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Zhewen Han<sup>a</sup>; Hongjiao Shen<sup>a</sup>; Qijin Zhang<sup>a</sup>; Kunsong Chen<sup>a</sup>

<sup>a</sup> Department of Applied Chemistry, University of Science and Technology of China Hefei, Anhui, China

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## STUDY ON THE KINETICS OF POLYMERIZATION OF TRIBUTYLTIN METHACRYLATE

ZHEWEN HAN, HONGJIAO SHEN, QIJIN ZHANG, and  
KUNSONG CHEN

Department of Applied Chemistry  
University of Science and Technology of China  
Hefei, Anhui, China

### ABSTRACT

The kinetics of polymerization of tributyltin methacrylate (TBTM) has been studied in benzene solution in the temperature range 60-75°C in the presence of azobisisobutyronitrile (AIBN). We have obtained the following polymerization rate equation:  $R_p = K_p [\text{TBTM}]^{1.5} [\text{AIBN}]^{0.5}$ . It shows that the dependence of the polymerization rate on the concentrations of the monomer TBTM and the initiator AIBN are 1.5 and 0.5 order, respectively. The activation energy of polymerization was found to be 18.1 kcal/mol. The activation energy for the degree of polymerization is approximately -12.3 kcal/mol.

### INTRODUCTION

Organotin carboxylate polymers and copolymers are known to be toxic to marine organisms and have found widespread applications in the marine industry as antifouling coatings [1, 2] and in other fields. Compared with low molecular weight organotin compounds, organotin polymers are considered to be longer lasting and environmentally safer antifouling coatings that depend upon the controlled slow release of toxin. Very little is known, however, about the polymerizability of various organotin monomers [3-5]. To develop the practical utility of organotin polymer materials, it is neces-

sary to study the synthesis of organotin monomers, their purification, and their homo- and copolymerization in detail.

In an attempt to understand the features of the polymerization behavior of organotin monomers, we have undertaken a series of studies on the polymerization kinetics of tributyltin methacrylate (TBTM). In this paper we describe a kinetic study of this monomer's polymerization in benzene solution at 60-75°C in the presence of azobisisobutyronitrile (AIBN) and report the dependence of the polymerization rate on the monomer and the initiator. The apparent activation energy of polymerization and the total activation energy for the degree of polymerization were also measured.

## EXPERIMENTAL

The monomer tributyltin methacrylate was synthesized from bis(tributyltin) oxide and methacrylic acid [6]. It was recrystallized three times from petroleum ether (30-60°C) and had a melting point of 18°C.

Azobisisobutyronitrile was chemical reagent grade and was recrystallized three times from methanol.

Benzene was washed with concentrated sulfuric acid, water, aqueous alkali, and water, and then distilled after drying over sodium metal wire.

The requisite amounts of monomer, initiator, and benzene solvent were charged into a 50-mL reaction flask and degassed by repeated freezing and thawing. The polymerization was carried out under nitrogen at 60-75°C in a well-thermostatted oil bath. The kinetics were studied by use of a 5DX-FTIR spectrometer. The infrared spectra were measured by placing samples taken at specified intervals of reaction time in a 0.05-mm KBr liquid cell. Sixty scans of the reaction mixture were taken for every measurement with 4 cm<sup>-1</sup> resolution.

The number-average degrees of polymerization of the polymers obtained by radical polymerization were measured by using a Corona Model 117 Molecular Weight Apparatus.

## RESULTS AND DISCUSSION

### Determination of the Band for Kinetics Measurement

The reaction mixture for kinetics measurements is a three-components system since the initiator can be neglected because of its very low concentration.

