Preparation of the Fine Powdery Copolymer of Glycidyl Methacrylate–Divinylbenzene and its Application as a Pigment

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Synopsis

In order to prepare the functional and fine powdery polymer, glycidyl methacrylate (GMA) and divinylbenzene (DVB) were polymerized in cyclohexane. This polymerization was heterogeneous. In the time–conversion curve, an autoaccelerating phenomenon and an apparently steady state were observed, and the activation energies for both reactions in the earlier stage and the steady state were calculated to be 28 kcal/mole and 11 kcal/mole, respectively. It is especially noteworthy that the increase in the DVB concentration decreased the polymerization rate. The diffusion of the monomers through the polymer matrix should be one of the most important factors. Some properties of the copolymer and its application as a mordant were studied.

INTRODUCTION

It has already been published that the polymerization of GMA and DVB in n-heptane was heterogeneous and resulted in fine powdery copolymer, available as a mordant to modify the poor dyeability of polypropylene.[1,2] However, no detail of the polymerization was investigated yet, although some heterogeneous polymerizations have so far been studied.[3,4] Therefore, the polymerization of GMA and DVB was investigated in this study, but a detailed investigation was difficult because of its complexity. The time–conversion curve was then studied in relation to various factors such as BPO, GMA, and DVB concentrations and polymerization temperature. In addition, some properties of the fine powdery copolymer and its application as a pigment were investigated.

EXPERIMENTAL

Materials

GMA and DVB were distilled under a reduced nitrogen atmosphere. The purity of commercial benzoly peroxide (BPO) used was more than 97%. Commercial DVB used was a mixture of pure divinylbenzene, ethylstyrene, and their isomers (m-DVB, 40.5%; p-DVB, 16.7%; o-DVB, 0.2%; and

2925

ethylstyrene and the others, 42.6%). The commercial DVB is expediently shown as DVB in this paper. Cyclohexane was distilled and then treated with a molecular sieve of 5 Å.

Polymerization

A glass reaction vessel was used of capacity about 200 ml. The solvent was put into the reaction vessel and the temperature of the solvent was elevated to a definite temperature under a nitrogen atmosphere. The monomer mixture containing BPO was then added and the total volume of the reactant solution was adjusted to 150 ml by adding some solvent. After the polymerization, the resultant was poured into a sufficient amount of cold methanol containing a small amount of hydroquinone, filtered, washed with methanol, and dried under vacuum. The conversion was shown by weight.
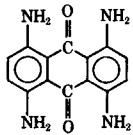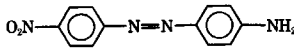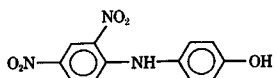
Measurement of Properties of the Fine Powdery Copolymer

The epoxy value was determined by the hydrochloric acid–dioxane method.[5] The bulk specific gravity was measured as follows: the fine powdery copolymer was placed into a measuring cylinder (100 ml), the bottom of the measuring cylinder was tapped onto a dense rubber sheet many times in order to make the fine powdery copolymer more compact, and its weight and apparent volume were measured.

Preparation of the Polymeric Pigment

The DVB content of the fine powdery copolymer used, DVB/(GMA + DVB), was 0.1 by weight. Commercial dyes used are shown in Table I. The dye, the fine powdery copolymer, water, and Monogen-W (an emulsifier from Daiichi Kogyo Seiyaku Co., Ltd.) were put into an autoclave made of stainless steel and were reacted with stirring. Then, the product was

