Approach to Ideal Network Formation Governed by Flory−Stockmayer Gelation Theory in Free-Radical Cross-Linking Copolymerization of Styrene with *m*-Divinylbenzene

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Received March 11, 1999; Revised Manuscript Received September 15, 1999

ABSTRACT: The critical conditions in which the classical Flory−Stockmayer gelation theory (F−S theory) is applicable to monovinyl−divinyl copolymerizations were pursued in detail. Thus, the cross-linking copolymerizations of styrene (St) with *m*-divinylbenzene (*m*-DVB) as a most typical monovinyl−divinyl system were discussed under the specified conditions where the occurrence of a thermodynamic excluded volume effect and intramolecular cross-linking as the primary and secondary factors, respectively, for the greatly delayed gelation in the free-radical monovinyl−divinyl copolymerizations was reduced. The ratio of the actual gel point to the theoretical one reached 1.3, supporting the good applicability of F−S theory. In addition, the more tailed molecular-weight distribution (MWD) curves were observed with conversion as a result of occurrence of intermolecular cross-linking reaction leading to ideal network formation governed by F−S theory. Also, the swelling ratio of the gel obtained just beyond the gel point was very high, suggesting no microgelation up to the gel-point conversion. On the contrary, in the solution copolymerization of St with *m*-DVB in toluene at a dilution of $^1/_3$ in the presence of a rather high amount of cross-linker, the considerable occurrence of intramolecular cross-linking reaction was clearly reflected on the greatly delayed gelation and the markedly changed MWD curve from a tailed one at a higher conversion.

Introduction

We have extensively investigated the free-radical cross-linking polymerization of a variety of symmetrical or asymmetrical divinyl compounds including diallyl dicarboxylates,[1] dimethacrylates,[2] bis(alkyl fumarate)s,[3] and allyl unsaturated carboxylates[4] in terms of cyclopolymerization and gelation, although our research goal is aimed at the elucidation of the cross-linking reaction mechanism and the control of network formation in order to molecular-design vinyl-type network polymers with high performance and high functionality.

Thus, we have recently reviewed the mechanistic discussion of the three-dimensional network formation in the radical polymerization of multivinyl compounds, based on the experimental results obtained mainly in our laboratory.[5] In particular, our attention has been focused on the clarification of the reasons for the greatly delayed gelation from Flory−Stockmayer gelation theory (F−S theory):[6] The primary factor is the significance of the thermodynamic excluded volume effect on the intermolecular cross-linking reaction between the growing polymer radical and prepolymer, especially at high molecular weight. Beyond the theoretical gel point, a secondary factor is related to the intramolecular cross-linking which becomes progressively important with conversion. The latter leads to the restriction of segmental motion of the prepolymer and, moreover, imposes steric hindrance, inducing the significance of the reduced reactivity of prepolymer as a tertiary factor.

Our interpretation of the greatly delayed gelation[5] suggests that the actual gel point should be close to the theoretical one if the experiment were done under the polymerization conditions in which the polymer concentration, at the theoretical gel point, would be high enough to reduce the significance of a thermodynamic excluded volume effect as a primary factor, and furthermore, the intramolecular cross-linking preceded by the intermolecular cross-linking could be suppressed. As our understanding has been verified for monomethacrylate−dimethacrylate copolymerizations in our previous papers,[7,8] we attempted to extend the similar discussion to the cross-linking copolymerization of styrene (St) with *m*-divinylbenzene (*m*-DVB)[9] as a most typical monovinyl−divinyl system; the results obtained are discussed in terms of ideal network formation governed by F−S theory.

Here it is worthy to note that the main trend in this field for the past decades was to extend the F−S theory to more realistic polymerization cases in the presence of cyclization and unequal reactivities. Since numerous papers have been published to report that gelation occurs 1−2 orders of magnitude than predicted, Dotson et al.[10] and Zhu et al.[11] made efforts to embellish the theory by removing the assumptions of the classical F−S theory, including no cyclizations and equal reactivities of all types of double bonds. In this connection, the establishment of the other extreme case governed by F−S theory would be significant. Moreover, the resulting prepolymers or precursors of ideal cross-linked-polymers are characterized as standard polymers for the

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10.1021/ma990368k CCC: $18.00

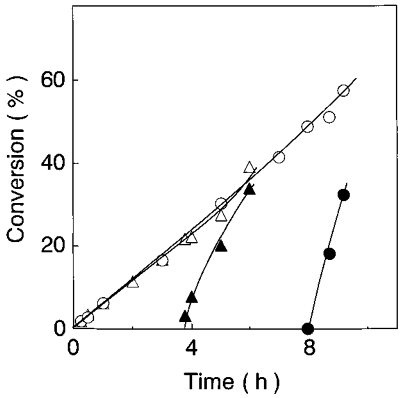

Figure 1. Conversion−time curves for the bulk copolymerizations of St with (○, ●) 0.25 and (△, ▲) 1 mol % of *m*-DVB using 0.04 mol dm^{-3} of AIBN at 60 °C. Open and full symbols correspond to total and gel polymers, respectively.

