Copolymerization of Glycidylmethacrylate–Methylmethacrylate–Divinylbenzene in Cyclohexane

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Synopsis

The copolymerization of glycidylmethacrylate–methylmethacrylate–divinylbenzene in cyclohexane was studied as an example of crosslinking precipitation copolymerization. The resultant copolymer is fine spheroidal. The copolymerization proceeds acceleratively at first, then steadily, and gradually slows down. The larger the divinylbenzene concentration, the smaller is the copolymerization rate. Glycidylmethacrylate is preferentially incorporated in the copolymer.

INTRODUCTION

We have reported the preparation of a fine powdery copolymer with crosslinkage (PFPC), and its application as a mordant to modify polypropylene dyeables.[1-3] PFPC can be prepared by copolymerizing vinylmonomer with crosslinking agent in a solvent that dissolves the monomers but not their polymers without crosslinkage. We have investigated details of the glycidylmethacrylate (GMA)–divinylbenzene (DVB) copolymerization in cyclohexane by using benzoylperoxide (BPO) as a polymerization initiator.[4] Some investigators have also reported that the use of a crosslinking agent in radical polymerization accelerates the polymerization rate owing to the gel effect.[5-10] On the other hand, we have found that the copolymerization rate in the crosslinking precipitation copolymerization of GMA–DVB decreases with the increasing DVB concentration in cyclohexane.[4]

This article reports on the copolymerization of GMA–methylmethacrylate (MMA)–DVB to confirm the tendency described previously for the ternary system and to investigate details of the crosslinking precipitation copolymerization.

EXPERIMENTAL

GMA, MMA, and DVB were washed successively with a dilute aqueous solution of NaOH and water, dried over anhydrous $CaCl_2$, and then distilled under reduced nitrogen atmosphere just before use. The purity of BPO was >97%. The DVB used was a mixture of m-DVB (41%), p-DVB (17%), ethylstyrene, and others (42%). Cyclohexane was dried successively over anhydrous $CaCl_2$ and Na metal pieces, and then distilled. Copolymerization procedure was the same as shown in the previous article.[4] The epoxy value was determined by the HCl–dioxane method.[11]
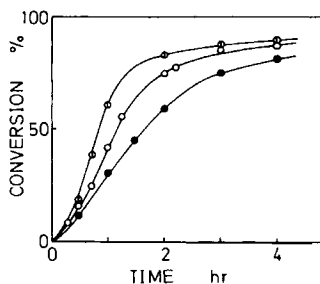
Fig. 1. Effect of DVB concentration on time–conversion curve at 80°C. GMA + MMA + DVB, 0.88 mol/liter; GMA/MMA, 1 by molar ratio; BPO, 10 mmol/liter; DVB: ☉, 0.04 mol/liter; ○, 0.08 mol/liter; ●, 0.16 mol/liter.

RESULTS AND DISCUSSION

The copolymerization proceeds acceleratively at first and then steadily and gradually slows down.   Soon after the copolymerization onset, the copolymerization system becomes turbid.   The copolymerization rate is affected by the stirring rate, so it was controlled at 1000 rpm.   Here, it is noteworthy that a detailed investigation is difficult because the copolymerization system consists of multicomponents and the resultant PFPC is crosslinked.

Figure 1 shows the DVB concentration effect on the time-conversion curve. Evidently, the larger the DVB concentration, the smaller the copolymerization rate.   This is similar to the result in the GMA–DVB system.[4]   This phenomenon must be characteristic in the crosslinking precipitation copolymerization.   The resultant polymer precipitates out, and DVB promotes the precipitation.   The precipitated copolymer is crosslinked and occludes the propagating radical.   So, the monomers must reach the active radical through the crosslinked matrix during the propagation.   This is probably the reason why the linear part is present in the time–conversion curve.   When the DVB concentration is larger, the resultant copolymer is more tightly crosslinked and the propagation should terminate earlier.   This presumption is supported by the tendency, observed by scanning electron microscopy, for the particle size to become smaller with increasing DVB concentrations.   For reference, in the cases of St–DVB copolymerization in the presence of Hypalon-20[6] and poly(vinyl chloride),[7] the copolymerization rate contrarily increases with the DVB concentration.