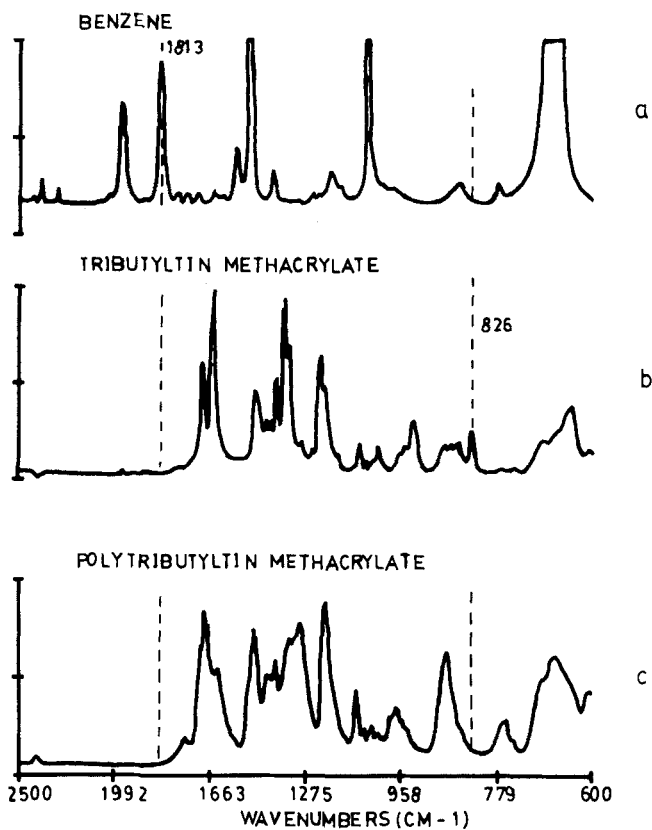


FIG. 1. Infrared absorbance spectra of (a) benzene, (b) TBTM, and (c) PTBTM.

By comparison with the spectra of the monomer (TBTM), the polymer (PTBTM), and benzene (Fig. 1), the  $826\text{ cm}^{-1}$  band in the IR spectrum of monomer can be assigned to the out-of-plane bending vibration of the vinylidene C-H bond of the monomer. There is no IR band in this region for the polymer and the solvent. We therefore chose the  $826\text{ cm}^{-1}$  band as the measurement band for the kinetic study. The change in intensity of the  $826\text{ cm}^{-1}$  band as a function of polymerization time should indicate the changes in monomer concentration.

In order to avoid the errors caused by small changes in the thickness of the

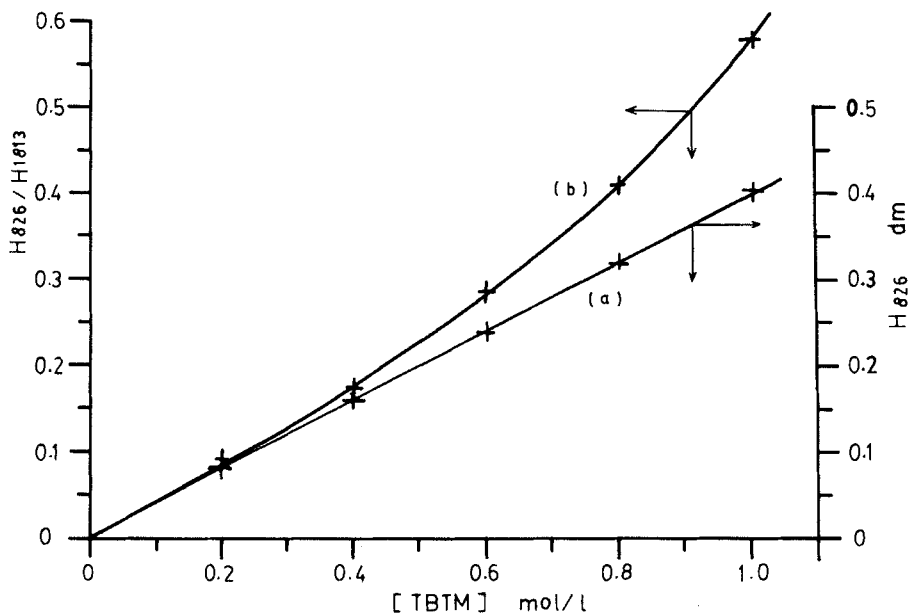


FIG. 2. Relation between monomer concentration and (a) peak height of the  $826\text{ cm}^{-1}$  band; (b) peak height ratio of the  $826\text{ cm}^{-1}$  to the  $1813\text{ cm}^{-1}$  band.

liquid cell and/or the measurement temperature, the band at  $1813\text{ cm}^{-1}$  in the IR spectrum of benzene was used as a normalization band, the intensity of which is of the same order of magnitude as the  $826\text{ cm}^{-1}$  band.

