Macromolecules **2004,** *37,* 8249−8255

Approach to Ideal Simultaneous Interpenetrating Network Formation via Topological Cross-Links between Polyurethane and Polymethacrylate Network Polymer Precursors

Tadahiro Kiguchi, Hiroyuki Aota, and Akira Matsumoto*

Department of Applied Chemistry, Faculty of Engineering and High Technology Research Center, Kansai University, Suita, Osaka 564-8680, Japan

Received April 12, 2004; Revised Manuscript Received August 9, 2004

ABSTRACT: The equimolar polyaddition cross-linking reaction of poly(methyl methacrylate-*co*-2-methacryloyloxyethyl isocyanate) with tri(oxytetramethylene) glycol leading to polyurethane (PU) networks was carried out in methyl benzoate at a 0.1 mol/L concentration of functional groups at 80 °C. Simultaneously, the free-radical cross-linking copolymerization of methyl methacrylate with tri(oxytetramethylene) dimethacrylate leading to polymethacrylate (PM) networks was progressed at a dilution of 1/10 in the presence of CBr_4 as a chain transfer agent. The simultaneous interpenetrating networks (SINs) were formed via the topological cross-links between PU and PM network structures introduced by the respective intramolecular cross-linking reactions. Under the same polymerization conditions, no gelation was observed for respective cross-linking homopolymerizations leading to PU and PM homo-networks because respective intramolecular cross-linking reactions would be enhanced at a diluted solution. The topological cross-link formation between PU and PM network polymer precursors was pursued by SEC monitored with a multichannel UV−vis spectrometer device. The enhanced occurrence of intermolecular cross-linking via the topological cross-link formation was reflected on the variations of both the UV−vis monitored SEC curves and the molecular weights of the resulting PU and PM network polymer precursors with conversion. In addition, the respective actual gel points were compared with the corresponding theories for PU and PM networks formation or gelation. The swelling ratio of the resulting gel was quite high, suggesting a rather low cross-link density of PU/PM SIN produced through the topological cross-link formation between PU and PM network polymer precursors.

Introduction

Interpenetrating polymer network (IPN) is defined as a combination of two or more network polymers in network form. A wide variety of IPNs[1−10] synthesized by combinations of several network polymers were reported since the first report of homo-IPN, as an IPN consisting of essentially two identical polymers, formed through cross-linking styrene/divinylbenzene copolymerization by Millar.[11] IPNs exhibit characteristic morphologies since the entropy of mixing is greatly decreased during the second polymer network formation and phase separation usually occurs. The phase separation in IPN would depend primarily on the miscibility of the constituent polymers, the cross-link density,[12,13] the reaction conditions including temperature and pressure,[14−16] and the relative reaction rates of network formation. If two immiscible polymers were formed into an IPN, the glass transition temperatures of the two polymers were shifted inward.[17,18] As an extreme, rather exceptional case, Frisch et al.[19] have reported that a homogeneous IPN formation was successfully accomplished consisting of polystyrene and poly(phenylene oxide), both of which form a compatible blend. Most of reports treated, so far, of the IPNs with the intention of the improvement of the mechanical properties of network polymers or thermosetting resins. However, a detailed cross-linking polymerization mechanism leading to IPN formation at a molecular level has not been established yet. Especially, the formation of a true simultaneous interpenetrating network (SIN) may appear doubtful considering the usual occurrence of phase separation in IPN.

Thus, we felt strongly the necessity of clarifying the IPN formation processes in terms of the reaction mechanism, especially in connection with our continuing studies aimed at the elucidation of the cross-linking polymerization mechanism and the control of network formation to molecularly design a variety of network polymers with high performance and high functionality. Our research target was focused on the IPNs consisting of both polyurethane (PU) and polymethacrylate (PM) networks, i.e., representatives of two typical types of network polymers formed through step growth and chain growth mechanisms, respectively. The reaction mechanism of a vinyl-type network polymer formation, especially through free-radical cross-linking monomethacrylate/dimethacrylate copolymerizations, has been clarified.[20] In addition, our work has been extended to the homopolymerization and copolymerization of multiallyl monomers in the presence of vinyl-type linear polymers in order to collect the basic data of semi-IPN formation.[21−23] On the other hand, a variety of PUs, obtained generally by the polyaddition reactions of isocyanates with diols, were used widely as intermediate materials between plastic and rubber, ranging from a general resin to a fine chemical product depending on the combination of raw materials.[24]

Our research program for clarifying the IPN formation mechanism is a successive understanding of (1) the polyaddition cross-linking reaction leading to PU network formation, (2) the reaction mechanism forming semi-IPNs consisting of PU networks and linear PMs, and (3) the reaction mechanism forming SINs consisting

---

* Corresponding author: Fax +81-6-6339-4026; e-mail amatsu@ipcku.kansai-u.ac.jp.

10.1021/ma040073t CCC: $27.50

of both PU and PM networks. In preceding articles,[25,26] we have discussed in detail the polyaddition cross-linking reactions leading to PU network formation. Thus, the equimolar polyaddition cross-linking reactions of poly(methyl methacrylate-*co*-2-methcryloyloxyethyl isocyanate)s (poly(MMA-*co*-MOI)s), having pendant isocyanate (NCO) groups, with ethylene glycol (EG), 1,6-hexanediol (HD), and 1,10-decanediol (DD), were explored in detail. The reason that we chose poly(MMA-*co*-MOI)s as novel multifunctional polyisocyanates is that poly(MMA-*co*-MOI)s are desirable for easier miscibility with our target PM networks, typical vinyl-type network polymers, as another component of SINs. Furthermore, the chain length of poly(MMA-*co*-MOI) is easily adjustable through changes in the amount of a chain transfer agent. The miscibility significantly depends 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. As an extension of the aforementioned PU network formation,[25,26] we have discussed the reaction mechanisms forming semi-IPNs consisting of both PU networks and linear PMs.[27] Notably, a direct evidence of semi-IPN formation was obtained by pursuing the incorporation of the linear PM into the resulting PU networks by ^{1}H NMR and ultraviolet−visible (UV−vis) spectroscopy. The copolymers containing a small amount of pyrenyl methacrylate (PyMA) were used as the probe for UV−vis spectroscopic determination.

