

Microwave Radiation Copolymerization of Dibutyltin Maleate and Allyl Thiourea

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ABSTRACT: This article reports on an investigation of microwave radiation copolymerization of dibutyltin maleate (DBTM) with allyl thiourea (AT) and the copolymers it produced. The effect of radiation energy, composition of monomer, amount of initiator, and amount and kind of inorganic oxide (Al_2O_3 or SiO_2) as reaction sensitizers on the copolymerization conversion and polymer-inherent viscosity were systematically studied, and simultaneously compared with the relevant conventional thermopolymerization. The reactivity ratios for DBTM and AT were determined using liquid chromatography. The copolymerization mechanism of microwave radiation was probed using a free-radical capturing agent (DPPH). The copolymers obtained were used as heat-stabilization agent of PVC resin. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 312–318, 2001

Key words: microwave irradiation; copolymerization; reactivity ratios; heat-stabilization agent

INTRODUCTION

Microwave is a nonionized electromagnetic energy. It has received considerable attention since Gidye first introduced it into organic synthesis in 1986.¹ However, until recently it has not been used in the polymerization reaction. There have been some reports on this aspect, mainly in the solidifying and crosslinking of polymers such as polyurea,² polyurethane,² and polyurethane–epoxy (PU–EP) IPN³ and in the bulk polymerization of polarity liquid monomers such as styrene⁴ and methyl methacrylate.⁵ But the copolymerization of DBTM and AT under microwave radiation had not been reported. This work provides a new approach to studying polymerization.

EXPERIMENTAL

Materials

Dibutyltin maleate (DBTM) and allyl thiourea (AT) were recrystallized. Alumina, silicon dioxide, and diphenylpicrylhydrazyl (DPPH) were analytically pure.

Mechanism of Copolymerization under Microwave Radiation

Series concentrations of DPPH solution were obtained using DMF as a solvent, and absorbance was determined by UV-VIS spectrophotometer. Thus the working curve was obtained by plotting absorbance versus concentration. A given amount of monomer or a mixture of monomer and carrier was radiated by a given microwave energy. After that, a given DPPH solution was added immediately. Absorbency was determined, so the concentration of the remaining DPPH was determined from the working curve. The difference between the initial DPPH concentration and the remain-

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ing DPPH concentration was the radical concentration generating from the system by microwave radiation. From this, radical concentrations under different conditions could be extrapolated. With these results we tried to assess the copolymerization mechanism under microwave radiation.

Copolymerization of DBTM and AT

Solid-state copolymerization of DBTM and AT was carried out in a small vial 10 mL in capacity. The reactants (or the mixture of reactants and inorganic carriers) were mixed by grinding, and the mixture obtained was placed in the vial and degassed with nitrogen for 30 min. The initial temperature was thus determined. The mixture was then radiated by the prescribed energy in a domestic microwave oven (which worked at 700 W), in which the temperature was kept at $44.0 \pm 1.0^\circ\text{C}$. After this, the mixture was poured into methanol. After 10 h the copolymer was obtained by filtration, purified by washing, and then dried under vacuum at room temperature. Conventional thermopolymerization was conducted using a heating method under nitrogen. The solution copolymerization was conducted in a tetrachloroethylene solution under microwave radiation at $44.0 \pm 1.0^\circ\text{C}$.

Measurement of Reactivity Ratio

Solid-state copolymerization was conducted with different mixtures of different monomeric compositions in the special vial. After a given energy radiation, the reaction was terminated by adding hydroquinone inhibitor to the solid system. The temperature of reaction was controlled at $44.0 \pm 1.0^\circ\text{C}$, and the conversion was controlled within 10%. The composition of the copolymer was determined by liquid chromatography, and reactivity ratios were obtained using the Lewis and Mayo equation.⁶

Measurement of Intrinsic Viscosity

The intrinsic viscosity of the copolymer was measured with a Ubbelohde viscometer at $30.0 \pm 0.5^\circ\text{C}$ in a solvent composed of trichloromethane and acetic acid at a 20 : 1 ratio.