discussion of network formation in free-radical monovinyl−divinyl copolymerizations.[8]

Experimental Section

St as monomer, 2,2′-azobis(isobutyronitrile) (AIBN) as initiator, and toluene as solvent were purified by conventional methods. *m*-DVB, supplied by Nissei Chemical Industry Co., Ltd., consisting of 94.0% of *m*-DVB, 5.2% of *p*-DVB, and 0.8% of ethylstyrene, was used without further purification.

Polymerization was carried out as described previously.[12] After a predetermined time of reaction, the copolymer was precipitated by pouring the reaction mixture into a large excess of methanol containing a small amount of hydroquinone as inhibitor. The purification of the polymer was done by reprecipitation from a toluene−precipitant system. The gel fraction of polymer at conversions beyond the gel point was separated by extracting the sol fraction with toluene.

The weight-average molecular weight, $\bar{M}_w$, and molecular-weight distribution (MWD) were measured by size-exclusion chromatography (SEC) using a dual detector system, set in the direction of flow, consisting of a multiangle laser light scattering (MALLS) device and a differential refractometer in sequence. SEC−MALLS measurements were carried out at 40 °C in tetrahydrofuran (THF) using a Shodex GPC KF-806L × 5 columns, at polymer concentrations 0.1−0.5% (w/v) and flow rate 1 mL/min. The MALLS device was a DAWN model F (Wyatt Technology Corp.) where the laser beam, of wavelength 632.8 nm, was focused on a 67 μL flow cell.

Results and Discussion

Determination of Actual Gel Point. In our previous works[7,8] concerned with monomethacrylate−dimethacrylate copolymerizations, the presence of lauryl mercaptan as a chain transfer agent and a small amount of solvent was required for keeping the primary chain length constant because otherwise the Trommsdorff effect[13] or gel effect was easily observed until the gel-point conversion under the polymerization condition of a high monomer concentration. Here we did not, however, need to employ any chain transfer agent and solvent for St-*m*-DVB copolymerization, and so our requirement for the highest monomer concentration was fulfilled to attain the research goal.

Figure 1 shows the conversion−time curves for the bulk copolymerizations of St with 0.25 and 1 mol % of *m*-DVB using 0.04 mol dm^{-3} of AIBN at 60 °C as typical examples; the rate of polymerization was not essentially changed by increasing the added amount of *m*-DVB from 0.25 to 1 mol %. The percentages of gel polymers are also plotted in Figure 1. The actual gel point was determined by extrapolating the gel formation curve to zero percentage. Thus, the conversion at which gel starts to form, i.e., the gel point, was estimated to be 21.5 and 48.8% for the copolymerizations of St with 1 and 0.25 mol % of *m*-DVB, respectively. Gelation was obviously delayed with a decrease in the amount of *m*-DVB as cross-linker. In addition, almost no gel effect was observed until the gel point, although a slight gel effect was observed beyond the gel point. Certainly, no occurrence of gel effect would be required for keeping the primary chain length constant in the case where the actual gel point is compared with the theoretical one estimated according to F−S theory, since the gel effect caused by a suppressed bimolecular termination reaction would enlarge the primary chain length.

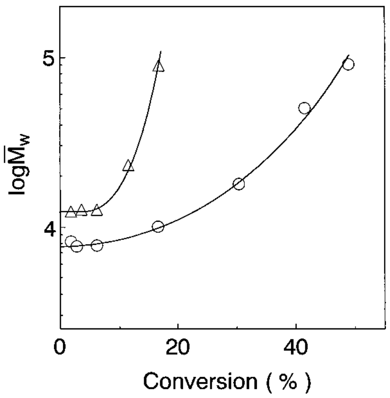

Figure 2. Dependence of $\bar{M}_w$ on conversion (see Figure 1).

Applicability of F−S Theory as Comparison of Actual Gel Point with Theoretical One. The actual gel points obtained above were then compared with the theoretical ones. Here the theoretical gel point was calculated according to the following Stockmayer's equation:[6]

$$\alpha_c = (1/\rho)(\bar{P}_w - 1)^{-1} \tag{1}$$

where α_c is obtained as the vinyl group conversion, $\bar{P}_w$ is the weight-average degree of polymerization of the primary chains which would result if all cross-links in the network at the gel point were cut, and ρ is the fraction of all double bonds residing on divinyl units in the initial system.