The present article deals with the pursuit of ideal SIN formation via topological cross-links based on both polyaddition cross-linking polyisocyanate/diol reaction and free-radical cross-linking monomethacrylate/dimethacrylate copolymerization. The origin of ideal SIN is in the topological cross-link formation between PU and PM network structures introduced by the respective intramolecular cross-linking reactions. In general, the phase separation occurs during IPN formation processes because of the immiscibility of two types of network polymer chains and the decreased entropy of mixing. This difficulty for ideal SIN formation would be surmounted by choosing two types of network polymers having similar structures and low primary polymer chains. The direct evidence for the occurrence of such a topological cross-linking could be obtainable by pursuing the interaction between PU and PM network polymer precursors. Here a lower concentration would be preferred as an appropriate polymerization condition to omit the possibility of a topological network formation due to the reinforced entanglement of both network polymer chains in a highly viscous solution at a higher concentration. Thus, the equimolar polyaddition cross-linking reaction of poly(MMA-*co*-MOI) with tri(oxytetramethylene) glycol (TOTMG) leading to PU networks was carried out in methyl benzoate (MBz). Simultaneously, the free-radical cross-linking copolymerization of MMA with tri(oxytetramethylene) dimethacrylate (TOTMDMA) leading to PM networks was progressed at a dilution of 1/10 in the presence of CBr_4 as a chain transfer agent (see Figure 1). Under these polymerization conditions, no gelation was observed for respective cross-linking homopolymerizations leading to PU and PM homo-networks because respective intramolecular cross-linking reactions would be enhanced at a diluted solution. On the contrary, the simultaneous cross-linking polymerizations resulting in PU/PM SIN led to the gel formation via the topological cross-links between PU and PM network structures introduced by the respective intramolecular cross-linking reactions.

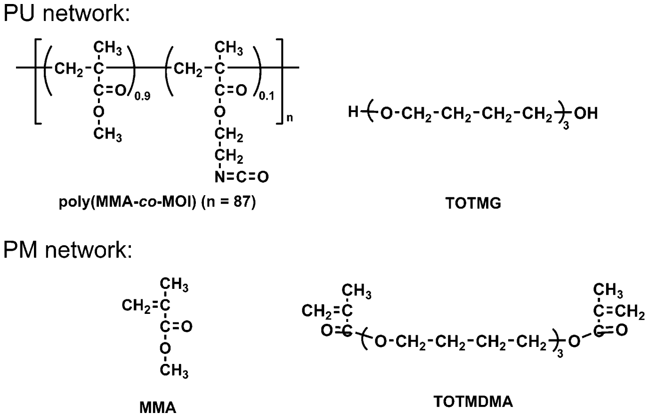

Figure 1. Chemical structures of poly(MMA-*co*-MOI), TOTMG, MMA, and TOTMDMA.

Experimental Section

Materials. MMA (Wako Pure Chemical Industries, Ltd.) was washed with 5% aqueous sodium hydroxide and distilled under reduced pressure. MOI (Showa Denko Co., Ltd.) was distilled under reduced pressure. MBz (Wako Pure Chemical Industries) was dehydrated over molecular sieves (4 Å) at room temperature before use. All other solvents (Wako Pure Chemical Industries) were treated with calcium hydride for the removal of H_2O. 2,2′-Azobis(*N*-butyl-2-methylpropionamide) (ABMPA; Wako Pure Chemical Industries), CBr_4 (Wako Pure Chemical Industries), 1,4-diazabicyclo[2.2.2]octane (DABCO; Wako Pure Chemical Industries), methacryloyl chloride (Wako Pure Chemical Industries), triethylamine (Wako Pure Chemical Industries), 1-butanol (Wako Pure Chemical Industries), 1-pyrenemethanol (PyOH; Aldrich Chemical Co.), TOTMG (Kyoeisha Chemical Co., Ltd.), and TOTMDMA (Kyoeisha Chemical Co.) were products of a super specific grade used without purification. PyMA was prepared by the Schotten−Baumann reaction of methacryloyl chloride with PyOH in benzene in the presence of triethylamine as a catalyst.

Polymerization Procedure. The preparation of poly(MMA-*co*-MOI) (MMA/MOI = 90/10), its polyaddition cross-linking reaction with TOTMG, and the free-radical cross-linking copolymerization of MMA with TOTMDMA were carried out in a glass ampule as described previously.[19,25−27] After a predetermined time of reaction, the ampule was cut off, and then the required amounts of PyOH, DABCO, and toluene for blocking the unreacted NCO groups were added to the reaction mixture. The NCO-blocking reaction with PyOH was carried out in the presence of a 0.1 mol/L concentration of DABCO in toluene at a 10 g/L polymer concentration under nitrogen for 48 h at room temperature. 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^{-1}, showing that the NCO-blocking reaction essentially went to completion.

