

# Crosslinking Polymerization Leading to Interpenetrating Polymer Network Formation.

## 3. Polyaddition Crosslinking Reaction of Poly(methyl methacrylate-co-2-methacryloyloxyethyl isocyanate) with Poly(oxytetramethylene) Glycol in the Presence of Linear Polymethacrylate Resulting in Semi-Interpenetrating Polymer Network

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**ABSTRACT:** As part of a series of our works concerned with the elucidation of the crosslinking polymerization mechanism leading to the interpenetrating polymer network (IPN) formation, in which IPN consists of both polyurethane (PU) and polymethacrylate (PM) networks, this article deals with the polyaddition crosslinking reactions of poly(methyl methacrylate-co-2-methacryloyloxyethyl isocyanate) poly-(MMA-co-MOI) [MMA/MOI = 99/1] as a novel multifunctional polyisocyanate with poly(oxytetramethylene) glycol [H-(OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>-OH (*n* = 28)] (POTMG-28) in the presence of two types of linear PMs, differently miscible with the resulting PU networks, leading to semi-IPN formation. Thus, poly(MMA-co-MOI) was prepared by the radical copolymerization of MOI with MMA in the presence of CBr<sub>4</sub> as a chain-transfer agent. No influence of the linear PM on the rate of polyaddition crosslinking reaction was observed. The actual gel points were compared with the theoretical ones calculated according to Macosko's equation: the deviation of the actual gel point from the theoretical one was rather small, close to the ideality, and the delayed gelation from theory tended to become a little smaller in the presence of PM. These are discussed mechanistically to deepen the

understanding of the PU network formation in the presence of a linear PM resulting in semi-IPN, along with the data of the intrinsic viscosities of resulting prepolymers. To collect a direct evidence of semi-IPN formation, we attempted to pursue the incorporation of the linear PM into the resulting PU networks by <sup>1</sup>H-NMR and UV-vis spectroscopy; in the latter case, the copolymers containing a small amount of pyrenyl methacrylate were used as linear PMs because the pyrenyl group was employed as the probe for UV-vis spectroscopic determination of the amount of the incorporated PM. The swelling ratio of the gel became lower in the presence of a linear PM. All data for the polyaddition crosslinking reactions of poly(MMA-co-MOI) with POTMG-28 in the presence of PM, along with the mechanistic discussion, demonstrate that the freely compatible molecular interaction would lead to a true semi-IPN formation as a result of the good miscibility between PU networks and a linear PM. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1198–1208, 2004

**Key words:** 2-methacryloyloxyethyl isocyanate; polyurethane; polymethacrylate; semi-IPN; crosslinking; gelation

### INTRODUCTION

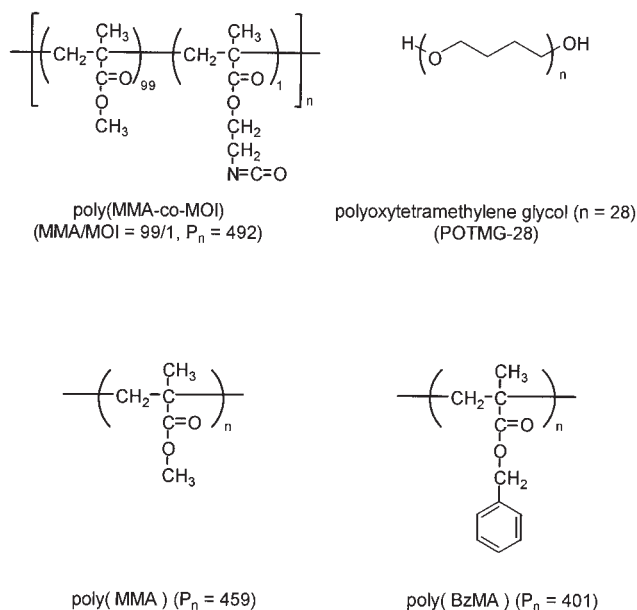
Multiphase polymer systems, essentially including interpenetrating polymer networks (IPNs), have been extensively employed to improve and satisfy the chemical and physical properties of polymeric materials required for various applications.<sup>1–7</sup> An IPN is defined as a combination of two crosslinked polymers, at least one of which has been formed and/or crosslinked in the immediate

presence of the other. IPNs are topologically related to polymer blends and block or graft polymers, but they can be distinguished from other multiphase polymer systems. IPNs swell in the presence of solvents, but do not dissolve. Moreover, IPNs exhibit characteristic morphologies since the entropy of mixing is greatly decreased during the second polymer network formation and phase separation usually occurs. The rather complicated morphology of the resulting IPNs has been the subject of many studies<sup>8–10</sup> in connection with the improvement of the mechanical properties of thermosets or cured resins. However, a detailed crosslinking polymerization mechanism leading to IPN formation has not been established yet.

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By considering the research background of the aforementioned IPNs, we felt strongly the necessity to clarify the IPN formation in terms of the reaction mechanism, especially in connection with our continuing studies aimed at the elucidation of the crosslinking polymerization mechanism and the control of network formation to molecularly design a variety of network polymers with high performance and high functionality.<sup>11</sup> Our research target was focused on IPN systems consisting of both polyurethane (PU) and polymethacrylate (PM) networks, these being representatives of two typical types of network polymers formed through step-growth and chain-growth mechanisms, respectively. The reason for the choice of PU/PM-type IPNs is as follows. So far, the reaction mechanism of vinyl-type network formation, especially through free-radical crosslinking monomethacrylate/dimethacrylate copolymerizations,<sup>12</sup> has been clarified. In addition, our work has been extended to the homopolymerization and copolymerization of multiallyl compound in the presence of a linear PM to collect the basic data of semi-IPN formation.<sup>13–15</sup> On the other hands, PUs were used widely as intermediate materials between plastic and rubber, ranging from a common resin to a fine chemical product depending on the combination of raw materials. Since PUs have characteristic features such as soft to hard, plastic, elastic or thermoset, and compact or foamed, they found a wide variety of applications, including flexible foam for upholstery, rigid foam for insulation, thermoplastic elastomers, high performance coatings, adhesives, and other materials.<sup>16</sup> Thus, the IPNs synthesized are often based on PUs and vinyl-type polymers such as poly(methyl methacrylate),<sup>17–39</sup> poly(ethyl methacrylate),<sup>40–43</sup> polystyrene,<sup>29,45–52</sup> poly(vinyl acetate),<sup>53,54</sup> and acrylic polymers.<sup>55–65</sup>