TABLE I
The Commercial Dyes

Dye	Chemical formula	N content, %
Celliton Blue Extra (CBE)		7.77
Miketon Fast Orange (MFO)	O_2N—◯—N=N—◯—NH_2	6.65
Dispersol Fast Yellow A 300 (DFY)	O_2N—◯—NH—◯—OH (with NO_2 substituent)	6.42

filtered, washed with methanol, and extracted with acetone. Unless otherwise noted, the recipe of the reactants and the reaction conditions were as follows: the fine powdery copolymer/dye = 2, the fine powdery copolymer/Monogen-W = 5, the fine powdery copolymer/water = $^1/_{40}$, reaction time 3 hr, and reaction temperature 120°C. The reaction degree of the dye (R_d) and the epoxy group (E_d) were calculated by the following equations from the elemental analysis of nitrogen:

$$E_d = \frac{z}{M} \cdot 100 \tag{1}$$

$$M = \frac{EWy}{1000 + EW}$$

$$R_d = \frac{z}{N} \cdot 100 \tag{2}$$

$$N = \frac{Bxy}{A + Bx}$$

where A = weight of the fine powdery copolymer (g); B = weight of the commercial dye (g); E = expoy value of the fine powdery copolymer (mmole/g); W = molecular weight of the pure dye; x = content of the pure dye in the commercial dye; y = nitrogen content of the pure dye; and z = nitrogen content of the product.

RESULTS AND DISCUSSION

Polymerization

In all cases, the polymerization proceeded acceleratively at first, and then steadily, and gradually slowed down. As soon as the polymerization was initiated, the reaction system became heterogeneous. Therefore, the stirring effect was studied preliminarily. The polymer yield increased with increase in the stirring rate to some extent, so the stirring rate was controlled at 1000 rpm.

The polymerization rate at the earlier stage (R_e) was arbitrarily defined as the average rate corresponding to 0- to 20-min and 0- to 40-min reaction time at 79.5°C and the average rate at a conversion smaller than 10% at 67°C and 56°C, as Bamford and Jenkins did.[8]

Figure 1 shows the effect of BPO concentration on the polymerization. As a matter of course, the polymerization rate increased with increase in the BPO concentration. In regard to the rule that polymerization rate varies as BPO^n, the exponent n was 0.7–0.8, calculated from the relation between $\log R_e$ and $\log [BPO]_0$ shown in Figure 2. This value shows that occlusion of the growing polymer radical in the polymer matrix occurred and the mutual coupling of the polymer radical was considerably difficult. Similar phenomena have been shown in the polymerization of methyl methacrylate in the presence of cyclohexane by Hayden and Melville[6]
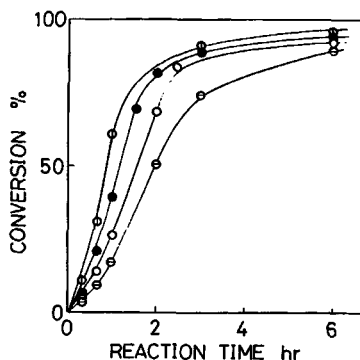
Fig. 1. Effect of BPO concentration on polymerization of GMA and DVB at 79.5°C: [GMA]$_0$, 0.498 mole/l.; [DVB]$_0$, 0.046 mole/l.; [BPO]$_0$, (◐) 9.7 mmole/l.; (●) 6.0 mmole/l., (○) 3.5 mmole/l.; (⊖) 2.0 mmole/l.

and the polymerization of acrylonitrile in aqueous solution by Dainton et al.[7]

Figure 3 shows that the increase in the GMA concentration increased the polymerization rate. The exponent of the GMA concentration was 0.3–0.4, determined from the linear relation between log R_e and log [GMA]$_0$ shown in Figure 2. This means that the GMA concentration was not so much important to the R_e value. When the GMA concentration was too high and conversion increased, it became rather difficult to maintain the reaction system at a definite temperature because the reaction system could not be stirred well.

Figure 4 shows the effect of DVB concentration on the polymerization. Remarkably, the increase in the DVB concentration decreased the polymerization rate. As is shown in Figure 2, when [DVB]$_0$ was 0.046–0.231 mole/l., an apparently linear relation could be observed and thus the exponent of DVB concentration was -0.3 to -0.4. However, when [DVB]$_0$ was 0.324 mole/l., the log R_e value deviated considerably from the
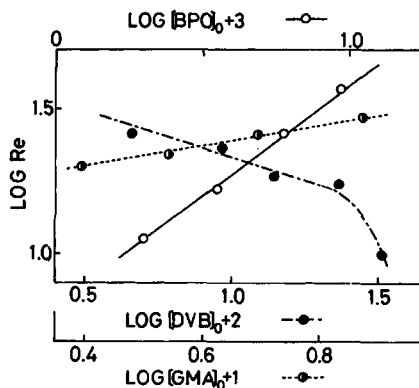

