Gel Formation in Free-Radical Crosslinking Copolymerization

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SYNOPSIS

Polymer gels with varying amounts of crosslinker and solvent were prepared by solution free-radical crosslinking copolymerization of methyl methacrylate/ethylene glycol dimethacrylate (MMA/EGDM) and styrene/*p*-divinyl benzene (S/*p*-DVB) comonomer systems. The structural characteristics of the gels were examined using equilibrium swelling in toluene and gel fraction measurements. Experimental results were compared with the predictions of a kinetic model developed recently for free-radical crosslinking copolymerizations. Experimental data on S/EGDM networks reported by Hild, Okasha, and Rempp were also used to test this model. It was found that the model correctly predicts the development of the gel properties in free-radical crosslinking copolymerization. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polymer gels with the ability to absorb many times their dry weight of solvent are widely used as absorbents in medical, chemical, and agricultural applications, and, therefore, have been the subject of a large number of studies. These materials are prepared mainly by free-radical copolymerization of monovinyl (MVM) and divinyl monomers (DVM) in a suitable solvent.[1,2] Previous studies have shown that the mechanism of network formation in free-radical crosslinking copolymerization and the properties of the resulting networks differ appreciably from ideal systems.[1-14] For example, the classical gelation theories of Flory[15] and Stockmayer[16,17] cannot be applied to MVM–DVM copolymerization due to the unequal vinyl group reactivities.[1] Cyclization reactions leading to the formation of intramolecular links[8,12,18-20] and, at high crosslinker contents, to microgel-like particles[21-26] with internal "frozen" vinyls and radical centers also cause deviation from theory. On the other hand, the drift in the primary chain length due to the decrease in termination rate constant (Trommsdorff effect), depletion of monomer and initiator, does not afford an ideal system for applying the ideal theories of network formation.[13]

Attention has recently been devoted to the kinetic network formation theories.[14,27-32] Compared to the statistical models, kinetic models take into account the kinetic feature of polymerization and so may offer a more realistic approach to the mechanism of network formation in free-radical polymerizations. Very recently, a kinetic model was proposed by one of the authors for the postgelation period of free-radical crosslinking copolymerization.[33-35] This model predicts important features of the postgelation period such as the weight fraction of sol and the chain length averages of both the primary and branched molecules in the sol. One single adjustable parameter to account for decreasing radical reactivity due to diffusion limitations is used for simulation of the whole network formation process.

In the present work, experiments were carried out to test the validity of this kinetic model. Of particular interest to us is the prediction of the structural characteristics of polymer networks prepared by free-radical crosslinking copolymerization. Two commonly used MVM–DVM systems were selected for this purpose, namely methyl methacrylate/ethylene glycol dimethacrylate (MMA/EGDM) and styrene/*p*-divinyl benzene (S/*p*-DVB) systems. A

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series of experiments with varying amounts of crosslinker and solvent were performed. The weight fraction of gel and its equilibrium degree of swelling were examined as a function of the reaction time, monomer concentration, and crosslinker content. Experimental data were compared with the predictions of the model. Recently, Hild, Okasha, and Rempp[36] offered experimental data for S/EGDM copolymerization with EGDM contents ranging from 2 to 20 mol %. Their data were also compared to the model predictions.

EXPERIMENTAL

Materials

The monomers methyl methacrylate (MMA), styrene (S), and ethylene glycol dimethacrylate (EGDM) were freed from the inhibitor by shaking with 5% aqueous NaOH, washing with water, and drying over $CaCl_2$. They were then distilled under reduced pressure. *p*-Divinyl benzene (*p*-DVB) was separated from the commercial mixture by means of its tetrabromide as described by Naumann.[37] Purity was checked by gel chromatography (GC) and found to be about 98%. The initiator 2,2′ azobisisobutyronitrile (AIBN) was recrystallized twice from methanol. The polymerization solvent, toluene, was distilled twice over sodium. All the other materials were used without further purification.