Our research program for clarifying the IPN formation mechanism is a successive understanding of (1) the polyaddition crosslinking reaction leading to PU network formation, (2) the reaction mechanism forming semi-IPNs consisting of PU networks and linear or branched PMs, and (3) the reaction mechanism forming sequential or simultaneous IPNs consisting of both PU and PM networks. In our previous articles,<sup>66,67</sup> we discussed in detail the polyaddition crosslinking reactions leading to PU network formation. Thus, the equimolar polyaddition crosslinking reactions of poly(methyl methacrylate-co-2-methacryloyloxyethyl isocyanate)s (poly(MMA-co-MOI)s), having pendant isocyanate (NCO) groups as novel multifunctional polyisocyanates, with ethylene glycol (EG),<sup>66</sup> 1,6-hexane diol (HD),<sup>67</sup> and 1,10-decane diol (DD)<sup>67</sup> were explored in detail. The rate constant, the deviation of the actual gel point from the theoretical one, the intrinsic viscosity of resulting prepolymer, and the swelling ratio of resulting gel were examined and these are discussed mechanistically in terms of the significant



**Figure 1** Molecular structures of poly(MMA-co-MOI), POTMG-28, poly(MMA), and poly(BzMA).

occurrence of intramolecular cyclization and intramolecular crosslinking reactions leading to the shrinkage of molecular size.

The present article deals with the reaction mechanism to form semi-IPN consisting of both PU networks and a linear PM. Here it should be noted that PU network-polymer with an appropriate network size is required for an easier formation of semi-IPN. Poly(MMA-co-MOI) [MMA/MOI = 99/1], a novel multifunctional polyisocyanate with a small amount of NCO groups, was employed for the polyaddition crosslinking reaction with poly(oxytetramethylene) glycol [H-(OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>-OH (*n* = 28)] (POTMG-28), probably leading to the network structure formation with an appropriate size required for semi-IPN formation. As the linear PM, we selected two kinds of PMs, i.e., poly(MMA) and poly(benzyl methacrylate) (poly(BzMA)), being differently miscible with the resulting PU networks (see Fig. 1).

## EXPERIMENTAL

MMA (Wako Pure Chemical Industries, Ltd.) was washed with 5% aqueous sodium hydroxide and distilled under reduced pressure. MOI (Showa Denko Co., Ltd.) and BzMA (Kyoeisha Chemical Co., Ltd.) were distilled under reduced pressure. *N*-Methyl pyrrolidone (MP) and POTMG-28 (Wako Pure Chemical Industries) were dehydrated over a molecular sieve (4 Å) at room temperature before use. All other solvents (Wako Pure Chemical Industries) were treated with calcium hydride for the removal of H<sub>2</sub>O.

*N*, *N'*-Azobisisobutyronitrile (AIBN; Wako Pure Chemical Industries) was recrystallized from methanol.  $\text{CBr}_4$ , 1,4-diazabicyclo [2.2.2] octane (DABCO; Wako Pure Chemical Industries), methacryloyl chloride, triethyl amine, *n*-butanol (Wako Pure Chemical Industries), and 1-pyrene methanol (PyOH; Aldrich Chemical Co.) were products of a superspecific grade used without purification.

The polyaddition crosslinking reaction of poly(MMA-*co*-MOI) with POTMG-28 in the presence of a linear PM was carried out in a glass ampule as described previously.<sup>66</sup> After a predetermined time of reaction, the ampule was cut off and then the required amounts of PyOH, DABCO, and toluene were added to the reaction mixture for blocking the unreacted NCO groups. The NCO-blocking reaction with PyOH was carried out in the presence of 0.1 mol L<sup>-1</sup> DABCO in toluene at a 10 g L<sup>-1</sup> polymer concentration under nitrogen for 24 h at 50°C. Then, the reaction mixture was poured into a large amount of a hexane/tetrahydrofuran (THF; 95/5) mixture to precipitate the polymer. The IR spectrum of the resulting polymer showed no absorption characteristic of the NCO group at 2275 cm<sup>-1</sup>, showing that the NCO-blocking reaction essentially went to completion.

IR measurements were performed with a Perkin-Elmer Spectrum 2000 (Perkin-Elmer Co.) with 4-cm<sup>-1</sup> resolution. The sample was directly dabbed into a KBr pellet. Ultraviolet-visible (UV-vis) measurements were carried out in CHCl<sub>3</sub> at room temperature with DP-L910/915 (Jasco Co., Ltd.).

Number-average molecular weights ( $M_n$ 's) and weight-average molecular weights ( $M_w$ 's) were measured by size exclusion chromatography (SEC) monitored with a dual-detector system set in the direction of the flow and 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 with five Shodex GPC KF-806L columns at a polymer concentration of 0.3% (w/v) and at a flow rate of 1 mL min<sup>-1</sup>. The MALLS device was a DAWN DSP (Wyatt Technology Corp.); the laser beam (wavelength = 632.8 nm) was focused on a 67- $\mu$ L flow cell.

The  $M_w$ 's of the resulting prepolymers as semi-IPN precursors were measured by light scattering (LS). LS measurements were carried out in THF at 30°C with an Otsuka Electronics DLS-7000 dynamic light scattering spectrophotometer over the angular range between 30 and 150°, using unpolarized light of wavelength of 632.8 nm.

The intrinsic viscosity ( $[\eta]$ ) was determined with an Ubbelohde-type viscometer in THF at 30°C.

The swelling ratio was estimated as the ratio of the weight of the swollen gel in THF for 48 h to that of the original gel.

The <sup>1</sup>H-NMR (270 MHz) measurements were carried out in CDCl<sub>3</sub> at 30°C.