The straight line in Fig. 2 shows that the height of band  $826\text{ cm}^{-1}$  is directly proportional to the monomer concentration, i.e., in the concentration region of the present work, the  $826\text{ cm}^{-1}$  band obeys Beer's law and is suitable for the kinetic measurement. Curve (b) in Fig. 2 shows the relation between the peak height ratio of the  $826\text{ cm}^{-1}$  and  $1813\text{ cm}^{-1}$  and the TBTM concentration. The initial monomer concentration and the change in monomer concentration during the polymerization could be measured by using this curve. The polymerization can be calculated by the following equation:

$$C_t\% = \frac{[\text{TBTM}]_0 - [\text{TBTM}]_t}{[\text{TBTM}]_0} \times 100$$

The initial polymerization rate can be also calculated by the following equation:

$$R_p = [\text{TBTM}]_0 \, dC/dt,$$

where  $[\text{TBTM}]_0$  is initial monomer concentration and  $[\text{TBTM}]_t$  is the monomer concentration in the reaction mixture at polymerization time  $t$ .

### Effect of Monomer Concentration on the Polymerization Rate

Polymerization kinetic measurements with different monomer concentrations were made in a  $60 \pm 0.2^\circ\text{C}$  thermostatted oil bath. The initiator concentration was fixed at  $5.03 \times 10^{-2}$  mol/L. The monomer conversion curves are shown in Fig. 3. Figure 4 shows that the plot of  $\log R_p$  calculated from the slope of the lines in Fig. 3 and using the polymerization rate equation against  $\log [\text{TBTM}]$  results in a straight line with a slope of 1.5.

The results indicate that the dependence of the polymerization rate on the monomer concentration is of the 1.5 order. This is due to the tributyltin substituent group of the monomer which is very large, so that the steric hindrance

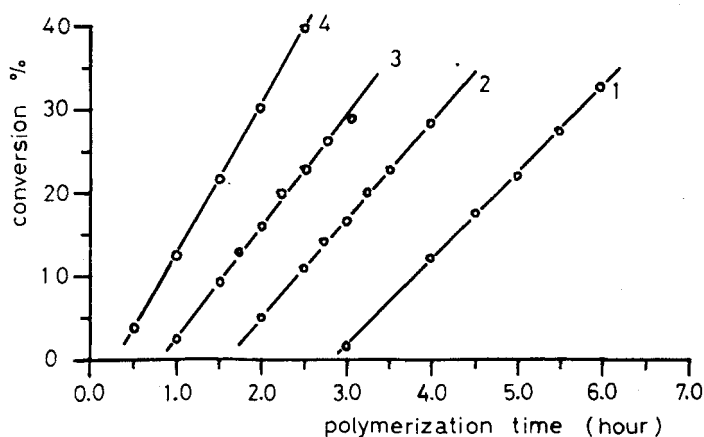


FIG. 3. Effect of TBTM concentration on polymerization.  $T = 60^\circ\text{C}$ ;  $[\text{AIBN}] = 50.3$  mmol/L in benzene solution.  $[\text{TBTM}]$ : (1) 0.40; (2) 0.50; (3) 0.60; (4) 0.70 mol/L.

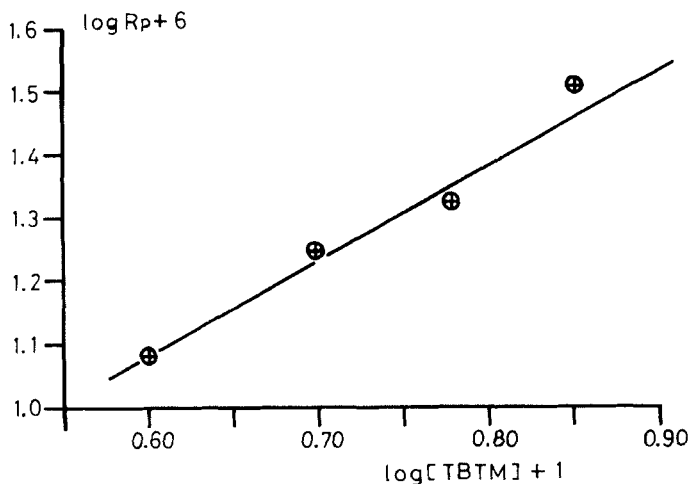


FIG. 4. Relation between  $\log R_p$  and  $\log [TBTM]$ . Polymerization conditions as in Fig. 3.

of the substituent group results in a slower initiation reaction in addition to a lower monomer concentration in the system studied. The initiation reaction rate is, therefore, not only controlled by the initiator but also by the monomer concentration.