Copolymerization

The reaction mixture containing monovinyl and divinyl monomers, AIBN, and toluene was poured into several glass tubes of 10 mm internal diameter and about 250 mm long. The tubes were degassed three times, sealed under vacuum (10^{-3} mm), and placed in a thermostat for a predetermined polymerization time. It was assumed that the surface/volume ratio of the glass tubes is high enough to assure an isothermal condition. Homologous series of polymer gels were prepared in this way allowing systematic variation of the crosslinker and toluene concentrations. The content of crosslinker is expressed in mole percent of the total monomers, and the monomer concentration (c) as volume percent of the initial monomer–toluene mixture.

Extraction of the Sol Fraction

Toluene was chosen as the extraction solvent and employed at room temperature. The crude gels, 10 mm in diameter, were cut into samples of 10–25 mm length. Each sample was placed in an excess of toluene containing a small amount of 1,4-benzoquinone as an inhibitor, and the solvent was replaced every other day over a period of 3 weeks until no further extractable polymer could be detected. The networks after extraction were carefully deswollen in a series of toluene–methanol mixtures with increasing methanol contents. They were then washed several times with methanol and dried at room temperature under vacuum to constant weight. The amount of soluble polymer in toluene solution was determined gravimetrically after evaporation and precipitation in methanol. The weight fraction of gel W_g was calculated as

$$W_g = \frac{g}{g + s} \tag{1}$$

where g and s are the weights of extracted network and soluble polymer, respectively.

Swelling Measurements

The swelling measurements were carried out in toluene at room temperature. In order to reach the equilibrium degree of swelling, the networks were immersed in toluene for at least 3 weeks; the swelling equilibrium was tested by weighing the samples. To achieve good precision, three measurements were carried out on samples of different weight taken from the same gel. The networks were then weighed in the swollen state and dried, after a solvent exchange with methanol as described above, under vacuum to constant weight. The extent of swelling was characterized by q_v, the volume swelling ratio, which was calculated as

$$q_v = 1 + \frac{(q_w - 1)d_p}{d_s} \tag{2}$$

where q_w is the ratio of weights of the gel in the swollen state and the dry state, d_p and d_s are the densities of polymer and solvent, respectively.

RESULTS AND DISCUSSION

A detailed development of the kinetic model is found in Refs 33–35. A summary of the model is given in the Appendix to enable the understanding of its applications presented in the current study. Here, the model was solved for batch isothermal solution copolymerizations of MMA/EGDM, S/*p*-DVB, and S/EGDM comonomer systems in toluene using AIBN

Table I Kinetic Parameters Used in the Model Calculations[a]

	Value for System			
Parameter	MMA/EGDM at 70°C	S/*p*-DVB at 60°C	S/EGDM at 60°C	Units
k_d	3.43×10^{-5} (38)	0.85×10^{-5} (39)	0.85×10^{-5} (39)	s^{-1}
k_{p1}	600[b]	145 (39)[f]	265[g]	$L\ mol^{-1}\ s^{-1}$
k_{p2}	600[c]	123 (40)	315 (43)	$L\ mol^{-1}\ s^{-1}$
k_{p3}	125[d]	38[d]	16[d]	$L\ mol^{-1}\ s^{-1}$
k_{tc}	1.06×10^{7} (10)	2.9×10^{7} (39)[f]	2.9×10^{7} (39)[f]	$L\ mol^{-1}\ s^{-1}$
k_{td}	1.01×10^{7} (10)	0 (39)[f]	0 (39)[f]	$L\ mol^{-1}\ s^{-1}$
f	0.59 (38)	0.77 (40, 41)	0.6[g]	—
m	2[b]	2[b]	1[b]	—
χ_1	0.496[e]	0.455 (42)	0.455 (42)	—
χ_2	0	−0.155 (42)	−0.155 (42)	—
χ_i $(i \geq 3)$	0	0 (42)	0 (42)	—
d_1	0.943	0.91	0.91	$g\ mL^{-1}$
d_2	1.08	0.91	1.08	$g\ mL^{-1}$
d_p	1.179	1.08	1.08	$g\ mL^{-1}$
MW_1	100	104	104	$g\ mol^{-1}$
MW_2	198	130	198	$g\ mol^{-1}$

