

Effect of Primary Polymer Chain Rigidity on Intramolecular Cyclization and Intramolecular Crosslinking in Free-Radical Crosslinking Monomethacrylate/Dimethacrylate Copolymerizations

Jun-ichi Ikeda,^{1,2} Yasuhide Hasei,¹ Yuduri Yasuda,¹ Hiroyuki Aota,¹ Akira Matsumoto¹

¹Department of Applied Chemistry, Faculty of Engineering and High Technology Research Center, Kansai University, Suita, Osaka 564-8680, Japan

²Kyoeisha Chemical Company, Limited, 5-2-5 Saikujyo-cho, Nara 630-8453, Japan

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ABSTRACT: *d*-Bornyl methacrylate (BoMA) was chosen as a typical example of bulky monomethacrylate monomers, the polymerization of which led to the formation of a rigid polymer chain. To discuss the effect of primary polymer chain rigidity on intramolecular cyclization, we compared the solution copolymerization results of BoMA with 1 mol % ethylene dimethacrylate (EDMA; $n = 1$) and poly(ethylene glycol dimethacrylate) [$\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}(\text{OCH}_2\text{CH}_2)_n\text{OCOC}(\text{CH}_3)=\text{CH}_2$, $n = 9$ (PEGDMA-9)] with those of methyl methacrylate (MMA) with 1 mol % EDMA and PEGDMA-9; the dependence of the weight-average degree of polymerization on conversion for the former BoMA copolymerization systems was completely opposed to that for the latter MMA systems, and this was a reflection of a reduced occurrence of intramolecular cyclization caused by the rigidity of the primary polymer chain. The effect of primary polymer chain rigidity on intramolecular crosslinking was discussed through a comparison of both BoMA/EDMA and MMA/EDMA copolymerizations. The correlations of the intrinsic viscosity, root-mean-square (rms) radius of gyration, and second virial coefficient with the molecular weight were examined for both BoMA/EDMA (90/10) and MMA/

EDMA (90/10) copolymerizations in a dilute solution because microgelation was observed in solution MMA/EDMA (90/10) copolymerization as a reflection of a locally extensive occurrence of intramolecular crosslinking. The logarithmic plots of both the intrinsic viscosity and rms radius of gyration versus the molecular weight for MMA/EDMA copolymerization were compared with those for the corresponding BoMA/EDMA copolymerizations. The second virial coefficients were greater than $10^{-5} \text{ mol cm}^3 \text{ g}^{-2}$ for BoMA/EDMA copolymers, even when the conversion was very close to the gel point, whereas they were quite low, that is, less than $10^{-5} \text{ mol cm}^3 \text{ g}^{-2}$, for an MMA/EDMA copolymer obtained at more than 15% conversion. These were ascribed to a suppressed occurrence of intramolecular crosslinking, a reflection of the lessened flexibility of the polymer main chain and a steric effect due to the bulky *d*-bornyl groups. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1086–1093, 2004

Key words: *d*-bornyl methacrylate; polyethylene glycol dimethacrylate; primary polymer chain rigidity; intramolecular cyclization; intramolecular crosslinking; crosslinking

INTRODUCTION

We are concerned with a mechanistic discussion of three-dimensional network formation in the free-radical crosslinking polymerization and copolymerization of multivinyl monomers.¹ For the network formation processes in a monovinyl/divinyl copolymerization, the following four elementary reactions of a growing polymer radical are essentially involved: (1) intermolecular propagation with two monomer types, (2) intramolecular cyclization leading to the formation of ring or loop structures, (3) intermolecular crosslinking with the prepolymer to form an effective crosslink

(eventually leading to the gel), and (4) intramolecular crosslinking leading to the formation of multiple crosslinks (see Fig. 1). A detailed understanding of the key factor for each elementary reaction is required for the molecular design of a vinyl-type network polymer with high performance and high functionality.

Dusek² and Dotson et al.³ emphasized the importance of cyclization, especially in connection with microgel formation at an early stage of polymerization, although they indiscriminately treated both intramolecular cyclization and intramolecular crosslinking as cyclization. On the other hand, we insisted that both reactions should be clearly discriminated for the discussion of gelation from the following standpoint.¹ Intramolecular cyclization leads only to the incorporation of the ring or loop structure into the primary polymer chain, although the crosslinked structure would be introduced only by the crosslinking reaction

Correspondence to: A. Matsumoto (amatsu@ipcku.kansai-u.ac.jp).