Measurement of Heat-Stabilizing Capacities of Organo-Tin Polymers

PVC resins (50 g), calcium stearate (0.1 g), zinc stearate (0.05 g), and dibutyl phthalate (3.0 g)

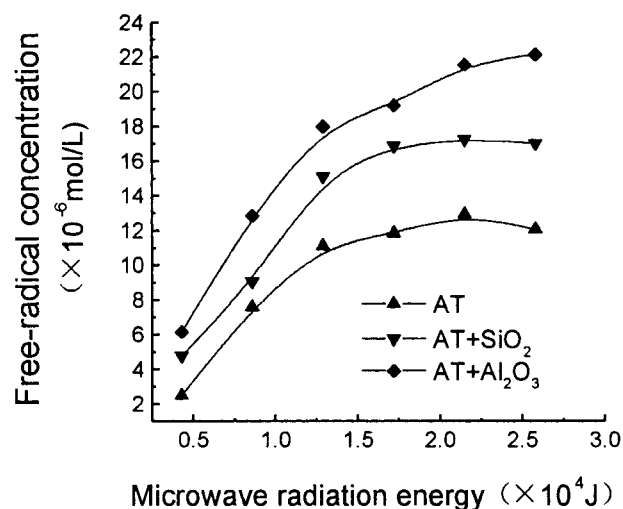


Figure 1 The relation between radiation energy and free-radical concentration in AT system.

were mixed by grinding, and the mixture obtained was heated at 100°C for 10 min. It was divided into 10 parts, and to every part 0.1 g organo-tin polymer was added. Then the mixture was ground and heated at 100°C for 15 mins and finally cooled naturally. Two currettes were filled $\frac{1}{3}$ full with the mixture, and Congo red indicator paper was placed on top of both currettes. One was heated slowly in an oil bath, and the temperature at which the indicator paper changed to blue was the degradation temperature of PVC resins. Timing was begun when the other curette was placed in an oil bath at a constant temperature ($190 \pm 1^\circ\text{C}$), and the time was the heat-stabilizing time of PVC resins while the indicator paper changed to blue.⁷

RESULTS AND DISCUSSION

Copolymerization Mechanism under Microwave Radiation

The relationships between the concentration of free radicals generating from an AT system and microwave radiation energy that of free radicals from a DBTM system with radiation energy are shown in Figure 1 and Figure 2, respectively. These figures show an overall trend of radical concentration increasing as microwave radiation energy increases. Because the polar molecule circumrotated and surged when it accepted microwave radiation energy, an active center, that is, free radicals, were generated. And the more tempestuously the polar molecule surged, the more free radicals were generated as radiation energy

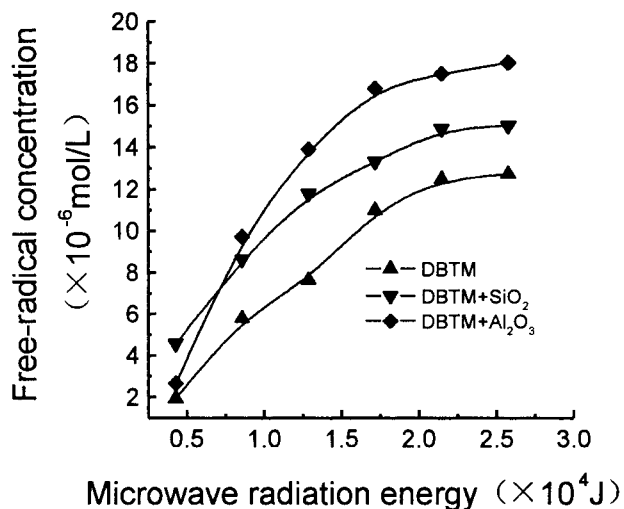


Figure 2 The relation between radiation energy and free-radical concentration in DBTM system.

increased. Figures 1 and 2 show that free-radical concentration in the DBTM system was lower than that in the AT system in conditions using no carriers and using Al_2O_3 (or SiO_2) as carrier, respectively. It was deduced that the reaction activity of DBTM was lower than that of AT under these conditions, which was confirmed by the results of the reactivity ratios of the monomers. In addition, the free-radical concentration obviously increased if carriers were used. And in addition, free-radical concentration in the Al_2O_3 system was higher than that in SiO_2 , which illuminated that Al_2O_3 and SiO_2 were not only carriers but also sensitizers, and the sensitive property of Al_2O_3 was better than that of SiO_2 .