Measurements. IR measurements were performed with a Perkin-Elmer Spectrum 2000 (PerkinElmer Co.) with 4 cm^{-1} resolution. The sample was directly dabbed into a KBr pellet. UV−vis measurements were carried out in $CHCl_3$ at room temperature with DP-L910/915 (Jasco Co., Ltd.). The number-average molecular weights (M_n's), weight-average molecular weights (M_w's), and molecular weight distribution of poly(MMA-*co*-MOI) and PM network polymer precursors obtained by the free-radical cross-linking copolymerization of MMA with TOTMDMA 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

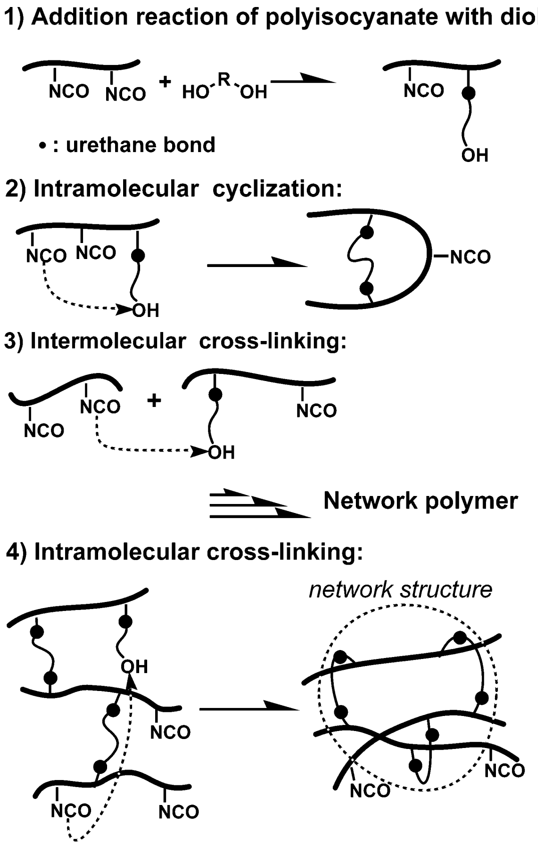

Figure 2. Reaction scheme for the network formation processes in the polyaddition cross-linking reaction of poly(MMA-*co*-MOI) with TOTMG.

sequence. SEC-MALLS measurements were carried out at 40 °C in THF with three Shodex GPC KF-806L columns at polymer concentration of 0.3% (w/v) and a flow rate of 1 mL/min. The MALLS device was a DAWN DSP (Wyatt Technology Corp.); the laser beam (wavelength = 632.8 nm) was focused on a 67 μL flow cell.

The resulting network polymer precursors were also characterized by SEC monitored with a dual-detector system set in the direction of the flow and consisting of a multichannel UV−vis spectrometer device and a differential refractometer in sequence. SEC measurements were carried out at 40 °C in THF with three Shodex GPC KF-806L columns at polymer concentration of 0.1% (w/v) and a flow rate of 1 mL/min. The multichannel UV−vis device was a DP-L910W (Jasco Co., Ltd.); the range of wavelength was from 200 to 800 nm.

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.

Results and Discussion

Ideal SIN Formation Mechanism. As is discussed in the preceding articles,[25,26] a reaction scheme to form PU networks by the polyaddition cross-linking reaction of poly(MMA-*co*-MOI) with TOTMG will be depicted in Figure 2. The intramolecular cyclization leading to the formation of loop structures, the intermolecular cross-linking leading to the formation of effective cross-links and eventually leading to gel, and the intramolecular cross-linking leading to the formation of multiple cross-links are characteristic reaction features of polyaddition cross-linking reactions. The intermolecular cross-linking reaction is the key reaction for the control of gelation for the formation of a three-dimensional network of indefinitely large size. The key reaction for the control of the network structure is the intramolecular cross-linking, which leads to the formation of multiple cross-links generating the network structure of PU networks. For our present discussion of ideal SIN formation, the latter intramolecular cross-linking is crucial as a generation of network structure, and its occurrence would be enhanced with dilution.

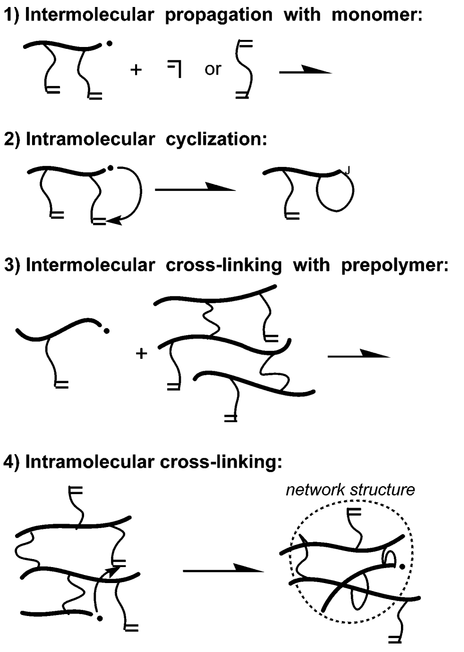

Figure 3. Reaction scheme for the network formation processes in the free-radical cross-linking copolymerization of MMA with TOTMDMA.

On the other hand, Figure 3 illustrates a reaction scheme to form PM networks by the free-radical cross-linking copolymerization of MMA with TOTMDMA as the formation of another component of our SINs. Thus, the scheme essentially involves four reactions of a growing polymer radical: intermolecular propagation with two types of monomer; intramolecular cyclization leading to the formation of ring or loop structures; intermolecular cross-linking with the prepolymer to form an effective cross-link, eventually leading to the gel; and intramolecular cross-linking leading to the formation of multiple cross-links. Here, the network structure of the resulting PM networks could be designed by controlling each elementally reaction, and again, the intramolecular cross-linking generating the network structure of PM networks would be crucial for SIN formation. Thus, the formation of the topological cross-links between PU and PM network structures introduced by the respective intramolecular cross-linking reactions would be an origin of an ideal SIN.