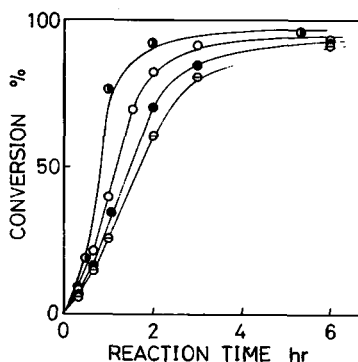Fig. 2. Log R_e vs. log [GMA]$_0$, log [BPO]$_0$, and log [DVB]$_0$.

Fig. 3. Effect of the GMA concentration on polymerization of GMA and DVB at 79.5°C; [DVB]$_0$, 0.046 mole/l.; [BPO]$_0$, 6 mmole/l.; [GMA]$_0$, (◐) 0.747 mole/l.; (○) 0.498 mole/l.; (●) 0.349 mole/l.; (⊖) 0.246 mole/l.

above linear relation. This fact indicates a complexity of this polymerization. When the GMA concentration was kept constant and the DVB concentration increased, it could be generally presumed that the polymerization rate should increase since one of the reactant concentrations increases. However, the experimental result was inconsistent with the presumption and was ascribed to the fact that the resultant polymer was crosslinked. Since the resultant polymer prepcipitates, the active radical should locate on the precipitated polymer, and in order to propagate the polymerization, the monomers must diffuse to the active radical. Since the resultant polymer is crosslinked, the diffusion of the monomers through the polymer matrix to the active radical, occluded in the growing polymer matrix, should become slower with the development of the crosslinking of the resultant polymer. Accordingly, it should be the reason why the increase in the DVB concentration decreased the polymerization rate. On the other hand, Hayden and Melville[6] have reported that the increase in the concentration of the divinyl monomer promoted an earlier autoacceleration
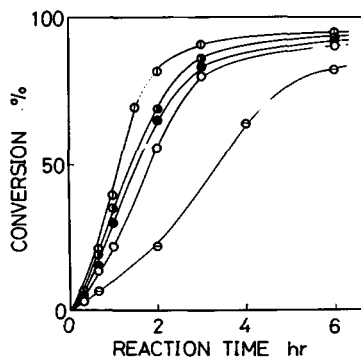

Fig. 4. Effect of DVB concentration on polymerization of GMA and DVB at 79.5°C: [GMA]$_0$, 0.498 mole/l.; [BPO]$_0$, 6 mmole/l.; [DVB]$_0$, (◐) 0.046 mole/l.; (◑) 0.093 mole/l.; (●) 0.139 mole/l.; (○) 0.231 mole/l.; (⊖) 0.324 mole/l.
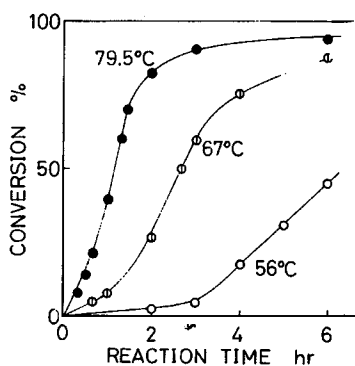
Fig. 5. Effect of reaction temperature on polymerization of GMA and DVB: $[GMA]_0$, 0.486 mole/l.; $[DVB]_0$, 0.046 mole/l.; $[BPO]_0$, 6 mmole/l.

in the bulk polymerization of methyl methacrylate and ethylene glycol dimethacrylate. In the bulk polymerization, the resultant polymer should well be swollen by the monomers; the monomers to propagate the polymer chain were sufficiently near the active radical. Accordingly, the increase in the ethylene glycol dimethacrylate concentration should be effective only for promoting the autoaccelerating effect, but not for depressing the diffusion of the monomers through the polymer matrix. Furthermore, it is interesting that the final conversion decreased with increase in DVB concentration.

