swelling ratio of the resulting gel just beyond the gel point is quite high for the homopolymerization of DAT as a reflection of no microgelation up to the gel point,[45] the swelling ratios of the gels obtained in the presence of **I** are not high even just beyond the gel points. This may suggest that the PAMA microsphere is preferentially incorporated into the gel.

Characterization of Fractionated Polymers by ^{1}H NMR Spectroscopy. The results obtained above demonstrate strongly the occurrence of the copolymerization of the PAMA microsphere with DAT at the surface; this was then checked by ^{1}H NMR spectroscopy. Thus, the polymer obtained at 11.3% conversion in the cross-linking polymerization of DAT in the presence of 9.1 wt % of **I** was fractionated, and then the highest-molecular-weight fraction was subjected to ^{1}H NMR measurement. Here the fractionation efficiency for the complete separation of DAT homopolymer from the resulting prepolymer was checked for the mixture of **I** and poly(DAT). In the ^{1}H NMR spectrum of the highest-molecular-weight fraction of resulting prepolymer, the absorption peaks corresponding to the protons of DAT units incorporated into the PAMA microsphere were detected clearly, supporting the copolymerization of microsphere with DAT.

Mechanistic Discussion. Now, we can discuss the cross-linking polymerization mechanism of DAT in the presence of the PAMA microsphere by considering the results obtained above. In the presence of a small amount of PAMA microsphere, the main locus of DAT polymerization would be in the free space among microspheres. In this connection, it is important to recall that, in the polymerization of a multiallyl compound such as DAT, only oligomer is obtained at an early stage of polymerization, and the resulting prepolymer would grow gradually with conversion through the intermolecular cross-linking of allyl groups of prepolymer with growing polymer radical to form a branched polymer, the extent of branching of the resulting DAT homopolymer being higher with the progress of polymerization. Concurrently, a minor portion of DAT polymerization would proceed at the surface of the microsphere through the copolymerization with the allyl groups present on the surface of the PAMA microsphere; this would lead not only to the growth of microsphere but also the remarkable increase in the number of allyl groups on the surface of the microsphere with conversion.

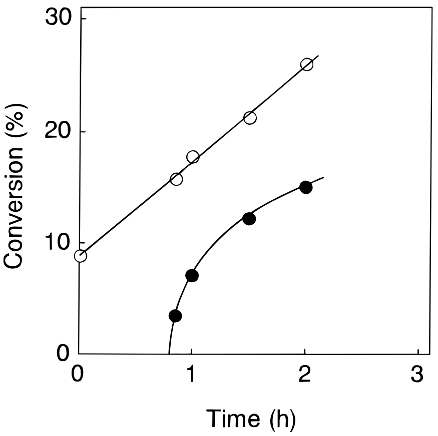

Figure 7. Conversion−time curve for the bulk copolymerization of DAT in the presence of 8.8 wt % of **II** using 0.05 mol dm^{-3} of BPO at 80 °C. Open and full symbols correspond to total and gel polymers, respectively.

Thus, the probability of the occurrence of the reaction between the microsphere and DAT branched prepolymer formed in the free space among microspheres should increase with the progress of polymerization, eventually leading to a formation of a macrogel as a result of bridging PAMA microspheres. This was clearly reflected in Figures 2 and 6. This kind of bridging reaction would be enhanced with an increase in the feed amount of PAMA microsphere to the cross-linking polymerization of DAT, leading to the promoted gelation. Here it should be noted that the direct bridging reaction between allyl groups of PAMA microspheres is essentially neglected because of the suppressed diffusion of microsphere as compared with DAT; however, this could become rather contributive to the gelation with increased concentration of microsphere.

As an extension of the above discussion, we may easily expect the promoted gelation when we employ **II** in place of **I**, since PAMA microsphere **II** having a higher swellability for DAT monomer would have a higher copolymerizability toward the DAT growing radical. Figure 7 shows the conversion−time curve for the cross-linking polymerization of DAT in the presence of 8.8 wt % of **II** along with the gel formation curve; the gel point was estimated to be 17.2% as compared to 27.5% for the polymerization in the presence of 9.1 wt % of **I**, the gelation being promoted obviously in conformity with our expectation.

