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Thermodynamic excluded volume effect on gelation in free-radical crosslinking copolymerization of allyl benzoate with diallyl terephthalate

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Abstract

In order to discuss further the significance of the thermodynamic excluded volume effect on gelation in free-radical monovinyl/divinyl crosslinking copolymerizations, allyl benzoate was copolymerized with diallyl terephthalate in the presence of poly(benzyl methacrylate) (poly(BzMA)) having different molecular weights. Thus, the deviation of actual gel point from theoretical one became smaller with an increase in the molecular weight of poly(BzMA) and, moreover, SEC-MALLS measurements clearly afforded supporting evidence for the increased occurrence of intermolecular crosslinking. These results are expected as a result of reduced contribution of the thermodynamic excluded volume effect on gelation. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

In a recent review [1], we dealt with network formation in the free-radical crosslinking polymerization and copolymerization of multivinyl compounds, especially including diallyl esters and dimethacrylates, by focusing attention on the discussion of deviations from Flory–Stockmayer (F–S) theory. First, the reasons for the greatly delayed gelation in diallyl polymerizations were discussed in detail mechanistically and the following conclusion was reached: the primary factor is the thermodynamic excluded volume effect on the intermolecular crosslinking reaction between a growing polymer radical and prepolymer, especially at high molecular weights. Beyond the theoretical gel point, a secondary factor is related to intramolecular crosslinking, which becomes progressively important with conversion. Such reaction leads to the restriction of segmental motion of the prepolymer and, moreover, imposes steric hindrance as a shielding effect [2] or a steric excluded volume effect, inducing the reduced reactivity of prepolymer as a tertiary factor. This discussion was satisfactorily extended to the network formation in common multivinyl polymerizations.

In this connection, the present article is related to the primary factor for the greatly delayed gelation, i.e. the thermodynamic excluded volume effect. Bulk copolymerizations of allyl benzoate (ABz) with diallyl terephthalate (DAT) were conducted in the presence of poly(benzyl methacrylate)s (poly(BzMA)) of high molecular weights and the effect of the addition of poly(BzMA) on the gelation in ABz/DAT crosslinking copolymerization is discussed, reconfirming a thermodynamic excluded volume effect.

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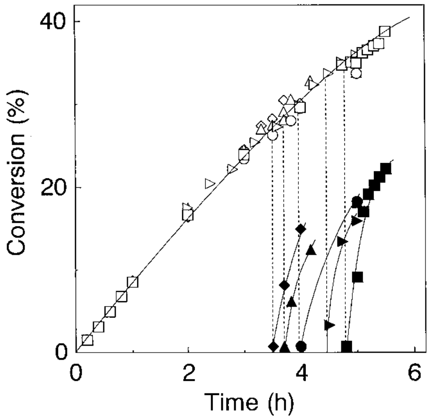

Fig. 1. Conversion–time curves for ABz/DAT (80/20) copolymerizations in the absence (□, ■) and presence of ca. 4.5 wt% of poly(BzMA) having different molecular weights ($\bar{M}_w = 0.85 \times 10^6$ (▷, ▶); 1.01×10^6 (○, ●); 3.12×10^6 (△, ▲); and 3.98×10^6 (◇, ◆)). Polymerizations were conducted in bulk using 0.1 mol/l of BPO at 80°C. Open and full symbols correspond to total and gel polymers, respectively.

2. Experimental

ABz and DAT, supplied by Daiso Co. Ltd, and BzMA, supplied by Kyoeisha Chemical Co. Ltd, as monomers and benzoyl peroxide (BPO) and 2,2′-azobisisobutyronitrile (AIBN) as initiators were purified by conventional methods as described previously [3,4].

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 reagent 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 up 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 as described previously [5]. After a predetermined reaction time, 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 gel fractions of polymer at conversions beyond the gel point were obtained 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 multi-angle 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 × 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.

3. Results and discussion

3.1. Promoted gelation in the presence of poly(BzMA)

Fig. 1 shows the conversion-time curves for the copolymerizations of ABz with 20 mol% of DAT in the absence and the presence of poly(BzMA) having different molecular weights; no influence was observed on the rate of polymerization although the viscosities of the polymerization solutions increased with an increase in the molecular weight of poly(BzMA). Moreover, no Trommsdorff effect [6] 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 [7]), 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 Fig. 1 along with the conversion–time curves; thus, the gel point was estimated as the conversion at which gel starts to form. Gelation was clearly promoted with increasing the molecular weight of poly(BzMA). Since the molecular structure of BzMA is similar to that of ABz, poly(BzMA) probably acts as pseudo-poly(ABz). Thus, the addition of poly(BzMA) inevitably shifts the polymerization system to a higher conversion by the amount of poly(BzMA), consequently reducing the thermodynamic excluded volume effect on gelation and leading to promoted gelation. In this connection, it is worthwhile noting that the thermodynamic excluded volume effect is predominantly operative at low conversions, i.e. especially around the theoretical gel point. Thus, ca. 4.5 wt% of poly(BzMA) was added because the theoretical gel point was estimated to be 5.93% conversion.