Figure 5 shows the effect of the polymerization temperature. The polymerization rates at the steady states (R_s) were determined from the slopes of the linear parts of the time–conversion curves. The R_e and R_s values are shown in Table II. From the Arrhenius plots, the apparent activation energies were calculated to be 28 kcal/mole for the reaction at the earlier stage and 11 kcal/mole for the reaction at the steady state. The former value was consistent with the value (27.4 kcal/mole) for the heterogeneous polymerization of acrylonitrile, in which BPO was used as an initiator,[8] but not with the value (19.9 kcal/mole) for the homogeneous polymerization of GMA in benzene at 50–80°C by the use of α,α'-azobis-isobutyronitrile as an initiator.[9] The reason for the difference between the activation energies relating to R_e and R_s is still obscure, but it can be assumed that the decomposition of BPO might be more effective at the earlier stage and the diffusion of the monomers, at the steady state. For reference, the activation energies for the spontaneous decomposition of BPO in cyclohexane at 80°C,[10] the diffusion of propane in polyethylene at

TABLE II
Polymerization Rates at Various Temperatures

	79.5°C	67°C	56°C
R_e, %/hr	26	7.4	1.5
R_s, %/hr	58	34	13.5

5–55°C,[11] and the diffusion of xylene in polyethylene at 30–85°C[12] are 29.2 kcal/mole, 10–13.6 kcal/mole, and 9–12 kcal/mole, respectively. However, the mechanism should clearly be elucidated in the future. In addition, it was elucidated that the polymerization of GMA–methyl methacrylate–DVB in cyclohexane was very similar to that shown in this study.

Properties of the Fine Powdery Copolymer

The resultant polymer was very fine-spheroidal, and its size was about 0.1 μ or less. GMA and DVB are soluble in cyclohexane, but poly-GMA is insoluble. Accordingly, the resultant polymer precipitates out of the solution. Then, DVB should promote the precipitation of the resultant polymer and should make the polymer very fine-spheroidal. Figure 6 shows the bulk specific gravity of the copolymer. Evidently, the increase in the DVB content made the fine powdery copolymer more bulky. Figure 7 shows the change in the epoxy value of the fine powdery copolymer corresponding to reaction time. The epoxy value was consistent with that calculated from the recipe of the monomers and was independent of the reaction time. In order to understand this constancy, the change in the monomer concentrations by adding the powdery copolymer and the copolymerizability of the monomers were studied as described below. Table III shows the result of the change in monomer composition in the bulk solution by adding the powdery copolymer, the composition of which was
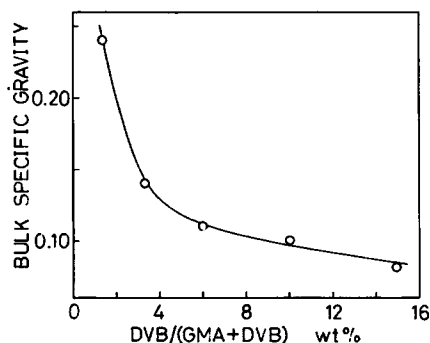

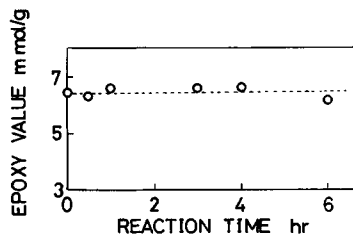Fig. 6. Bulk specific gravities of the fine powdery copolymers at room temperature.

Fig. 7. Epoxy value of the fine powdery copolymer: (-------) calculated value from the recipe.

TABLE III

Changes in GMA and DVB Concentrations in Bulk Solution Upon Addition of
Powdery Copolymer at Room Temperature After 40 Hr[a]

Polymer particles, g/100 ml	GMA, mole/l.	DVB mole/l.	DVB/GMA
0	0.500	0.050	0.10
2	0.493	0.049	0.10
4	0.475	0.046	0.10
6	0.474	0.049	0.11

[a] The GMA and DVB concentrations were determined respectively from the optical densities $D_{1732 \text{ cm}^{-1}}$ and $D_{706 \text{ cm}^{-1}}$, measured by the use of a Hitachi Perkin Elmer 125 grating infrared spectrophotometer from Hitachi Ltd.