## RESULTS AND DISCUSSION

### Preparation and characterization of linear PMs and poly(MMA-*co*-MOI)

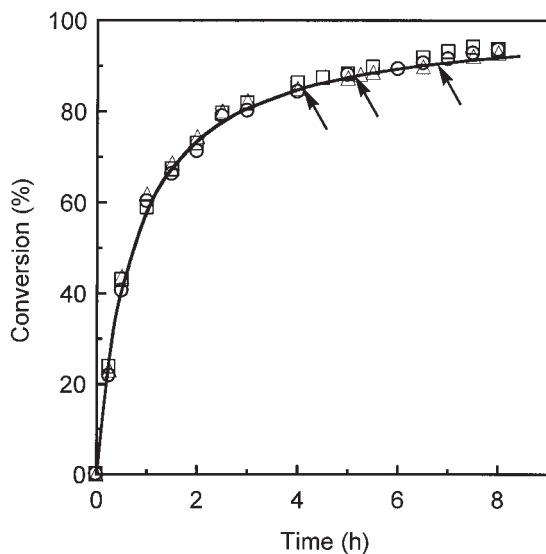
Pyrenyl methacrylate (PyMA) was prepared by the Schotten-Baumann reaction of methacryloyl chloride with PyOH in benzene in the presence of triethyl amine as a catalyst. Poly(MMA), poly(BzMA), poly(MMA-*co*-PyMA) [MMA/PyMA = 99/1], and poly(BzMA-*co*-PyMA) [BzMA/PyMA = 99/1] were prepared by the homopolymerizations of MMA and BzMA and their copolymerizations with PyMA in benzene at a dilution of 1/2 using 0.05 mol L<sup>-1</sup> AIBN at 50°C for 24 h in the presence of CBr<sub>4</sub> as a chain-transfer agent. The  $M_n$  ( $M_w/M_n$ ) values of resulting PMs were estimated by SEC-MALLS to be 45,900 (1.63), 70,600 (1.82), 44,200 (1.73), and 67,900 (1.91) for poly(MMA), poly(BzMA), poly(MMA-*co*-PyMA), and poly(BzMA-*co*-PyMA), respectively.

In the present work, poly(MMA-*co*-MOI) [MMA/MOI = 99/1], a novel multifunctional polyisocyanate with a small amount of NCO groups, was employed considering the results of our previous papers<sup>66,67</sup> because the PU network-polymer with a appropriate network size is required for an easier formation of semi-IPN. Poly(MMA-*co*-MOI) obtained in 89% yield was characterized as follows. For <sup>1</sup>H-NMR (CDCl<sub>3</sub> at room temperature),  $\delta$  was equal to 0.5–2.0 (m, backbone protons and CCH<sub>3</sub>), 3.0–3.7 (m, -OCH<sub>3</sub> of MMA and -OCH<sub>2</sub>CH<sub>2</sub>- of MOI), and 4.1 ppm (m, -OCH<sub>2</sub>CH<sub>2</sub> of MOI). For IR (KBr pellet), the characteristic absorption for the NCO group appeared at 2275 cm<sup>-1</sup>. The  $M_n$  ( $M_w/M_n$ ) and  $[\eta]$  values were estimated to be 49,500 (1.76) and 0.28 dL g<sup>-1</sup>, respectively.

### Polyaddition crosslinking reaction kinetics of poly(MMA-*co*-MOI) with POTMG in the presence of linear PM

The NCO group is moisture sensitive and, therefore, the polymer having pendant NCO groups has no good stability in the air. Eventually, this results in the formation of network polymer through the following successive reactions: the formation of carbamic acid by the addition of H<sub>2</sub>O to NCO group, the dicarboxylation of the resulting carbamic acid to generate amine, and the subsequent addition of the amine to the NCO group belonging to another polymer to form the crosslink. Therefore, the resulting polymers having unreacted NCO groups were immediately subjected to the reaction with PyOH to block the unreacted NCO groups.

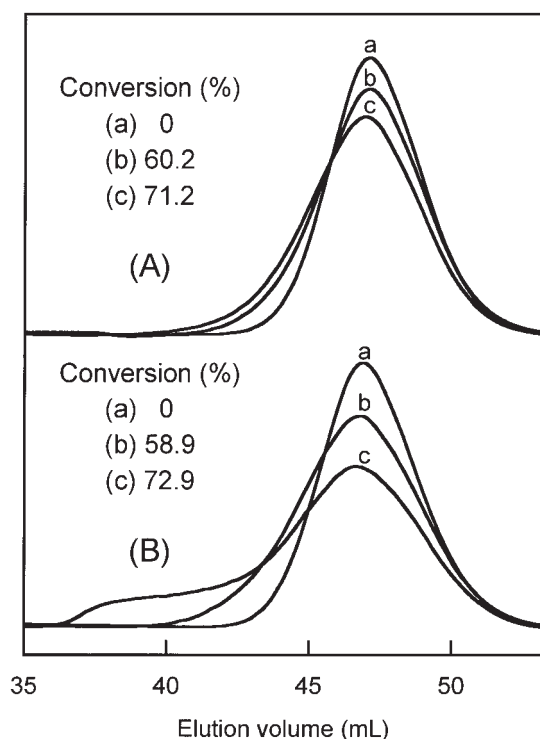
Figure 2 shows the conversion-time curves for the solution polyaddition crosslinking reactions of



**Figure 2** Conversion versus time curves for the equimolar polyaddition crosslinking reactions of poly(MMA-co-MOI) with POTMG-28 in the absence (○) and the presence of 16.7 wt % of (△) poly(MMA) or (□) poly(BzMA). Reactions were carried out in MP at a  $0.03 \text{ mol L}^{-1}$  concentration of functional groups at  $80^\circ\text{C}$ . The arrows denote gel points.

poly(MMA-co-MOI) with POTMG-28 in MP in the absence and the presence of 16.7 wt % of poly(MMA) or poly(BzMA) at a  $0.03 \text{ mol L}^{-1}$  concentration of functional groups at  $80^\circ\text{C}$ , where the feed ratio  $[\text{NCO}]/[\text{OH}]$  of both functional groups was equimolar. With the progress of reaction, the solution became turbid in the presence of poly(BzMA) before gelation, whereas in the presence of poly(MMA) the solution was transparent during the reaction. The former turbidity is caused by a poor miscibility of PU prepolymer with poly(BzMA), although poly(MMA) was easily miscible with PU prepolymer due to their structural resemblance (see Fig. 1). The consumption of the NCO group was followed by UV-vis spectroscopy;<sup>66,67</sup> thus, the conversion was calculated from the decreased absorption at 345 nm, assignable to the pyrene unit of the NCO-blocked polymer. No influence of the linear PM on the rate of polyaddition crosslinking reaction was observed although the viscosity of the solution became high by the addition of poly(MMA) or poly(BzMA). Also, the gelation was promoted in the following order: in the presence of poly(BzMA) > in the presence of poly(MMA) > in the absence of a linear PM. This was reflected in the variation of both the SEC curves and the molecular weights of the recovered prepolymers, determined by LS, with conversion (see Figs. 3 and 4). The SEC profiles were clearly broadened toward a higher molecular weight side with conversion in the presence of poly(BzMA) and the conversion dependency of  $M_w$  became remarkable in the same order for the promoted gelation.

