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Effect of antimony catalyst on solid-state polycondensation of poly(ethylene terephthalate)

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Abstract

The effect of antimony trioxide (Sb_2O_3) catalyst on the solid-state polycondensation (SSP) of poly(ethylene terephthalate) (PET) has been rigorously studied. It has been determined that the rate constant increases, while the activation energy decreases, linearly with increasing catalyst concentration within the range of 0–100 ppm Sb. The SSP rate reaches its maximum value at about 150 ppm Sb. The activation energies are 30.7 and 23.3 kcal/mol respectively for the uncatalyzed and fully catalyzed SSP. The frequency factor decreases with increasing catalyst concentration due to the decreased mobility of catalyzed end groups. A mechanism of Sb catalysis has been proposed to explain these observations.

Keywords: Poly(ethylene terephthalate); Solid-state polycondensation; Catalyst

1. Introduction

Condensation polymers, such as polyesters and polyamides, can undergo further polycondensation in the solid state at temperatures between the glass transition temperature and the crystalline melting point of the polymer. This phenomenon has been advantageously utilized to manufacture very high molecular weight (i.e. >24,000) poly(ethylene terephthalate) (PET) resins for carbonated soft drink bottle, frozen food tray, and tire cord applications. First, a moderately high molecular weight prepolymer is produced by a melt polymerization process. The prepolymer is then solid-state polymerized to the molecular weight required for the end-use application. It is well known that the existing polycondensation catalyst (normally antimony trioxide) in the prepolymer remains active during SSP. In fact, if the catalyst concentration is sufficient to achieve the maximum polycondensation rate in melt polymerization, it will also achieve the maximum polycondensation rate in SSP. Therefore, no additional catalyst or new catalyst is needed for SSP.

Antimony trioxide (Sb_2O_3) is the preferred polycondensation catalyst because it offers a high (although not the highest) catalytic activity, does not engender undesirable colors, and has a low tendency to catalyze side reactions. In the commercial process, it is first dissolved in ethylene glycol (EG) at about 150 °C under a nitrogen blanket to form antimony glycolate before being added to the polycondensation reactor. In small-scale lab polymerization experiments, dry Sb_2O_3 can be directly added to the reactor at the beginning of the polycondensation stage. The Sb_2O_3 added is readily dissolved because there is still ample free EG in the reaction mixture. It is understood that the presence of a stabilizer can substantially reduce the efficiency of the antimony catalyst. This is especially true if the stabilizer is a trivalent phosphorous compound (i.e. phosphorous acid or a phosphite) because it can reduce part of the antimony catalyst to metallic Sb, which is inert. The catalyst and stabilizer concentrations in most commercial PET resins are 190–300 ppm Sb and 20–100 ppm P respectively. Of course, when considering the catalytic effect, only the active Sb concentration counts.

Challa [1] first used a second order kinetics to describe the melt polycondensation of PET. Thus the forward reaction rate is given as

$$-\frac{dC}{dt} = 2kC^2 \tag{1}$$

where C is the end group concentration, t, the polycondensation time, and k, the forward reaction rate constant. This rate equation has been widely used in the studies of the polycondensation of polyesters.

Hovenkamp [2] studied the catalyzed reactions in the formation of PET using mixtures of model compounds,

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glycolmonobenzoate, glycoldibenzoate, and EG. He found that Sb (a polycondensation catalyst) behaves quite differently from ester interchange catalysts (Mn, Zn, and Ca). While ester interchange catalysts are very active in media having both a high and a low hydroxyl concentration, [OH], they are easily poisoned by very small amounts of carboxyl end groups. The polycondensation catalyst Sb is not hurt by the presence of carboxyl end groups. However, its activity is inversely proportional to [OH]. He determined that the forward rate constant increased linearly with the amount of Sb_2O_3 added.