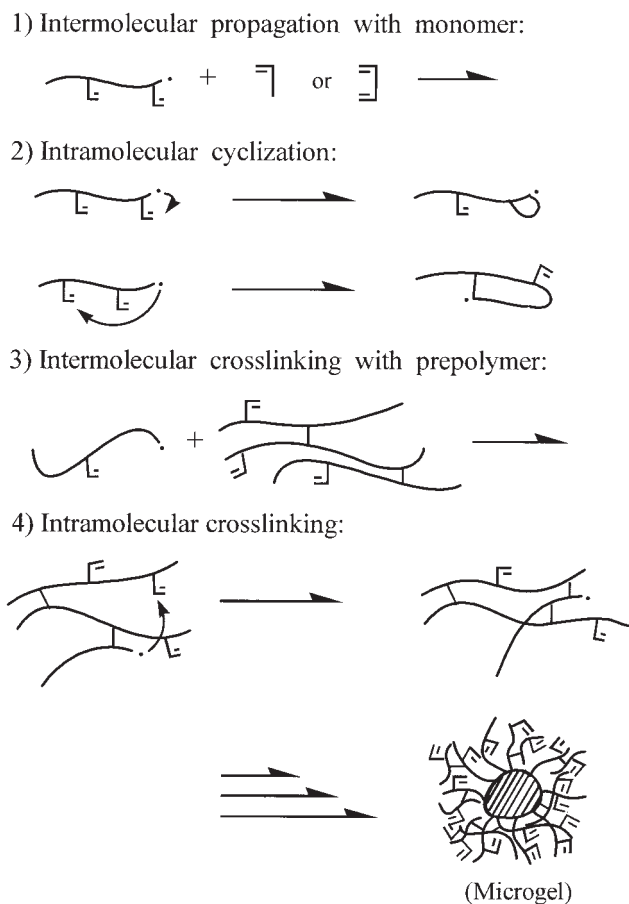


Figure 1 Reaction scheme for the network formation processes in the free-radical monovinyl/divinyl copolymerization.

between primary polymer chains. However, intramolecular crosslinking inevitably leads to the formation of a multiple-crosslinked structure generating the network structure of the crosslinked polymer, and so it acts as the key reaction for the control of the network structure. Moreover, the occurrence of intramolecular crosslinking should be preceded by intermolecular crosslinking, whereas intramolecular cyclization would occur during the growth of a propagating radical, regardless of the occurrence of intermolecular crosslinking, and it always competes with intermolecular propagation with two monomer types as a lengthening reaction of the primary polymer chain. In addition, the locally extensive occurrence of intramolecular crosslinking would induce microgelation, leading not only to delayed gelation⁴⁻¹⁷ but also to the inhomogeneity of the network structures of three-dimensional crosslinked polymers, being closely related to their properties.¹⁸⁻²⁸

We have dealt with loop structure formation via intramolecular cyclization in common monovinyl/multivinyl copolymerizations in connection with gelation, including the copolymerizations of methyl

methacrylate (MMA) with several poly(ethylene glycol dimethacrylate)s [CH₂=C(CH₃)CO(OCH₂CH₂)_n-OCOC(CH₃)=CH₂, *n* = 1, 2, 3, 4, 9, or 23 (PEGDMA-*n*)]^{29,30} and styrene (St) with PEGDMAs.³¹ These were extended to the free-radical crosslinking copolymerizations of *tert*-butyl methacrylate (*t*BuMA) with PEGDMAs.³² To deepen the understanding of the key factor for each elementary reaction in a monovinyl/divinyl copolymerization, here we further discuss the effect of primary polymer chain rigidity on intramolecular cyclization and intramolecular crosslinking in the free-radical crosslinking monomethacrylate/dimethacrylate copolymerizations. *d*-Bornyl methacrylate (BoMA) was chosen as a typical example of bulky monomethacrylate monomers, the polymerization of which leads to the formation of rigid polymer chain. Besides, this work provides useful information for a full understanding of three-dimensional network formation in free-radical crosslinking monovinyl/divinyl copolymerizations as part of 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.^{1,33-37}

EXPERIMENTAL

BoMA and ethylene dimethacrylate (EDMA) as monomers, 2,2'-azobisisobutyronitrile (AIBN) as an initiator, and 1,4-dioxane and benzene as solvents were purified by conventional methods. PEGDMA-9 (Kyocera Chemical Co., Nasa, Japan) as a monomer was used without further purification.

Polymerization was carried out in a glass ampule containing the required amounts of the monomers, solvent, and AIBN. The ampule was degassed three times by the usual freezing and thawing technique *in vacuo*, flushed with nitrogen, and then sealed off. It was then placed in a thermostat regulated at 50 ± 0.1°C. After a predetermined reaction time, the polymer was precipitated by the reaction mixture being poured into a large excess of methanol containing a small amount of hydroquinone as an inhibitor. For PEGDMA-9 copolymerizations, a methanol/water (5:1 v/v) mixture was used in place of methanol as a precipitant. The polymer was purified by reprecipitation from a tetrahydrofuran (THF)-precipitant system. The gel fraction of the polymer at conversions beyond the gel point was separated by the extraction of the sol fraction with THF.

The weight-average molecular weight (*M_w*), the root-mean-square (rms) radius of gyration ($\langle S^2 \rangle^{1/2}_Z$), and the second virial coefficient (*A₂*) were measured with light scattering (LS). LS measurements were carried out in THF at 30°C with an Otsuka Electronics DLS-7000 dynamic LS spectrophotometer (Osaka, Japan) over the angular range of 30–150° with unpolar-

ized light with a wavelength of 632.8 nm. The molecular weight distribution (MWD) was measured by size exclusion chromatography (SEC) with a dual-detector system, set in the direction of the 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 THF with Shodex GPC KF-806L (Tokyo, Japan) $\times 5$ columns at polymer concentrations of 0.2–0.8% (w/v) and at a flow rate of 1 mL/min. The MALLS device was a Dawn F (Wyatt Technology Corp., Santa Barbara, CA); the laser beam (wavelength = 632.8 nm) was focused on a 67- μ L flow cell.

