Influence of Structural Parameters on the Degradation of Ultrahigh-Molecular-Weight Vinyl-Type Network-Polymer Precursors During Elution Through Size Exclusion Chromatography Columns

Jun-Ichi Ikeda,[1] Hiroaki Oe,[2] Hiroyuki Aota,[2] Akira Matsumoto[2]

[1]*Kyoeisha Chemical Co., Ltd., 5-2-5 Saikujyo-cho, Nara 630-8453, Japan*
[2]*Department of Applied Chemistry, Faculty of Engineering and High Technology Research Center, Kansai University, Suita, Osaka 564-8680, Japan*

ABSTRACT: Network-polymer precursors obtained in various crosslinking monovinyl/divinyl copolymerization systems, including benzyl methacrylate/1,6-hexanediol dimethacrylate, benzyl acrylate (BzA)/1,6-hexanediol diacrylate (HDDA), and vinyl benzoate/divinyl adipate, were subjected to degradation during elution through size exclusion chromatography (SEC) columns, although the copolymerizations were conducted under specified conditions where the factors for the greatly delayed gelation from the Flory–Stockmayer gelation theory were reduced. The most remarkable degradation was observed for the BzA/HDDA copolymerization, which provided prepolymers with the most flexible backbone chains. Thus, the BzA/HDDA precopolymers were chosen, and their degradation behavior during elution through SEC columns was explored in detail as one of the representatives of vinyl-type network-polymer precursors. The results were correlated with the structural parameters of network-polymer precursors, including primary polymer chain length, branched structure, and multiple crosslink or network structure. The degradation became more remarkable with decreased primary polymer chain length, that is, the increment of branching, whereas reduced degradation was observed with the incorporation of loop and network structures into the prepolymer. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 577–582, 2003

Key words: degradation; branched; networks; copolymerization; crosslinking

INTRODUCTION

Our previous article[1] dealt with the crosslinking copolymerization of styrene (St) with *m*-divinylbenzene (*m*-DVB) as an extension of our continuing studies concerned with the mechanistic discussion of the three-dimensional network formation in the free-radical polymerization and copolymerization of multivinyl compounds.[2] During the detailed pursuit of the variation in molecular weight distribution (MWD) curves with conversion with a size exclusion chromatography (SEC) columns equipped with a multiangle laser light-scattering (MALLS) device (SEC–MALLS), we noticed by chance that the degradation of an ultrahigh-molecular-weight poly(styrene-*co-m*-divinylbenzene) [poly(St-*co-m*-DVB)] prepolymer obtained at conversion close to the gel point occurred significantly during elution through SEC columns. The specific degradation of prepolymer depended on the primary polymer chain length ($\bar{P}_{w,0}$), branched structure, and

multiple crosslink or network structure as the characteristic features of network-polymer precursor.

This prompted us to extend our discussion to the degradation of common network-polymer precursors obtained in various crosslinking monovinyl/divinyl copolymerization systems, including benzyl methacrylate (BzMA)/1,6-hexanediol dimethacrylate (HDDMA),[3,4] benzyl acrylate (BzA)/1,6-hexanediol diacrylate (HDDA),[5] and vinyl benzoate (VBz)/divinyl adipate (DVA). The degradation of the resulting network-polymer precursors occurred most remarkably for the BzA/HDDA copolymerization, which provided prepolymers with the most flexible backbone chains. Therefore, the BzA/HDDA precopolymers were chosen, and their degradation behavior during elution through SEC columns was explored in detail as one of the representatives of vinyl-type network-polymer precursors. The degradability was correlated with the structural parameters of network-polymer precursor including $\bar{P}_{w,0}$, branched structure, and multiple crosslink or network structure.