Finally, it may be noteworthy to treat the copolymerization with ABz in place of DAT because ABz is a monoene counterpart of DAT, and the copolymerization of allyl groups present on the surface of the PAMA microsphere with ABz would reduce the number of allyl groups at the surface of the microsphere responsible for cross-linking, leading to the reduced cross-linking reactivity of the microsphere with conversion as completely opposed to the case of the copolymerization with DAT. Then, PAMA microsphere **I** was copolymerized with ABz under the same polymerization conditions mentioned above. Figure 8 shows the results obtained; for the copolymerization in the presence of 9.1 wt % of **I** no gelation was observed even at 43.6% conversion as

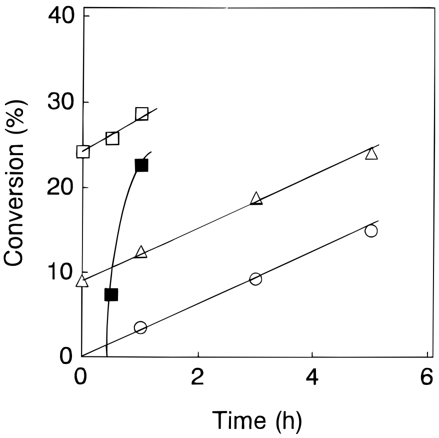

Figure 8. Conversion−time curves for the bulk copolymerizations of ABz in the absence (○) and presence of (△) 9.1 and (□, ■) 24.8 wt % of **I** using 0.05 mol dm^{-3} of BPO at 80 °C. Open and full symbols correspond to total and gel polymers, respectively.

compared to the case of DAT in which gelation occurred at 27.5%. On the contrary, in the presence of 24.8 wt % of **I**, very close to the extrapolated value of ca. 26% in Figure 2, in which the PAMA microsphere can easily collide each other, the gelation was observed at 26.0% conversion, although for DAT polymerization in the presence of 25.1 wt %, gelation was observed at 28.2% conversion. The difference between ABz and DAT polymerizations may be ascribed to a steric effect on the reaction of allyl groups present on the surface of microsphere with ABz or DAT growing polymer radical because the reacting site of DAT growing radical would be sterically much crowded compared to the case of ABz, thus having a reduced reactivity toward the allyl group belonging to microsphere as a sterically hindered monomer.

Conclusion

We have discussed in detail the cross-linking polymerization of DAT in the presence of PAMA microsphere or pseudo-microgel as reactive cross-linked polymer microsphere or microgel-like polymer with abundant pendant allyl groups in order to clarify the polymerization behavior of microgel in the free-radical cross-linking polymerization of multivinyl compounds and, moreover, the reactivity of cross-linked polymer microspheres. In the presence of a small amount of microsphere the wide, free space among microspheres will be a main polymerization locus of DAT, and concurrently, a small portion of DAT will copolymerize with the allyl groups present on the surface of microsphere. With the progress of polymerization, the structure of the resulting prepolymer in the free space would grow to be a more branched form through cross-linking reaction, whereas the number of pendant allyl groups on the surface of microsphere, responsible for cross-linking, would increase remarkably through the copolymerization with DAT. Eventually, the polymerization system would reach the critical point at which gelation occurs as a result of the intermolecular cross-linking reaction between microspheres, although the gelation would be promoted with an increase in the feed amount of PAMA microsphere.

