Microwave Radiation Copolymerization in Solid State of Maleic Anhydride and Allylthiourea

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ABSTRACT: Microwave radiation copolymerization of maleic anhydride and allylthiourea was studied in solid state. Composition of the monomer feed and the power and time of microwave radiation on conversion and intrinsic viscosity were discussed. Reactivity ratios for maleic anhydride and allylthiourea were also determined. Values of r_1 and r_2 were 0.875 and 0.650 for maleic anhydride and allylthiourea, respectively. The copolymer can be used as soluble macromolecular complexing agents for metal ions. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1563–1566, 1998

Key words: maleic anhydride; allylthiourea; microwave; solid-state copolymerization

INTRODUCTION

In recent years, microwave radiation was widely studied in the chemical field. In organic chemistry, especially, the microwave has received considerable attention due to its excellent properties in organic compound synthesis. However, it has not been used in the reaction of polymerization until recently. Polymerization in solid state by the microwave has not yet been reported. In this work, we studied previously unreported copolymerization of maleic anhydride and allylthiourea in the solid state by microwave initiation in the domestic microwave oven. The power and time of microwave radiation on conversion and intrinsic viscosity were discussed. Composition of the monomers on copolymerization was also discussed at the same wave frequency and power. At the same time, the reactivity ratios of maleic anhydride and allylthiourea were measured by ultraviolet absorption spectrometry. The fact that, in this system, the microwave initiated the reaction of copolymerization may provide a new viewpoint for heating effect and unheating effect, which people

pay close attention to. In the meantime, the copolymer was used in isolation metal ions for the first time.

EXPERIMENTAL

Material

Maleic anhydride and allylthiourea were recrystallized from chloroform.

Microwave Polymerization

Solid-state copolymerization of maleic anhydride and allylthiourea was conducted in a special vial as depicted in Figure 1. The reactants were mixed by grinding; then, the mixture obtained was placed in the vial and degassed with nitrogen for 30 min. The beginning temperature and weight of the mixture were determined. The mixture was radiation at prescribed power and time in a domestic microwave oven (which worked at 700 W and 2450 MHz). After this, the temperature and weight of the mixture were determined again. The mixture was poured into a mixture of toluene and acetone at the ratio of 1 : 1. The polymer was obtained by filtration and purified by washing
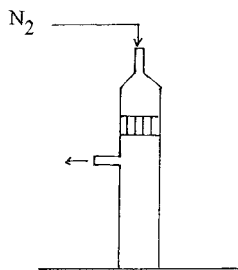
Figure 1   Special vial under microwave radiation.

and then dried under a vacuum at 50°C. The yield of the polymer was determined by dividing the weight of the monomer by the weight of the polymer.[1–3]

Measurement of the Reactivity Ratio

Solid-state copolymerization was conducted in the special vial with a different mixture of different monomer composition. After a given time of radiation at the power of 430 W, the reaction was ended by adding hydroquinone inhibitor to the solid system.

The temperature of reactants was controlled at $55 \pm 1°C$, and the conversion was controlled within 10%. The composition of the copolymer was determined by ultraviolet absorption spectrometry. The reactivity ratios were obtained by the Lewis and Mayo equation.

Measurement of Complexing Capacities of Metal Ion

The copolymer complexes with metal ions by means of membrane filtration (refs. 4–6). Membrane filtration was conducted in a system as depicted in Figure 2. The membrane filtration unit
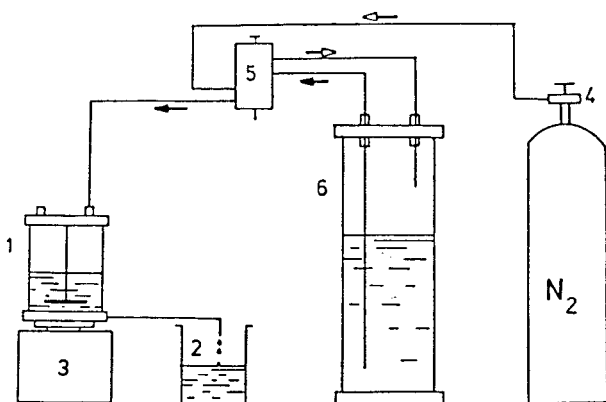

Figure 2   Membrane filtration unit: (1) filtration cell with solution of polymeric complex; (2) membrane filtrate; (3) magnetic stirrer; (4) pressure trap; (5) selector; (6) reservoir with solution of metal salt.

consists of the membrane filtration cell with a magnetic stirrer, the coupled reservoir, the dialysate reservoir, the selector, and the pressure source using a selector that allow the addition of the washing fluid simultaneously corresponding to the elution volume and therewith continuous membrane filtration.