[a] Reference numbers are given in parenthesis.
[b] Estimated from time versus conversion data.
[c] Equal reactivity assumption of monomeric vinyls based on the previous experimental data.[7,20]
[d] Estimated from the experimental gel point data as described in Ref. 33.
[e] Estimated from the equilibrium swelling degrees.
[f] Rate constant for homopolymerization of styrene.
[g] Estimated from the experimental data given in Ref. 43.

as an initiator. The kinetic parameters used in the calculations are listed in Table I. Most of these parameters were taken directly from the literature. The rate constant of crosslinking reactions, k_{p3}, was estimated from the experimental gel point data. The adjustable parameter m, representing the extent of the gel effect in the postgelation period, was estimated by fitting the experimental time versus con-

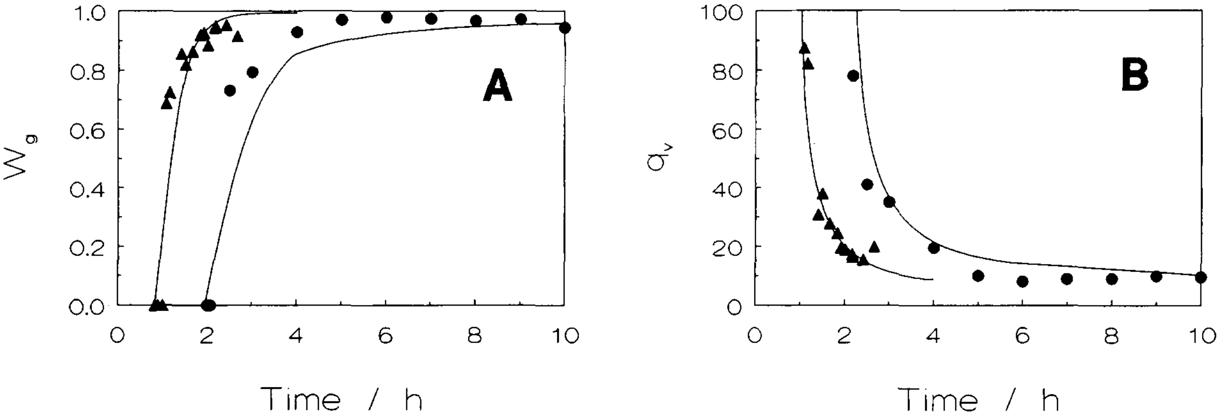

Figure 1 Weight fraction of gel W_g (A) and the equilibrium volume swelling ratio of the gel in toluene q_v (B) plotted as functions of the reaction time for MMA/EGDM copolymerization in toluene at 70°C using an AIBN concentration of 0.3 wt %. Initial monomer concentration = 50 vol %. (●) EGDM = 0.23 and (▲) 0.46 mol %. The curves were calculated using the kinetic model with the kinetic parameters listed in Table I.

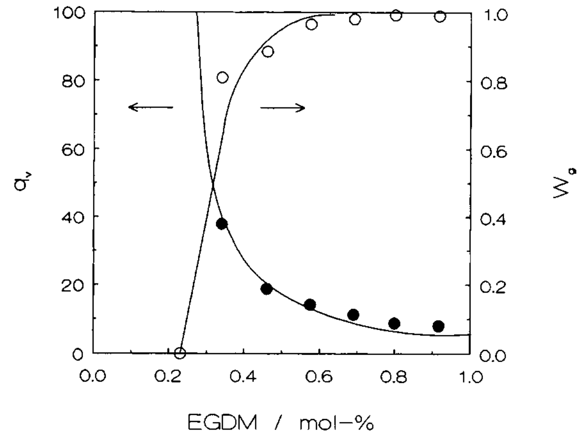

Figure 2 Volume swelling ratio q_v and the weight fraction of gel W_g shown as function of the EGDM concentration for MMA/EGDM copolymerization in toluene at 70°C with 0.3 wt % AIBN. Polymerization time = 2 h. Initial monomer concentration = 50 vol %. Experimental data are shown as filled (q_v) and empty circles (W_g). The curves were calculated using the kinetic model.