#### Effect of Initiator Concentration on the Polymerization Rate

The conversion of polymerization with different initiator concentrations was measured at 60°C. The monomer concentration was fixed at 0.601 mol/L. The relationship between the initial polymerization rate and the initiator concentration is shown in Fig. 5. It is almost a straight line with a slope of 0.5. This 0.5 order dependence is consistent with the mechanism of a polymerization initiated by thermal decomposition of the initiator.

The polymerization rate inferred from Figs. 4 and 5 follows the equation

$$R_p = K_p [TBTM]^{1.5} [AIBN]^{0.5}.$$

#### Effect of Polymerization Temperature on the Polymerization Rate

The polymerization was investigated at 60, 65, 70, and 75°C at constant concentrations of the monomer and the initiator of 0.5 mol/L and 50.3 mmol/L,

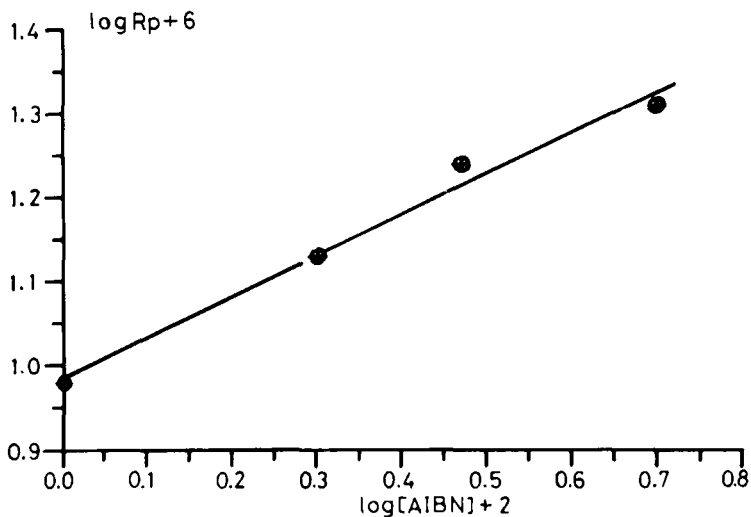


FIG. 5. Relation between  $\log R_p$  and  $\log [AIBN]$ .  $T = 60^\circ\text{C}$ ; in benzene solution;  $[TBTM] = 0.60 \text{ mol/L}$ ;  $[AIBN] = 1.0, 2.0, 3.0, 4.0 \times 10^{-2} \text{ mol/L}$ .

respectively. The polymerization rate increases with increasing temperature. The Arrhenius plot is shown in Fig. 6. The activation energy  $E_a$  of polymerization, calculated from the slope of the straight line in Fig. 6, is 18.1 kcal/mol.

#### Effect of Temperature on Degree of Polymerization

The number-average degrees of polymerization for the polymers obtained from polymerizations in benzene solution at 55, 60, 65, 70, and 75°C, with monomer and initiator concentrations of 0.50 and 0.05 mol/L, respectively, were measured. Figure 7 shows that the polymer molecular weight decreases with increasing reaction temperature. The plot of  $\ln X_n$  versus  $1/T$  allows the determination  $E_x$ .  $E_x$ , the activation energy for the degree of polymerization, is approximately -12.3 kcal/mol.