Shah et al. [3] investigated the effects of the type and concentration of catalyst on the melt polycondensation of bis(2-hydroxyethyl) terephthalate (BHET). They concluded that Sb, with the third highest activity (next to Ti and Sn) and the lowest tendency to catalyze degradation reactions, is the most suitable catalyst for polycondensation among the catalysts they tested (Ti, Sn, Sb, Mn, Zn, and Pb).

Yokoyama et al. [4] studied the influences of catalyst (Sb_2O_3), stabilizer (triphenyl phosphite), and temperature on the melt polycondensation of PET. They determined that the polycondensation rate constant k can be expressed as the sum of two terms. The first term represented the rate constant of uncatalyzed polycondensation, k_0, and the second term, which was proportional to the antimony concentration, [Sb], but decreased with increasing stabilizer concentration, represented the contribution due to the presence of the catalyst and the stabilizer

The SSP of PET has been investigated by many researchers [5–15]. Bamford and Wayne [5] pointed out that the SSP of PET has a couple of peculiar features. First, the reaction rate constant appears to increase with increasing prepolymer molecular weight. Second, there exists a limiting molecular weight for each prepolymer molecular weight at each temperature. If Eq. (1) is used to fit the SSP data, the rate constant k will appear to decrease with time and eventually approach zero. This means that Eq. (1) is not adequate for SSP. Nevertheless, Eq. (1) has been used in most of the published models for the SSP of PET [8–12].

The inadequacy of Eq. (1) for SSP has been addressed by Chen and Chen [7] and Duh [13] using different approaches. Chen and Chen [7] proposed a rate equation, in which the rate constant decreases as the SSP proceeds, according to an end-group diffusion controlled model. Duh [13] postulated that part of the functional end groups remains inactive during SSP and the solid-state polycondensation (transesterification) follows a second-order kinetics with respect to the active end group concentration. Thus,

$$-\frac{dC}{dt} = 2k(C - C_i) \tag{2}$$

where C_i is the inactive end group concentration. This model is capable of satisfactorily describing the SSP behaviors of PET and fits the experimental data very well. Therefore it was used in this study to determine the kinetic parameters.

There are very few published articles [14,15] concerning the influence of Sb catalyst on the SSP of PET. Furthermore, none of these works are without deficiencies, uncertainties, or inadequacies.

In US Patent 4,205,157 [14], Duh presented experimental data for the average SSP rates of PET with various Sb concentrations. However, because of limited data, the reaction rate constants and activation energies were not determined.

Kokkalas et al. [15] investigated the effect of Sb_2O_3 concentration on the SSP of PET in the temperature range of 180–210 °C and determined the reaction rate constants and activation energies using the rate equation proposed by Chen and Chen [7]. However, at least a couple of issues regarding their experiments merit further discussion. First, because the prepolymers contained 127 ppm manganese and up to 2000 ppm Sb_2O_3, the observed catalyst effect was the effect of mixed catalysts, and not the effect of Sb_2O_3 as implied by the title of the article. Secondly, because dried Sb_2O_3 was mixed into the prepolymer melt in the absence of free EG, the Sb catalyst must be incorporated directly into the polymer chain ends to become effective. This is a very slow process. Therefore, it is believed that only small fractions of the Sb_2O_3 added to the prepolymers melt were properly incorporated and became active. This is supported by the facts that most commercial PET resins contain no more than 300 ppm Sb (requiring no more than 300 ppm Sb catalyst to achieve maximum melt-phase and solid-state polycondensation rate) and that the prepolymer with 2000 ppm Sb_2O_3 had not attained the maximum SSP rate in their study.

Therefore, it is the purpose of this article to present a rigorous study on the catalytic activity of Sb for the solid-state polycondensation of PET. In order to simplify the treatment of the experimental data and to increase the accuracy of the results, the study will be focused on the effect of the Sb concentration on the major polycondensation reaction, transesterification, by using prepolymers with negligible carboxyl contents.

