

NOTES

Copolymerization of Poly(allyl methacrylate) Crosslinked Polymer Microspheres with Allyl Benzoate

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(Received April 2, 2001; Accepted June 11, 2001)

KEY WORDS Allyl Methacrylate / Allyl Benzoate / Microsphere / Crosslinking / Gelation / Microgel /

In the preceding article,¹ we have discussed in detail the crosslinking polymerization of diallyl terephthalate (DAT) in the presence of microgel-like poly(allyl methacrylate) microsphere (PAMA microsphere) with abundant pendant allyl groups in order to clarify the polymerization behavior of microgel in the free-radical crosslinking polymerization of multivinyl compounds² and, moreover, the reactivity of crosslinked polymer microspheres. In the presence of a small amount of microsphere the wide, free space among microspheres is a main polymerization locus of DAT and, concurrently, a small portion of DAT copolymerizes with the allyl groups present on the surface of microsphere. With the progress of polymerization, the structure of resulting prepolymer in the free space grows to be a more branched form through crosslinking reaction, whereas the number of pendant allyl groups on the surface of microsphere, responsible for crosslinking, increases remarkably through the copolymerization with DAT. Eventually, the polymerization system reaches the critical point at which gelation occurs as a result of the intermolecular crosslinking reaction between microspheres. Thus, the gelation is promoted with an increase in the feed amount of PAMA microsphere. In this connection, the copolymerization with allyl benzoate (ABz) is treated in place of DAT. Because ABz is a monoene counterpart of DAT, the copolymerization of allyl groups present on the surface of PAMA microsphere with ABz reduces the number of allyl groups at the surface of microsphere responsible for crosslinking, leading to the reduced crosslinking reactivity of microsphere with the progress of polymerization as completely opposed to the case of the copolymerization with DAT. The results obtained are in a good agreement with the above mechanistic discussion.

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In the present article, the latter copolymerization with ABz was extended to the further discussion of the characteristic polymerization behavior of PAMA microsphere as reactive crosslinked polymer microsphere or pseudo-microgel. The clarification of polymerization characteristics of microgel is considered to be significant because microgelation leads not only to delayed gelation,^{3–16} but also to the inhomogeneity of network structures of three-dimensional crosslinked polymers as closely related to their properties.^{17–26}

EXPERIMENTAL

ABz, supplied by Daiso Co., Ltd., as monomer was purified by vacuum distillation under nitrogen. Benzoyl peroxide (BPO) was purified by repeated precipitation from a chloroform solution with methanol.

Copolymerization was carried out as described previously.²⁷ After a predetermined time of reaction, the copolymer was precipitated by pouring the reaction mixture into a large excess of cooled hexane containing a small amount of *t*-butylcatechol as inhibitor. The purification of the soluble copolymer or precopolymer obtained at conversions up to the gel point was done by reprecipitation from a tetrahydrofuran (THF)-precipitant system. The gel fraction of the copolymer obtained at conversions beyond the gel point was separated by extracting the sol fraction with THF.

Fractionation of the resulting polymer 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 up to dissolve the precipitated polymer, and subsequently, the solution was gradually cooled to obtain a high-molecular-weight fraction of the polymer, *i.e.*,

PAMA/ABz copolymer. Then, ABz homopolymer was recovered from a supernatant solution by evaporating solvents.

The weight-average molecular weight \overline{M}_w , the r.m.s. radii of gyration $\langle s^2 \rangle_z^{1/2}$, and the second virial coefficients A_2 of the resulting polymers were measured by light scattering. 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 30–150°, using unpolarized light of wavelength 632.8 nm. The intrinsic viscosity $[\eta]$ was determined with Ubbelohde viscometer in THF at 30°C.

RESULTS AND DISCUSSION

Microgel-like PAMA microspheres, **I–IV**, were prepared according to our previous work.²⁸ That is, PAMA microspheres **I**, **II**, and **III** having different swellabilities for ABz were prepared as the polymers at *ca.* 80, 51, and 15% conversions, respectively, by the emulsion polymerization of AMA under the same polymerization conditions. Besides, PAMA microsphere **IV** having smaller particle size than **I** was prepared similarly, except that five-fold amount of emulsifier was employed. All PAMA microspheres are characterized as shown in Table I.

