NOTE

Basic Study on Vinyl-Type Semi-Interpenetrating Polymer Network Formation. I. Free-Radical Crosslinking Copolymerization of Allyl Benzoate with Diallyl Terephthalate in the Presence of Chemically Inactive Poly(benzyl Methacrylate)

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In the preceding article,[1] allyl benzoate (ABz) was co-polymerized with diallyl terephthalate (DAT) in the presence of poly(benzyl methacrylate) [poly(BzMA)] having different molecular weights, with the aim to discuss further the significance of the thermodynamic excluded volume effect[2] on gelation in free-radical monovinyl/divinyl crosslinking copolymerizations as a primary factor for the greatly delayed gelation from Flory–Stockmayer theory.[3]

In the present article, the above copolymerization proceeded to a late stage of polymerization, i.e., beyond the gel-point conversion, in order to study the incorporation of poly(BzMA) as a chemically inactive, linear polymer into ABz–DAT network formed, providing the basic data for molecular-designing the vinyl type semi-interpenetrating polymer network (semi-IPN).

EXPERIMENTAL

ABz and DAT (each Daiso Co.), and BzMA (Kyoeisha Chemical Co.) as monomers, and benzoyl peroxide (BPO) and 2,2′-azobisisobutyronitrile (AIBN) as initiators, were purified by conventional methods as described previously.[4,5]

Poly(BzMA)s having different molecular weights were prepared from the bulk polymerizations of BzMA monomer in the absence and the presence of small amounts of lauryl mercaptan as a chain transfer agent using AIBN at 50°C, followed by the fractionation of each resulting polymer from the benzene–methanol system: thus, methanol was added dropwise into ca. 2% (w/v) solution of the polymer sample in benzene 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.

Polymerization was carried out in ampoules as described previously.[6] After the required time, the reaction mixture was poured into a large excess of chilled methanol containing a small amount of hydroquinone as inhibitor to precipitate the polymer. The sol–gel separation of the polymer samples obtained at conversions beyond the gel point was done by extracting the sol fraction with benzene.

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 tetrahydrofuran using a Shodex GPC KF-806L $\times$ 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.

RESULTS AND DISCUSSION

Promoted Gelation in the Presence of Poly(BzMA) as a Reflection of the Thermodynamic Excluded Volume Effect

In the preceding article,[1] the copolymerizations of ABz with 20 mol % of DAT in the absence and the presence

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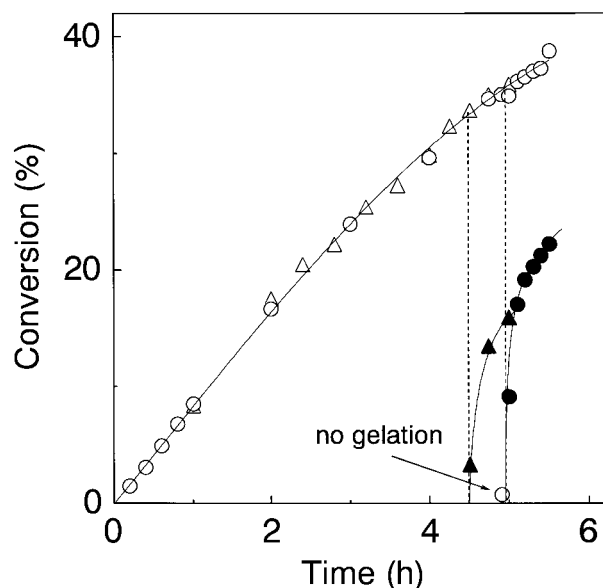
Figure 1 Conversion-time curves for ABz/DAT (80/20) copolymerizations in the absence (○, ●) and the presence (△, ▲) of 4.76 wt % of poly(BzMA) ($\bar{M}_w$ = 8.44 × 10⁵). Open and full symbols correspond to total and gel polymers, respectively.

of poly(BzMA) having different molecular weights have been explored in detail. Here it should be noted that poly(BzMA) probably acts as pseudo-poly(ABz) since the molecular structure of BzMA is similar to that of ABz. Thus, the deviation of actual gel point from the theoretical one became smaller with an increase in the molecular weight of poly(BzMA), and moreover, SEC-MALLS measurements clearly afforded direct supporting evidence for the increased occurrence of intermolecular crosslinking. These results were in conformity with our expectation as a result of reduced contribution of the thermodynamic excluded volume effect on gelation.