Figure 3 shows the relationship between free-radical concentration generating from DBTM-AT copolymerization system and radiation energy. Because free radicals induced by microwave radiation increased as the radiation increased, the free-radical concentration decreased after the radiation energy reached a given value. In addition, free-radical concentration in the system without carriers was lower than that in the system using carriers, and free-radical concentration was higher in a Al_2O_3 system than that in a SiO_2 system, which was the same as the previously mentioned.

Reactivity Ratios of Monomers

The composition equation of Lewis and Mayo is

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

where $[M_1]$ and $[M_2]$ are the concentrations of AT and DBTM, and r_1 and r_2 are the competitive ratios of AT and DBTM, respectively. If $b = [M_1]/[M_2]$, $a = d[M_1]/d[M_2]$, eq. (1) is simplified and presented as

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

or

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

Monomers of various compositions (value of b) were copolymerized under various conditions by microwave radiation (controlling conversion: 10%). The relative value of a is

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

where $[M_1]_0$ and $[M_2]_0$ are the concentrations of AT and DBTM respectively before reaction, which were the composition of monomers; $[M_1]$ and $[M_2]$ are the concentrations of AT and DBTM respectively after reaction, which were measured by liquid chromatography. The lines were obtained by $(b - b/a)$ as the longitudinal coordinate and (b/a) as the horizontal coordinate. The linear slope is r_1 , and the linear intercept $-r_2$. The results are represented in Table I.

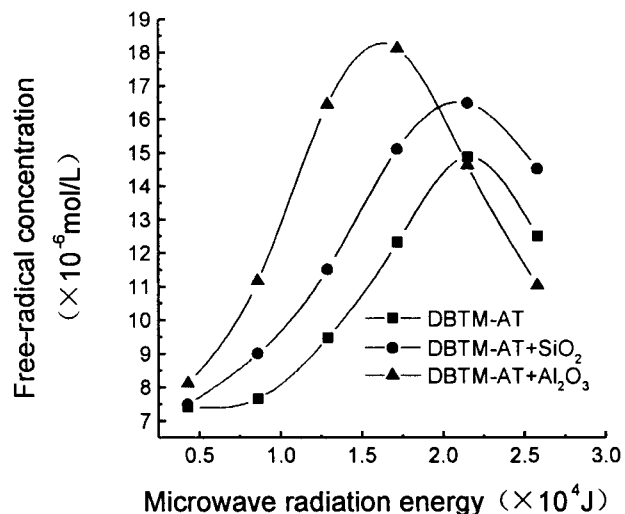


Figure 3 The relation between radiation energy and free-radical concentration in DBTM-AT system.

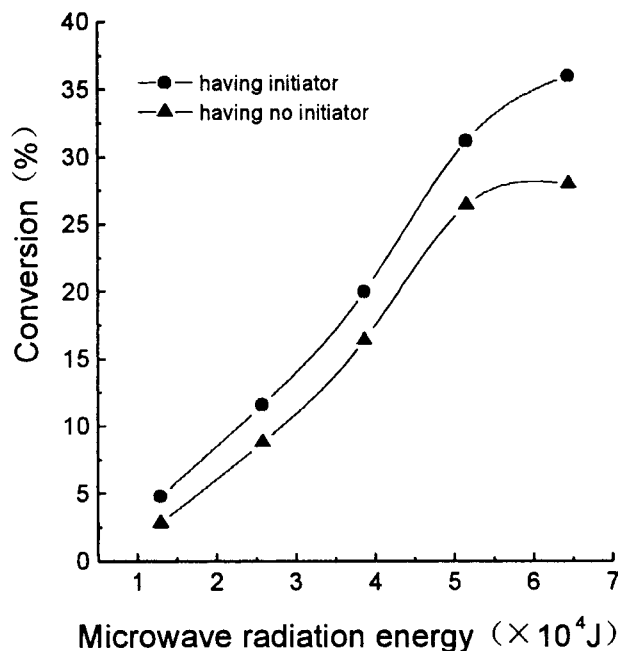


Figure 4 The relation between microwave radiation energy and polymerization conversion; AT : DBTM = 1 : 1; concentration of initiator = 0.4%.