Since the molecular structure of methyl methacrylate (MMA) is similar to the monomer TBTM, we compared the polymerization behavior of the two monomers by using some literature data for MMA [7]. In the free-radical polymerization of MMA in benzene solution in the presence of AIBN, the chain transfer reaction should be negligible. The activation energy of degree of polymerization  $E_x$  could be calculated by the following equation:



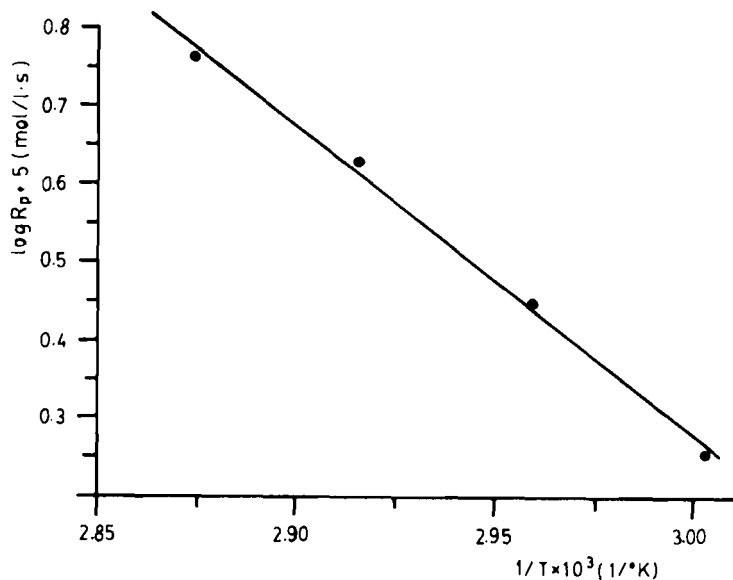


FIG. 6. Effect of temperature on TBTM polymerization rate. [TBTM] = 0.50 mol/L; [AIBN] = 50 mmol/L; in benzene solution;  $T = 60, 65, 70,$  and  $75^\circ\text{C}$ .

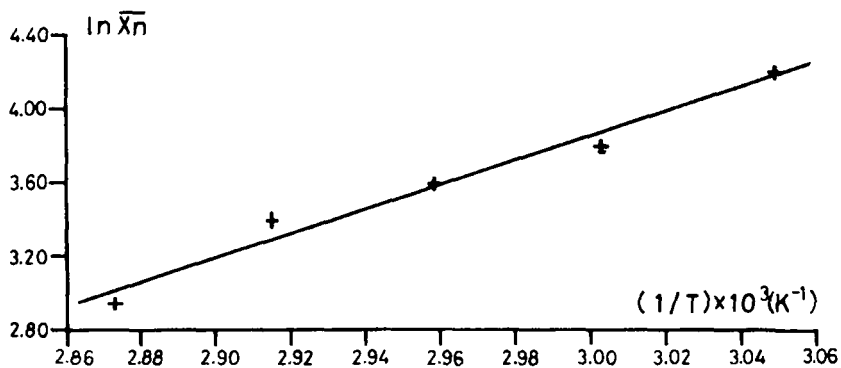


FIG. 7. Effect of temperature on the degree of polymerization of TBTM. [TBTM] = 0.50 mol/L; [AIBN] = 50 mmol/L; in benzene solution;  $T = 55, 60, 65, 70,$  and  $75^\circ\text{C}$ .

$$E_x = E_p - 1/2E_t - 1/2E_d.$$

Here  $E_d$ ,  $E_p$ , and  $E_t$  are the activation energies of AIBN thermal decomposition (29.5 kcal/mol at 60°C), of MMA radical propagation (4.7 kcal/mol), and of chain radical termination (1.2 kcal/mol), respectively. The  $E_x$  of MMA polymerization calculated from the above equation is -10.6 kcal/mol. The  $E_x$  of TBTM obtained by us is -12.3 kcal/mol, which suggests that the decrease of the degree of TBTM polymerization with increasing temperature is bigger than that for MMA.

The number-average molecular weights are about 0.72 to  $2.52 \times 10^4$ . They are smaller at the higher initiator concentration, lower monomer concentration, and higher polymerization temperature. In order to obtain a higher molecular weight sample, the polymerization of TBTM was done at 50°C, with ~1.0 mol/L monomer concentration. The concentrations of initiator AIBN were 4.7 and 1.8 mmol/L, respectively. The intrinsic viscosities (in toluene, at 30°C) of the resulting two PTBTM samples were 19.40 and 27.69, respectively, corresponding to viscosity-average molecular weights of  $5.0 \times 10^5$  and  $8.3 \times 10^5$  by the Mark-Houwink equation we established [8].

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