Appropriate Polymerization Conditions for Discussion of SIN Formation. The preliminary experiments were done to fix the appropriate polymerization conditions for the discussion of SIN formation via topological cross-links based on both polyaddition cross-linking polyisocyanate/diol reaction and free-radical cross-linking monomethacrylate/dimethacrylate copolymerization. For example, PU network was prepared by the equimolar polyaddition cross-linking reaction of poly(MMA-*co*-MOI) with TOTMG in MBz at a 0.1 mol/L concentration of functional groups at 80 °C. Simultaneously, PM network was formed by the free-radical cross-linking copolymerizations of MMA with different amounts of TOTMDMA at a dilution of 1/10 using 0.04 mol/L ABMPA in the presence of CBr_4 ([CBr_4]/[total monomer] = 1/25), mainly focusing on the added amount

Table 1. SIN Formation via Topological Cross-Links Based on Both Polyaddition Cross-Linking Polyisocyanate/Diol Reaction, and Free-Radical Cross-Linking Monomethacrylate/Dimethacrylate Copolymerization[a]

run	PU/PM (wt/wt)	TOTMDMA (mol %)	total polymer concn (g/L)	gelation[b]
1	1/0		100	no
2	0/1	0	100	no
3	0/1	5	100	no
4	0/1	10	100	no
5	1/1	0	200	no
6	1/1	5	200	no
7	1/1	10	200	yes

[a] PU and PM networks were prepared by the equimolar polyaddition cross-linking reaction of poly(MMA-*co*-MOI) with TOTMG in MBz at a 0.1 mol/L concentration of functional groups and simultaneously, by the free-radical cross-linking copolymerization of MMA with different amounts of TOTMDMA at a dilution of 1/10 using 0.04 mol/L ABMPA in the presence of CBr_4 ($[CBr_4]$/[total monomer] = 1/25). [b] Reaction time was 36 h.

of TOTMDMA as cross-linker. The results obtained are summarized in Table 1. In respective PU and PM homonetworks formation, no gelation was observed even beyond 90% conversion (runs 1−4). This would be ascribed to the enhanced occurrence of respective intramolecular cross-linking reactions at a diluted solution. On the other hand, gelation was clearly observed by adding 10 mol % of TOTMDMA for simultaneous PU/PM network formation (run 7). By the addition of only 5 mol % TOTMDMA (run 6), no gelation was observed but the solution viscosity increased with conversion. These results suggest the formation of the topological cross-links between PU and PM network structures introduced into the corresponding network polymer precursors by the respective intramolecular cross-linking reactions. Therefore, we chose the 10 mol % TOTMDMA cross-linker content as the appropriate polymerization conditions for the following discussion of SIN formation.

Equimolar Polyaddition Cross-Linking Reaction of Poly(MMA-*co*-MOI) with TOTMG Accompanied by SIN Formation. In the present work, poly(MMA-*co*-MOI) [MMA/MOI = 90/10] having M_n (M_w/M_n) of 9200 (1.95) was used for the polyaddition cross-linking reaction with TOTMG. The poly(MMA-*co*-MOI) obtained in 89% yield was characterized as described previously.[25] The polymer having pendant NCO groups has no good stability in the air because the NCO group is moisture-sensitive. Therefore, the resulting polymers having unreacted NCO groups were immediately subjected to the reaction with PyOH to block the unreacted NCO groups and prevent the occurrence of post-cross-linking reaction leading to the formation of network polymer.[25−27]

Figure 4 shows the NCO conversion vs time curves in PU networks and PU/PM SIN formation. Thus, the equimolar polyaddition cross-linking reactions of poly(MMA-*co*-MOI) with TOTMG were carried out in MBz at 0.1 mol/L NCO group concentration at 80 °C. Simultaneously, MMA was copolymerized with 5 and 10 mol % of TOTMDMA at a dilution of 1/10 using 0.04 mol/L ABMPA in the presence of CBr_4 ($[CBr_4]$/[total monomer] = 1/25). The solution was transparent throughout the reaction in all the polymerization systems. This suggests the good miscibility between PU and PM network polymer precursors, being due to their structural similarity and, moreover, their low primary polymer chain lengths. The rate of NCO group consumption was not influenced by SIN formation. Notably, the viscosity of the solution increased with the progress of polymerization as a reflection of the occurrence of intermolecular cross-linking via the topological cross-links between PU and PM network polymer precursors.

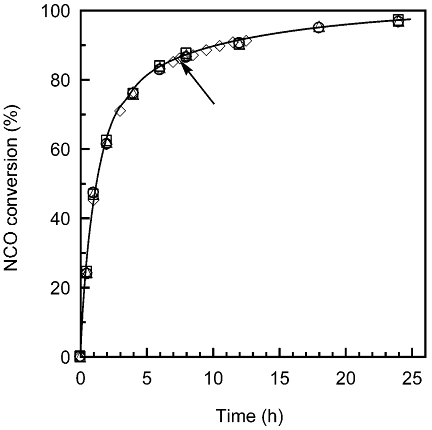

Figure 4. NCO conversion vs time curves for the equimolar polyaddition cross-linking reactions of poly(MMA-*co*-MOI) with TOTMG in (○) PU networks, (△) PU/PM semi-IPN, and PU/PM (MMA/TOTMDMA = (□) 95/5 and (◇) 90/10) SIN formation. Reactions were carried out in MBz at 0.1 mol/L concentration of functional groups at 80 °C. The arrow denotes the gel point.