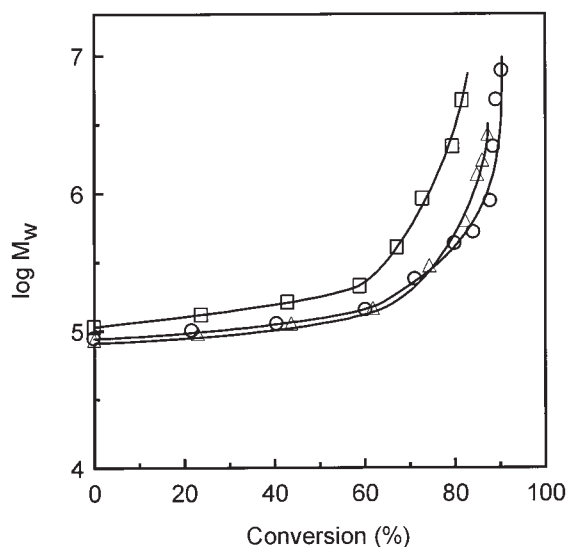
Then, the rate constants were estimated according to the ordinary second-order kinetic equation:



**Figure 3** Variation of refractive-index-monitored SEC curves with conversion for the equimolar polyaddition crosslinking reactions of poly(MMA-co-MOI) with POTMG-28 (A) in the absence of a linear PM and (B) in the presence of 16.7 wt % of poly(BzMA) (see Fig. 2).

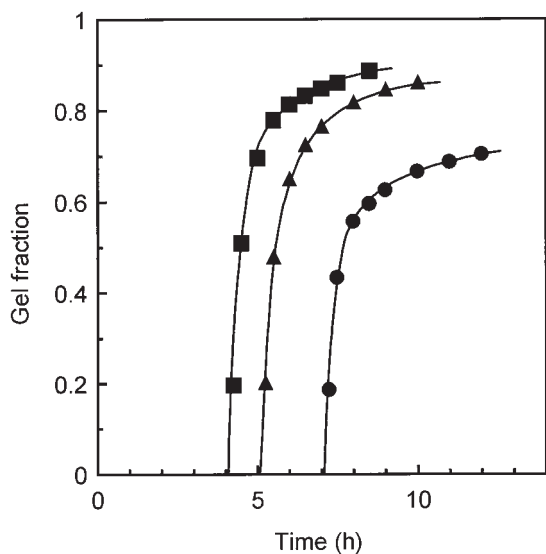
$$1/[\text{NCO}] - 1/[\text{NCO}]_0 = k_2 t \quad (1)$$

The reciprocal of the NCO group concentration was plotted against time;<sup>66,67</sup> the linear relationship governed by Eq. (1) was valid until about 90% conversion. Thus, the second-order rate constant ( $k_2$ ) was deter-



**Figure 4** Dependence of  $M_w$  on conversion (see Fig. 2).





**Figure 5** Increment of gel fraction with the progress of reaction beyond the gel point for the equimolar polyaddition crosslinking reactions of poly(MMA-co-MOI) with POTMG-28 in the absence (●) and the presence of 16.7 wt % of (▲) poly(MMA) or (■) poly(BzMA) (see Fig. 2).

mined from the slope of the straight line to be  $1.29 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$ . Here it should be recalled that the  $k_2$  values for the equimolar polyaddition reactions of poly(MMA-co-MOI) [MMA/MOI = 90/10] with EG, HD, and DD were 9.06, 5.46, and  $2.97 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$ , respectively, accompanied by the decrease in the rate constant with a longer chain diol.<sup>67</sup> Therefore, the high  $k_2$  value in the present polyaddition crosslinking reaction might be caused by the ether bonds of POTMG-28, although the true nature of the interaction between the ether bonds of POTMG-28 and the NCO and/or OH groups is not clear. In this connection, Cooper et al.<sup>68</sup> reported the kinetics of the reactions of *p*-phenylene diisocyanate with various diols, including three kinds of POTMGs ( $n = 2, 9, \text{ and } 19$ ); clearly, the  $k_2$  value increased with an increase in the number of oxytetramethylene unit, i.e., 3.2 times higher from  $n = 2$  to 19.

#### Comparison of the actual gel point with the theoretical one

As is shown in Figure 2, gelation occurred for all the reaction systems; the gel point was determined as the conversion at which gel started to form. Thus, the gel fraction of the polymer at conversion beyond the gel point was separated by the extraction of the sol fraction with THF. Figure 5 shows the increment of the gel fraction with the progress of reaction beyond the gel point for the solution polyaddition crosslinking reaction of poly(MMA-co-MOI) with POTMG-28 in MP in the absence and the presence of poly(MMA) or poly-

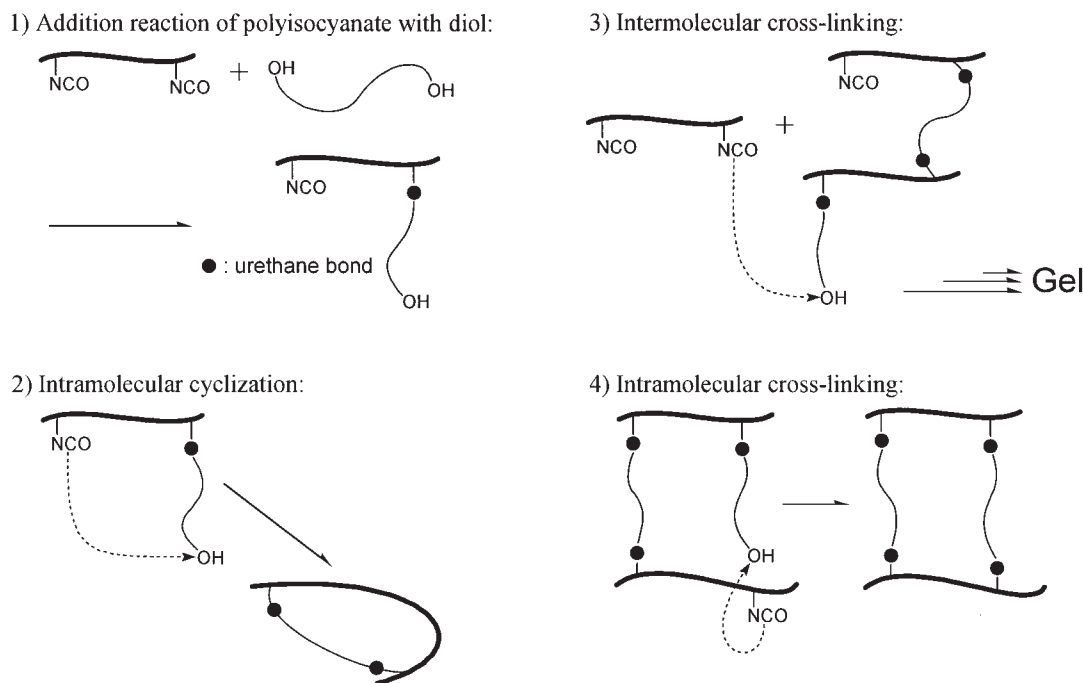
(BzMA) at a  $0.03 \text{ mol L}^{-1}$  concentration of functional groups at  $80^\circ\text{C}$ . The gel formation curve leveled off at a higher gel fraction in the presence of PM than that without PM; this may suggest the incorporation of the linear PM into the resulting PU networks leading to the formation of semi-IPN.