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

RESULTS AND DISCUSSION

Effect of primary polymer chain rigidity on intramolecular cyclization

Soper et al.³⁸ investigated the copolymerization of St with divinylbenzene; $[\eta]$ of the resulting polymer was measured to explore the occurrence of intramolecular cyclization leading to the formation of a loop structure that inevitably results in the reduced viscosity of the polymer. This kind of intramolecular cyclization was extensively discussed in connection with the gelation in the copolymerizations of MMA with PEGDMAs with different numbers of oxyethylene units;²⁹ evidently, the enlargement of the primary polymer chain length, closely related to gelation, was observed with an increasing oxyethylene number of PEGDMA. This was ascribed to the suppression of the intermolecular termination between growing polymer radicals with a loop structure formed through intramolecular cyclization; moreover, the MWD of the polymer obtained during an early stage of polymerization was broad.³⁰ Furthermore, the copolymer obtained at an early stage of polymerization in MMA/trimethylolpropane trimethacrylate copolymerizations was examined in detail by SEC monitored with a low-angle laser LS detector;³⁹ the intensity of LS at a low elution volume was enhanced in comparison with the calculated value under the assumption of a linear polymer, but no intensified LS was observed for the MMA/EDMA copolymer with a linear primary polymer chain ($[\eta]_0/[\eta]_L = 0.98$) as expected. In addition, this kind of primary polymer chain enlargement (see Fig. 2) suggests that it is not always reasonable to employ the value of the weight-average degree of polymerization (P_w) of the polymer obtained in the homopolymerization of a monovinyl monomer as the substituted value of the primary polymer chain length ($P_{w,0}$) of a monovinyl/divinyl copolymerization system for calculating the theoretical gel point according to the Flory–Stockmayer (FS) gelation theory.⁴⁰

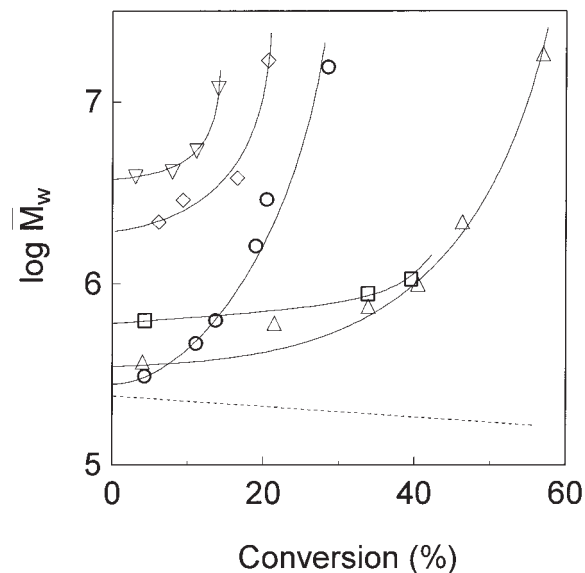


Figure 2 Dependence of M_w on the conversion in the copolymerizations of MMA with (○) EDMA, (△) PEGDMA-2, (□) PEGDMA-3, (◇) PEGDMA-9, and (▽) PEGDMA-23 and (---) in the homopolymerization of MMA.

As a matter of course, this kind of intramolecular cyclization, leading to the formation of a loop structure, is influenced by the flexibility of the polymer chain, the content of pendant double bonds, and the primary polymer chain length. In this connection, the effect of the rigidity of the primary polymer chain on intramolecular cyclization was examined preliminarily in *t*BuMA/PEGDMA copolymerizations,³² and the results were compared with those of MMA/PEGDMA copolymerizations. The oxyethylene number dependency of the primary polymer chain length was quite small in *t*BuMA/PEGDMA copolymerizations; the longest primary polymer chain length was obtained for $n = 23$, but it was only 1.8 times higher than that for $n = 1$, whereas in MMA/PEGDMA copolymerizations, it reached 10.6 times.²⁹ In addition, the deviation of the actual gel point from the FS theory⁴⁰ became greater for $n = 1$ in *t*BuMA/PEGDMA copolymerizations; it reduced a bit with an increase in the oxyethylene number, whereas in MMA/PEGDMA copolymerizations, the opposite dependency was observed as a remarkably enhanced deviation with an increased oxyethylene number. The former *t*BuMA/PEGDMA copolymerization results were ascribed to a suppressed occurrence of intramolecular cyclization accompanied by the loop structure formation as well as intermolecular crosslinking and intramolecular crosslinking, as a reflection of a lessened flexibility of the primary polymer chain and a steric effect due to the bulky *tert*-butyl groups.³²

To deepen the effect of primary polymer chain rigidity on intramolecular cyclization, we tried to explore the free-radical crosslinking BoMA/PEGDMA

copolymerizations because the copolymer backbone mainly consisting of BoMA units inevitably generated a more rigid primary polymer chain than *t*BuMA/PEGDMA copolymerizations. The solution BoMA/PEGDMA copolymerizations were carried out in 1,4-dioxane at a dilution of 1/5 with 0.04 mol/L AIBN at 50°C. Figure 3 shows the dependence of P_w on conversion in the copolymerizations of BoMA with 1 mol % EDMA ($n = 1$) and PEGDMA-9 ($n = 9$). By extrapolating the curve to zero conversion, we estimated the $P_{w,0}$ value to be 1960 for BoMA/PEGDMA-9 copolymerization, which is even lower than that of BoMA/EDMA copolymerization ($P_{w,0} = 2290$). This result is completely opposed to the copolymerizations of MMA with 1 mol % EDMA and PEGDMA-9 (see Fig. 2),²⁹ in which the oxyethylene number dependency of the primary polymer chain length was quite high and the $P_{w,0}$ value obtained for $n = 9$ was 5.9 times higher than that for $n = 1$ (see Fig. 4 for the structures of MMA, BoMA, EDMA, and PEGDMA as monomers). The $P_{w,0}$ value thus obtained was then employed to calculate the theoretical gel point (α_c) according to Stockmayer's equation:⁴⁰

$$\alpha_c = (1/\rho)(P_{w,0} - 1)^{-1}$$

where ρ is the fraction of all double bonds residing on the divinyl units in the initial system.