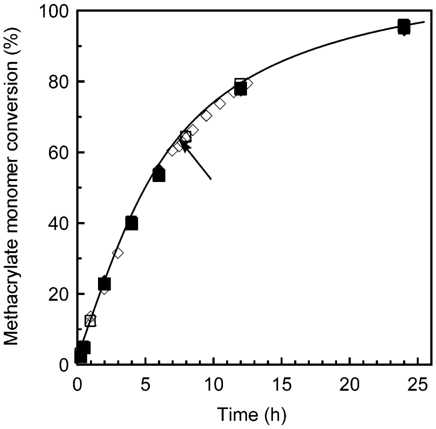

Figure 5. Methacrylate monomer conversion vs time curves for the free-radical cross-linking copolymerizations of MMA with TOTMDMA in (▲) PM linear polymer, PM (MMA/TOTMDMA = (■) 95/5 and (◆) 90/10) networks, (△) PU/PM semi-IPN, and PU/PM (MMA/TOTMDMA = (□) 95/5 and (◇) 90/10) SIN formation (see Figure 4). Polymerizations were carried out in MBz at a dilution of 1/10 using 0.04 mol/L ABMPA at 80 °C in the presence of CBr_4 ($[CBr_4]$/[total monomer] = 1/25). The arrow denotes the gel point.

Free-Radical Cross-Linking MMA/TOTMDMA Copolymerizations Accompanied by SIN Formation. Figure 5 shows the methacrylate monomer conversion vs time curves for the free-radical cross-linking copolymerizations of MMA with 5 and 10 mol % of TOTMDMA in MBz at a dilution of 1/10 using 0.04 mol/L ABMPA in the presence of CBr_4 ($[CBr_4]$/[total monomer] = 1/25) at 80 °C. Simultaneously, the equimolar polyaddition cross-linking reaction of poly(MMA-*co*-MOI) with TOTMG was progressed at 0.1 mol/L NCO group concentration. The gelation occurred only by adding 10 mol % of TOTMDMA. Moreover, no gel effect[28] was observed even beyond the gel point conversion as were the cases of the bulk polymerizations of multiallyl monomers.[29,30] This is ascribed to chain transfer from the growing polymer radical to the monomer in allyl polymerization;[31] the degradative chain transfer is essentially the termination reaction of growing polymer radical to form a dead polymer, thus acting to keep the primary chain length constant. This is an important fact for our mechanistic discussion of the network formation in the free-radical cross-linking polymerization and copolymerization of multivinyl monomers because the primary chain length is expected to contribute significantly to the gelation by theory.[32] In the present work, the chain transfer reaction of the growing polymer radical to CBr_4 would play an important role for no observation of gel effect because of the essential termination reaction of oligomeric growing polymer radical to form a dead polymer and, moreover, for keeping the primary chain length constant.

Pursuit of Topological Cross-Link Formation between PU and PM Network Polymer Precursors by SEC. We tried to pursue the topological cross-link formation between PU and PM network polymer precursors by SEC monitored with a multichannel UV–vis spectrometer device. Here poly(MMA-*co*-PyMA-*co*-MOI) (MMA/PyMA/MOI = 89/1/10), a multifunctional polyisocyanate, and MMA/PyMA/TOTMDMA (89/1/10) methacrylate monomer mixture were used for PU/PM SIN formation. Respective PU and PM homo-networks were formed by employing poly(MMA-*co*-MOI) (MMA/MOI = 90/10) and MMA/TOTMDMA (90/10) methacrylate monomer mixture. In addition, the NCO-blocking reaction was carried out by using 1-butanol in place of PyOH. Thus, the pyrenyl groups of PyMA units in poly(MMA-*co*-PyMA-*co*-MOI) and MMA/PyMA/TOTMDMA (89/1/10) network polymer precursor were employed as the probe for SEC measurement monitored with the multichannel UV–vis spectrometer device.

The enhanced occurrence of intermolecular cross-linking, via the topological cross-link formation between PU and PM network polymer precursors, would lead to gelation in PU/PM (MMA/TOTMDMA = 90/10) SIN formation. This was reflected on the variations of both the UV–vis monitored SEC curves and the molecular weights of the resulting PU network polymer precursors with NCO conversion. Thus, the SEC profiles were clearly broadened toward a higher molecular weight side with conversion. Concurrently, the conversion dependency of M_w became steeper in the order PU/PM (MMA/TOTMDMA = 90/10) SIN > PU/PM (MMA/TOTMDMA = 95/5) SIN > PU homo-networks (see Figures 6 and 7). Similarly, Figures 8 and 9 show the variation of UV–vis monitored SEC curves and the molecular weights of the resulting PM network polymer precursors with methacrylate monomer conversion for the free-radical cross-linking MMA/TOTMDMA copolymerizations for PM (MMA/TOTMDMA = 95/5 and 90/10) homo-networks and PU/PM (MMA/TOTMDMA = 95/5 and 90/10) SIN formation, respectively. Both SEC profiles and conversion dependencies of M_w supported the topological cross-link formation between PU and PM network polymer precursors for simultaneous polyaddition/free-radical cross-linking PU/PM (MMA/TOTMDMA = 90/10) polymerization resulting in PU/PM SIN. Especially, supporting evidence came from the comparison of the SEC curve of PM network polymer precursor obtained at 54.9% conversion with that of PU/PM SIN one obtained at 55.1% conversion (see Figure 8).

Comparison of Actual Gel Point with Theoretical One. As is discussed above, gelation occurred for simultaneous PU/PM (MMA/TOTMDMA = 90/10) network formation. The gel point was determined as the conversion at which gel started to form. The gel fraction of the polymer at conversion beyond the gel point was separated by the extraction of the sol fraction with THF. Figure 10 shows the increment of the gel fraction with the progress of gelation for the SIN formation through both polyaddition cross-linking poly(MMA-*co*-MOI)/TOTMG reaction and free-radical cross-linking MMA/TOTMDMA (MMA/TOTMDMA = 90/10) copolymerization at 80 °C. The actual gel points, determined by extrapolating the gel formation curves to zero percentage, were 86.1 and 61.6% conversions based on NCO group and methacrylate monomer, respectively. The actual gel points thus obtained were then compared with the theoretical ones.