The actual gel points, determined by extrapolating the gel formation curves to zero percentage, were 90.8, 87.6, or 84.9% conversions for the reactions in the absence and the presence of poly(MMA) or poly(BzMA), respectively. The actual gel points thus obtained were then compared with the theoretical ones. The theoretical gel point was calculated according to Macosko's equation for  $f$ -functional polyisocyanate/diol polyaddition crosslinking reactions, in which the feed ratio  $[\text{NCO}]/[\text{OH}]$  is equimolar and the intramolecular reaction is ruled out.<sup>69</sup>

$$\alpha_c^2 = 1/(f - 1) \quad (2)$$

where  $\alpha_c$  is the conversion of the functional group at the gel point and  $f$  is the weight-average number of the NCO group of polyisocyanate. The  $f$  value was estimated to be 9 for our novel multifunctional poly(MMA-co-MOI) and then the theoretical gel point was calculated to be 35.4%. The ratios of the actual gel points to the theoretical ones were estimated to be 2.56, 2.47, or 2.40 for the reactions in the absence and the presence of poly(MMA) or poly(BzMA), respectively. In all systems, the actual gel point clearly deviated from theory. As one of the reasons for the delayed gelation from theory, we could point out the occurrence of intramolecular crosslinking reaction, which was ruled out for the derivation of Eq. (2). Moreover, the deviation became a little smaller in the presence of PM; by considering a rather high polymer concentration of  $360 \text{ g L}^{-1}$  in the present reaction systems, the linear PM could be topologically captured by the PU prepolymers with progressing the polyaddition crosslinking reaction, especially close to the gel-point conversion, and concurrently, the intramolecular crosslinking preceded by the topological crosslinking may act as an enhancement of intermolecular crosslinking. In addition, the topological interaction of PU network with a less compatible poly(BzMA) would induce the decrease of the interaction between polymer segment and solvent or the relatively enforced interaction between polymer chains leading to an enhanced occurrence of intermolecular crosslinking leading to a more promoted gelation.

Noteworthy, it should be recalled that the ratio of the actual gel point to the theoretical one was estimated to be 3.8 and 5.2 for the polyaddition crosslinking reactions of poly(MMA-co-MOI)s [MMA/MOI = 90/10 and 80/20] with EG at a  $0.25 \text{ mol L}^{-1}$  concentration of functional groups.<sup>66</sup> In this connection,



**Figure 6** Reaction scheme for the network formation processes in the polyaddition crosslinking reaction of poly(MMA-*co*-MOI) with POTMG-28.

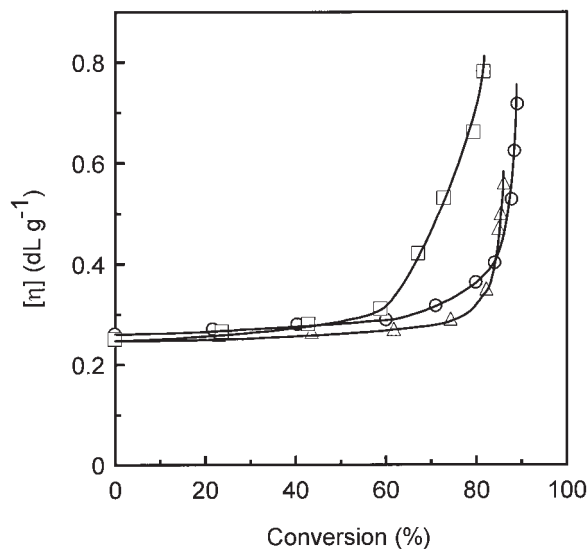
the present polyaddition crosslinking reaction behavior of poly(MMA-*co*-MOI) [MMA/MOI = 99/1] is close to the ideality, regardless of the lower concentration of functional groups as  $0.03 \text{ mol L}^{-1}$ , although the deviation from theory became smaller with a decrease in the pendant vinyl group content, responsible for crosslinking, for a free-radical crosslinking monovinyl/divinyl copolymerization.<sup>12</sup>

#### PU network formation accompanied by topological incorporation of linear PM

A reaction scheme to form PU networks by the polyaddition crosslinking reaction of poly(MMA-*co*-MOI) with POTMG-28 is illustrated in Figure 6; the intramolecular cyclization leading to the formation of loop structures, the intermolecular crosslinking leading to the formation of effective crosslinks and eventually leading to gel, and the intramolecular crosslinking leading to the formation of multiple crosslinks are characteristic reaction features of polyaddition crosslinking reactions. The intermolecular crosslinking reaction is the key reaction for the control of gelation for the formation of a three-dimensional network of indefinitely large size, whereas the key reaction for the control of the network structure is the intramolecular crosslinking, which leads to the formation of multiple crosslinks generating the network structure of PU. In the presence of a linear PM, the latter intramolecular crosslinking reaction would be accompanied by a topological incorporation of PM

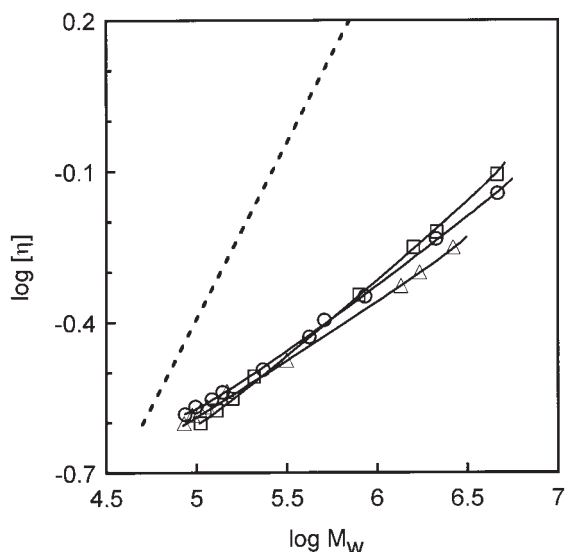
into PU network and, therefore, our subsequent discussion will be focused on this type of topological interaction leading to semi-IPN formation, evidenced by the detailed characterization of the resulting prepolymers and network polymers.