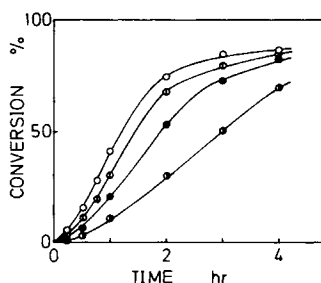Figure 2 shows the BPO concentration effect on the time–conversion curve.

Fig. 2. Effect of BPO concentration on time–conversion curve at 80°C. GMA, 0.4 mol/liter; MMA, 0.4 mol/liter; DVB, 0.08 mol/liter: BPO: ◐, 1 mmol/liter; ●, 3 mmol/liter; ☉, 5 mmol/liter; ○, 10 mmol/liter.
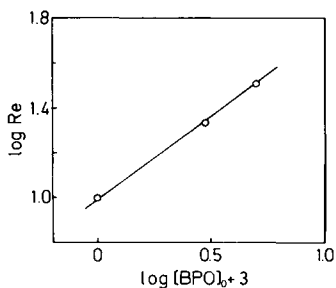
Fig. 3. Relation between $\log R_e$ and $\log [\mathrm{BPO}]_0$.

The copolymerization rate at an earlier stage (R_e) is arbitrarily defined as the average rate at the conversion smaller than 10%, as defined by Bamford and Jenkins.[12] When the BPO concentration was 10 mmol/liter, the copolymerization was too fast to estimate the R_e value. Figure 3 shows the relation between $\log R_e$ and $\log [\mathrm{BPO}]_0$. According to the rule that the polymerization rate varies as $[\mathrm{BPO}]^n$, the exponent is 0.7–0.8 and is consistent with that in the GMA–DVB system.[4] This value shows that the crosslinked copolymer matrix occludes the growing polymer radical and hinders the termination reaction by their mutual coupling. This is why the autoacceleration occurs at the earlier stage. Similar phenomena occur in the case of radical polymerization in viscous media[9,10] and in precipitation polymerization even without any crosslinking agent.[13]

Figure 4 shows the temperature dependency of the time–conversion curves. Here the copolymerization rate at the steady state (R_s) was determined graphically and the R_e value was determined as described before. From the Arrhenius plot in Figure 5, the activation energies were calculated to be 26 kcal/mol for the reaction at the earlier stage and 10 kcal/mol for the reaction at the steady state. These values are consistent with those of the GMA–DVB system (28 kcal/mol for the reaction at the earlier stage and 11 kcal/mol for the reaction at the steady state).[4] Also, these values are approximate to those for the spontaneous decomposition of BPO in cyclohexane (29.2 kcal/mol),[14] and for the diffusion of propene and xylene in polyethylene (9–13.6 kcal/mol),[15,16] respectively. So, it might be presumed that the BPO decomposition and the diffusion of the monomers to the active radical are the rate-determining processes at the earlier stage and the steady state, respectively.

Figure 6 shows the effect of the GMA/MMA molar ratio on the time–conversion curves. With increasing GMA/MMA molar ratio, the copolymerization proceeds more rapidly.
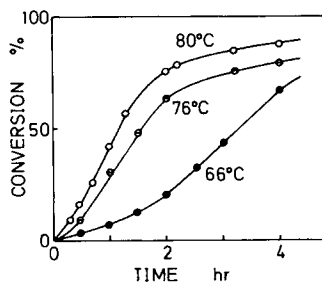

Fig. 4. Temperature effect on time–conversion curve. Monomer concentrations shown in Fig. 2 and BPO, 10 mmol/liter. Reaction temperature: ●, 66°C; ⊖, 76°C; ○, 80°C.
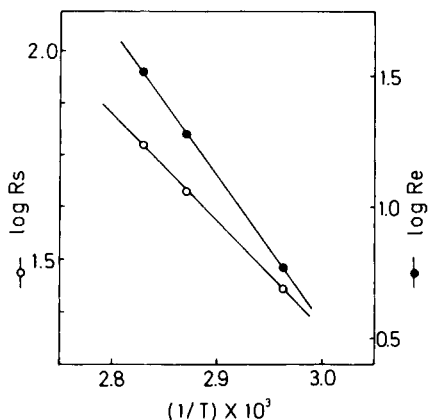
Fig. 5. Arrhenius plot of $\log R_s$ and $\log R_e$.

