

Microwave Radiation Solid-State Copolymerization in Binary Maleic Anhydride–Dibenzyl Maleate Systems

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ABSTRACT: The microwave radiation copolymerization of maleic anhydride and dibenzyl maleate was studied in the solid state at 45°C. The composition of the monomer ratio on conversion and intrinsic viscosity and the amount of initiator on intrinsic viscosity were discussed. The copolymer can be used as a suspending agent synthesizing superabsorbent oil resin. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 129–133, 1997

Key words: microwave; copolymerization; maleic anhydride; dibenzyl maleate

INTRODUCTION

Radiation solid-state copolymerization of various vinyl and cyclic monomers was studied, and the results were published in several reviews and articles. Binary systems involved eutectic mixtures, solid solutions, glassy states, and other molecular complexes. Copolymerization of maleic anhydride (MAH) with acrylamide in the solid state was first studied by Zurakowska-Orszagh and Wojno.¹ In recent years, the use of microwave for chemical reaction has been successfully documented. The technique provides a new way for the production of polymer at high rates and conversions. In this article, the previously unreported copolymerization of MAH with dibenzyl maleate (MDE) in the solid state is investigated by microwave radiation. The method of microwave radiation solid-state copolymerization provides a new technique for polymerization.

EXPERIMENT

Copolymerization of MAH and MDE

Materials

MAH was recrystallized three times from chloroform. MDE was prepared by the esterification of

MAH and benzyl alcohol, 20 mL of benzene, 35 mL of benzyl alcohol, 12.25 g of maleic anhydride, and 5 mL of sulfuric acid were added to a three-neck round-bottomed flask, which had a thermometer, separating water equipment, and stirring equipment. The mixture was heated and dehydrated. When the amount of evolved water was 5–6 mL, the reaction mixture was cooled and the evolved water was neutralized by 13.78 g of sodium carbonate. A white solid was formed from the reaction mixture. The solid, MDE, was dried under vacuum.

Copolymerization Procedure

Solid-state copolymerization of MAH and MDE was carried out in small vial of 10-mL capacity. The reactants were mixed by grinding, and then the mixture obtained was placed in the vial and degassed with nitrogen. The mixture was irradiated for 32 sec (intermittent radiation) in a domestic microwave oven (which worked at 700 W and 2,450 MHz). Reaction temperature was kept at 45°C by controlling power. Immediately after irradiation, the polymer formed was isolated by being poured into 200 mL of methanol and was washed with refluxing methanol for 3 h. The polymer was dried under vacuum at 60°C for 10 h. The yield of the copolymer was 94%, and the intrinsic

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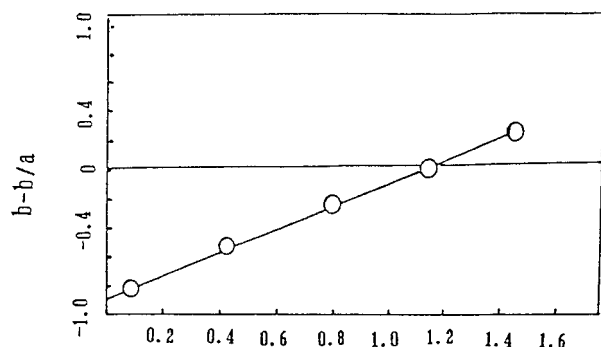


Figure 1 The linear relation between $b - b/a$ and b^2/a .

viscosity was $2.75 \text{ cm}^3/\text{g}$, which was measured at a 1 : 1 water and Tetrahydrofuran ratio at 25°C . The copolymer was prepared by a conventional thermal method at 45°C for 2 h under nitrogen. The yield was 89%, and the intrinsic viscosity was $2.16 \text{ cm}^3/\text{g}$.

Copolymer as W/O Suspending Agent in Superabsorbent Oil Resin

Materials

Dodecyl acrylate, isobutyl acrylate monomers, and diethylene glycol diacrylate crosslinker were purified by distilling under vacuum.