First, we examined the intrinsic viscosities of resulting polymers because the intramolecular crosslinking inevitably led to the reduction of viscosity as a reflection of the shrinkage of the molecular size of the resulting prepolymer. Figure 7 shows the variation of  $[\eta]$  of the recovered prepolymers with conversion for the polyaddition crosslinking reaction of poly(MMA-*co*-MOI) with POTMG-28 in the absence and the presence of poly(MMA) or poly(BzMA). The conversion dependency of  $[\eta]$  became remarkable in the same order for the promoted gelation. Figure 8 shows the double logarithmic plots of  $[\eta]$  versus  $M_w$  based on the data of Figures 4 and 7, along with the dotted line for a linear poly(MMA). The rather curved lines for the recovered prepolymers were clearly cited below the dotted line, with a quite low slope of less than 0.3; this demonstrates the significance of intramolecular crosslinking in the polyaddition crosslinking reaction of poly(MMA-*co*-MOI) with POTMG-28, regardless of the presence of a linear PM. In addition, the correlation line for the recovered prepolymers in the presence of poly(BzMA) was a little steeper compared to that in the presence of poly(MMA), suggesting the relatively enhanced occurrence of intermolecular crosslinking compared to intramolecular crosslinking for the reac-

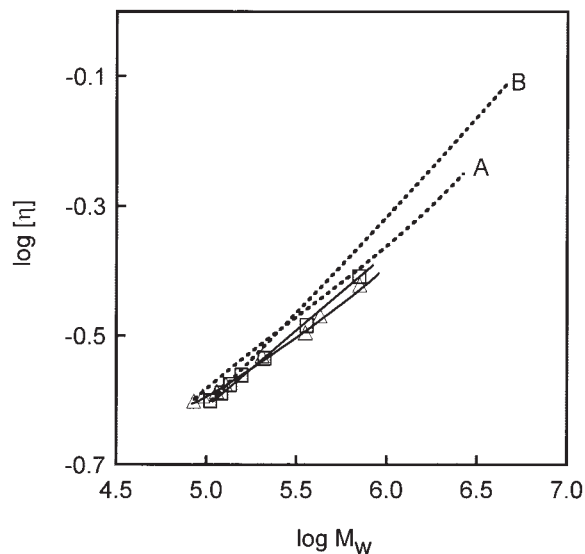


**Figure 7** Variation of  $[\eta]$  of the recovered prepolymers with conversion (see Fig. 4).

tion in the presence of poly(BzMA) as discussed above. Figure 9 shows the double logarithmic plots of  $[\eta]$  versus  $M_w$  for the mixtures of poly(MMA) or poly(BzMA) and the recovered prepolymers for the corresponding reaction in the absence of PM. The correlation lines for the recovered prepolymers became higher compared to those for the corresponding mixtures; probably the poly(MMA) or poly(BzMA) chain would be topologically captured by the PU prepolymers even before gelation, inducing the enhanced occurrence of intermolecular crosslinking reaction. Thus, the occurrence of the intramolecular crosslinking reaction accompanied by a topological incorporation of



**Figure 8** Double logarithmic plots of  $[\eta]$  versus  $M_w$  (see Figs. 4 and 7). The dotted line denotes a plot of poly(MMA).

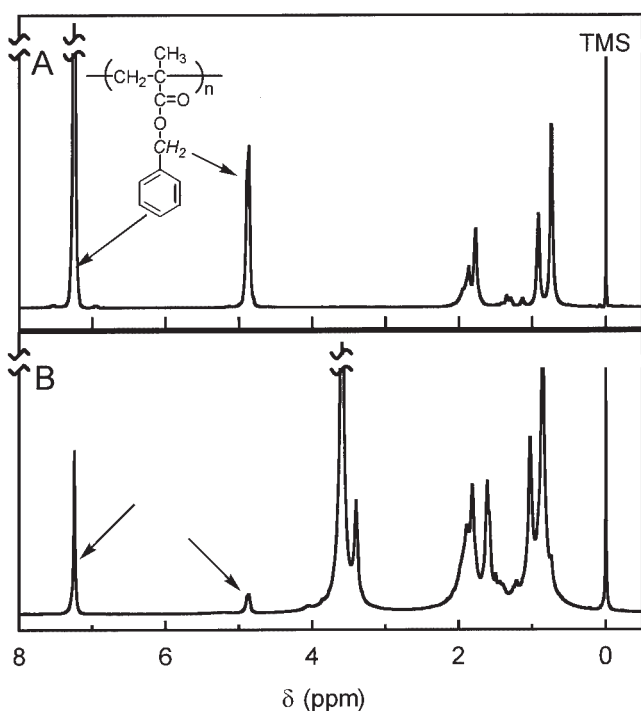


**Figure 9** Double logarithmic plots of  $[\eta]$  versus  $M_w$  for the mixtures of ( $\Delta$ ) poly(MMA) or ( $\square$ ) poly(BzMA) and the recovered prepolymers for the corresponding reaction in the absence of PM. The dotted lines denote plots for the equimolar polyaddition crosslinking reactions of poly(MMA-co-MOI) with POTMG-28 in the presence of 16.7 wt % of (A) poly(MMA) or (B) poly(BzMA).

PM into PU network was evidenced indirectly for the polyaddition crosslinking reaction of poly(MMA-co-MOI) with POTMG-28 in the presence of a linear PM.