Table I summarizes the results obtained as a comparison of actual gel points with theoretical ones for BoMA/EDMA (99/1) and BoMA/PEGDMA-9 (99/1) copolymerizations, along with the copolymerization results of MMA with 1 mol % EDMA and PEGDMA-9.

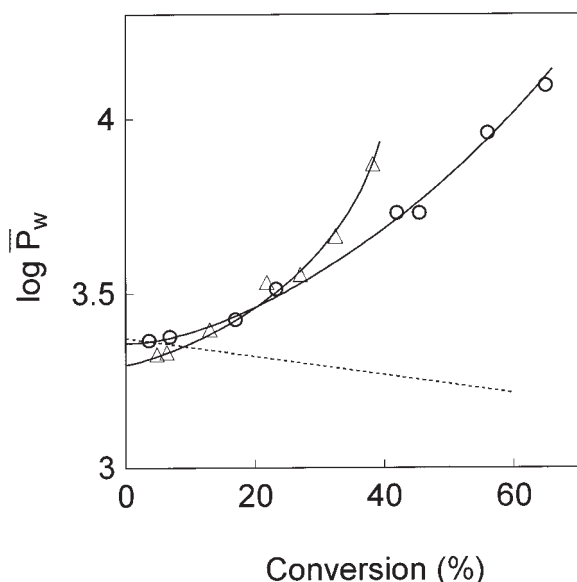


Figure 3 Dependence of P_w on the conversion in the copolymerizations of BoMA with (○) EDMA and (△) PEGDMA-9 and (---) in BoMA homopolymerization.

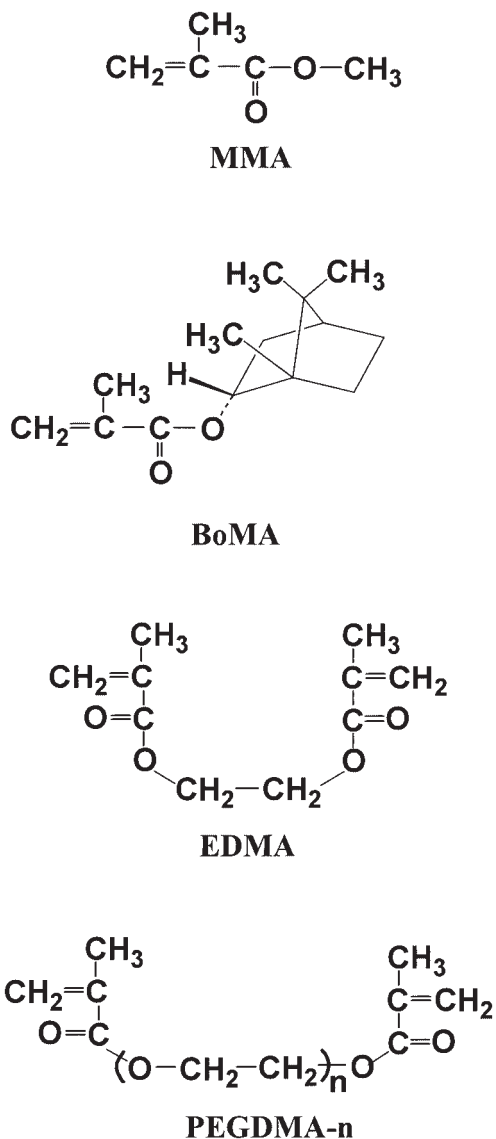


Figure 4 Structural formulas of the monomers.

The actual gel point was quite delayed from the theoretical one for each polymerization system, and the deviation (i.e., the ratio of the actual gel point to the theoretical one) became smaller, from 31 to 19, with an increase in the oxyethylene number, from 1 to 9, for BoMA systems, whereas for MMA systems, it became remarkably larger from 16 to 81. The latter deviation for MMA systems could be ascribed to the increased primary polymer chain length caused by the suppression of the intermolecular termination between growing polymer radicals having a loop structure formed through intramolecular cyclization.²⁹ The former reversed result for BoMA systems may come not only from a suppressed occurrence of intramolecular cyclization leading to the formation of a loop structure but also from an enhanced occurrence of intermolecular crosslinking of the rigid growing BoMA radical with unreacted methacrylic double bonds present at

TABLE I
Comparison of the Actual and Theoretical Gel Points in the Crosslinking Copolymerizations of
BoMA or MMA with 1 mol % EDMA or PEGDMA-9^a

Monovinyl/divinyl	$P_{w,0} \times 10^{-3}$	Gel point (%)		Actual gel point ^d
		Theoretical ^b	Actual ^c	Theoretical gel point ^b
BoMA/EDMA	2.29	2.21	70.0 (69.4) ^d	31
BoMA/PEGDMA-9	1.96	2.58	48.8 (48.2) ^d	19
MMA/EDMA	2.94	1.72	28.0 (27.5) ^d	16
MMA/PEGDMA-9	17.4	0.29	24.6 (23.4) ^d	81

^a In 1,4-dioxane, dilution-1/5, [AIBN] = 0.04 mol/L, 50°C.