The complexing polymer solution was placed into the membrane filtration cell and the metal salt solution added from the reservoir. The polymer concentration in the cell was constant. After isolation of the complex formed, the proportion of nonbound ions could be determined by atomic absorption spectroscopy of the filtrate that was collected in fractions.

Measurement of Intrinsic Viscosity

Intrinsic viscosity was measured by the one-point method in the solvent mixture: THF and isopropanol, 1 : 1 at $25 \pm 0.1°C$.

RESULTS AND DISCUSSION

Reactivity Ratio of Two Monomers

The Lewis and Mayo composition equation is represented as follows:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \times \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} . \quad (1)$$

In the above equation, $[M_1]$ and $[M_2]$ are the concentration of maleic anhydride and allylthiourea, and r_1 and r_2 are the reactivity ratios of maleic anhydride and allylthiourea copolymerization, respectively. If $b = [M_1]/[M_2]$, $a = d[M_1]/d[M_2]$, eq. (1) was simplified and represented as:

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

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

Various compositions of monomers (value of "b") were copolymerized by the microwave (controlling conversion < 10%). The relative value of "a" is

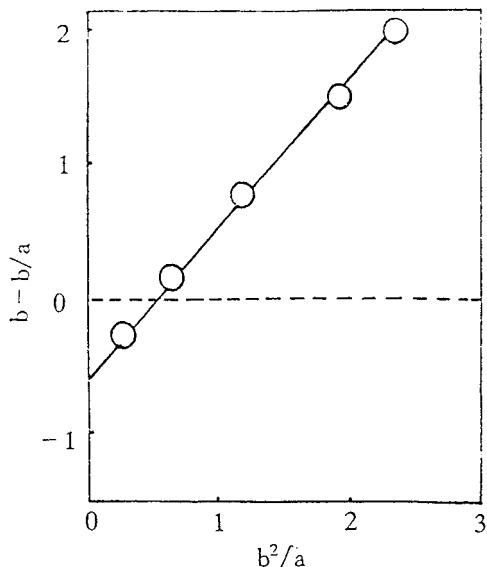$$a = \frac{d[M_1]}{d[M_2]} = \frac{([M_1]_0 - [M_1])}{([M_2]_0 - [M_2])} \quad (3)$$

Figure 3 Linear relationship of $b - b/a$ to b^2/a.

Here, $\sqrt{[M_1]_0}$ and $[M_2]_0$ are the concentration of maleic anhydride and allylthiourea before reaction, respectively, which were compositions of monomers. $[M_1]$ and $[M_2]$ are the concentration of maleic anhydride and allylthiourea after reaction, respectively, which were measured by ultraviolet absorption spectrometry. The line (Fig. 3) was obtained by $(b - b/a)$ as the longitudinal coordinate and (b^2/a) as the horizontal coordinate. The linear slope was r_1. The linear intercept was r_2. Herein, $r_1 = 0.875$ and $r_2 = 0.650$. Therefore, allylthiourea was the major component of polymers that were formed initially.

Effect of Monomer Ratio on Intrinsic Viscosity

The relationship between monomer ratio and the copolymer intrinsic viscosity at the same microwave radiation time and power was showed in Figure 4. It is apparent that intrinsic viscosity decreases as the maleic anhydride increases. This is because r_1 of maleic anhydride is higher than r_2 of allylthiourea ($r_1 = 0.875$, $r_2 = 0.650$). Namely, reactive activity of two copolymerization monomers is maleic anhydride higher than allylthiourea. An increase of lower active allylthiourea content would increase the copolymerization velocity and intrinsic viscosity.

Effect of Microwave Radiation Power and Time on Polymer Yield

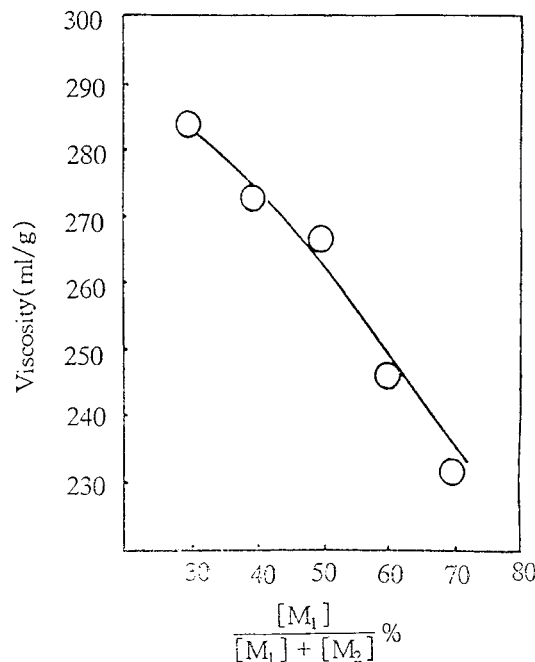The microwave radiation power and time were the major factors. Figure 5 shows the effect of