Synthesis of Superabsorbent Oil Resin

Water (9 mL) and a 0.25-g copolymer of MAH and MDE were placed in three-neck round-bottomed flask, which had a thermometer, condenser, and stirring apparatus. The mixture was heated until the copolymer was dissolved; then, this reactive system was cooled to 40°C . A sample of 4.6 g of dodecyl acrylate, 7.9 g of isobutyl acrylate, 0.1 g of diethylene glycol diacrylate, and 0.13 g of benzoyl peroxide was added to the flask and stirred. The stirring speed was controlled at 500 revolutions/min. The reactive solution was heated under nitrogen to $90\text{--}95^\circ\text{C}$ and reacted for 4 h. After the reactive solution was cooled, the copolymer was recovered by filtration and washed with water three times. The copolymer was dried under vacuum at 70°C for 5 h.

Measurements of Resin Property

Absorbent Oil Power. Absorbent oil resin (1 g) was combined with 30 g of benzene in a 100-mL

Erlenmeyer flask. After 2 h, the resin was isolated by filtration. Residual benzene weight was determined by

absorbent oil power (g/g)

$$= \frac{\text{amount of benzene} - \text{amount of residual benzene}}{\text{amount of resin}} \quad (1)$$

Absorbent Oil Ratio. Absorbent oil resin (1 g) was combined with 30 g of benzene in a 100-mL Erlenmeyer flask. After the resin absorbed the benzene in various time, the resin was isolated by filtration. Residual benzene weight was determined by the difference. The relation between absorbent time and absorbent power was obtained.

RESULTS AND DISCUSSION

Copolymerization of MAH and MDE

It is difficult to polymerize 1,2-disubstitute ethylene (such as MAH or MDE) by conventional thermal methods because of the steric effects of these monomers. In this article, microwave radiation is utilized to easily copolymerize MAH and MDE.

Measurements of R_1 and R_2

The composition equation of Lewis and Mayo is as follows:

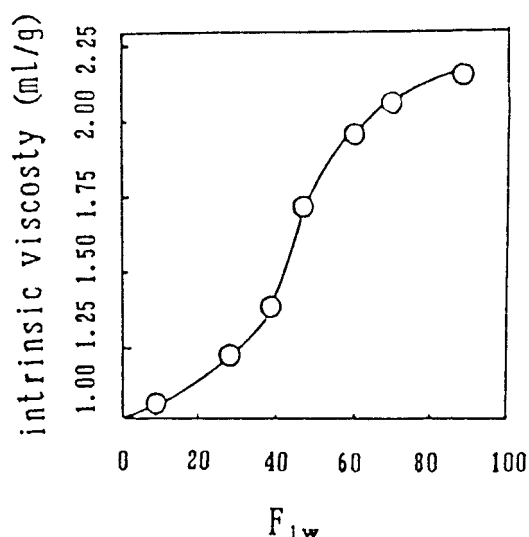


Figure 2 The effect of monomer ratio on the intrinsic viscosity of copolymer.

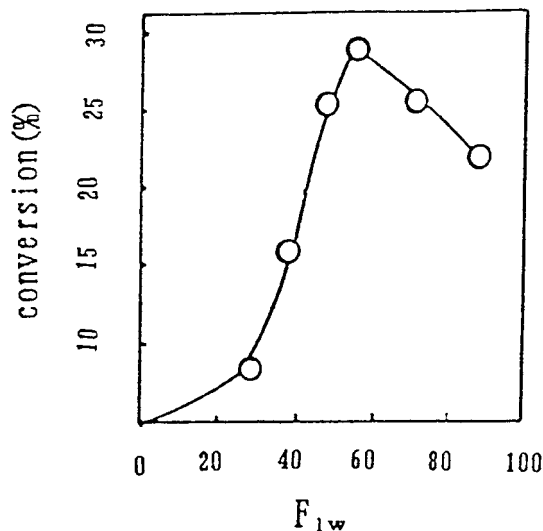


Figure 3 The effect of different monomer ratios on polymer yields.