In this connection, let us recall that the chain scission during elution through SEC columns has been observed for ultrahigh-molecular-weight polystyrene.[6–11] Barth and Carlin[8] reviewed the polymer shear degradation in SEC and presented guidelines involving operational parameters. High-molecular-

weight polymers are fairly sensitive to shear forces, which can lead to chain scission. Because of velocity gradients generated during flow in SEC columns, a polymer becomes extended. Bonds near the middle of the chain become stretched and can rupture if shear rates are great enough. As the end segments of a chain maintain their coiled shape, the maximum strain is usually focused near the center of the polymer. In general, the most probable sites of stress concentration on the polymer chain for the application of shear force are (1) side chain links to the main chain, that is, branch points; (2) crosslink points in networks; (3) points of inclusion of heteroatoms and quaternary carbon atoms; and (4) dissymmetry between adjacent atoms, which promotes the rupture of the chain by stretching forces. The former two points are closely related to our vinyl-type network-polymer precursors. Furthermore, we point out that the degradation of prepolymers during elution through SEC columns is significantly related not only to the discussion of network formation but also to the discussion of branching with SEC.[12–14]
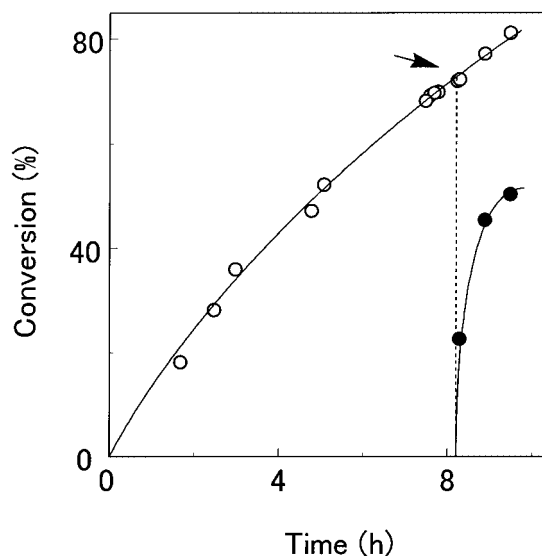
EXPERIMENTAL

VBz and DVA, supplied by Japan VAM & POVAL Co., Ltd. (Osaka, Japan), and BzMA, BzA, HDDMA, and HDDA, supplied by Kyoeisha Chemical Co., Ltd. (Nara, Japan), as monomers, were purified by vacuum distillation under nitrogen.

2,2'-Azobisisobutyronitrile (AIBN) and 1,1'-azo-biscyclohexane-1-carbonitrile (ACHCN) as initiators and 1,4-dioxane and t-butylbenzene (t-BB) as solvents were purified by conventional methods. Lauryl mercaptan (LM), as a chain-transfer agent (a commercially available, extrapure reagent), was used without further purification.

Polymerization was carried out in a glass ampule containing the required amounts of monovinyl monomer, divinyl monomer, initiator, solvent, and LM. 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 $50 \pm 0.1°C$. After a predetermined time of reaction had passed, we precipitated the copolymer by pouring the reaction mixture into a large excess of methanol containing a small amount of hydroquinone as an inhibitor. The purification of the polymer was performed by reprecipitation from a tetrahydrofuran (THF)–precipitant system. The percentage of conversion was calculated from the weight of the vacuum-dried polymer. The gel fraction of polymer at conversions beyond the gel point was separated by extraction of the sol fraction with THF.

Fractionation of poly(BzA-*co*-HDDA) was carried out with a THF–methanol system. Methanol was added dropwise into about a 2% (w/v) THF solution of the polymer sample until the solution became turbid. The turbid solution was then warmed up to dissolve the precipitated polymer, and subsequently, the solution was gradually cooled to obtain a high-molecular-weight fraction of the polymer.

The weight-average molecular weight (M_w) and MWD were measured by SEC with a dual detector system, set in the direction of flow and consisting of a MALLS device and a differential refractometer in sequence. SEC–MALLS measurements were carried out at 40°C in THF with a Shodex GPC KF-806L (Tokyo, Japan) × 5 columns, at polymer concentrations of 0.1–0.5% (w/v) and a flow rate of 1 mL min^{-1}. The MALLS device was a DAWN DSP (Wyatt Technology Corp., Santa Barbara, CA), where the laser beam (wavelength = 632.8 nm) was focused on a 67-μL flow cell. M_w was also measured by light scattering. The measurements were carried out in THF at 30°C with an Otsuka Electronics DLS-700 dynamic light-scattering spectrophotometer (Osaka, Japan) over an angular range between 30 and 150°, with unpolarized light of wavelength 632.8 nm.