2. Experimental

2.1. Preparation of prepolymers

Six prepolymers having intrinsic viscosities (IV's) of 0.235 ± 0.005 dl/g and carboxyl contents of ≤ 3 μmol/g and containing various amounts of Sb (0, 20, 50, 100, 150, and 210 ppm) were prepared in a tube reactor using a base polymer provided by Goodyear Tire and Rubber Co. The base polymer, which had an IV of 0.246 dl/g and a carboxyl content of 12 μmol/g and contained no catalyst or stabilizer, was produced from terephthalic acid (TPA) and EG in a 25-pound reactor according to a procedure described in US Patent 4,205,157 [14]. Incidentally, the highest prepolymer catalyst concentration was chosen

based on the fact that Goodyear tire cord resin contained 210 ppm Sb and 20 ppm P and that this formulation achieved the maximum polycondensation rates in melt polymerization and SSP.

The tube reactor has a tube-shape body, 40 mm in diameter and 30 cm long, and a top with 3 necks to accommodate the agitator, the nitrogen supply, and the vacuum line. The body of the reactor was immersed in a thermostated oil bath. To prepare a prepolymer, 120 g ground base polymer and 15 ml EG were charged into the reactor with the oil temperature set at 270 °C. The base polymer was allowed to melt under a nitrogen blanket. After the base polymer was melted, a desired amount of Sb_2O_3 was added to the reactor and the reactor content was mixed with a spiral agitator turning at 60 rpm for 15 min. Because of the presence of free EG and the low viscosity of the mixture, the Sb_2O_3 added was readily dissolved and uniformly mixed into the polymer melt. Then the reactor pressure was gradually reduced to full vacuum (<1 mm Hg) over 60 min to effect polycondensation. After 25–60 min under full vacuum, depending on the amount of Sb_2O_3 added, the polycondensation operation was stopped and the resulting prepolymer melt was poured into cold water to solidify. The goal was to prepare prepolymers with nearly equal IV's, negligible carboxyl contents, and various Sb concentrations. The additional EG, the relatively low reaction temperature, and short polycondensation time used were conducive to producing prepolymers with very low carboxyl contents.

The prepolymer without Sb was first prepared with 60 min polycondensation time under full vacuum. Then the prepolymers with various desired Sb concentrations were prepared by varying the polycondensation time. It took 3–8 runs to obtain each of the suitable prepolymers with Sb catalyst. The IV, carboxyl content, and Sb concentration of each of the six chosen prepolymers are listed in Table 1.

The prepolymers thus obtained were ground and classified with the fraction that passed through the 100-mesh screen but remained on the 150-mesh screen saved for the SSP experiments. Therefore the particle size of the prepolymers used in the experiments was 106–150 μm. Because the carboxyl content of each prepolymer was very small (less than 1% of total end groups), esterification during SSP was negligible in comparison with transesterification.

Table 1
Sb concentrations, IV's, and carboxyl contents of prepolymers used in the SSP runs

Prepolymer	Sb concentration (ppm)	IV (dl/g)	Carboxyl content (μmol/g)
A	0	0.236	1
B	20	0.239	2
C	50	0.232	2
D	100	0.238	3
E	150	0.236	2
F	210	0.235	3

2.2. Solid-state polymerization

Each of the prepolymers was solid-state polymerized in a fluid-bed reactor with nitrogen as the fluidizing gas. The reactor used to conduct the SSP experiments was constructed of a 50 cm long glass column with a diameter of 37 mm. The bottom of the column was fitted with a porous filter for supporting the powdered polymer and distributing the purge gas (nitrogen). Below the filter, the column was necked down and connected to a 7 mm diameter, 150 cm long nitrogen supply tube, which was coiled up around the lower half of the column. During the experimental runs, the reactor with its nitrogen supply tube was immersed in a thermostated oil bath about 30 cm deep. The temperature of the oil bath could be controlled to within ±0.1 °C. The nitrogen supply tube also served as the heat exchanger which heated the incoming nitrogen to the desired experiment temperatures.