^b Theoretical gel point; $\alpha_c = (1/\rho)(P_{w,0} - 1)^{-1}$.

^c Obtained on monomer basis.

^d Obtained as the vinyl group conversion calculated by the assumption of the equal reactivity of each vinyl group belonging to monovinyls and divinyls.

the terminals of long poly(oxyethylene) segments ($n = 9$) in PEGDMA-9 units incorporated into other primary polymer chains in comparison with short ones ($n = 1$) in EDMA units. In addition, the intermolecular crosslinking in BoMA/EDMA copolymerization should be quite reduced as a reflection of a steric effect due to the bulky *d*-bornyl groups, the ratio of the actual gel point to the theoretical one being 31 (16 for MMA/EDMA copolymerization).

Effect of primary polymer chain rigidity on intramolecular crosslinking

In a free-radical crosslinking monovinyl/multivinyl copolymerization, intermolecular crosslinking is the key reaction for the control of gelation during the formation of a three-dimensional network of an indefinitely large size, whereas the key reaction for the control of the network structure is intramolecular crosslinking, which leads to the formation of multiple crosslinks generating the network structure of the crosslinked polymer. The latter intramolecular crosslinking preceded by the former intermolecular crosslinking is not a primary factor for greatly delayed gelation, but its significance becomes important with the progress of polymerization.¹ That is, when the theoretical gel point⁴⁰ is quite low (at a quite early stage of polymerization), the occurrence of intermolecular crosslinking is negligible, at least up to the theoretical gel point, and under these circumstances no contribution of intramolecular crosslinking is expected for the greatly delayed gelation. With the progress of polymerization, the prepolymer concentration inevitably becomes high, and so the occurrence of intermolecular crosslinking is enhanced, inducing subsequent intramolecular crosslinking. The extent of the occurrence of intramolecular crosslinking becomes higher with an increasing number of primary polymer chains in the prepolymer or an increased degree of branching of the prepolymer. The occurrence of intramolecular crosslinking leads to the complication of

the prepolymer structure sterically influencing the intermolecular crosslinkability of pendant vinyl groups; the steric effect is more remarkable for the vinyl groups located in the inner part of the branched prepolymer molecule. Theoretically, it is assumed that all double bonds residing in the polymerization system should have equal reactivity,⁴⁰ and thus the sterically suppressed reactivity of pendant vinyl groups significantly contributes to the greatly delayed gelation as a shielding effect⁵ or a steric excluded volume effect.¹ This kind of complication of the prepolymer structure induced by intramolecular crosslinking influences not only the intermolecular crosslinking but also the bimolecular termination between growing polymer radicals.^{41,42} The latter living type of radical formation leads to the enlargement of the primary polymer chain length and, furthermore, may play an important role in microgelation.¹

Thus, we discuss the effect of primary polymer chain rigidity on intramolecular crosslinking in the free-radical crosslinking monomethacrylate/dimethacrylate copolymerizations. As shown in Table I, the gelation in BoMA/EDMA copolymerization was quite delayed in comparison with that in MMA/EDMA copolymerization. This could be ascribed to a suppressed occurrence of intermolecular crosslinking as a reflection of the rigidity of the primary polymer chain mainly consisting of the bulky *d*-bornyl groups. In this connection, the dependence of P_w on conversion was quite different in MMA/EDMA (see Fig. 2) and BoMA/EDMA (see Fig. 3) copolymerizations. This kind of suppressed intermolecular crosslinking was also reflected in the conversion dependencies of the MWD curves (see Figs. 5 and 6); a broadened MWD curve was clearly observed at a 19.8% conversion for MMA/EDMA copolymerization, although the gel-point conversion was 28.0%, whereas for BoMA/EDMA copolymerization, the occurrence of intermolecular crosslinking was not significant even at a 23.4% conversion, although eventually gelation occurred at a 70.0% conversion. Next, we tried to check the effect of

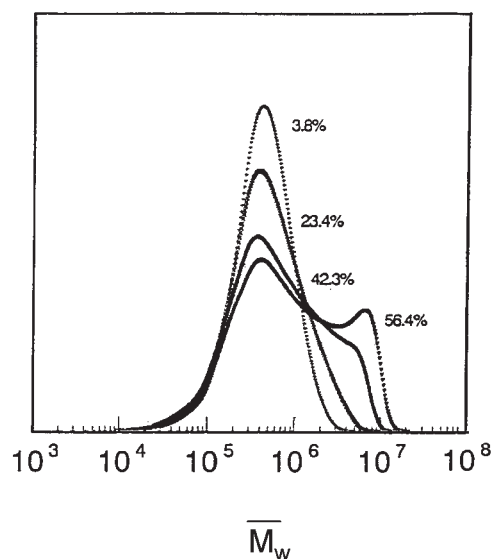


Figure 5 Variation of the MWD curves with the conversion in BoMA/EDMA (99/1) copolymerization.