Figure 1 Conversion–time curve for the solution copolymerization of BzMA with 0.04 mol % HDDMA in *t*-BB at a dilution of 2:3 in the presence of 7.8×10^{-4} mol L^{-1} LM with 0.025 mol L^{-1} AIBN at 50°C. Open and filled symbols correspond to the total and gel polymers, respectively. The arrow denotes the gel point.

RESULTS AND DISCUSSION

Degradation of network-polymer precursors obtained in various crosslinking monovinyl/divinyl copolymerization systems

We adjusted the polymerization conditions considering the fact[1] that the degradation of resulting poly(St-*co*-*m*-DVB) prepolymers became remarkable with the reduced occurrence of intramolecular crosslinking, that is, with approaching the ideal network formation governed by Flory–Stockmayer (FS) gelation theory.[15]
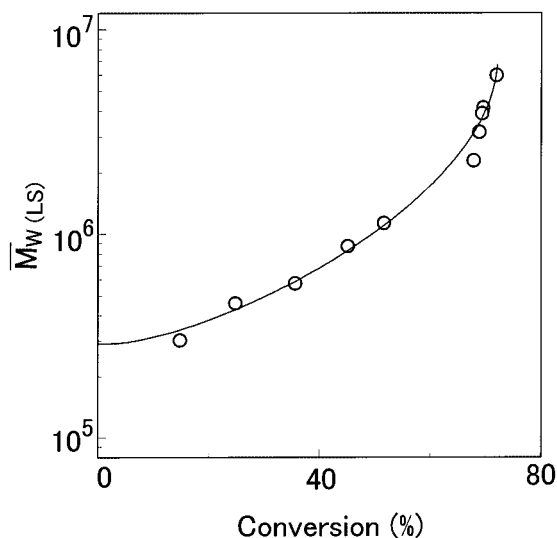
Figure 2 Dependence of M_w (LS) of the resulting prepolymers determined by LS on conversion (see Fig. 1).

Thus, BzMA/HDDMA (99.96:0.04 molar ratio), BzA/HDDA (99.94:0.06 molar ratio), and VBz/DVA (99.9:0.1 molar ratio) copolymerizations were conducted in bulk or in solution with AIBN or ACHCN as an initiator in the presence of LM as a chain-transfer agent at 50°C.

Figure 1 shows the conversion–time curve for the solution copolymerization of BzMA with 0.04 mol % HDDMA in t-BB at a dilution of 2:3 in the presence of 7.8×10^{-4} mol L^{-1} LM as a chain-transfer agent with 0.025 mol L^{-1} AIBN at 50°C as an example. The percentages of the gel polymers are also plotted in Figure 1. The actual gel point was determined by extrapolation of the gel formation curve to 0%. Thus, the conversion at which gel started to form, that is, the gel point, was estimated to be 73.1%. Similarly, the gel points were estimated to be 90.7 and 71.2% for the BzA/HDDA (99.94:0.06) and VBz/DVA (99.9:0.1) copolymerizations, respectively. In addition, no gel effect[16] was observed in all of the copolymerizations. Certainly, no occurrence of the gel effect would be required for keeping $\bar{P}_{w,0}$ constant in the case where

the actual gel point was compared with the theoretical gel point (α_c) estimated according to FS theory because the gel effect caused by a suppressed bimolecular termination reaction would enlarge $\bar{P}_{w,0}$.

Figure 2 shows the conversion dependence of M_w of the resulting prepolymers determined by LS. $\bar{P}_{w,0}$ was estimated from the initial weight-average molecular weight ($M_{w,0}$) value determined by the extrapolation of the curve to zero conversion. Then, the $\bar{P}_{w,0}$ value was employed to calculate α_c according to Stockmayer's equation:[15]