Although the preceding discussion is in line with our expectation of the significance of the thermodynamic excluded volume effect on the greatly delayed gelation in comparison with F–S theory in the monovinyl–divinyl copolymerizations, the promoted gelation may also be related to chain transfer to poly(BzMA), which could incorporate poly(BzMA) into poly(ABz-co-DAT).

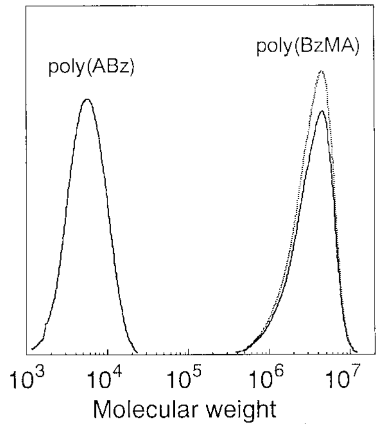

Fig. 2. MWD curves for the original poly(BzMA) (dotted curve) and the mixture (solid curves) of poly(BzMA) and poly(ABz) obtained at ca. 5% conversion.

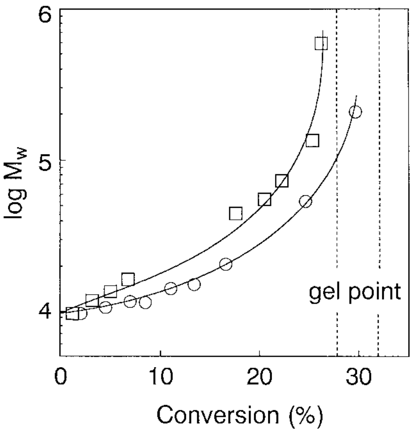

Fig. 4. Dependence on $\bar{M}_w$ of resulting precopolymers on conversion for ABz/DAT (80/20) copolymerizations in the absence (○) and presence (□) of ca. 4.5 wt% of poly(BzMA).

3.2. No chain transfer to poly(BzMA)

Homopolymerization of ABz was carried out in the presence of ca. 4.5 wt% of poly(BzMA) ($\bar{M}_w = 4.86 \times 10^6$) under the same conditions for the preceding ABz/DAT (80/20) copolymerizations. Fig. 2 shows MWD curves of the recovered polymer at ca. 5% ABz conversion; clearly, two peaks corresponding to poly(ABz) and poly(BzMA), respectively, were observed and the curve of poly(BzMA) was not changed at all, indicating no chain transfer. The similar supporting evidence was also obtained for the copolymerizations of ABz with DAT. These results clearly demonstrate that the chain transfer reaction of growing polymer radicals to poly(BzMA) does not occur.

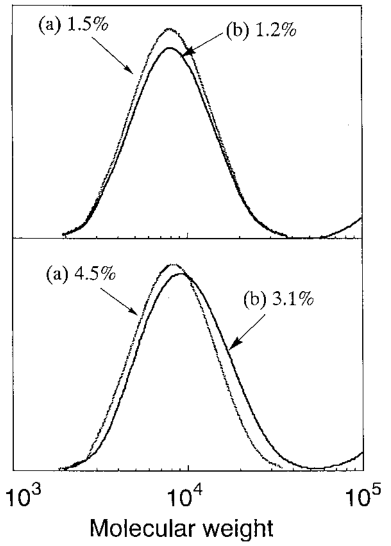

Fig. 3. MWD curves for the poly(ABz-co-DAT) obtained at different conversions in the absence (a, dotted line) and presence (b, solid line) of ca. 4.5 wt% of poly(BzMA).

3.3. Significance of thermodynamic excluded volume effect on gelation

Although the significance of the thermodynamic excluded volume effect on gelation is supported by the promoted gelation with an increase in the molecular weight of the added poly(BzMA), more direct supporting evidence would be obtained from SEC–MALLS measurements of the polymers obtained around the theoretical gel point for an ABz/DAT (80/20) copolymerization. Fig. 3 shows the effect of addition of poly(BzMA) ($\bar{M}_w = 4.86 \times 10^6$) on the MWD curves of resulting poly(ABz-co-DAT). Clearly, the curve corresponding to poly(ABz-co-DAT) obtained at 3.1% conversion in the presence of poly(BzMA) is shifted towards a higher molecular weight, compared with that of poly(ABz-co-DAT) obtained at 4.5% conversion in the absence of poly(BzMA), although almost no difference is observed for poly(ABz-co-DAT) obtained at low conversions; this difference indicates the promotion of intermolecular crosslinking by adding poly(BzMA). The promoted occurrence of intermolecular crosslinking reaction is also illustrated as the dependence of the molecular weights of precopolymers on conversion for ABz/DAT (80/20) copolymerizations in the absence and presence of poly(BzMA) ($\bar{M}_w = 4.86 \times 10^6$) as shown in Fig. 4; clearly, the intermolecular crosslinking is promoted by adding poly(BzMA). This is in line with our discussion on the thermodynamic excluded volume effect on gelation.

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