For each SSP run, 10 g of powdered prepolymer was charged into the reactor. High purity nitrogen was introduced to the bottom of the reactor through the coiled tube at a superficial velocity of 1.5 m/min, which was about five times the minimum fluidizing velocity, to maintain a stable fluidized bed. The bath temperature was first maintained at 140 °C for 1 h to dry the prepolymer to a moisture content below 0.005% to prevent hydrolytic degradation during the subsequent SSP step. During this drying period no significant IV change took place. Then the reactor with its nitrogen supply tube was transferred to another oil bath whose temperature had been controlled at the desired SSP temperature. By using another oil bath it was possible to heated the dried prepolymer to the reaction temperature within 2 min. The reaction was allowed to proceed at the constant SSP temperature for 8 h. Samples, about 1 g each, were taken after 1, 2, 3.5, 5, 6.5, and 8 h of SSP. Each sample was tested for the IV. Each prepolymer was solid-state polymerized at three temperatures, 220, 230, and 240 °C for the prepolymer without catalyst, and 210, 220, and 230 °C for all other prepolymers.

According to a recent work by Duh [13], which used similar apparatus and procedure to conduct solid state polymerization of low IV PET, maximum SSP rate of PET in a fluidized bed is achieved when the polymer particle size is reduced to below 180 μm and the superficial nitrogen velocity is increased to above 0.9 m/min. Therefore, under the experimental conditions used (with a particle size of 106–150 μm and a superficial nitrogen velocity of 5 m/min), the byproduct diffusion resistance was negligible and the byproduct concentration in the gas phase was low enough not to cause significant backward reaction. This means that the byproduct EG was removed immediately as soon as it was

Table 2
Calculated C_i and k values for SSP of PET prepolymers with various Sb concentrations

Prepolymer	Sb conc. (ppm)	C_0[a] (μmol/g)	C_i (μmol/g)				$k \times 10^3$ (μmol/g)$^{-1}$h^{-1}			
			210 °C	220 °C	230 °C	240 °C	210 °C	220 °C	230 °C	240 °C
A	0	424.33		42.86	30.31	22.37	0.1243[b]	0.2366	0.4471	0.8022
B	20	416.52	49.95	40.49	29.72		0.2642	0.4915	0.8855	
C	50	435.13	52.73	42.57	33.91		0.5264	0.9188	1.6068	
D	100	419.10	50.87	41.88	31.18		0.9092	1.5522	2.5917	
E	150	424.33	52.07	42.44	31.54		1.0994	1.8432	2.9290	
F	210	426.99	53.37	42.82	32.03		1.1083	1.8013	2.9099	

[a] Prepolymer end group concentration.
[b] Extrapolated value.

generated and the SSP is reaction-controlled. Therefore the proposed SSP rate equation (Eq. (2)) is applicable.

2.3. Determinations of carboxyl content and intrinsic viscosity

The carboxyl contents were determined only for the base polymer and the prepolymers according to the Pohl's method [16].

All IV measurements were conducted at 25 °C in a Ubbelohde 1B viscometer using 60/40 phenol/tetrachloroethane as the IV solvent. The number average molecular weight $\overline{M}_n$ is related to the IV by the Moore equation [17],

$$\mathrm{IV} = 7.50 \times 10^{-4} \overline{M}_n^{0.68} \tag{3}$$

The total end group concentration C in the unit of μmol/g is related to $\overline{M}_n$ by the following equation:

$$C = \frac{2 \times 10^6}{\overline{M}_n} \tag{4}$$

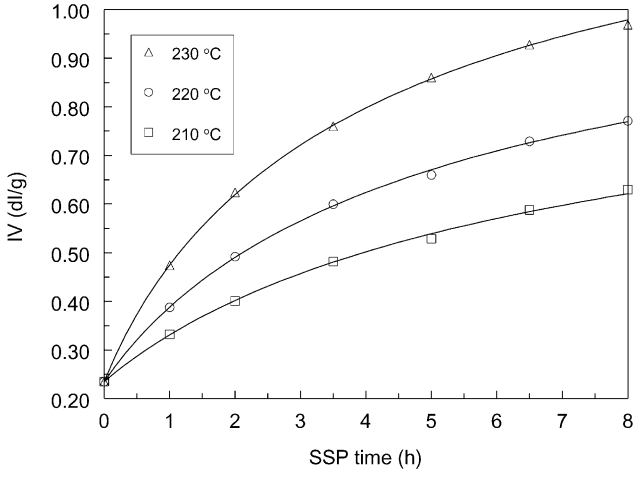


Fig. 1. Curve fittings of solid-state polycondensation data for PET prepolymer with 210 ppm Sb. Curves are predicted by the kinetic model.

3. Results and discussion

3.1. Values of rate constants and inactive end group concentrations

The rate equation proposed by Duh [13] was used to calculate the kinetic parameters because of its simplicity and adequacy. The derivation of the related mathematical equations and the procedure for the calculation of the rate constant k and the inactive end group concentration C_i are given in Appendix A. Table 2 lists the calculated k and C_i values for the SSP of the six prepolymers.

3.2. Adequacy of the kinetic model used

To see whether the kinetic model used is adequate and whether the calculated kinetic parameters are valid, we need to determine whether the model fits the experimental data well. As an example, Fig. 1 shows the curve fittings of the SSP data for the prepolymer with 210 ppm Sb. It can be seen that the rate equation used fits the data very well. Similarly curve fittings for the SSP of all other prepolymers are also very good. Fig. 2 shows the IV build-up curves for the six

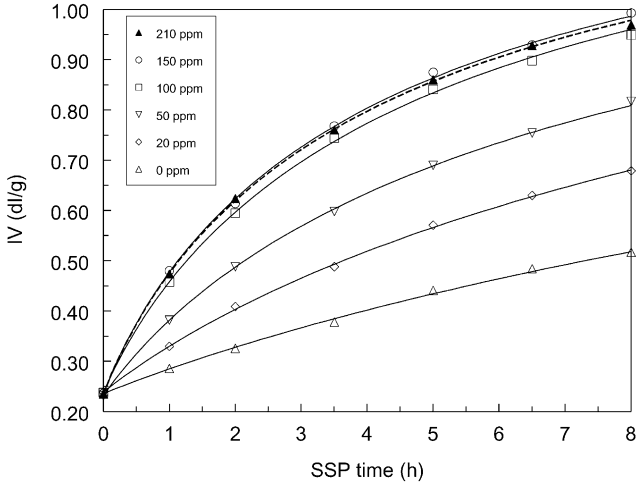


Fig. 2. Intrinsic viscosity build-up curves for solid-state polycondensation of PET prepolymers with various Sb concentrations at 230 °C. Curves are predicted by the kinetic model.

prepolymers with various Sb concentrations at 230 °C. Obviously, maximum SSP rate can be achieved with about 150 ppm Sb.

3.3. Effects of Sb concentration and temperature on inactive end group Concentration

Based on the C_i data in Table 2, it is obvious that C_i is insensitive to the Sb catalyst concentration. This is not surprising. During SSP, it is believed that most of the end groups are located in the amorphous phase. However, there are always some end groups that are trapped in the crystalline phase. These are the inactive end groups according to the kinetic model [13] used. C_i is determined mainly by the crystallinity. Since the addition of Sb catalyst does not significantly affect the crystallinity, especially if all the Sb catalyst remains soluble, C_i should not be significantly affected by the Sb concentration.

However, C_i decreases with increasing temperature because, as the temperature is increased, part of the end groups that are inactive originally will be sufficiently motivated and become active (i.e. move from the crystalline phase into the amorphous phase). This is one of the reasons why the SSP rate increases with increasing temperature. Taking the average values of C_i for different temperatures, C_i can be fitted with the following equation:

$$C_i = -0.9902T + 530.07 \qquad (210\,^{\circ}\text{C} \le T \le 230\,^{\circ}\text{C}) \quad (5)$$

where T is the absolute temperature in °K.