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

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

Table I summarizes the comparison of actual gel points with α_c's. The ratios of the actual gel points to α_c's reached 1.5, 1.4, and 1.9, respectively, for the BzMA/HDDMA (99.96:0.04), BzA/HDDA (99.94:0.06), and VBz/DVA (99.9:0.1) copolymerizations, which supported the good applicability of FS theory, although gelation is well-known to occur frequently 1–2 orders of magnitude later than predicted.[2] FS theory suggests that the MWD curves of resulting prepolymers should rapidly broaden toward a higher molecular weight side with conversion as a result of exclusive intermolecular crosslinking reactions, leading to ideal network formation governed by theory.[15,17,18] SEC is commonly used to determine the molecular weight and the MWD of resulting prepolymers. However, as a technique, it is not always applicable to our crosslinking polymerization systems because the structure of the prepolymer changes from a linear to a branched form with progressing polymerization, and moreover, the content of ring or loop structures introduced into the linear portion or primary polymer chain and the content of multiple crosslink or network structures in the branched form depend on the polymerization conditions. However, SEC–MALLS was expected to be a very useful and efficient tool in the characterization of our prepolymers because the use of

TABLE I
Comparison of the Actual Gel Point and α_c in Various Crosslinking Monovinyl/Divinyl Copolymerizations

Monovinyl/divinyl	$\bar{P}_{w,0} \times 10^{-3}$	Gel point (%)		Actual gel point[c]
		α_c[a]	Actual[b]	α_c[a]
BzMA/HDDMA[d]	1.70	49.1	73.1 (72.9)[c]	1.5
BzA/HDDA[e]	1.59	62.9	90.7 (90.5)[c]	1.4
VBz/DVA[f]	2.22	37.5	71.2 (70.9)[c]	1.9

[a] $\alpha_c = (1/\rho)(\bar{P}_{w,0} - 1)^{-1}$.
[b] Obtained on a monomer basis.
[c] Obtained as the vinyl group conversion calculated by the assumption of equal reactivities of each vinyl group belonging to monovinyls and divinyls.
[d] HDDMA = 0.04 mol% in t-BB, dilution = 2:3, [AIBN] = 0.025 mol L^{-1}, [LM] = 7.8×10^{-4} mol/L^{-1}, 50°C.
[e] HDDA = 0.06 mol% in dioxane, dilution = 2:3, [ACHCN] = 0.01 mol L^{-1}, [LM] 2×10^{-3}, 50°C.
[f] DVA = 0.1 mol% in bulk, [AIBN] = 0.1 mol L^{-1}, [LM] = 1.5×10^{-3}, 50°C.
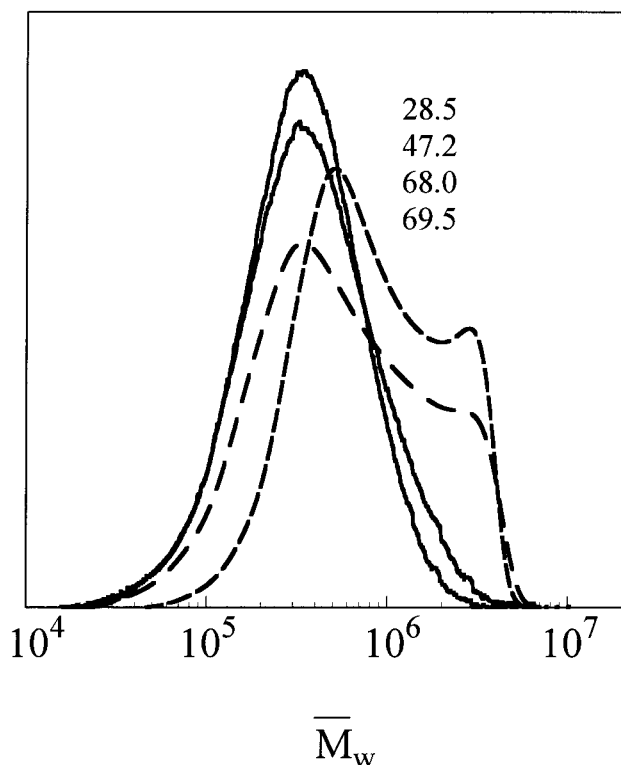
Figure 3 Broadened MWD curves toward higher molecular weight sides with conversion (see Fig. 1).