$$\frac{dM_1}{dM_2} = \frac{M_1}{M_2} \cdot \frac{r_1 M_1 + M_2}{r_2 M_2 + M_1} \quad (2)$$

In the above equation, M_1 and M_2 are the concentration of MDE and MAH, respectively. r_1 and r_2 are the competitive ratio of MDE and MAH copolymerization, respectively. If the ratio of monomers is

$$b = \frac{M_1}{M_2} \quad \text{and} \quad a = \frac{dM_1}{dM_2}$$

then eq. (2) was simplified and represented as

$$\frac{a-1}{b} = r_1 - r_2 \frac{a}{b^2} \quad (3)$$

or

$$\frac{b(a-1)}{a} = -r_2 + r_1 \frac{b^2}{a}$$

Table I Particle Diameter and Absorbent Oil Power for Some Resins

Suspending agent no.	11	12	15	21	22	24	25	0 ^a
Particle diameter (mm)	0.27	0.23	0.54	0.17	0.38	0.33	0.24	0.21
Power (g/g)	17.0	15.0	18.0	15.0	13.2	16.5	16.0	17.0

^a 0, colla taurina.

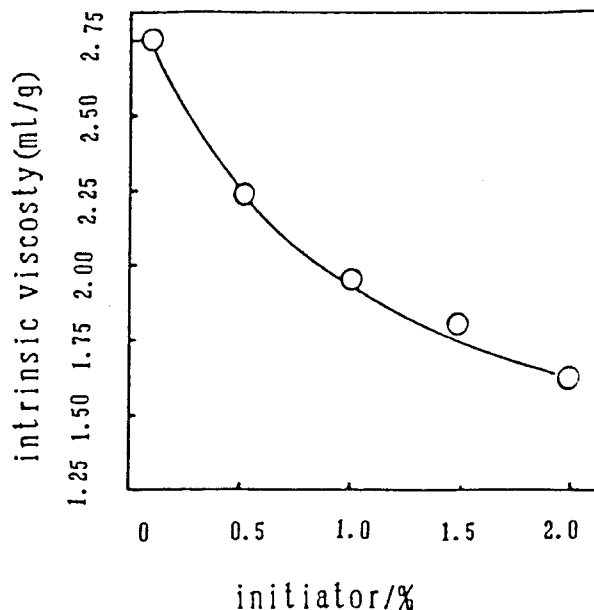


Figure 4 The relation between amount of initiator and intrinsic viscosity of polymer.

The variations of the composition of monomers (b value) were copolymerized by microwave (controlling conversion < 10%). Relative a values were measured through ultraviolet absorption spectrometry. The line (Fig. 1) was obtained by $b - b/a$ as longitudinal coordinate and b^2/a as horizontal coordinate. The linear slope is r_1 ($=0.900$). The linear intercept is $-r_2$ ($=0.775$).

Monomer Ratio

The effect of monomer ratio on the intrinsic viscosity of the copolymer is shown in Figure 2. It is apparent from Figure 2 that intrinsic viscosity increases as the MDE content of the mixture increases. This is because r_1 of MDE is higher than r_2 of MAH, that is, the reactive activity of MAH is higher than that of MDE. An increase in the lower active MDE content would increase the two

Table II Relation Among Suspending Property and Intrinsic Viscosity, Monomer Ratio, and Initiator

Suspending Agent no.	11	12	13	14	15	21	23	24	25
Intrinsic viscosity (cm/g)	0.950	1.275	1.250	1.750	2.125	2.750	2.075	1.950	1.850
f_{1w}^a	50	40	30	10	90	50	50	50	50
BPO (%)	1	1	1	1	1	0.1	0.5	1.5	2
Suspending property ^b	B	B	C	C	A	A*	B	B	B

^a f_{1w} , MDE.