In this connection, we may suspect that the promoted gelation could also be related to chain transfer to poly(BzMA), which would incorporate poly(BzMA) into poly(ABz-co-DAT). However, no detection of the chain transfer reaction of growing polymer radicals to poly-(BzMA) was experimentally confirmed, i.e., poly-(BzMA) was chemically inactive.

Incorporation of Poly(BzMA) into ABz-DAT Network

In general, the free-radical polymerization and copolymerization of divinyl monomers leads to the formation of a gel polymer, except for rather special cases in which only cyclic, linear polymers are obtained.[6] Therefore, both intramolecular cyclization and intermolecular crosslinking reactions are characteristic of the polymerization of divinyl monomers as distinct from

monovinyl monomers. At an early stage of polymerization, linear or loop-structured prepolymer is formed, consisting of cyclized and uncyclized units, the latter having pendant double bonds. The crosslinking reaction between the pendant double bond of the resulting prepolymer and the growing polymer radical gradually becomes more important with the progress of polymerization accompanied by the change of the structure of prepolymer from a linear form to a branched one. The extent of branching increases with conversion, and eventually, gelation occurs and the viscosity of the system suddenly increases sharply. This was attributed by Carothers[7] to the formation of a three-dimensional network of indefinitely large size. The free-radical crosslinking copolymerization of ABz with DAT, taken up in this work, would fall on the same category; accordingly, in the ABz/DAT copolymerization in the presence of poly-(BzMA) as chemically inactive polymer, poly(BzMA) would be topologically incorporated into ABz-DAT network, thus vinyl type semi-IPN being formed.

Figure 1 shows the conversion-time curves for the bulk copolymerizations of ABz with 20 mol % of DAT in the absence and the presence of 4.76 wt % of poly-(BzMA) ($\bar{M}_w$ = 8.44 × 10⁵) using 0.1 mol/L of BPO at 80°C; gelation was clearly promoted by the addition of poly(BzMA) as discussed previously.[1] In Figure 2 is shown the MWD curve of the recovered prepolymer at 3.1% conversion, i.e., at an early stage of polymerization in which crosslinking is negligible. Clearly, two distinct peaks corresponding to poly(ABz-co-DAT) and poly(BzMA), respectively, were observed, and the
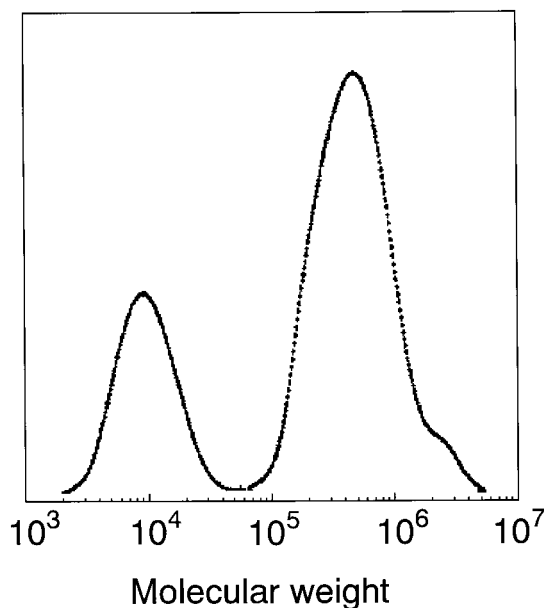

Figure 2 MWD curve for the polymer recovered at 3.1% conversion in the ABz/DAT (80/20) copolymerization in the presence of 4.76 wt % of poly(BzMA) ($\bar{M}_w$ = 8.44 × 10⁵).

MWD curve of poly(BzMA) was not changed at all from the original one, indicating no chain transfer to poly-(BzMA). The percentages of gel polymer were also plotted in Figure 1; the incorporation rate of sol polymer into the gel polymer was very rapid and it tended to be somewhat decreased by the addition of poly(BzMA).

Figure 3 shows MWD curves of the sol polymers recovered beyond the gel-point conversion for the ABz/DAT (80/20) copolymerization in the absence and the presence of 4.76 wt % of poly(BzMA) ($\bar{M}_w = 4.81 \times 10^6$), although poly(BzMA) of higher molecular weight than the above one was employed for an easier chromatographic separation of the peak of poly(ABz-co-DAT) sol from that of the original poly(BzMA). Here it is worthy to note that the gel points were estimated to be 34.4 and 26.4%, respectively, in the absence and the presence of poly(BzMA). The peak at the highest molecular weight side, which was observed only in the presence of poly(BzMA), would correspond to poly-(BzMA) remained in the sol fraction; this was confirmed from IR and ^{1}H-NMR spectra of the fractionated polymer sample of highest molecular weight.