Solid-State Copolymerization of AT and DBTM

Microwave Radiation Energy

The effects of microwave radiation energy on polymer conversion and intrinsic viscosity are shown in Figures 4 and 5, respectively. In Figure 4 it can be seen that conversion increased if radiation energy was increased because microwave

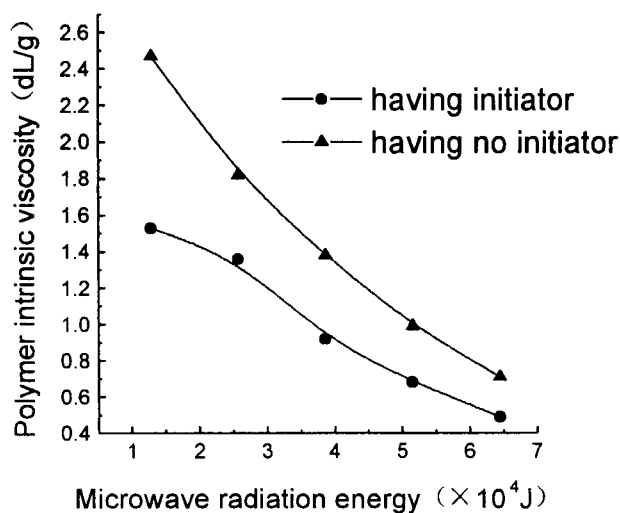


Figure 5 The relation between microwave radiation energy and polymer intrinsic viscosity; AT : DBTM = 1 : 1; concentration of initiator = 0.4%.

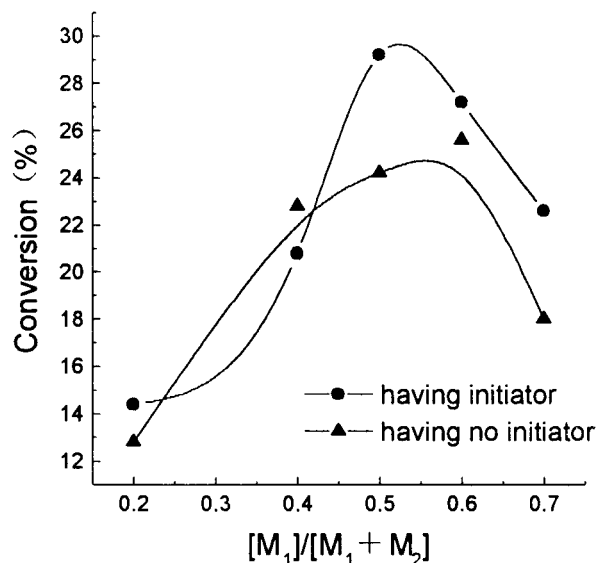


Figure 6 The relation between monomer ratio and conversion (microwave radiation energy = 5.05×10^4 J; concentration of initiator = 0.4%; M_1 —AT, M_2 —DBTM).

radiation initiated the forming of the active center, that is, free radicals. The amount of active center would also increase if we increased radiation energy, which resulted in the increase in conversion. From Figure 4 we also learned that at a given radiation energy the conversion using initiator was higher than that without using it. This is because the amount of active center while using initiator is higher than that without using it.