primary polymer chain rigidity on the intramolecular crosslinking by SEC-MALLS measurements as follows:⁴³ Figure 7 shows the variation of the refractive-index-monitored SEC curves and the correlations of the molecular weight versus the elution volume with conversion for BoMA/EGDMA copolymers. The copolymers were obtained at 17.6 and 34.0% conversions; clearly, both correlation curves were superimposed, demonstrating almost no occurrence of intramolecular crosslinking. Moreover, the occurrence of intramolecular crosslinking, which does not affect the molecular weight, leads to the shrinkage of the molecular size in solution;

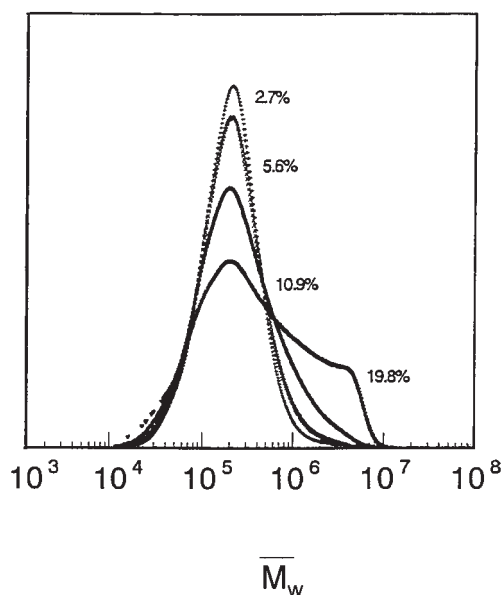


Figure 6 Variation of the MWD curves with the conversion in MMA/EDMA (99/1) copolymerization.

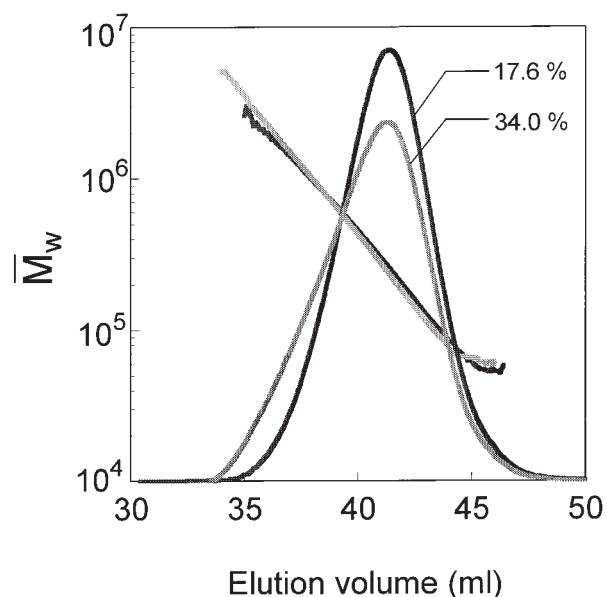


Figure 7 Refractive-index-monitored SEC curves and correlations of the molecular weight versus the elution volume for BoMA/EDMA (99/1) copolymers obtained at 17.6 and 34.0% conversions.

this is reflected in the correlation of $[\eta]$ with the molecular weight.^{13,39,44} Here the solution copolymerization of BoMA with 10 mol % EDMA was carried out in benzene at a dilution of 1/10 with 0.04 mol/L AIBN at 50°C because microgelation was observed at a dilution of 1/10 in the solution MMA/EDMA (90/10) copolymerization in 1,4-dioxane as a reflection of a locally extensive occurrence of intramolecular crosslinking.¹⁵ Figure 8 shows

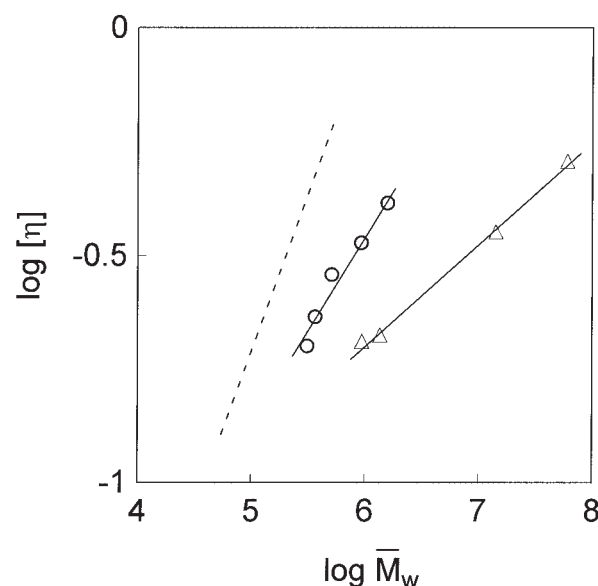


Figure 8 Double logarithmic plots of $[\eta]$ versus M_w for (O) BoMA/EDMA (90/10) and (Δ) MMA/EDMA (90/10) copolymers.