References and Notes

(1) Flory, P. J. *J. Am. Chem. Soc.* **1941**, *63*, 3083, 3091, 3096.
(2) (a) Stockmayer, W. H. *J. Chem. Phys.* **1943**, *11*, 45. (b) Stockmayer, W. H. *J. Chem. Phys.* **1944**, *12*, 125.
(3) Walling, C. *J. Am. Chem. Soc.* **1945**, *67*, 441.
(4) Gordon, M.; Roe, R. J. *J. Polym. Sci.* **1956**, *21*, 27, 39, 75.
(5) Jokl, J.; Kopecek, J.; Lim, D. *J. Polym. Sci., Part A-1* **1968**, *6*, 3041.
(6) Horie, K.; Otagawa, A.; Muraoka, M.; Mita, I. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 445.
(7) Galina, H.; Dusek, K.; Tuzar, Z.; Bohdanecky, M.; Stokr, J. *Eur. Polym. J.* **1980**, *16*, 1043.
(8) Spevacek, J.; Dusek, K. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 2027.
(9) Dusek, K.; Spevacek, J. *Polymer* **1980**, *21*, 750.
(10) Whitney, R. S.; Burchard, W. *Makromol. Chem.* **1980**, *181*, 869.
(11) Shah, A. C.; Parsons, I. W.; Haward, R. N. *Polymer* **1980**, *21*, 825.
(12) Hild, G.; Okasha, R. *Makromol. Chem.* **1985**, *186*, 389.
(13) Matsumoto, A.; Matsuo, H.; Oiwa, M. *Makromol. Chem. Rapid Commun.* **1987**, *8*, 373.
(14) Landin, D. T.; Macosko, C. W. *Macromolecules* **1988**, *21*, 846.
(15) Zhu, S.; Hamielec, A. E. *Macromolecules* **1989**, *22*, 3093.
(16) Zhu, S.; Tian, Y.; Hamielec, A. E. *Polymer* **1990**, *31*, 154.
(17) Dotson, N. A.; Diekmann, T.; Macosko, C. W.; Tirrell, M. *Macromolecules* **1992**, *25*, 4490.
(18) Matsumoto, A. *Makromol. Chem., Macromol. Symp.* **1993**, *76*, 33.
(19) Storey, B. T. *J. Polym. Sci.* **1965**, *A3*, 265.
(20) Malinsky, J.; Klaban, J.; Dusek, K. *J. Macromol. Sci., Chem.* **1971**, *A5*, 1071.
(21) Soper, B.; Haward, R. N.; White, E. F. T. *J. Polym. Sci., Part A-1* **1972**, *10*, 2545.
(22) Kwant, P. W. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 1331.
(23) Okasha, R.; Hild, G.; Rempp, P. *Eur. Polym. J.* **1979**, *15*, 975.
(24) Leicht, R.; Fuhrmann, J. *Polym. Bull.* **1981**, *4*, 141.
(25) Fink, J. K. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *18*, 195.
(26) Hild, G.; Rempp, P. *Pure Appl. Chem.* **1981**, *53*, 1541.
(27) Hild, G.; Okasha, R. *Makromol. Chem.* **1985**, *186*, 93.
(28) Antonietti, M.; Rosennauer, C. *Macromolecules* **1991**, *24*, 3434.
(29) Simpson, W.; Holt, T.; Zetie, R. J. *J. Polym. Sci.* **1953**, *10*, 489.
(30) Gordon, M. *J. Chem. Phys.* **1954**, *22*, 610.
(31) Simpson, W.; Holt, T. *J. Polym. Sci.* **1955**, *18*, 335.
(32) Oiwa, M.; Ogata, Y. *Nippon Kagaku Zasshi* **1958**, *79*, 1506.
(33) Matsumoto, A.; Yokoyama, S.; Khono, T.; Oiwa, M. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 127.
(34) Matsumoto, A.; Ogasawara, Y.; Nishikawa, S.; Aso, T.; Oiwa, M. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 839.
(35) Dusek, K. In *Developments in Polymerisation-3*; Applied Science Publishers: Oxford, 1982; p 143.
(36) Dotson, N. A.; Macosko, C. W.; Tirrell, M. In *Synthesis, Characterization, and Theory of Polymeric Networks and Gels;* Plenum Press: New York, 1992; p 319.
(37) Zhu, S.; Hamielec, A. E. *Macromol. Chem., Macromol. Symp.* **1993**, *69*, 247.
(38) Matsumoto, A. *Adv. Polym. Sci.* **1995**, *123*, 41.
(39) Staudinger, H.; Husemann, E. *Chem. Ber.* **1935**, *68*, 1618.
(40) Matsumoto, A.; Nakajima, H.; Oiwa, M. *Netsukokasei Jushi (J. Thermoset. Plast. Jpn.)* **1988**, *9*, 141.
(41) Matsumoto, A.; Yamashita, Y.; Oiwa, M. *Netsukokasei Jushi (J. Thermoset. Plast. Jpn.)* **1991**, *12*, 135.
(42) Matsumoto, A.; Yamashita, Y.; Oiwa, M. *Netsukokasei Jushi (J. Thermoset. Plast. Jpn.)* **1993**, *14*, 139.
(43) Matsumoto, A.; Takahashi, S.; Oiwa, M. *ACS Polym. Prepr.* **1990**, *31*, 149.
(44) Matsumoto, A.; Takahashi, S.; Morita, T. *J. Net. Polym. Jpn.* **1996**, *17*, 139.
(45) Matsumoto, A.; Mitomi, D.; Aota, H.; Ikeda, J. *Polymer* **2000**, *41*, 1321.
(46) Matsumoto, A.; Kodama, K.; Mori, Y.; Aota, H. *J. Macromol. Sci., Pure Appl. Chem.* **1998**, *A35*, 1459.
(47) Matsumoto, A.; Oiwa, M. *J. Polym. Sci., Part A-1* **1970**, *8*, 751.
(48) Trommsdorff, E.; Kohle, H.; Lagally, P. *Makromol. Chem.* **1948**, *1*, 169.
(49) Bartlett, P. D.; Altschul, R. *J. Am. Chem. Soc.* **1945**, *67*, 816.
(50) Matsumoto, A.; Oiwa, M. *Nippon Kagaku Zasshi* **1969**, *90*, 1278.

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