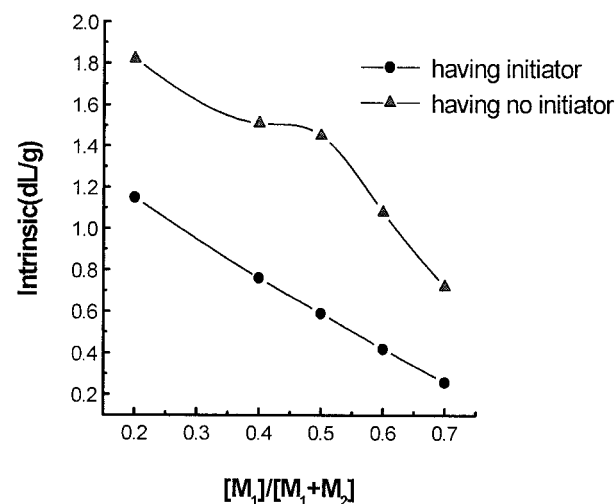


Figure 7 The relation between monomer ratio and intrinsic viscosity (microwave radiation energy = 5.05×10^4 J; concentration of initiator = 0.4%; M_1 —AT, M_2 —DBTM).

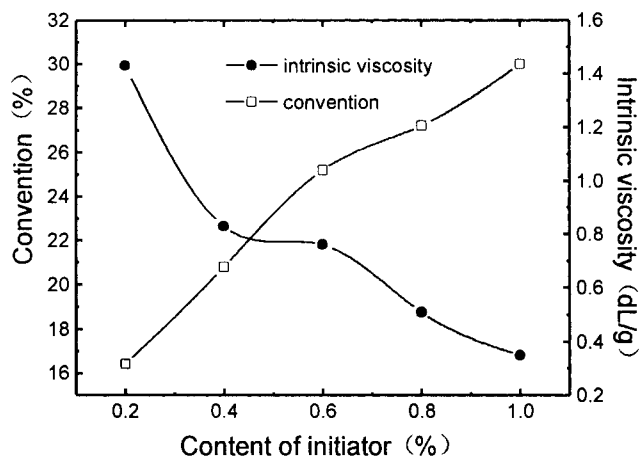


Figure 8 The relation between content of initiator with conversion and polymer intrinsic viscosity (AT : DBTM = 1 : 1, microwave radiation energy = 4.3×10^4 J).

It is obvious from Figure 5 that polymer intrinsic viscosity decreased as the radiation energy increased, and at a given radiation energy, intrinsic viscosity without using initiator was higher than where it was used. The number of free radicals generated increased with increasing microwave radiation dosage, and the number of polymer chains initiated was close to the number of initiating radicals generated. And for the same monomer concentration, the higher the number of initiating radicals, the higher were the number of

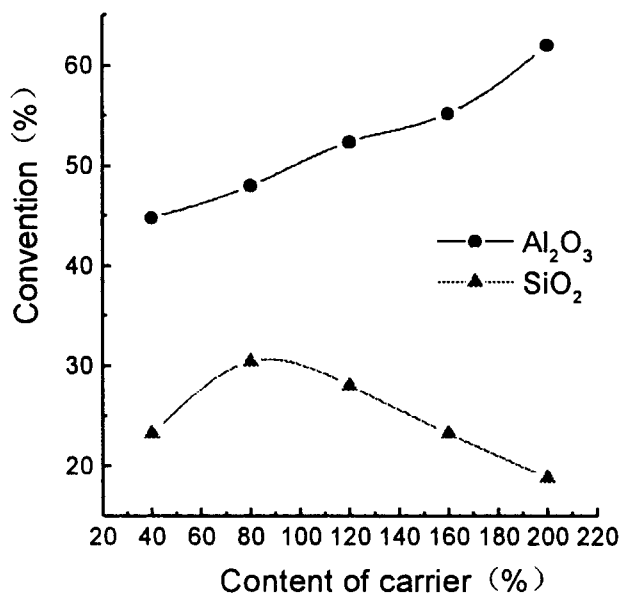


Figure 9 The relation between content of carrier with conversion (microwave radiation energy = 9.03×10^4 J; DBTM : AT = 1 : 1).