MALLS as an absolute detector enables the molecular weight and MWD to be determined directly without any calibration.[4]

Figure 3 shows the variations in MWD with conversion in the copolymerization of BzMA with 0.04 mol % of HDDMA. Instead of our expectation that the more tailed MWD curves would be observed at a higher conversion as a reflection of ideal network formation, a big bulge appeared clearly at the tail ends of the SEC curves of the prepolymers obtained at 68.0 and 69.5% conversions close to the gel point, that is, 73.1%. Moreover, the peak top of the bulge corresponded to a molecular weight of 2.9×10^6, although the exclusion limit of SEC was much higher at 2×10^7. This may suggest the occurrence of the degradation of ultrahigh-molecular-weight poly(BzMA-co-HDDMA) during elution through the SEC columns. The molecular weights determined by SEC–MALLS were then compared with those by determined by LS.

Figure 4 shows the plot of M_w (SEC–MALLS)/M_w (LS) versus M_w (LS) for the BzMA/HDDMA (99.96:0.04) copolymerization, along with those for the BzA/HDDA (99.94:0.06) and VBz/DVA (99.9:0.1) copolymerizations. The results for the St/m-DVB (99.83:0.17) copolymerization[1] are also plotted as a dotted line. Because M_w (SEC–MALLS)/M_w (LS) would be a measure of the degradation of the prepolymer during elution through the SEC columns, the resulting prepolymers in four crosslinking monovinyl/divinyl copolymerization systems degraded easier in the order

BzMA/HDDMA < VBz/DVA < St/m-DVB[1] < BzA/HDDA. The degradation of resulting network-polymer precursors occurred most remarkably for BzA/HDDA copolymerization, which provided the prepolymers with the most flexible backbone chains. Earlier, Slagowski et al.[6] reported that the chain scission in SEC columns was observed for ultrahigh-molecular-weight polystyrene ($M_w = 4.4 \times 10^7$), and its molecular weight decreased to 1.9×10^7. With this in mind, we prepared ultrahigh-molecular-weight poly(BzMA), poly(BzA), and poly(VBz) [M_w (LS) = 7.9 $\times 10^6$, 9.2×10^6, and 8.0×10^6, respectively] by conventional emulsion polymerization, and then, these linear polymers were subjected to SEC–MALLS measurement to give corresponding M_w (SEC–MALLS)/M_w (LS) values of 0.41, 0.11, and 0.23, respectively. Here, the poly(BzA), that is, acrylate polymer, was again the most degradable during elution through the SEC columns. Thus, the BzA/HDDA precopolymers were chosen, and their degradation behavior during elution through the SEC columns was explored in more detail as one of the representatives of vinyl-type network-polymer precursors. The degradability was correlated with the structural features of network-polymer precursors, including $\bar{P}_{w,0}$, branched structure, and multiple crosslink or network structure.

Correlation of degradability with $\bar{P}_{w,0}$ and branched structure

We tried to examine the dependence of degradation of the resulting prepolymers on the $\bar{P}_{w,0}$ because the shorter primary polymer chain inevitably led to a more highly branched structure to produce an ultra-
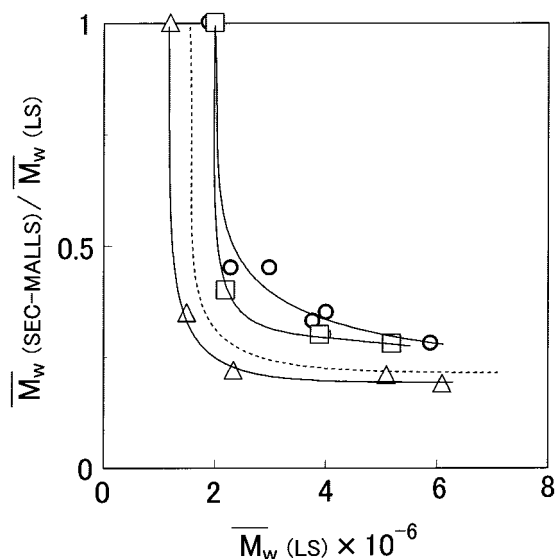
Figure 4 Degradation of the resulting prepolymers in (○) BzMA/HDDMA (99.96:0.04), (△) BzA/HDDA (99.94:0.06), and (□) VBz/DVA (99.9:0.01) copolymerizations. The dotted line corresponds to the St/m-DVB (99.83:0.17) copolymerization.