3.4. Effects of Sb concentration and temperature on rate constant

Fig. 3 shows the rate constant vs. Sb concentration plots for the SSP of PET at 210, 220, and 230 °C. It can be seen that the rate constant k reaches the maximum value at about 150 ppm Sb. This is approximately equal to the Sb concentration required to achieve the maximum melt polycondensation rate for PET without stabilizer according to Shah et al. [3]. In US Patent 4,205,157 [14], the Sb concentration required to achieve the maximum SSP rate for 0.250 dl/g IV prepolymer with 0 carboxyl content was estimated to be about 100 ppm. This lower value is probably due to the fact that the prepolymer particle size used was not small enough for truly reaction-controlled SSP and the value was obtained by extrapolation.

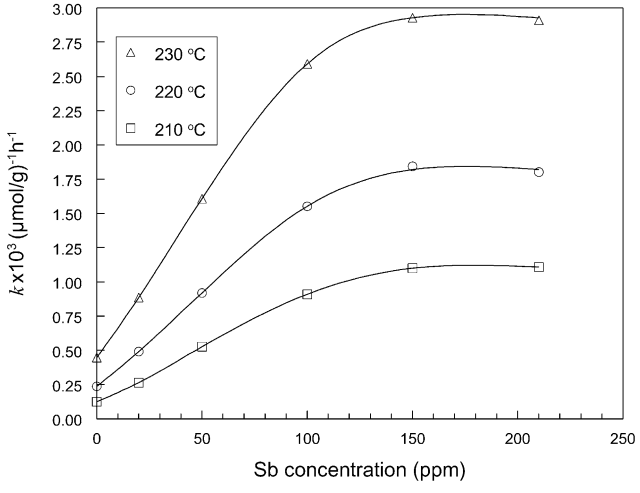


Fig. 3. Effects of Sb concentration on rate constants for solid-state polycondensation of PET at various temperatures.

It is apparent that the three curves in Fig. 3 are approximately linear within the Sb concentration range of 0–100 ppm. Therefore within this Sb concentration range, k for each temperature can be represented by the following equation:

$$k = k_0 + \alpha[\text{Sb}] \qquad ([\text{Sb}] \le 100 \text{ ppm}) \quad (6)$$

where k_0 is the uncatalyzed rate constant, α, the proportionality constant, and [Sb] is the Sb concentration in ppm. This rate equation has a similar form with that given by Hovenkamp [2] for the melt polycondensation in his model system. The difference is that the second term in Hovenkamp's rate equation is inversely proportional to [OH] while the second term in Eq. (6) is independent of [OH]. This is probably because of the presence of free EG in Hovenkamp's model system (to be further explained later).

Using linear regression technique, the values for k_0 and α are obtained for the three SSP temperatures and listed in Table 3. It is further found that k_0 and α can be fitted with exponential functions of $1/T$. Thus the rate constant can be expressed in the following form:

$$k = 1.0732 \times 10^{11} \exp\left\{\frac{-33,050}{RT}\right\} + 6.8235 \times 10^{5}[\text{Sb}]\exp\left\{\frac{-24,174}{RT}\right\} \quad (7)$$

([Sb] ≤ 100 ppm)

The first term on the right hand side represents the uncatalyzed rate constant k_0 and the second term represents the increase in the rate constant k due to the catalysis of the Sb. Eq. (7) has the same form as the rate equation given by Yokoyama et al. [4] for melt polycondensation of PET with zero stabilizer concentration.