Now, we need to estimate the $\bar{P}_w$ values. Figure 2 shows the conversion dependence of weight-average molecular weight, $\bar{M}_w$, of the prepolymer determined by GPC−MALLS; the prepolymer of a higher $\bar{M}_w$ value was obtained for the copolymerization with a higher *m*-DVB mole percent in a feed monomer mixture. The primary chain length $\bar{P}_w$ was estimated by the extrapolation of the curves shown in Figure 2 to zero conversion, the theoretical gel point being calculated according to eq 1.

Table 1 summarizes the comparison of actual gel points with theoretical ones for St/*m*-DVB copolymerizations. The higher the theoretical gel point, the smaller the ratio of the actual gel point to the theoretical one. In the presence of 0.17 mol % of *m*-DVB, it reached 1.3, close to unity, supporting the good applicability of F−S theory, although gelation is well-known to occur frequently 1−2 orders of magnitude later than predicted.

In this connection, we have reported that in the copolymerization of methyl methacrylate with 0.03 mol % of ethylene dimethacrylate,[7] butylene dimethacrylate,

Table 1. Comparison of Actual and Theoretical Gel Points in the Copolymerization of St with *m*-DVB[a]

m-DVB, mol %	$\bar{P}_{w,0}$[b] × 10^{-3}	gel point (%) theoret[e]	gel point (%) actual[c]	actual gel point[d] / theoret gel point[e]
1	1.19	4.25	21.5 (21.2)[d]	5.0
0.5	0.79	13.3	33.3 (33.1)[d]	2.5
0.25	0.74	27.1	48.8 (48.6)[d]	1.8
0.17	0.67	43.5	54.9 (54.7)[d]	1.3

[a] In bulk, [AIBN] = 0.04 mol dm^{-3}, 60 °C. [b] Estimated by SEC–MALLS. [c] Obtained on monomer basis. [d] Obtained as the vinyl group conversion calculated by assuming equal reactivity of St and *m*-DVB vinyl groups. [e] Theoretical gel point: $\alpha_c = (1/\rho)(\bar{P}_{w,0} - 1)^{-1}$.

or nonapropylene glycol dimethacrylate,[8] the ratio of the actual gel point to the theoretical one reached 1.3, 1.05, or 1.06, respectively. Here it should be noted that the lower cross-linker content (0.03 mol %) was required for monomethacrylate–dimethacrylate copolymerizations compared to 0.17 mol % for St/*m*-DVB copolymerization; this may be due to a lower primary chain length and the rigidity of polymer chain for the latter case as the delay of gelation from theory became smaller for shorter primary chain length[5] and for more rigid polymer chain.[14]

MWD Curves Governed by F–S Theory. The F–S theory also suggests that the MWD curves should rapidly broaden toward a higher-molecular-weight side with conversion as a result of exclusive occurrence of intermolecular cross-linking reaction leading to ideal network formation governed by theory.[6,15] SEC is commonly used to determine the molecular weight and the MWD of prepolymers. However, as a technique, it is not always applicable to our cross-linking polymerization systems because the structure of prepolymer changes from a linear to a branched form with the progress of polymerization and, moreover, the content of ring or loop structure introduced into the linear portion or primary chain and the content of multiple cross-linkage in the branched form depend on the polymerization conditions. On the other hand, SEC–MALLS is expected to be a very useful and efficient tool in characterizing our prepolymers because the use of MALLS, as an absolute detector, enables the molecular weight and MWD to be determined directly without any calibration.[8] Of course, even when MALLS is used, true MWD profiles may not be obtained because for a nonlinear polymer mixture, the polymer molecules whose hydrodynamic volume is the same but having different molecular weights exist within the same elution volume of SEC.

Figure 3 shows the variations of MWD curves with conversion in the copolymerization of St with 0.5 and 0.17 mol % of *m*-DVB as the ratios of the actual gel points to the theoretical ones were 2.5 and 1.3, respectively. For the latter copolymerization, tailed curves were observed in conformity with our expectation as a reflection of ideal network formation.

This kind of ideal network formation should lead to the highly swellable gel as completely opposed to the common cases accompanied by microgelation[16–21] in free-radical monovinyl–divinyl copolymerizations. Here it is worthy to note that microgelation occurs under the polymerization conditions in which the intramolecular cross-linking preceded by the intermolecular cross-linking could be enhanced extensively and locally.

High Swelling Ratio of Resulting Gel Just beyond the Gel Point. The swelling ratios in toluene were tentatively determined for the gels obtained just beyond the gel points (48.8 and 21.5%) in the copolymerizations of St with 0.25 and 1 mol % of *m*-DVB as follows [*m*-DVB mol %, conversion (%), swelling ratio (g/g)]: 0.25, 51.2, 27.7; 1, 24.8, 22.5. In conformity with our expectation, the swelling ratio of the resulting gel just beyond the gel point is quite high, supporting again the ideal network formation with no occurrence of microgelation up to the gel point conversion. Besides, the gels obtained at a higher *m*-DVB mole percent in feed showed the lower swellability, reflecting a higher cross-link density of network caused by an intramolecular cross-linking.