TABLE II
Comparison of The Actual Gel Point and α_c in the Crosslinking Copolymerizations of BzA with HDDA[a]

[LM] $\times 10^3$ (mol L^{-1})	HDDA (mol %)	$\bar{P}_{w,0} \times 10^{-3}$	Gel point (%)		Actual gel point[d]
			α_c[b]	Actual[c]	α_c[b]
0.5	0.04	3.41	36.7	88.9 (88.8)[d]	2.4
2.2	0.06	1.23	67.8	92.0 (91.9)[d]	1.4
3.0	0.1	0.88	56.9	91.1 (91.0)[d]	1.6

[a] In 1,4-dioxane, dilution = 2:3, [ACHCN] = 0.01 mol L^{-1}, 50°C.
[b] $\alpha_c = (1/\rho)(\bar{P}_{w,0} - 1)^{-1}$.
[c] Obtained on a monomer basis.
[d] Obtained as the vinyl group conversion calculated by the assumption of equal reactivities of BzA and HDDA vinyl groups.

high-molecular-weight prepolymer of the same molecular weight. Thus, two kinds of poly(BzA-*co*-HDDA) prepolymers with different $\bar{P}_{w,0}$ values were prepared as follows: BzA/HDDA (99.96:0.04, 99.94:0.06, and 99.9:0.1) copolymerizations were conducted in 1,4-dioxane at a dilution of 2:3 in the presence of 5 $\times 10^{-4}$, 2.2 $\times 10^{-3}$, and 3 $\times 10^{-3}$ mol L^{-1} LM, respectively, as a chain-transfer agent with 0.01 mol L^{-1} ACHCN at 50°C. The $\bar{P}_{w,0}$ values of the resulting prepolymers were estimated to be 3410, 1230, and 880, respectively. Table II summarizes the comparison of actual gel points with α_c's. The deviation of the actual gel point from α_c became smaller with decreasing $\bar{P}_{w,0}$ as expected.[2] Figure 5 shows the plots of M_w (SEC–MALLS)/M_w (LS) versus M_w (LS). Obviously, the degradation of prepolymers became more remarkable with decreasing $\bar{P}_{w,0}$, that is, with the increment of branching, as was the case in the St/*m*-DVB copolymerization.[1]

Then, the more degradable BzA/HDDA (99.94:0.06) prepolymer [M_w (LS) = 6.2 $\times 10^6$], with a $\bar{P}_{w,0}$ of 1230,
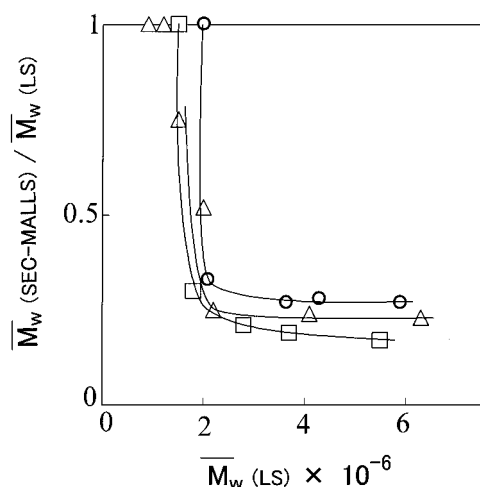
was fractionated to give about 10 wt % of a higher molecular weight fraction of M_w (LS) = 8.9 $\times 10^6$. Both the original and fractionated samples were subjected to SEC–MALLS measurement to give the MWD curves shown in Figure 6; the values of M_w (SEC–MALLS)/M_w (LS) were calculated as 0.176 and 0.145, respectively. The higher molecular weight fraction degraded easier, as we expected.