version data. For the polymerization systems considered, the chain transfer to monomer and to solvent reactions can be neglected because of the low transfer constants.[39] Cyclization is neglected in the present study due to the low crosslinker concentration. Figures 1–5 compare the calculated and observed gel properties–synthesis conditions profiles. Since no replication was done, it is difficult to estimate the experimental error. However, agreement between the model calculations and the experimental data is good. The model predicts every trend observed by experiments.

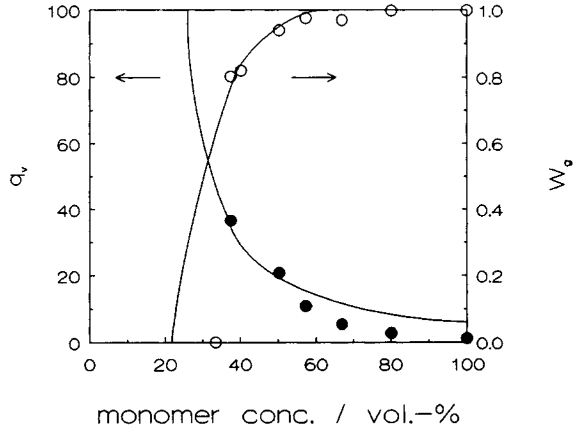

Figure 3 Volume swelling ratio q_v and the weight fraction of gel W_g shown as function of the monomer concentration for MMA/EGDM copolymerization in toluene at 70°C with 0.3 wt % AIBN. Polymerization time = 2 h. EGDM = 0.48 mol %. Experimental data are shown as filled (q_v) and empty circles (W_g). The curves were calculated using the kinetic model.

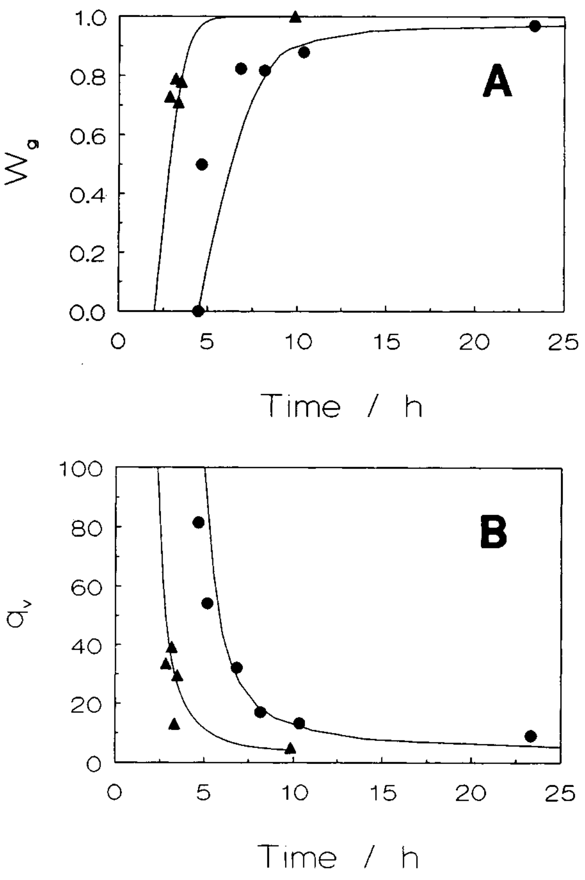

Figure 4 Weight fraction of gel W_g (A) and the equilibrium volume swelling ratio of the gel in toluene q_v (B) plotted as functions of the reaction time for S/p-DVB copolymerization in toluene at 60°C using an AIBN concentration of 3 wt %. Initial monomer concentration = 47 vol %. (●) p-DVB = 2 and (▲) 4 mol %. The curves were calculated using the kinetic model with the kinetic parameters listed in Table I.