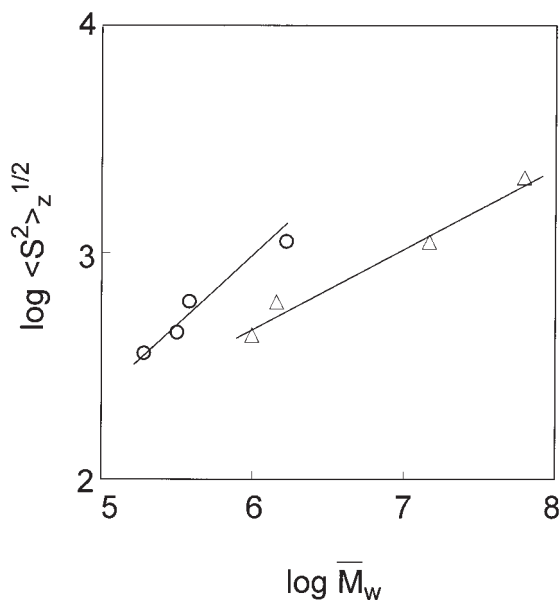


Figure 9 Double logarithmic plots of $\langle S^2 \rangle_z^{1/2}$ versus \bar{M}_w for (○) BoMA/EDMA (90/10) and (△) MMA/EDMA (90/10) copolymers.

the double logarithmic plots of $[\eta]$ versus \bar{M}_w for BoMA/EDMA and MMA/EDMA copolymers; the plot of the MMA/EDMA copolymers can be clearly seen below, in comparison with that of BoMA/EDMA copolymers, as a reflection of an enhanced occurrence of intramolecular crosslinking. This is in line with the double logarithmic plots of $\langle S^2 \rangle_z^{1/2}$ versus \bar{M}_w for BoMA/EDMA and MMA/EDMA copolymers (see Fig. 9); again, the plot of MMA/EDMA copolymers can be seen below. A_2 was also quite low, that is, less than 10^{-5} mol $\text{cm}^3 \text{g}^{-2}$, for MMA/EDMA copolymers obtained at more than 15% conversion, whereas for BoMA/EDMA copolymers, the A_2 values were greater than 10^{-5} mol $\text{cm}^3 \text{g}^{-2}$, even when the conversion was very close to the gel point.

CONCLUSIONS

To deepen our understanding of the key factor behind each elementary reaction in a monovinyl/divinyl copolymerization, we have discussed the effect of primary polymer chain rigidity on intramolecular cyclization and intramolecular crosslinking in free-radical crosslinking monomethacrylate/dimethacrylate copolymerizations. Here BoMA was chosen as a typical example of bulky monomethacrylate monomers, the polymerization of which led to the formation of a rigid polymer chain. First, BoMA/PEGDMA copolymerizations were explored to discuss the effect of primary polymer chain rigidity on intramolecular cyclization because the copolymer backbone, mainly consisting of BoMA units, inevitably generated a rigid primary polymer chain. The solution copolymeriza-

tions of BoMA with 1 mol % EDMA and PEGDMA-9 were carried out in 1,4-dioxane at a dilution of 1/5. The dependence of P_w on the conversion was completely opposed to the copolymerizations of MMA with 1 mol % EDMA and PEGDMA-9. Then, the deviation of the actual gel points with the theoretical ones for both BoMA/EDMA (99/1) and BoMA/PEGDMA-9 (99/1) copolymerizations was compared with those of the corresponding MMA/EDMA and MMA/PEGDMA-9 copolymerizations; the opposite result was observed. Although the deviation for MMA systems could be explained by the increased primary polymer chain length caused by the suppression of the intermolecular termination between growing polymer radicals having a loop structure formed through intramolecular cyclization, the opposite result for BoMA systems may come not only from a suppressed occurrence of intramolecular cyclization but also from an enhanced occurrence of intermolecular crosslinking of the rigid growing BoMA radical with unreacted methacrylic double bonds present at the terminals of long poly(oxyethylene) segments in PEGDMA-9 units incorporated into other primary polymer chains in comparison with short ones in EDMA units. Second, we discussed the effect of primary polymer chain rigidity on intermolecular and intramolecular crosslinkings in BoMA/EDMA and MMA/EDMA copolymerizations. The gelation in BoMA/EDMA (99/1) copolymerization was quite delayed in comparison with that in the corresponding MMA/EDMA copolymerization. This could be ascribed to a suppressed occurrence of intermolecular crosslinking as a reflection of the rigidity of the primary polymer chain mainly consisting of the bulky *d*-bornyl groups. This kind of suppressed intermolecular crosslinking was also reflected in the conversion dependencies of MWD curves. The effect of primary polymer chain rigidity on intramolecular crosslinking was examined through the variation of the refractive-index-monitored SEC curves and the correlations of the molecular weight versus the elution volume with the conversion for BoMA/EGDMA (99/1) copolymers by SEC-MALLS measurements. The occurrence of intramolecular crosslinking led to the shrinkage of the molecular size, as reflected in the correlations of $[\eta]$, $\langle S^2 \rangle_z^{1/2}$, and A_2 with the molecular weight. The results obtained for both BoMA/EDMA (90/10) and MMA/EDMA (90/10) copolymers were in line with our expectations; the plots of the MMA/EDMA copolymers were seen below in comparison with those of the corresponding BoMA/EDMA copolymers; this was a reflection of an enhanced occurrence of intramolecular crosslinking.

References

1. Matsumoto, A. *Adv Polym Sci* 1995, 123, 41.
2. Dusek, K. *Developments in Polymerisation 3*; Applied Science: London, 1982; p 143.