Here it is worthy to note that in the preceding article,¹ PAMA microsphere **I** is copolymerized with ABz as compared to its copolymerization with DAT. Thus, for the copolymerization of ABz with 9.1 wt% of **I** no gelation is observed even at 43.6% conversion, while gelation occurs at 27.5% in the case of DAT. On the contrary, for the copolymerization with 24.8 wt% of **I**, in which the PAMA microsphere can easily collide each other, the gelation is observed at 26.0% conversion. These results are interpreted as follows: In the presence of PAMA microspheres, the main locus of ABz polymerization would be in the free space among

Table I. Preparation of PAMA Microspheres

PAMA microsphere	I ^a	II ^a	III ^a	IV ^b
Conversion/%	80	51	15	82
Noncyclic unit/%	89	91	94	91
$\overline{M}_w \times 10^{-7}$	7.7	7.2	2.7	7.2
$\langle s^2 \rangle_z^{1/2} \times 10^{-2}/\text{Å}$	2.5	2.5	2.6	2.9
$A_2 \times 10^7/\text{mol cm}^3 \text{ g}^{-2}$	2.2	9.7	14	3.6
$[\eta]/\text{dL g}^{-1}$	0.10	0.18	0.41	0.14
\overline{D}/nm	87	62	43	56

^aEmulsion polymerization of AMA was carried out in an ampoule at 50°C according to the following recipe: AMA, 10 g; water, 90 g; sodium dodecyl sulfate (SDS), 1.3 g; and potassium peroxodisulfate, 0.03 g. ^bFive-fold amount of SDS as an emulsifier was employed to prepare a smaller sized microsphere.

microspheres, and concurrently, a small portion of ABz will copolymerize with the allyl groups present on the surface of microsphere, reducing the number of allyl groups at the surface of the microsphere responsible for crosslinking. Thus, the gelation is observed only under the polymerization condition in which the PAMA microspheres collide each other.

In the present article, the above-mentioned, interesting copolymerization behavior of PAMA microsphere was explored in more detail. First, we pursued the critical polymerization condition under which the gelation would be observed. Figure 1 shows the conversion-time curves for the copolymerizations of ABz with 18 and 21 wt% of **I** using 0.05 mol L⁻¹ of BPO at 80°C. Here the conversion was calculated as follows:

$$\text{Conversion}(\%) = \{[\text{PAMA} + \text{poly}(\text{ABz}) + \text{poly}(\text{PAMA} - \text{co} - \text{ABz})]/(\text{PAMA} + \text{ABz})\} \times 100$$

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 34.5% for the copolymerization with 21 wt% of **I**, although no gelation occurred for 18 wt% of **I** even when the copolymerization proceeded until 82% conversion. The critical amount of **I** required for gelation would be roughly estimated to be *ca.* 20 wt% since the gelation was not observed even for the copolymerization of ABz with 19 wt% of **I**.

As an extension of the above discussion to pursue the critical polymerization condition leading to gelation, we tried to explore the copolymerization of ABz with

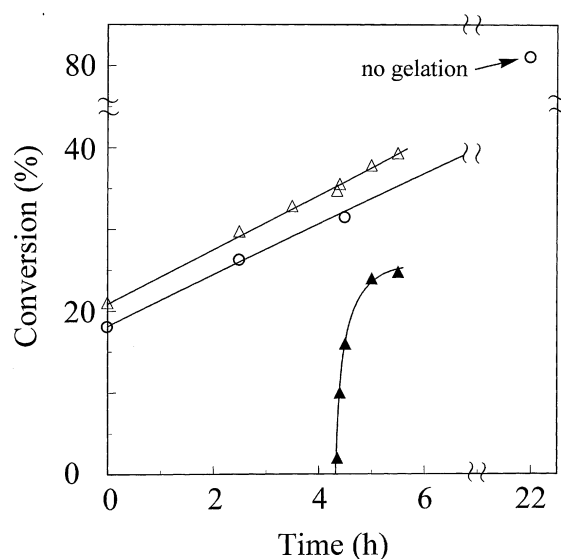


Figure 1. Conversion-time curves for the bulk copolymerizations of ABz with (○) 18 and (△) 21 wt% of **I** using 0.05 mol L⁻¹ of BPO at 80°C. Open and full symbols correspond to total and gel polymers, respectively.

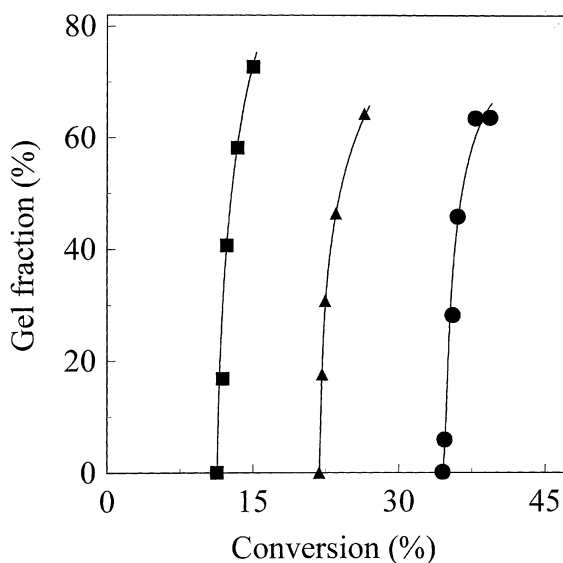


Figure 2. Increment of gel fraction with the progress of polymerization beyond the gel point for the bulk copolymerizations of ABz with (■) 21, (▲) 18, and (●) 9 wt% of **I**, **II**, and **III**, respectively (see Figure 1).