^b A*, fairly good; A, good; B, general; C, no good.

monomers' collision probability and therefore would increase copolymerization probability and increase intrinsic viscosity.

The effect of different monomer ratios on polymer yields is shown in Figure 3. Polymer yields reached a highest value for different monomer ratios in Figure 2. It is probable that r_1 is similar to r_2 . When the monomer ratio is 50% MDE content, copolymerization is probably easy under microwave radiation so that the yields increase. The yields decrease as MAH content increases because MAH homopolymerization is difficult. On the other hand, the yields also decrease as MDE decreases, but the decrease in the value of yields is less than that of MAH. It is probable that homopolymerization can take place more easily for MDE than for MAH because the r_1 of MDE is equal to 0.900.

Initiator

Figure 4 exhibits the relation between the amount of initiator and the intrinsic viscosity of polymer.

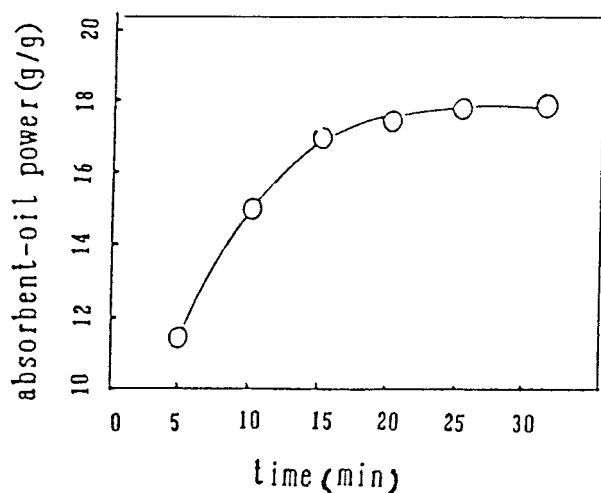


Figure 5 Absorbent-benzene ratio.

The intrinsic viscosity of the polymers decreases as the amount of initiator increases. This specific property corresponds to a radical mechanism. We conclude that the copolymerization of microwave radiation for this system is probably a radical mechanism.

Synthesis of Superabsorbent Oil Resin

Choice of Synthetic Condition

In order to get a stable suspending polymer system, it is necessary to choose a proper polymer condition. Optimized synthetic conditions are as follows: phase ratio = oil phase volume/water phase volume = 1 : 3; amount of suspending agent = 2% (relative to amount of monomer); amount of initiator = 1% (relative to amount of monomer); amount of crosslinker = 0.8% (relative to amount of monomer); ratio of monomers = dodecyl acrylate/isobutyl acrylate = 0.58.

Property of Superabsorbent Oil Resin

Particle Diameter and Absorbent Oil Power. Table I exhibits particle diameter and absorbent oil power for some resins.

Absorbent Oil Ratio. Figure 5 exhibits the absorbent-benzene ratio. Absorbent-benzene power reached the highest value in 30 min. The ratio is faster than other systems which had previously studied.

Choice of Suspending Agent

A suspending agent is a type of surface active agent, composed of a hydrophilic group and a lipophilic group. Its properties depend on HLB (hydrophilic water-lipophilic oil equilibrium value) volume. The test showed that an HLB volume of

11.8–12.4 is fit to the w/o suspending polymerization in this system. HLB volume depended on the molecular weight and composition of the copolymer. The suspending properties of the copolymer are shown in Table II.

Table II shows intrinsic viscosities in the 2.125–2.750 cm³/g range, and compositions of copolymerization (f_{1w}) in the 50–90% range are good suspending agents for the system. The synthetic superabsorbent oil resin can separate the mixture of 1 : 1 benzene and alcohol. The separating effect reached 92.72% benzene content.

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