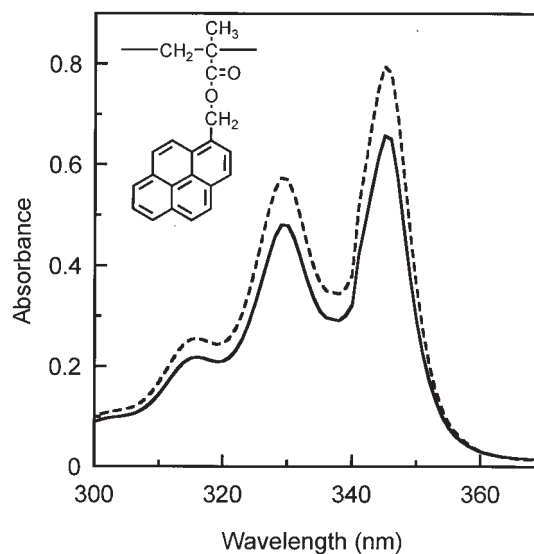
Then, we attempted to pursue in more detail the incorporation of the linear PM into the resulting PU networks to collect a direct evidence of semi-IPN formation. The highly swellable gel fraction of the resulting polymer obtained beyond the gel-point conversion, as will be shown later in Figure 14, was subjected to  $^1\text{H-NMR}$  measurement demonstrating directly the incorporation of the linear PM into the PU networks to form semi-IPN. Figure 10 shows the comparison of the spectrum of the original poly(BzMA) with that of the gel fraction obtained at 93.0% conversion for the equimolar polyaddition crosslinking reaction of poly(MMA-co-MOI) with POTMG-28 in the presence of 16.7 wt % of poly(BzMA). In the spectrum of the gel fraction, the characteristic absorption peaks of poly(BzMA) clearly appeared at 7.3 and 4.9 ppm, assignable to aromatic and methylene protons, respectively, supporting strongly the incorporation of poly(BzMA) into the PU networks.

Next, we tried to determine the amount of the linear PM incorporated into the resulting PU networks by UV-vis spectroscopy. Here poly(MMA-co-PyMA) and poly(BzMA-co-PyMA) were used in place of poly(MMA) and poly(BzMA), respectively. Moreover, the NCO-blocking reaction was carried out by using *n*-butanol in place of PyOH because the pyrenyl groups of PyMA units in poly(MMA-co-PyMA) and poly(BzMA-co-PyMA) were employed as the probe



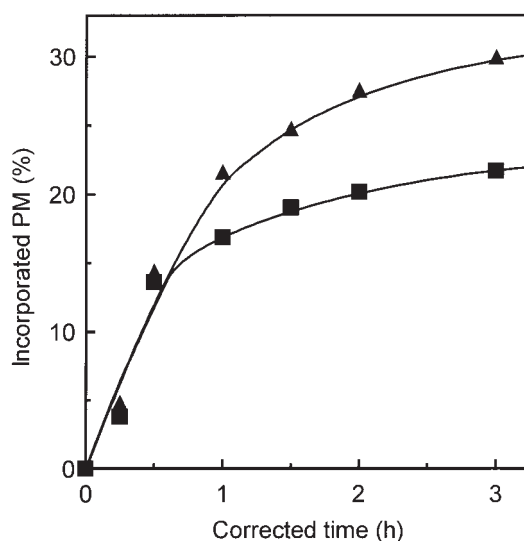
**Figure 10**  $^1\text{H-NMR}$  spectra of (A) the original poly(BzMA) and (B) the gel fraction obtained at 93.0% conversion for the equimolar polyaddition crosslinking reactions of poly(MMA-co-MOI) with POTMG-28 in the presence of 16.7 wt % of poly(BzMA). (see Fig. 2).

for UV-vis spectroscopic determination. Thus, the amount of the linear PM remaining in the sol fraction, without incorporating into the PU networks, was determined by measuring the absorption intensity at 345 nm, assignable to the pyrene unit. It was then compared with that of the linear PM calculated by assuming no incorporation of PM into PU networks; the decreased amount of the PM remained in the sol fraction would inevitably correspond to the increased one of the PM incorporated into the resulting PU networks, forming semi-IPN. Figure 11 shows the comparison of UV-vis spectrum of the sol fraction of the recovered polymer at 93.0% conversion beyond the gel point for the polyaddition crosslinking reaction of poly(MMA-co-MOI) with POTMG-28 in the presence of 16.7 wt % of poly(BzMA-co-PyMA) with that of the original poly(BzMA-co-PyMA), corresponding to no incorporation of PM into PU networks, as an example. Figure 12 shows the increase in the amount of the linear PM incorporated into the resulting PU networks with the progress of reaction beyond the gel-point conversion. The incorporation of PM into PU networks became more remarkable in the presence of poly(MMA-co-PyMA) than poly(BzMA-co-PyMA). Then, we calculated the amount of PM topologically captured by PU networks, based on the data of Figures 5 and 12. Figure 13 shows the correlation of the incorporated PM (in milligrams) per PU networks (in



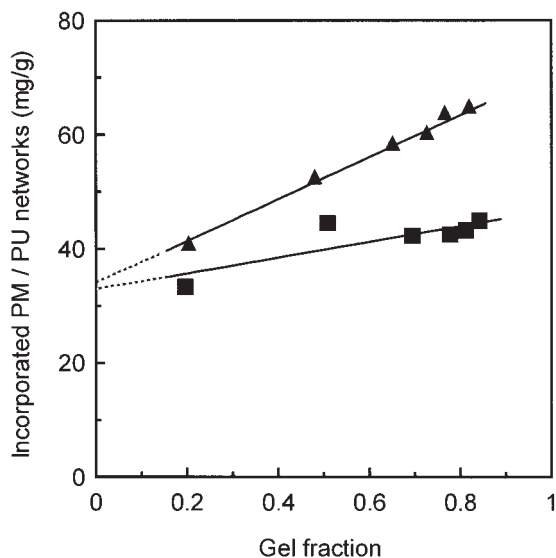
**Figure 11** Comparison of UV-vis spectrum of (—) the sol fraction of the recovered polymer at 93.0% conversion beyond the gel point for the polyaddition crosslinking reaction of poly(MMA-co-MOI) with POTMG-28 in the presence of 16.7 wt % of poly(BzMA-co-PyMA) with (---) that of the original poly(BzMA-co-PyMA) (see Fig. 2).

grams) with the gel fraction; the incorporation of PM into PU networks increased with the progress of reaction beyond the gel point. Also, the correlation curves were extrapolated to the gel-point conversion, i.e., zero gel fraction; clearly the positive intercepts were



**Figure 12** Increment of the amount of the linear PM incorporated into the resulting PU networks with the progress of reaction beyond the gel point for the polyaddition crosslinking reaction of poly(MMA-co-MOI) with POTMG-28 in the presence of 16.7 wt % of (▲) poly(MMA-co-PyMA) or (■) poly(BzMA-co-PyMA). Time in the abscissa is corrected so that the corresponding gel time is zero.