MMA/EGDM copolymerizations were carried out in toluene at 70°C using an AIBN concentration of 0.3 wt % (with respect to the monomers). The weight fraction of gel, W_g, and its equilibrium volume swelling ratio in toluene, q_v, are shown in Figure 1 as a function of the polymerization time for 0.23 and 0.46 mol % EGDM. The initial monomer concentration is 50 vol %. The gelation times were found to be 2 and 0.83 h, respectively, compared to 1.92 and 0.82 h predicted by the model. The rate of change in W_g and in q_v is rapid, up to 4 and 2 h for 0.23 and 0.46 mol % EGDM, respectively; thereafter, it slows down owing to the small amount of crosslinking agent set in and as a result of the low rate constant of the crosslinking reactions (Table I). For the same monomer concentration, the variations of q_v and W_g with the EGDM concentration are shown in Figure 2. The reaction time is 2 h. Experiments showed that no gelation occurs below 0.20–0.23 mol % EGDM, compared to 0.231 mol % predicted by the model.

Figure 3 illustrates the dependences of q_v and W_g on the initial monomer concentration (c) for a reaction time of 2 h and for 0.48 mol % EGDM. Again, the prediction of the model is in good agreement with the experimental data. Deviations appearing between the theoretical and experimental values in highly diluted polymerization systems can be attributed to the intramolecular crosslinking reactions.

S/p-DVB copolymerizations were carried out in toluene at 60°C using an AIBN concentration of 3 wt %. The initial monomer concentration was 47 vol %. The variations of W_g and q_v with the polymerization time are shown in Figure 4 for 2 and 4 mol % p-DVB. The increase in the p-DVB concentration promotes the onset of gelation (from 4.5 to 2 h). Similar trends are also seen in Figure 5. Here, q_v is plotted against the reaction time for S/EGDM copolymerization in toluene with EGDM contents ranging from 2 to 20 mol %. The data points are the results of measurements of Hild et al.[36] The agreement of model and experiment is remarkably good, even thought the crosslinker concentration changes by a factor of 10.

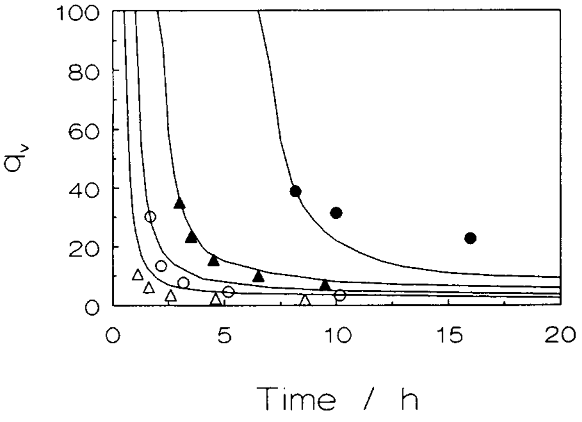

Figure 5 Variation of the equilibrium swelling ratio of the gels q_v with the reaction time for S/EGDM copolymerization in toluene at 60°C. $[M_1]_0$ = 4 mol L^{-1}, $[I]_0$ = 0.08 mol L^{-1}, EGDM = (●) 2, (▲) 5, (○) 10, and (△) 20 mol %. Experimental results of Hild et al.[36] are shown as symbols. The curves were calculated using the kinetic model.

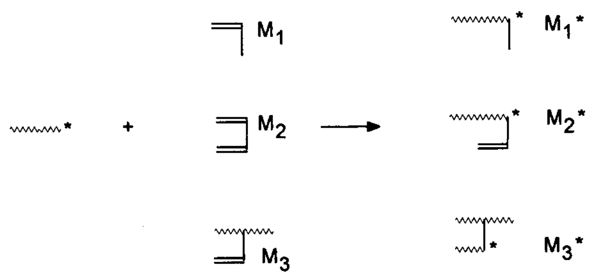

Figure 6 Types of vinyl groups and radical centers in MVM–DVM copolymerization.