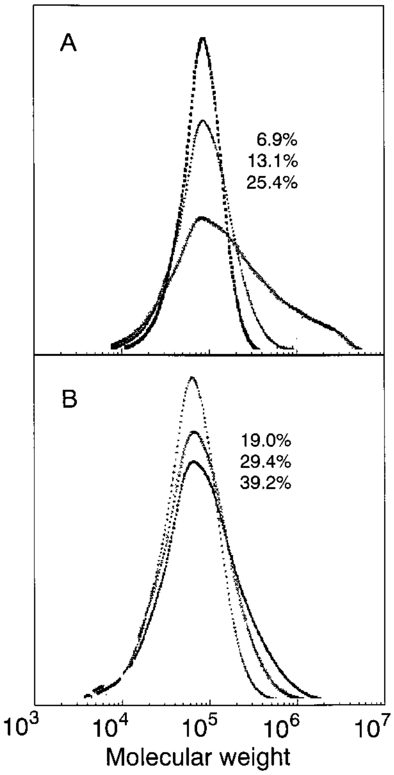

Figure 3. Variation of MWD curves with conversion for the bulk copolymerizations of St with (A) 0.5 and (B) 0.17 mol % of *m*-DVB (see Figure 1).

Occurrence of Intramolecular Cross-Linking Leading to Delayed Gelation from F–S Theory. Regarding the mechanistic discussion and understanding of network formation in free-radical monovinyl–divinyl copolymerizations, the detailed characterization of resulting prepolymers is significant. The intramolecular cyclization leading to the formation of ring or loop structures, the intermolecular cross-linking to form effective cross-linkages, and the intramolecular cross-linking leading to the formation of multiple cross-linkages are characteristic reaction features of polymerizations involving divinyl monomer, all of which influence the molecular weight, the MWD, and the structures of resulting prepolymers. The ideal network formation mentioned above was the special case in which the exclusive occurrence of intermolecular cross-linking is observed.

Finally, we tried to pursue the detailed behaviors of the cross-linking polymerization under the condition where the intramolecular cross-linking would occur significantly as would be the opposite case of ideal network formation. Thus, the solution copolymerization of St with 3 mol % of *m*-DVB in toluene was conducted

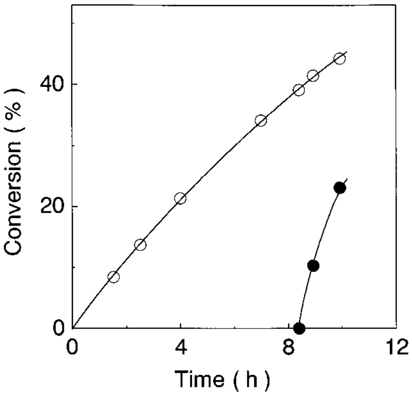

Figure 4. Conversion−time curves for the solution copolymerizations of St with 3 mol % of *m*-DVB in toluene at a dilution of $^1/_3$ using 0.04 mol dm^{-3} of AIBN at 60 °C. Open and full symbols correspond to total and gel polymers, respectively.

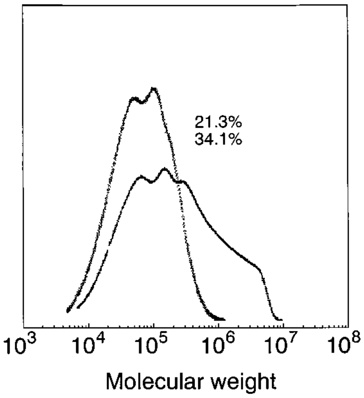

Figure 5. Variation of MWD curves with conversion (see Figure 4).

at a dilution of $^1/_3$ using 0.04 mol dm^{-3} of AIBN at 60 °C. Figure 4 shows the conversion−time curve along with the gel formation curves; no gel effect was observed even in the presence of a rather high amount of cross-linker, and the gel point was estimated to be 39.2%. The primary chain length $\bar{P}_w$ determined by SEC−MALLS was 410, and then the theoretical gel point was calculated to be 4.1%. Thus, the ratio of the actual gel point to the theoretical one was 9.6, indicating a greatly delayed gelation from F−S theory. Figure 5 shows the variation of MWD curves with conversion; the shape of the curve of the prepolymer obtained at a higher conversion changed markedly from a tailed MWD curve governed by F−S theory (see Figure 3) as a reflection of the enhanced occurrence of intramolecular cross-linking reaction.

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MA990368K