It shows that the copolymerization rate of GMA is larger than that of MMA. As elucidated so far, the outline of the copolymerization of the GMA–MMA–DVB system is similar to that of the GMA–DVB system,[4] and also the particle size of PFPC is about 0.1 μm or less. This similarity should suggest the common feature of these crosslinking precipitation copolymerization.

Figure 7 shows the relation between the epoxy value of PFPC and the conversion. The epoxy value is larger at the lower conversion and decreases with the conversion to the value calculated from the recipe, clearly showing the preferential incorporation of GMA into PFPC. For reference, the epoxy value of the GMA–DVB system is independent of the conversion.[4]
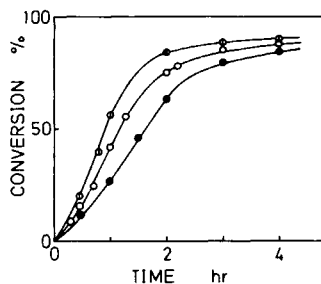

Fig. 6. Effect of GMA/MMA molar ratio on time-conversion curve at 80°C. GMA + MMA + DVB, 0.88 mol/liter; DVB, 0.08 mol/liter; BPO, 10 mmol/liter; GMA/MMA (molar ratio): ●, 1/3; ○, 1; ◑, 3.
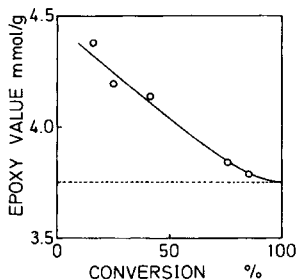

Fig. 7. Relation between epoxy value of copolymer and conversion at 80°C. Reactant concentrations are those in Fig. 4.

TABLE I
Copolymerizability Parameters

M_1	M_2	M_3	Parameter				Remark
GMA	MMA		r_{12}:	1.05	r_{21}:	0.80	ref. [17]
	MMA	m-DVB	r_{23}:	0.41	r_{32}:	0.61	ref. [18]
GMA		m-DVB	r_{13}:	0.21	r_{31}:	0.14	calculated from Q and e values[a]

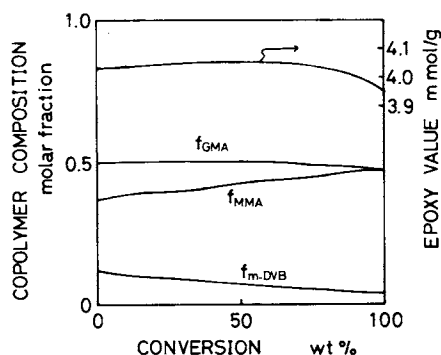[a] GMA: $Q = 0.85$, $e = 0.10$; m-DVB: $Q = 3.35$, $e = -1.77$.[19]

Fig. 8. Relation among copolymer composition, epoxy value of copolymer, and conversion. f_{GMA}, f_{MMA}, $f_{m\text{-}DVB}$ are molar fraction of GMA, MMA, and m-DVB units in copolymer, respectively. Molar fraction of recipe: GMA, 0.48; MMA, 0.48; and m-DVB, 0.04.

In order to consider the factor regulating the copolymerization, the relation between the copolymer composition and the conversion was calculated for the GMA–MMA–DVB system from the copolymerizability parameters shown in Table I. It is necessary to note that the components other than m-DVB, in the recipe shown in Figure 7, were neglected for brevity because the quantities of p-DVB, ethylstyrene, and the others are low in comparison to those of GMA and MMA. Figure 8 shows the result calculated with aid of a computer by the method reported by Chan and Meyer,[20] based on the assumption that the monomer reactivity depends only on the terminal unit and the reaction proceeds steadily for the free radical species. The epoxy value calculated from the copolymer composition is rather independent of the conversion under 70% and then decreases, as shown in Figure 8. This result is inconsistent with the experimental result shown in Figure 7. This inconsistency can be considered to suggest the presence of some unknown factor regulating the crosslinking precipitation copolymerization. Accordingly, the copolymerization mechanism must be investigated in more detail.

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