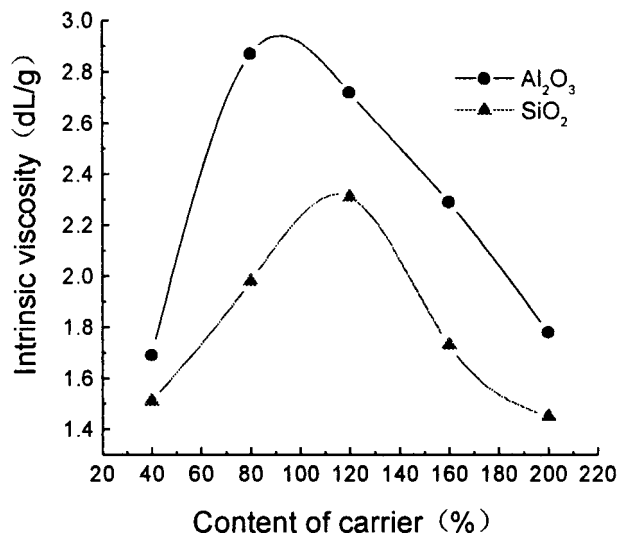


Figure 10 The relation between content of carrier with polymer intrinsic viscosity (microwave radiation energy = 9.03×10^4 J; DBTM : AT = 1 : 1).

polymer chains formed and the shorter the chain length. The shorter chain length explains decreasing intrinsic viscosity.

Monomer Ratio

The effect of monomer ratio on polymer conversion and intrinsic viscosity is shown in Figures 6 and 7, respectively. Polymer conversion reached its highest value for different monomer ratios, and intrinsic viscosity decreased as the AT content of the mixture increased. This was because the reactivity of AT was higher than that of DBTM in a solid state under microwave radiation

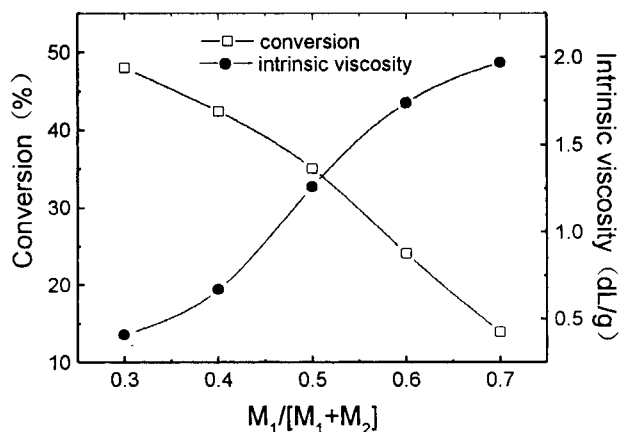


Figure 11 The relation between monomer ratio with polymer conversion and intrinsic viscosity (microwave radiation energy = 9.03×10^4 J; M_1 —AT, M_2 —DBTM).

Table I Reactivity Ratios of 2 Monomers

	Solid-State (Without Carriers or Initiator)	Solid-State (Using Initiator but no Carriers)	Solid-State (Using SiO ₂ as Carrier but no Initiator)	Solid-State (Using Al ₂ O ₃ as Carrier but no Initiator)	Solution Copolymerization (without Carriers or Initiator)
R_{AT}	1.127	1.577	1.640	2.181	0.612
R_{DBTM}	0.102	0.364	0.262	0.417	1.373

without using initiator, as we had known from the copolymerization mechanism, which was also verified by the fact that the r_1 of AT was higher than the r_2 of DBTM. An increase in the higher active AT content would increase the monomer collision probability and therefore result in a increase in polymer conversion. It was probably because of the homopolymerization of AT, which resulted in a decrease in polymer conversion when the AT content in monomer mixture was higher than 60%.

It was apparent that the intrinsic viscosity decreased as the amount of AT increased in copolymerization system. Increase in the amount of higher active AT would cause a decrease in the polymer intrinsic viscosity.