3. Dotson, N. A.; Macosko, C. W.; Tirrell, M. *Synthesis, Characterization, and Theory of Polymeric Networks and Gels*; Plenum: New York, 1992; p 319.
4. Walling, C. *J Am Chem Soc* 1945, 67, 441.
5. Storey, B. T. *J Polym Sci Part A: Gen Pap* 1965, 3, 265.
6. Horie, K.; Otagawa, A.; Muraoka, M.; Mita, I. *J Polym Sci Polym Chem Ed* 1975, 13, 445.
7. Galina, H.; Dusek, K.; Tuzar, Z.; Bohdanecky, M.; Stokr, J. *Eur Polym J* 1980, 16, 1043.
8. Spevacek, J.; Dusek, K. *J Polym Sci Polym Phys Ed* 1980, 18, 2027.
9. Shah, A. C.; Parsons, I. W.; Haward, R. N. *Polymer* 1980, 21, 825.
10. Leicht, R.; Fuhrmann, J. *Polym Bull* 1981, 4, 141.
11. Matsumoto, A.; Nakajima, H.; Oiwa, M. *J Thermoset Plast Jpn* 1988, 9, 141.
12. Matsumoto, A.; Takahashi, S.; Oiwa, M. *Polym Prepr (Am Chem Soc Div Polym Chem)* 1990, 31(2), 149.
13. Matsumoto, A.; Yamashita, Y.; Oiwa, M. *J Thermoset Plast Jpn* 1991, 12, 135.
14. Matsumoto, A.; Yamashita, Y.; Oiwa, M. *J Thermoset Plast Jpn* 1993, 14, 139.
15. Matsumoto, A.; Takahashi, S.; Morita, T. *J Thermoset Plast Jpn* 1996, 17, 139.
16. Aota, H.; Sanai, Y.; Matsumoto, A.; Kamachi, M. *Polym J* 1996, 28, 867.
17. Matsumoto, A.; Fujise, K.; Morita, T.; Terada, S.; Yamamoto, Y.; Aota, H.; Ikeda, J. *Wiley Polymer Networks Group Review Series*; Wiley: New York, 1998; Vol. 1, p 197.
18. Staudinger, H.; Huseman, E. *Chem Ber* 1935, 68, 1618.
19. De Boer, J. H. *Trans Faraday Soc* 1936, 32, 10.
20. Erath, E. H.; Robinson, M. *J Polym Sci Part C: Polym Symp* 1963, 3, 65.
21. Matsumoto, A.; Aoki, K.; Oiwa, M.; Ochi, M.; Shimbo, M. *Polym Bull* 1983, 10, 438.
22. Matsumoto, A.; Kurokawa, M.; Oiwa, M. *J Thermoset Plast Jpn* 1988, 9, 85.
23. Matsumoto, A.; Kurokawa, M.; Oiwa, M. *Eur Polym J* 1989, 25, 207.
24. Matsumoto, A.; Mori, Y.; Takahashi, S.; Aota, H. *J Thermoset Plast Jpn* 1995, 16, 131.
25. Funke, W.; Okay, O.; Joos-Muller, B. *Adv Polym Sci* 1998, 136, 139.
26. Aota, H.; Nishizawa, K.; Matsumoto, A. *Macromol Mater Eng* 2000, 275, 26.
27. Aota, H.; Nishizawa, K.; Matsumoto, A. *Macromol Mater Eng* 2000, 278, 1.
28. Matsumoto, A.; Nishizawa, K.; Yamashita, Y.; Morita, T.; Aota, H. *J Appl Polym Sci* 2001, 81, 1187.
29. Matsumoto, A.; Matsuo, H.; Oiwa, M. *Macromol Chem Rapid Commun* 1987, 8, 373.
30. Matsumoto, A.; Matsuo, H.; Oiwa, M. *J Polym Sci Part C: Polym Lett* 1988, 26, 287.
31. Matsumoto, A.; Yonezawa, S.; Oiwa, M. *Eur Polym J* 1988, 24, 703.
32. Matsumoto, A.; Hasei, Y.; Aota, H. *J Thermoset Plast Jpn* 1994, 15, 117.
33. Matsumoto, A. *Prog Polym Sci* 2001, 26, 189.
34. Matsumoto, A. *Macromol Symp* 2002, 179, 141.
35. Matsumoto, A.; Fujise, K.; Ikeda, J.; Aota, H. *J Net Polym Jpn* 2002, 23, 81.
36. Kiguchi, T.; Aota, H.; Matsumoto, A. *J Polym Sci Part A: Polym Chem* 2003, 41, 3243.
37. Doura, M.; Naka, Y.; Aota, H.; Matsumoto, A. *Macromolecules* 2003, 36, 8477.
38. Soper, B.; Haward, R. N.; White, E. F. T. *J Polym Sci Part A-1: Polym Chem* 1972, 10, 2545.
39. Matsumoto, A.; Ando, H.; Oiwa, M. *Eur Polym J* 1989, 25, 385.
40. Stockmayer, W. H. *J Chem Phys* 1944, 12, 125.
41. Landin, D. T.; Macosko, C. W. *Macromolecules* 1988, 21, 846.
42. Zhu, S.; Hamielec, A. E. *Macromolecules* 1989, 22, 3093.
43. Matsumoto, A.; Okamoto, A.; Okuno, S.; Aota, H. *Angew Makromol Chem* 1996, 240, 275.
44. Matsumoto, A.; Ando, H.; Oiwa, M. *Kobunshi Ronbunshu* 1989, 46, 583.