Table 3
Values of k_0 and α in Eq. (6)

Temperature (°C)	$k_0 \times 10^4$ $(\mu\text{mol/g})^{-1}\text{h}^{-1}$	$\alpha \times 10^4$ $(\mu\text{mol/g})^{-1}$ $\text{h}^{-1}(\text{ppm Sb})^{-1}$
210	1.1902	0.0793
220	2.3789	0.1322
230	4.6801	0.2152

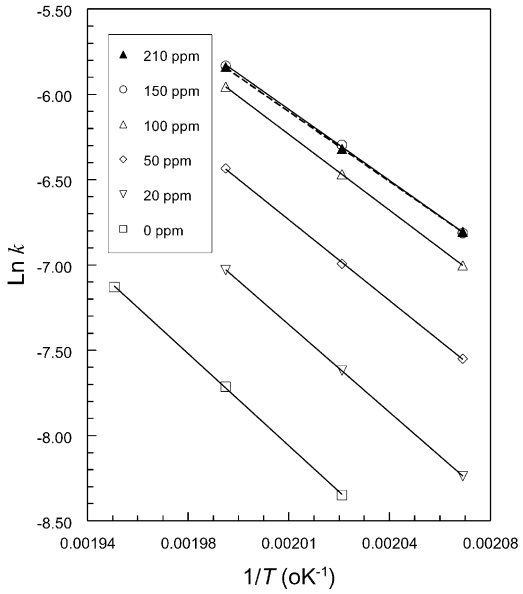


Fig. 4. Arrhenius plots for rate constants for solid-state polycondensation of PET prepolymers with various Sb concentrations.

3.5. Effects of Sb concentration and temperature on frequency factor and activation energy

Fig. 4 shows the Arrhenius plots for the rate constants for the SSP of the six prepolymers with various Sb concentrations. Straight lines with various slopes are obtained. Therefore, the temperature dependence of the rate constant can be represented by the Arrhenius equation,

$$k = A \exp\left\{\frac{-E}{RT}\right\} \tag{8}$$

where A is the frequency factor and E, the activation energy. The values of A and E for each prepolymer can be determined from the intercept and the slope, respectively, of the corresponding straight line and are listed in Table 4. It is obvious that both the frequency factor and the activation energy decrease with Sb concentration.

It appears that the activation energy is close to its lowest value at a catalyst concentration of 210 ppm Sb. Since it is widely believed or assumed that the activation energy is insensitive to the molecular weight and has the same value in melt polycondensation or SSP, it will be interesting

Table 4
Values of frequency factors and activation energies for solid-state polycondensation of PET with various antimony concentrations

Prepolymer	Sb concentration (ppm)	A (μmol/g)$^{-1}$h^{-1}	E (kcal/mol)
A	0	9.5256×10^9	30.684
B	20	4.2936×10^9	29.193
C	50	8.0689×10^8	26.932
D	100	1.2167×10^8	24.583
E	150	5.6114×10^7	23.657
F	210	3.8567×10^7	23.297

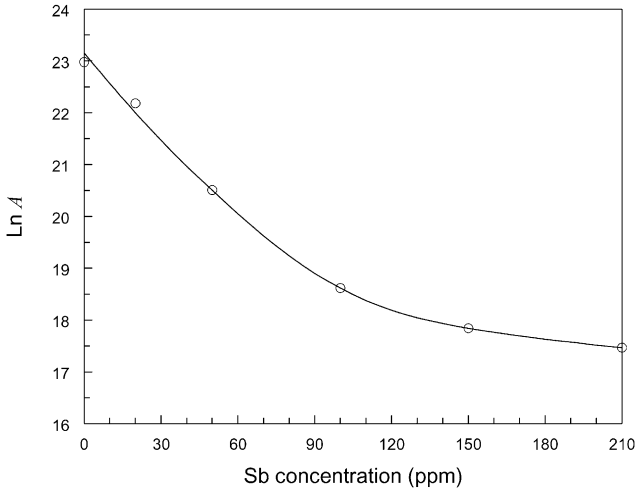


Fig. 5. Natural logarithm of frequency factor vs. Sb concentration plot for solid-state polycondensation of PET.

to compare the values of activation energy reported by various researchers. The activation energy for uncatalyzed SSP is 30.7 kcal/mol according to this study, compared with 23, 21, and 40 kcal/mol according to Challa [1], Hovenkamp [2], and Yokoyama et al. [4] respectively for uncatalyzed melt polycondensation. The activation energy for fully catalyzed SSP is 23.3 kcal/mol according to this study, compared with 18.5 kcal/mol according to Yokoyama et al. [4] for fully catalyzed melt polycondensation, and 24.0 and 23.6 kcal/mol according to Chen and Chen [7] and Duh [13] respectively for fully catalyzed SSP.