Initiator

Figure 8 exhibits the effect of the amount of initiator on polymer conversion and intrinsic viscosity. It is apparent from Figure 8 that polymer conversion increased and intrinsic viscosity decreased as the amount of initiator increased. This specific property corresponds to a radical mechanism. We could conclude that copolymerization under microwave radiation for this system is probably a radical mechanism.

Inorganic Carrier

The effect of the amount of inorganic carrier on polymer conversion and intrinsic viscosity are shown in Figures 9 and 10, respectively.

Figure 9 exhibits that polymer conversion increased in a Al₂O₃ carrier system as the amount of Al₂O₃ increased within the experimental range. However, in an SiO₂ carrier polymer conversion appeared as a peak value as the amount of SiO₂ carrier increased. And polymer conversion in the Al₂O₃ carrier system was higher than that in the SiO₂ carrier system accordingly for the same reason as previously described. Figure 10 shows that intrinsic viscosity in both the Al₂O₃ and SiO₂ carrier systems appeared as a peak value, and

intrinsic viscosity in the Al₂O₃ system was higher than that in the SiO₂ system, which also illuminates that the sensitive property of the Al₂O₃ carrier was better than that of the SiO₂ carrier.

Solution Copolymerization

The copolymer obtained by solution copolymerization was also white powder. The effect of the monomer ratio on copolymerization without using initiator under microwave radiation was studied, and the results are shown in Figure 11.

It is apparent from Figure 11 that intrinsic viscosity increased but polymer conversion decreased as AT content in the monomers increased because the r_1 of AT was lower than the r_2 of DBTM (Table I), that is, the reactive activity of AT was lower than that of DBTM. An increase in the lower active AT content would increase the polymer intrinsic viscosity and decrease the polymer conversion.

Conventional Thermopolymerization of DBTM and AT

The monomers did not copolymerize by conventional heating for 7 h without using initiator. If initiator were used, a spot of polymers was obtained in the same condition. Compared with copolymerization under microwave radiation, it is apparent that microwave radiation has a deterministic function on copolymerization; at the same time, it is instructive that microwaves have not only a thermal effect but a nonthermal effect as well depending only on which polymerization is carried out.

Heat-Stabilizing Capacities of Organo-tin Polymers

The results are shown in Table II. The degradation temperature of PVC resins without using organo-tin polymers was 180°C and that using organo-tin polymers obtained by microwave radiation was higher, above 240°C. The heating-sta-

Table II Heat-Stabilizing Capacities of Organo-tin Polymer

	<i>F</i> (AT/DBTM)	Degradation Temperature of PVC (°C)	Heat-Stabilizing Time (min)
1#	2.33	244	17
2#	1.50	250	18
3#	1.00	248	16
4#	0.67	246	14
5#	0.43	243	15

bilizing time was above 14 mins. But the degradation temperature of PVC resins using organotin polymers obtained by conventional heating method was 220°C and heating-stabilizing time was 11 mins. It is apparent that the heating-stabilizing capacities of organo-tin polymers obtained by microwave radiation are better than

that by a conventional heating method, and it has potential future applications.

REFERENCES

1. Gedye, R.; Smith, F.; Westaway, K.; Ali, H.; Baldisera, L.; Laberge, L.; Rousell, J. *Tetrahedron Lett* 1986, 27, 279.
2. Silinski, B.; Kuzmycz, C.; Gourdenne, A. *Eur Polym J* 1987, 23(4), 273.
3. Weihua, L.; Jingyuan, W.; Yaoxian, L.; Fuan, L.; Yuwei, L.; Xinyi, T. *ACTA Polymerica Sinica* 1994, 4, 509.
4. Chia, H. L.; Jacob, J.; Boey, E. Y. C. *J Polym Sci, Part A: Polym Chem* 1996, 34(11), 2087.
5. Jie, L.; Jianging, Z.; Jiarui, S. *Synthetic Rubber Industry* 1997, 20(1), 53.
6. Mayo, F. R.; Lewis, F. M. *J Am Chem Soc* 1944, 66, 1594.
7. Rongbao, W.; Ya, L.; Qifeng, X. *ACTA Polymerica Sinica* 1994, 5, 543.