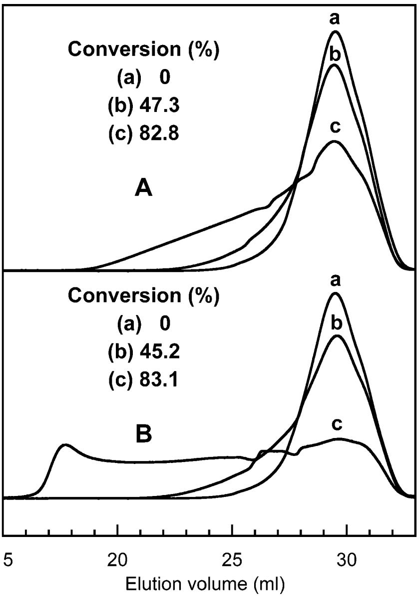

Figure 6. Comparison of UV–vis monitored (345 nm) SEC curves with conversion for the equimolar polyaddition cross-linking reactions of poly(MMA-*co*-MOI) with TOTMG in (A) PU networks and (B) PU/PM (MMA/TOTMDMA = 90/10) SIN formation (see Figure 4).

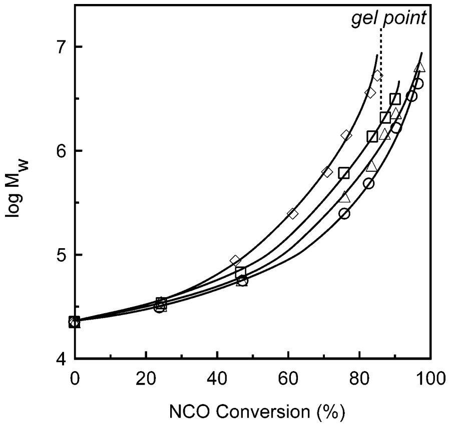

Figure 7. Dependence of M_w of PU network polymer, PU/PM semi-IPN, and PU/PM (MMA/TOTMDMA = 95/5 and 90/10) SIN precursors on conversion (see Figure 4).

The theoretical gel point of PU network formation was calculated according to Macosko's equation for *f*-functional polyisocyanate/diol polyaddition cross-linking reactions, in which the feed ratio [NCO]/[OH] is equimolar and the intramolecular reaction is ruled out:[33]

$$\alpha_c^{\,2} = 1/(f - 1) \qquad (1)$$

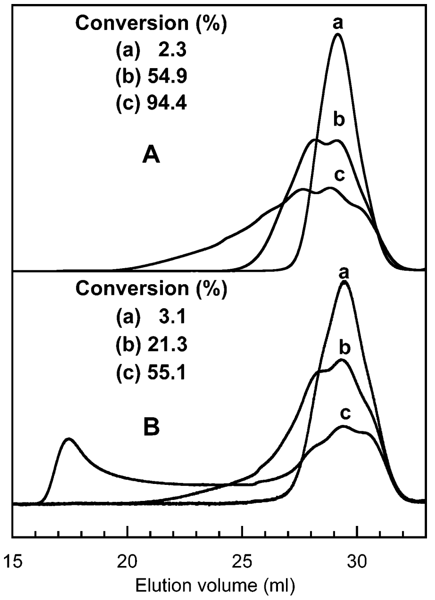

Figure 8. Comparison of UV−vis monitored (345 nm) SEC curves with conversion for the free-radical cross-linking copolymerizations of MMA with 10 mol % of TOTMDMA in (A) PM networks and (B) PU/PM (MMA/TOTMDMA = 90/10) SIN formation (see Figure 5).

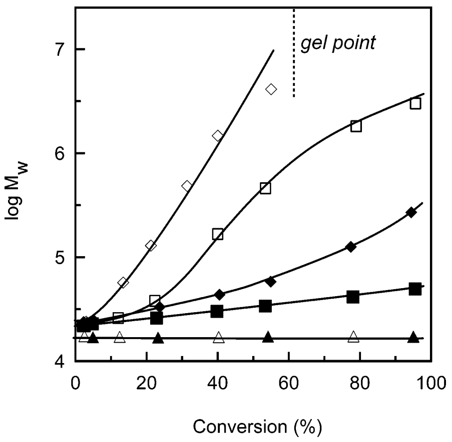

Figure 9. Dependence of M_w of PM linear polymer, PM (MMA/TOTMDMA = 95/5 and 90/10) networks, PU/PM semi-IPN, and PU/PM (MMA/TOTMDMA = 95/5 and 90/10) SIN precursors on conversion (see Figure 5).

where α_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 17 in this system, and then, the theoretical gel point was calculated according to eq 1 to be 25.0%. The ratio of the actual gel point to the theoretical one was estimated to be 3.4. Interestingly, the deviation from theory was quite similar to our previous results of PU homo-networks formation through the polyaddition cross-linking reactions of poly(MMA-*co*-MOI) with EG, HD, and DD.[25−27]

The theoretical gel point of PM network formation was calculated according to Flory−Stockmayer's equation for free-radical cross-linking monovinyl/divinyl copolymerization:[32]

$$\alpha_c = (1/\rho)/(P_{w,o} - 1)^{-1} \qquad (2)$$

where ρ is the fraction of all double bonds residing on divinyl units in the initial systems and $P_{w,o}$ is the