Correlation of degradability with multiple crosslink or network structure

Three types of prepolymers containing different amounts of loop and network structures were prepared by the solution copolymerization of BzA with 1 mol % HDDA in 1,4-dioxane at dilutions of 2:3, 1:3, and 1:5 in the presence of 2 $\times 10^{-3}$, 1.5 $\times 10^{-3}$, and 1.2 $\times 10^{-3}$ mol L^{-1} LM, respectively, as a chain-transfer agent with 0.01 mol L^{-1} ACHCN at 50°C. Table III summarizes the comparison of actual gel points with
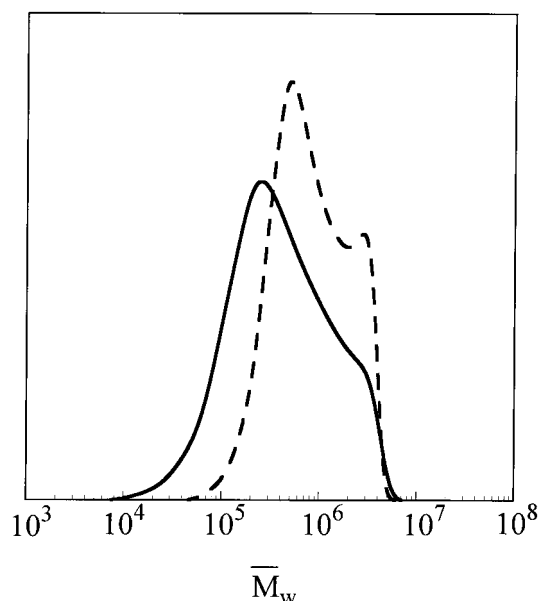
Figure 5 Degradation of poly(BzA-*co*-HDDA) prepolymers obtained in the solution copolymerization of BzA with 0.04, 0.06, and 0.1 mol % HDDMA in 1,4-dioxane at a dilution of 2:3 in the presence of (○) 5 $\times 10^{-4}$, (△) 2.2 $\times 10^{-3}$, and (□) 3 $\times 10^{-3}$ mol L^{-1} LM, respectively, with 0.01 mol L^{-1} ACHCH at 50°C. The $\bar{P}_{w,0}$ values were 3410, 1230, and 880, respectively.

Figure 6 MWD curves of the (—) original and (– – –) fractionated BzA/HDDA (99.94:0.06) prepolymers with M_w (LS) values of 6.2 $\times 10^6$ and 8.9 $\times 10^6$, respectively.

TABLE III
Comparison of The Actual Gel Point and α_c in the Crosslinking Copolymerization of BzA with HDDA[a]

Dilution	$[LM] \times 10^3$ (mol L^{-1})	$P_{w,0} \times 10^{-3}$	Gel point (%)		Actual gel point[d]
			α_c[b]	Actual[c]	α_c[b]
2:3	2.0	0.98	5.2	35.1 (34.6)[d]	6.6
1:3	1.5	0.85	5.9	49.3 (48.6)[d]	8.2
1:5	1.2	0.81	6.2	64.4 (63.5)[d]	10.2

[a] HDDA = 1 mol % in 1,4-dioxane, [ACHCN] = 0.01 mol/L^{-1}, 50°C.
[b] $\alpha_c = (1/\rho)(\bar{P}_{w,0} - 1)^{-1}$.
[c] Obtained on a monomer basis.
[d] Obtained as the vinyl group conversion calculated by the assumption of equal reactivities of BzA and HDDA vinyl groups.

α_c's; the gelation occurred quite later than predicted as a reflection of the extensive occurrence of intramolecular cyclization and crosslinking reactions, which led to the enhanced formation of loop and network structures. Figure 7 shows the plots of M_w (SEC–MALLS)/M_w (LS) versus M_w (LS). The degradation of the prepolymers became less remarkable from 2:3 to 1:5, that is, at a higher dilution, which suggests the reduced occurrence of degradation by the incorporation of loop and network structures into the prepolymer. $\bar{P}_{w,0}$ was lower for the prepolymers obtained at a higher dilution, despite the previous result that a shorter primary polymer chain led to the promoted occurrence of degradation.