**Figure 13** Dependence of the incorporated PM per PU networks on gel fraction (see Fig. 12).

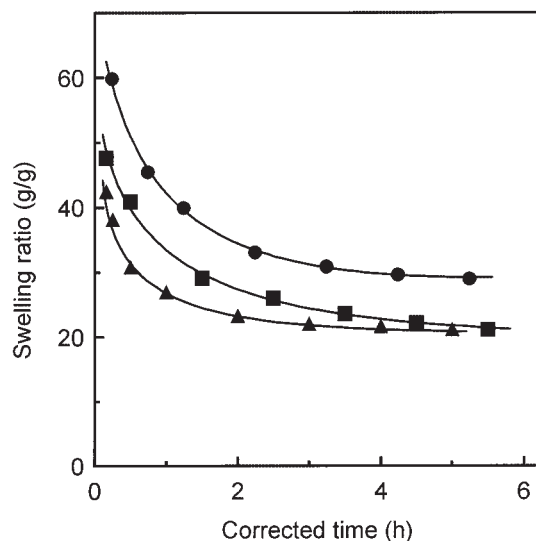
observed, suggesting the topological incorporation of PM into prepolymers as precursors of semi-IPNs.

Finally, the variation of swelling ratios of resulting gels in THF with the progress of reaction beyond the gel point was examined for the polyaddition crosslinking reactions of poly(MMA-*co*-MOI) with POTMG-28 in the absence and the presence of poly(MMA) or poly(BzMA). As is shown in Figure 14, the swelling ratio tended to decrease gradually with the progress of reaction beyond the gel point. Moreover, the swelling ratio of the gel was higher in the order: in the absence of a linear PM > in the presence of poly(BzMA) > in the presence of poly(MMA). These results would also be related to an occurrence of intramolecular crosslinking reaction beyond the gel-point conversion and the incorporation of the linear PM into the resulting PU networks leading to semi-IPN formation.

### CONCLUSION

The present article deals with the reaction mechanism to form semi-IPN consisting of both PU networks and a linear PM. Poly(MMA-*co*-MOI) [MMA/MOI = 99/1], a novel multifunctional polyisocyanate with a small amount of NCO groups, was employed for the polyaddition crosslinking reaction with POTMG-28 leading to the network structure formation with an appropriate size required for an easier formation of semi-IPN. As the linear PM, we selected two kinds of PMs, i.e., poly(MMA) and poly(BzMA), being differently miscible with the resulting PU networks. Thus, the radical copolymerization of MOI with MMA was carried out in the presence of CBr<sub>4</sub> as a chain-transfer agent and the resulting poly(MMA-*co*-MOI) was re-

acted with POTMG-28 in the presence of a linear PM. No influence of the linear PM on the rate of polyaddition crosslinking reaction was observed. The actual gel points were compared with the theoretical ones calculated according to Macosko's equation<sup>69</sup> for the *f*-functional polyisocyanate/diol polyaddition crosslinking reaction. The deviation of the actual gel point from the theoretical one was rather small, close to the ideality, and the delayed gelation from theory tended to become a little smaller in the presence of PM. The linear PM could be topologically captured by the PU prepolymers, thus leading to an enhanced occurrence of intermolecular crosslinking causing a promoted gelation. A mechanistic discussion was given to deepen the understanding of the PU network formation in the presence of a linear PM resulting in semi-IPN, along with the data of the intrinsic viscosities of resulting prepolymers because the intramolecular crosslinking reaction inevitably led to the shrinkage of the molecular size of the resulting prepolymer. Then, we attempted to pursue the incorporation of the linear PM into the resulting PU networks to collect direct evidence of semi-IPN formation. The highly swella- ble gel fraction of the resulting polymer obtained beyond the gel-point conversion was subjected to <sup>1</sup>H-NMR measurement. For example, the characteristic absorption peaks of poly(BzMA) clearly appeared, supporting strongly the incorporation of poly(BzMA) into the PU networks. Then, we tried to determine the amount of the linear PM incorporated into the resulting PU networks by UV-vis spectroscopy. Here poly(MMA-*co*-PyMA) and poly(BzMA-*co*-PyMA), possessing 1 mol % of PyMA unit, were used in place of poly(MMA) and poly(BzMA), respectively. Moreover, the NCO-



**Figure 14** Decrease in the swelling ratio of the resulting gel in THF with the progress of reaction beyond the gel point (see Fig. 5). Time in the abscissa is corrected so that the corresponding gel time is zero.

blocking reaction was carried out by using *n*-butanol in place of PyOH because the pyrenyl group was employed as the probe for UV-vis spectroscopic determination. The incorporation of PM into PU networks became more remarkable in the presence of poly(MMA-*co*-PyMA) than in the presence of poly(BzMA-*co*-PyMA). The swelling ratio of the gel tended to decrease gradually with the progress of polymerization beyond the gel point and it became lower in the presence of a linear PM. These would be related to an occurrence of intramolecular crosslinking reaction beyond the gel-point conversion and the incorporation of the linear PM into the resulting PU networks leading to semi-IPN formation.

As is obvious from the above discussion, the evidence to support a true semi-IPN formation was obtained for the polyaddition crosslinking reactions of poly(MMA-*co*-MOI) with POTMG-28 in the presence of a linear PM, although the semi-IPN formation depended on the miscibility between PU networks and a linear PM. The miscibility would significantly depend on the chain length, especially for polymers of intermediate molecular weights between the low-molecular-weight (or oligomeric) and high-molecular-weight (or polymeric) molecules. In this connection, the solution was transparent during the reaction in the presence of poly(BzMA) ( $P_n = 76$ ), although the solution became turbid in the presence of poly(BzMA) ( $P_n = 401$ ). The chain length of poly(MMA-*co*-MOI), i.e., the primary polymer chain length in the PU networks, would also play a significant role on the miscibility with a linear PM, although for our novel multifunctional polyisocyanates their chain lengths are easily adjustable through changes in the amount of  $\text{CBR}_4$  as a chain-transfer agent. More detailed study of semi-IPN formation is now in progress.

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