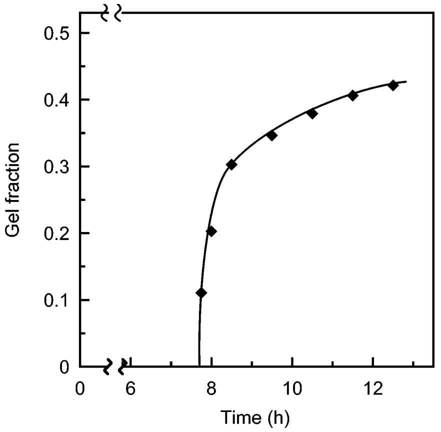

Figure 10. Increment of gel fraction with the progress of gelation for the SIN formation through both polyaddition cross-linking poly(MMA-*co*-MOI)/TOTMG reaction and free-radical cross-linking MMA/TOTMDMA (MMA/TOTMDMA = 90/10) copolymerization (see Figures 4 and 5).

weight-average degree of polymerization of the primary polymer chains. Now, we need the $P_{w,o}$ value for calculating the theoretical gel point according to eq 2. Thus, the primary chain length, $P_{w,o}$, was estimated to be 191 by the extrapolation of the conversion dependency of M_w of the network polymer precursor to zero conversion (see Figure 9), and then, the theoretical gel point was calculated according to eq 2 to be 2.9%. The ratio of the actual gel point to the theoretical one was estimated to be 17, although the actual gel point obtained above was corrected as 49.2% of the vinyl group conversion under the assumption of equal reactivity of MMA and TOTMDMA. Here it should be noted that no gelation was observed for PM homo-networks formation under the present polymerization conditions because of the enhanced occurrence of intramolecular cross-linking reaction.

Swelling Ratio of Resulting Gel. The variation of swelling ratios of resulting gels in THF with the progress of polymerization beyond the gel point was examined for PU/PM (MMA/TOTMDMA = 90/10) SIN formation through both polyaddition cross-linking poly(MMA-*co*-MOI)/TOTMG reaction and free-radical cross-linking MMA/TOTMDMA (MMA/TOTMDMA = 90/10) copolymerization. The results obtained are shown in Figure 11, along with the result for the polyaddition cross-linking poly(MMA-*co*-MOI)/DD reaction.[26] The time was corrected such that the corresponding gel time was zero. The swelling ratio tended to decrease gradually with the progress of polymerization beyond the gel point. The swelling ratio of the PU/PM (MMA/TOTMDMA = 90/10) SIN became much higher than that of poly(MMA-*co*-MOI)/DD networks or PM homo-networks. This result suggests a rather low cross-link density of PU/PM (MMA/TOTMDMA = 90/10) SIN produced through the topological cross-link formation between PU and PM network polymer precursors.

Conclusion

The present article deals with the pursuit of ideal SIN formation via topological cross-links based on both polyaddition cross-linking polyisocyanate/diol reaction and free-radical cross-linking monomethacrylate/dimethacrylate copolymerization. Thus, the equimolar polyaddition cross-linking reaction of poly(MMA-*co*-MOI) with TOTMG leading to PU networks was carried

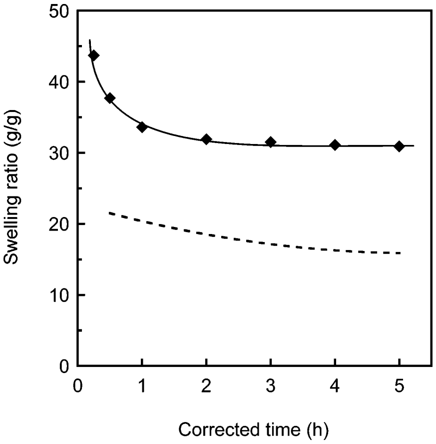

Figure 11. Decrease in swelling ratios of the resulting gels in THF with the progress of gelation (◆) for the SIN formation (see Figure 10), along with that of (- - -) the polyaddition cross-linking poly(MMA-*co*-MOI)/DD reaction.[26] Time in the abscissa is corrected such that the corresponding gel time is zero.

out in MBz at 0.1 mol/L NCO group concentration at 80 °C. Simultaneously, the free-radical cross-linking copolymerization of MMA with TOTMDMA leading to PM networks was progressed at a dilution of 1/10 in the presence of CBr_4 as a chain transfer agent. Under these polymerization conditions, no gelation was observed for respective cross-linking homopolymerizations leading to PU and PM homo-networks. Respective intramolecular cross-linking reactions would be enhanced at a diluted solution. On the contrary, the simultaneous cross-linking polymerizations resulting in PU/PM SIN led to the gel formation via the topological cross-links between PU and PM network structures introduced by the respective intramolecular cross-linking reactions. The rate of NCO group consumption was not influenced by SIN formation. The viscosity of the solution increased with the progress of polymerization as a reflection of the occurrence of intermolecular cross-linking via the topological cross-links between PU and PM network polymer precursors. For the rate of the methacrylate monomer consumption, no gel effect was observed even beyond the gel point conversion. This is ascribed to the chain transfer reaction of the growing polymer radical to CBr_4, being essentially the termination reaction of oligomeric growing polymer radical to form a dead polymer and, moreover, keeping the primary chain length constant. Then, the topological cross-link formation between PU and PM network polymer precursors was pursued by SEC monitored with a multichannel UV−vis spectrometer device. The pyrenyl groups of PyMA units in poly(MMA-*co*-PyMA-*co*-MOI) and MMA/PyMA/TOTMDMA (89/1/10) network polymer precursor were employed as the probe. The enhanced occurrence of intermolecular cross-linking via the topological cross-link formation led to gelation. This was clearly reflected on the variations of both the UV−vis monitored SEC curves and the molecular weights of the resulting PU and PM network polymer precursors with NCO and methacrylate monomer conversion, respectively. In addition, the respective actual gel points were compared with the corresponding theories for PU and PM networks formation or gelation. The swelling ratio of the resulting gel was much higher than that of poly(MMA-*co*-MOI)/DD networks or PM homo-networks. This suggests a rather low cross-link density of PU/PM (MMA/TOTMDMA = 90/10) SIN produced through the topological cross-link formation between PU and PM network polymer precursors.