CONCLUSIONS

In this work, we tried to generalize the degradation of ultrahigh-molecular-weight poly(St-*co-m*-DVB) pre-

polymer[1] during elution through SEC columns to the common network-polymer precursors obtained in various crosslinking monovinyl/divinyl copolymerization systems, including BzMA/HDDMA, BzA/HDDA, and VBz/DVA. The degradation of resulting network-polymer precursors occurred most remarkably for the BzA/HDDA copolymerization, which provided the prepolymers with the most flexible backbone chains. Thus, the BzA/HDDA precopolymers were chosen, and their degradation behavior during elution through SEC columns was explored in detail as one of the representatives of vinyl-type network-polymer precursors. The degradability was correlated with the structural features of network-polymer precursor, including $\bar{P}_{w,0}$, branched structure, and multiple crosslink or network structure.

References

1. Matsumoto, A.; Oe, H.; Aota, H. Polym J 2002, 34, 242.
2. Matsumoto, A. Adv Polym Sci 1995, 123, 41.
3. Matsumoto, A.; Okuno, S.; Aota, H. Macromol Symp 1995, 93, 1.
4. Matsumoto, A.; Okamoto, A.; Okuno, S.; Aota, H. Angew Makromol Chem 1996, 240, 275.
5. Matsumoto, A.; Taniguchi, A. Polym J 1999, 31, 711.
6. Slagowski, E. L.; Fetters, L. J.; McIntyre, D. Macromolecules 1974, 7, 394.
7. McIntyre, D.; Shih, A. L.; Savoca, J.; Seeger, R.; MacArthur, A. ACS Symposium Series 245; American Chemical Society: Washington, DC, 1984; p 227.
8. Barth, H. G.; Carlin, F. J. J Liq Chromatogr 1984, 7, 1717.
9. Chubarova, E. V.; Nesterov, V. V. Vysokomol Soedin A 1994, 38, 1372.
10. Zigon, M.; Ke The, N.; Shuyao, C.; Grubisic-Gallot, Z. J Liq Chromatogr Relat Technol 1997, 20, 2155.
11. Aust, N.; Parth, M.; Lederer, K. Int J Polym Anal Charact 2001, 6, 245.
12. Kurata, M.; Okamoto, H.; Iwama, M. Polym J 1972, 3, 739.
13. Park, W. S.; Graessley, W. W. J Polym Sci Polym Phys Ed 1977, 15, 85.
14. Axelson, D. E.; Knapp, W. C. J Appl Polym Sci 1980, 25, 119.
15. Stockmayer, W. H. J Chem Phys 1944, 12, 125.
16. Trommsdorff, E.; Kohle, H.; Lagally, P. Makromol Chem 1948, 1, 169.
17. Oiwa, M. Nippon Kagaku Zasshi 1955, 76, 684.
18. Tobita, H. Macromol Theory Simul 1998, 7, 225.
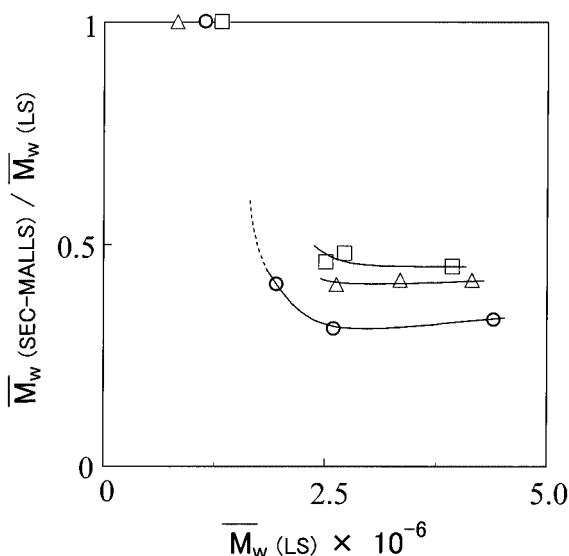
Figure 7 Degradation of poly(BzA-*co*-HDDA) prepolymers obtained in the solution copolymerization of BzA with 1 mol % HDDMA in 1,4-dioxane at dilutions of (○) 2:3, (△) 1:3, and (□) 1:5 in the presence of 2×10^{-3}, 1.5×10^{-3}, and 1.2×10^{-3} mol L^{-1} LM, respectively, with 0.01 mol L^{-1} ACHCN at 50°C. The $\bar{P}_{w,0}$ values were 980, 850, and 810, respectively.