PAMA microspheres **II** and **III** in place of **I** since the A_2 and $[\eta]$ values of three kinds of PAMA microspheres increased in the order **I** < **II** < **III** (see Table I) as a reflection of crosslink density of microsphere. The lower the crosslink density, the easier the gelation. Thus, the copolymerizations were conducted under the same conditions and the gel points were estimated to be 21.8 and 11.3%, respectively, for the copolymerizations of ABz with 18 wt% of **II** and 9 wt% of **III**. The gelation was clearly promoted in the order **I** < **II** < **III**, being in conformity with our expectation.

In addition, we examined the effect of particle size on the gelation since the surface area of PAMA microsphere would increase with decreased particle size and thus, the probability of collision between PAMA microspheres should increase, leading to an easier gelation. Here PAMA microsphere **IV** was employed in place of **I** since **IV** has a smaller size than **I** and other properties of both microspheres **I** and **IV** are similar (see Table I). The gel point was estimated to be 23.0% for the copolymerization of ABz with 18 wt% of **IV**; obviously, the gelation was promoted with decreased particle size, in contrast with the case that no gelation occurred for 18 wt% of **I**. These are in line with our previous discussion¹ that the gelation is observed only under the polymerization condition in which the PAMA microspheres collide each other.

Then, the resulting gels were examined; Figure 2 shows the increment of gel fraction with the progress of gelation for the copolymerizations of ABz with 21, 18, and 9 wt%, respectively, of **I**, **II**, and **III**. Beyond the gel point, the sol fraction was rapidly incorporated

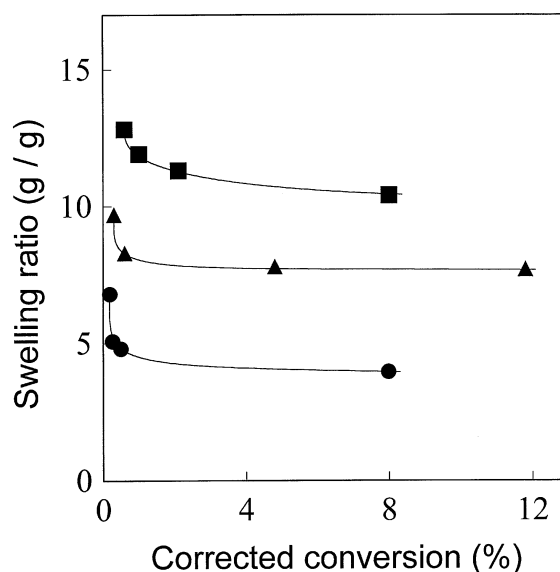


Figure 3. Decrease in swelling ratio of resulting gel in THF with the progress of polymerization beyond the gel point (see Figures 1 and 2). Conversion in the abscissa is corrected such as the corresponding gel point is 0% of conversion.

into the gel and its tendency became to a certain extent steeper from **I** to **III** as a reflection of decreased crosslink density of PAMA microsphere. In Figure 3, the swelling ratios of resulting gels were plotted against conversion. Here the conversion is corrected such as the corresponding gel point is 0% of conversion. The swelling ratio tended to decrease gradually with the progress of polymerization beyond the gel point. Moreover, the swelling ratios became relatively higher in the order **I** < **II** < **III**. These results would support the preferential incorporation of PAMA microsphere into the gel, demonstrating again the importance of the reaction of allyl groups present on the surface of microsphere in the copolymerization of PAMA microsphere with ABz.

Finally, we will discuss briefly the polymerization characteristics of microgel by ¹H NMR spectroscopy. Here it should be recalled that ¹H NMR spectra of the crosslinked polymer microspheres, **I**, obtained at high conversions in the emulsion crosslinking polymerization of AMA were characteristic of the microgel-like polymers.²⁸ That is, the absorption of the unreacted allyl groups was clearly observed at 4.7, 5.3, and 6.0 ppm corresponding to methylene, vinyl methylene, and vinyl methine protons, respectively, whereas the absorption peaks at a higher magnetic field corresponding to the protons of polymer backbone were weakened as compared with those of unreacted pendant allyl groups. The ratio of the peak area of polymer backbone protons to that of allyl group protons decreased clearly with conversion as a reflection of increased crosslink density, although no absorption was reported for microgel due to the complete loss of segmental

motion.⁷ In this connection, the ¹H NMR spectra of the resulting PAMA/ABz copolymers clearly changed with conversion, *i.e.*, the absorption peaks corresponding to the protons of unreacted pendant allyl groups were weakened with the progress of polymerization and, eventually, disappeared completely at 58% conversion, whereas those of benzene rings belonging to ABz units, present on the surface of microsphere, increased clearly with conversion.

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