Here it should be also noted that poly(BzMA) was easily incorporated into the polymer network. Therefore, the incorporation behavior of linear polymers into ABz–DAT network was examined in detail by changing the molecular weight of poly(BzMA), and furthermore,
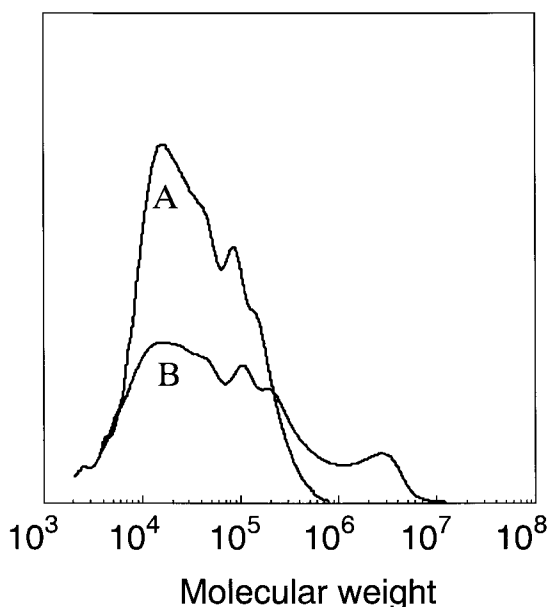
Table I   The Incorporation of Linear Polymers into ABz–DAT Network[a]

Linear Polymer[b]	Corrected Conversion[c] (%)	Incorporated Linear Polymer[d] (%)
Poly(BzMA) ($\bar{M}_w = 8.4 \times 10^5$)	3.8	74
	5.9	85
Poly(BzMA) ($\bar{M}_w = 4.72 \times 10^6$)	0.9	78
	3.4	91
	5.1	93
Poly(MA) ($\bar{M}_w = 1.53 \times 10^6$)	0.8	33
	3.0	50
	3.8	61

[a] ABz : DAT = 80 : 20 (by mole), in bulk, [BPO] = 0.1 mol/L, 80°C.
[b] Total monomer : linear polymer = 100 : 5 (w/w).
[c] The values denote the corrected conversion as the gel point corresponds to 0%.
[d] Obtained by the determination of the amount of linear polymer in the sol fraction.

the structure of linear polymer from poly(BzMA) to poly(methyl acrylate) [poly(MA)]. Table I summarizes the results obtained. Clearly, the amount of incorporated poly(BzMA) increased with the progress of gelation and it was enhanced with an increase in the molecular weight of poly(BzMA). On the other hand, the incorporation of poly(MA) into the polymer network was quite reduced as compared with poly(BzMA). Although poly(BzMA) acts as pseudo-poly(ABz),[1] poly(MA) would be incompatible with the ABz–DAT network. In this connection, the polymerization solution became turbid near the gel-point conversion in the ABz–DAT copolymerization in the presence of poly(MA).

Figure 3   MWD curves for the sol polymers recovered at 35.0 and 28.2% conversions, respectively, in the ABz/DAT (80/20) copolymerizations in the absence (A) and the presence (B) of 4.76 wt % of poly(BzMA) ($\bar{M}_w = 4.81 \times 10^6$).

REFERENCES

1. Matsumoto, A.; Yokoyama, K.; Aota, H. Eur Polym J 2000, 36, 201.
2. Matsumoto, A. Adv Polym Sci 1995, 123, 41.
3. Stockmayer, W. H. J Chem Phys 1944, 12, 125.
4. Matsumoto, A.; Yokoyama, S.; Khono, T.; Oiwa, M. J Polym Sci Polym Phys Ed 1977, 15, 127.
5. Matsumoto, A.; Aso, T.; Oiwa, M. J Polym Sci Polym Chem Ed 1973, 11, 2357.
6. Butler, G. B. Cyclopolymerization and Cyclocopoly-merization; Marcel Dekker: New York, 1992.
7. Carothers, W. H. Chem Rev 1931, 8, 402.