CONCLUSIONS

The kinetic model proposed recently correctly predicts the development of the gel properties in free-radical crosslinking copolymerization of MMA/EGDM, S/p-DVB, and S/EGDM systems. In order to apply this model to highly diluted polymerization systems or to systems with a high crosslinker content, one has to consider the effect of cyclization reactions as well as the conversion dependence of the elementary rate constants such as those of termination and crosslinking reactions. However, in view of the current results, this model seems to be applicable to systems of practical interest.

APPENDIX

The kinetic model was proposed for free-radical copolymerization of monovinyl (MVM) and divinyl monomers (DVM). The rate equations for the concentration of various species and the moment equations for branched molecules as well as for primary chains were published previously.[33-35] In the following is provided a brief review of the kinetic model.

1. The model distinguishes three types of vinyl groups with different reactivities, as shown in Figure 6: (i) on MVM (M_1), (ii) on DVM (M_2), and (iii) on polymer chains, i.e., pendant vinyls (M_3).

Accordingly, MVM–DVM copolymerization involves three kinetically distinguishable radicals and, as in terpolymerizations, 4 initiation, 9 propagation, and 12 termination reactions. In order to simplify the kinetic treatment of the system, a series of instantaneous rate constants for propagation and termination reactions is defined. Note that these constants are equivalent to the average rate constants of Fukuda et al.[44] Applying the instantaneous rate constants, the copolymerization system may be viewed as consisting of three propagation reactions with instantaneous rate constants k_{pi}, where i is the type of the vinyl group M_i ($i = 1, 2$, and 3) participating the reaction.

2. Although cyclization is not accounted for in the model, these reactions can easily be included into the model using constants for primary and secondary cyclization[20] (multiple crosslinking[45]). As recently summarized by Tobita and Hamielec, primary and secondary cyclization reactions are very important in free-radical copolymerization of MMA/EGDM and S/*p*-DVB systems.[12] However, these reactions are neglected in the present study due to the low concentration of DVMs used.

3. The model assumes steady-state concentration for the radicals in the reaction system. Thus, the radical concentration is simply given by $[R^*] = (2fk_d[I]/k_t)^{1/2}$ where f is the initiator efficiency, k_d is the decomposition rate constant of the initiator I, and k_t is the sum of the instantaneous termination rate constants by coupling and by disproportionation, i.e., $k_t = k_{tc} + k_{td}$. Termination reactions are assumed to be chemically controlled prior to gelation, but diffusion-controlled beyond gelation. The decrease of the termination rate of radicals is given by the empirical relation

$$k_t = k_t^0 m \left(\sum_{i=1}^{m} \varepsilon^i \right)^{-1}$$

where k_t^0 represents the chemically controlled termination rate constant, m is an adjustable parameter, which can take on integral values, and ε is the crosslinking density of primary chains, i.e., the number of crosslinked units per weight-average primary molecule. Beyond the gel point, the radical concentration in the sol is assumed to decrease as the volume of the sol fraction decreases, but not faster. It must be noted that a rapid rise of radical concentration during autoacceleration in polymerization rate may invalidate the steady-state hypothesis. Indeed, Zhu and Hamielec recently found that for high crosslinker levels the steady-state hypothesis is clearly invalid.[14] Therefore, the model is applicable for low crosslinker contents.

4. The model assumes the validity of the limitations following from the Flory lattice theory and the theory of rubber elasticity. Thus, the equilibrium volume swelling ratio of the gel, q_v, can be calculated from the crosslinking density of the gel and the polymer–solvent interaction parameter χ using the Flory's swelling equation.[46] Note that the polymer–solvent interaction parameter χ, in general, depends on q_v and on the temperature. At constant temperature, this dependence is given by[47] $\chi = \chi_1 + \chi_2 q_v^{-1} + \chi_3 q_v^{-2} + \cdots$ where $\chi_1, \chi_2, \chi_3, \cdots$ are empirical constants.

5. Due to the differences in the densities of MVM (d_1), DVM (d_2), and the polymer (d_p), the reaction volume will change during the polymerization. Assuming ideal solutions, this change is accounted for in the model.

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