Figure 4 Relationship between composition of monomers and viscosity of polymer.

the microwave radiation power and time on polymer yield. It is shown that, at a given power, the yield increases if we prolong the reaction time. Because copolymerization was initiated by
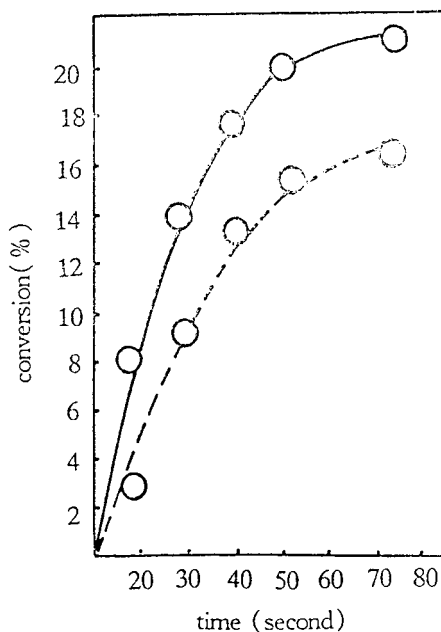

Figure 5 Relationship between power and time of radiation and conversion of monomer: $(- - -)$ power $= 270$ W; $(—)$ power $= 430$ W.

microwave radiation, the activation center would increase if we prolong the radiation time, which resulted in yield increases while power increases. This is also because energy absorbed by reactants increases and the activation center increases, whereas power increases and, as a result, the yield increases.

Effect of Microwave Radiation Time and Power on Copolymer Intrinsic Viscosity

It is obvious in Figure 6 that intrinsic viscosity decreases as the radiation time increases. This is because the activation center increases as the time is prolonged. As the activation center increases more and more, lower molecular weight and higher polymer yield would appear. From Figure 6, we also learn that the polymer intrinsic viscosity is high at the content of allylthiourea (50%) and low at 30%. This conclusion was the same as in the Effect of Monomer Ratio on Intrinsic Viscosity section (i.e., the copolymerization reaction is favorable and the intrinsic viscosity increases while the ratio of allylthiourea increases).
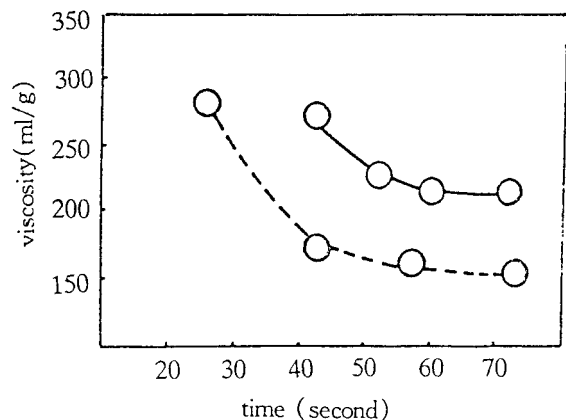

Figure 6 Relationship between power and time of radiation and viscosity of polymer: (– – –) containing 30 wt % allylthiourea; (—) containing 50 wt % allylthiourea. Power = 430 W.

Table I   Results by Membrane Filtration

Metal Ion	pH	Molar Capacity (mmol g^{-1})
Ni(II)	2.5	0.45
Ni(II)	2.0	0.31
Cu(II)	2.5	0.49
Hg(II)	2.5	0.50
Pd(II)	2.5	0.86

Copolymer from Maleic Anhydride and Allylthiourea-Soluble Macromolecular Complexing Agent

Water-soluble polymer complexes are not only of theoretical importance, but also of increasing practical interest for the potentiality of versatile application in chemistry. The copolymer of maleic anhydride and allylthiourea is water-soluble at pH ≤ 2.5 and at pH 2.5 has complexing capacities of metal ion. We obtained the result by membrane filtration (see Table I).

A very strong dependency exists between capacity and pH. Capacity was influenced by both types of functional groups in copolymer and type of metal ions. Generally, complexing capacity increases as pH rised. In this system, when pH is 2.5 and 2, the complexing capacity for Ni(II) is 0.45 and 0.31 mmol g^{-1}, respectively. Although pH ≥ 2.5, an insoluble polymer, was obtained, it caused considerable disadvantages for reactions in the heterogeneous phase and long contenting time.

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