DVB/(GMA + DVB) = 0.1 by weight. The ratio of DVB/GMA was not changed, and this result shows that the monomers diffuse from the bulk solution into the polymer particles with the same ratio as that in the bulk solution. Here, the good copolymerizability of the monomers was confirmed by the method shown by Ham[13] by which, since reactivity ratios for the systems styrene (M_1)–GMA (M_2)[14] and styrene–m-DVB or p-DVB (M_3)[15,16] are known, reactivity ratio for system M_2–M_3 could be predicted as follows: $r_{23} = 0.08$, $r_{32} = 0.07$ for m-DVB and $r_{23} = 0.05$–0.06, $r_{32} = 0.14$–0.4 for p-DVB. Thus, it was confirmed that GMA is well copolymerizable with p-DVB and m-DVB. Also, it is not clear yet whether ethylstyrene is well copolymerizable, but styrene derivatives often show the properties analogous to styrene,[13] which is well copolymerizable with GMA.[16] Accordingly, it may be an understandable explanation for the constancy of the epoxy value that GMA and DVB diffuse at similar rates through the polymer matrix from the bulk solution, and as soon as the monomers arrive at the active radical, the monomers are well copolymerized.

Application of the Fine Powdery Copolymer as a Pigment

The fine powdery copolymer has epoxy groups which are reactive, so some dyes containing an amino group and/or a phenolic hydroxy group can be bonded to prepare the colored and fine powdery copolymer, a pigment. From a preliminary experiment, water was favorable as a reaction medium and the reaction time for 3 hr was adequate. Figure 8 shows the effect of reaction temperature on the R_d and E_d values. Both values reasonably increased with elevation in reaction temperature. Figure 9 shows the effect of the ratio of dye/powdery copolymer to both values, and the result was reasonable. As shown in Figures 8 and 9, the reactivity order of the dyes was as follows: MFO > CBE > DFY. In the case of CBE, the situation should be complicated because CBE is tetrafunctional. Clearly, the hydroxyl group of DFY was less reactive than the amino group of MFO, since both dyes are monofunctional. The use of the mixed
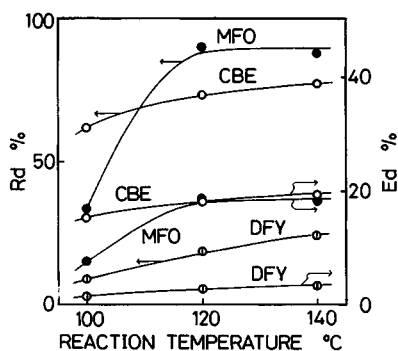
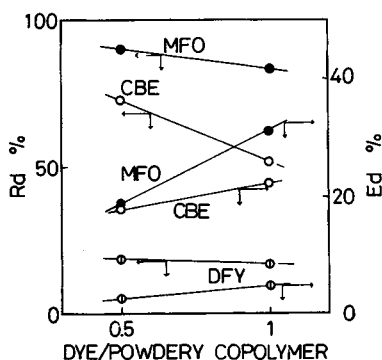Fig. 8. Effect of reaction temperature on R_d and E_d values.

Fig. 9. Effect of dye concentration on R_d and E_d values.

dyes (1:1) of CBE–MFO, MFO–DFY, and DFY–CBE resulted in pigments of black, orange, and green, respectively. Here, the E_d values were rather less, and this should suggest that the bulky molecules of the dyes might react with difficulty with the epoxy groups on the crosslinked matrix. The improvement of the E_d value is then a project for the future. The pigments obtained were blended into polypropylene and poly(vinyl chloride) without any trouble such as color change by heat. Both polymers were well colored by blending 0.5–1% pigments. The plates of polypropylene was opaque, but that of poly(vinyl chloride) was clearly transparent, and the presence of pigment in both plates could not be seen with the naked eye.

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