Acknowledgment. This research was financially supported by the Kansai University Grant-in-Aid for the Faculty Joint Research Program, 2003.

References and Notes

(1) Paul, D. R.; Barlow, J. W.; Keskkula, H. *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Wiley-Interscience: New York, 1987; Vol. 12, pp 399−461.
(2) Utracki, L. A.; Ajji, A.; Dumoulin, M. M. *Polymeric Materials Encyclopedia: Synthesis, Properties, and Applications*; CRC Press: Boca Raton, FL, 1996; Vol. 1, pp 166−188.
(3) Klempner, D.; Frisch, K. C. *Polymer Science and Technology Series: Polymer Alloys III: Blends, Blocks, Grafts, and Interpenetrating Networks*; Plenum Press: New York, 1983; pp 191−218/233−252.
(4) Dickie, R. A.; Labana, S. S.; Bauer, R. S. *Crosslinked Polymers: Chemistry, Properties, and Applications*; American Chemical Society: Washington, DC, 1988; pp 244−268/269−296/297−310.
(5) Sperling, L. H.; Mishra, V. *Polymeric Materials Encyclopedia: Synthesis, Properties, and Applications*; CRC Press: Boca Raton, FL, 1996; Vol. 5, pp 3292−3302/3303−3308.
(6) Klempner, D.; Berkowski, L. *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Wiley-Interscience: New York, 1987; Vol. 8, pp 279−340.
(7) Kim, S. C.; Sperling, L. H. *IPNs Around the World: Science and Engineering*; John Wiley & Sons: New York, 1997; pp 75−102/155−202.
(8) Sperling, L. H. *Interpenetrating Polymer Networks and Related Materials*; Plenum Press: New York, 1981; pp 80−101.
(9) Klempner, D.; Sperling, L. H.; Utracki, L. A. *Interpenetrating Polymer Networks*; American Chemical Society: Washington, DC, 1994; pp 305−332/427−448/557−570.
(10) Klempner, D.; Frisch, K. C. *Advances in Interpenetrating Polymer Networks*; Technomic Pub. Co.: Lancaster, 1994; Vol. 4, pp 109−140/243−286.
(11) Millar, J. R. *J. Chem. Soc.* **1960**, 1311.
(12) Donatelli, A. A.; Sperling, L. H.; Thomas, D. A. *Macromolecules* **1976**, *9*, 671.
(13) Donatelli, A. A.; Sperling, L. H.; Thomas, D. A. *Macromolecules* **1976**, *9*, 676.
(14) Kim, S. C.; Lee, D. S. *Macromolecules* **1984**, *17*, 268.
(15) Kim, S. C.; Lee, D. S. *Macromolecules* **1984**, *17*, 2193.
(16) Kim, S. C.; Lee, D. S. *Macromolecules* **1985**, *18*, 2173.
(17) Kim, S. C.; Klempner, D.; Frisch, K. C.; Frisch, H. L. *Macromolecules* **1976**, *9*, 263.
(18) Yenwo, G. M.; Sperling, L. H.; Pulido, J.; Manson, J. A.; Conde, A. *Polym. Eng. Sci.* **1977**, *17*, 251.
(19) Frisch, H. L.; Klempner, D.; Yoon, H. K.; Frisch, K. C. *Macromolecules* **1980**, *13*, 1016.
(20) Matsumoto, A. *Adv. Polym. Sci.* **1995**, *123*, 41.
(21) Matsumoto, A.; Yokoyama, K.; Aota, H. *Eur. Polym. J.* **2000**, *36*, 201.
(22) Matsumoto, A.; Yokoyama, K.; Aota, H. *J. Appl. Polym. Sci.* **2000**, *78*, 692.
(23) Matsumoto, A.; Kiguchi, T.; Aota, H. *Macromol. Rapid Commun.* **2000**, *21*, 1201.
(24) Oertel, G. *Polyurethane Handbook: Chemistry−Raw Materials−Processing−Application−Properties*, 2nd ed.; Hanser Publishers: Munich, 1993; pp 33−34.
(25) Kiguchi, T.; Aota, H.; Matsumoto, A. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 606.
(26) Kiguchi, T.; Aota, H.; Matsumoto, A. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3243.
(27) Kiguchi, T.; Aota, H.; Matsumoto, A. *J. Appl. Polym. Sci.* **2004**, *94*, 1198.
(28) Trommsdorff, E.; Kohle, H.; Laggaly, P. *Makromol. Chem.* **1948**, *1*, 169.
(29) Matsumoto, A.; Yokoyama, S.; Khono, T.; Oiwa, M. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 127.
(30) Matsumoto, A.; Inoue, H.; Matsumoto, T.; Oiwa, M. *J. Macromol. Sci., Chem.* **1989**, *A26*, 1279.
(31) Bartlett, P. D.; Altschul, R. *J. Am. Chem. Soc.* **1945**, *67*, 812.
(32) Stockmayer, W. H. *J. Chem. Phys.* **1944**, *12*, 125.
(33) Macosko, C. W.; Miller, D. R. *Macromolecules* **1976**, *9*, 199.

MA040073T