Figs. 5 and 6 shows respectively the Ln A vs. Sb concentration and E vs. Sb concentration plots. It can be seen that A and E appear to decrease with increasing Sb concentration and level off after a certain Sb concentration is reached. Also the curves in these two figures are approximately linear within the Sb concentration range of 0–100 ppm. Thus

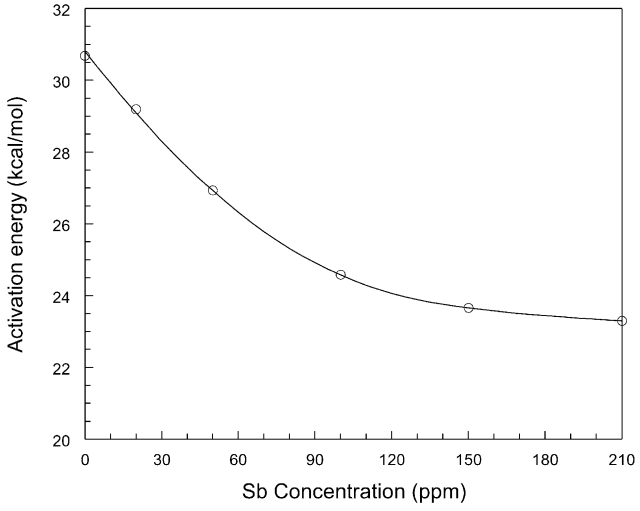


Fig. 6. Activation energy vs. Sb concentration plot for solid-state polycondensation of PET.

within this Sb concentration range, the frequency factor and the activation energy can be expressed as

$$A = 9.3011 \times 10^9 \exp(-0.0443[\mathrm{Sb}]) \quad (9)$$

$$E = -60.9[\mathrm{Sb}] + 30,435 \quad (10)$$

Inserting Eqs. (9) and (10) in Eq. (8) leads to

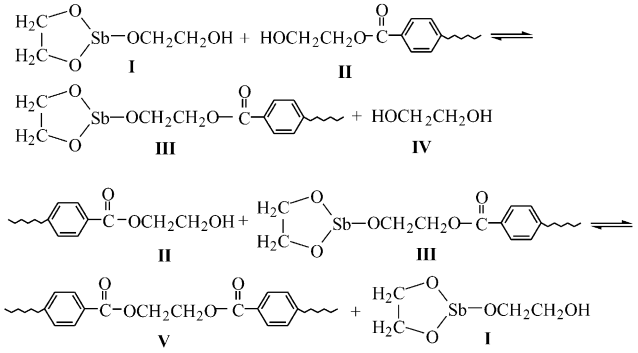
$$k = 9.3011 \times 10^9 \exp(-0.0443[\mathrm{Sb}]) \exp\left\{\frac{-30,435 + 60.9[\mathrm{Sb}]}{RT}\right\}$$

$$([\mathrm{Sb}] \leq 100 \text{ ppm}) \quad (11)$$

This equation should give more accurate values for A and E than Eq. (7) and is therefore the preferred form.

3.6. Mechanism of antimony catalysis

The following mechanism is proposed to explain the observed Sb catalysis:



The Sb catalyst is usually added to the melt reactor in the form of glycolate (I) in a glycol solution. If Sb_2O_3 is added directly into the reactor, it is readily converted to glycolate by reaction with the free glycol in the system. The glycolate may have several forms. Form (I) is chosen to demonstrate the mechanism because of its simplicity. It must first attach itself to the end group of a polymer chain (II) to impart catalytic activity for the polycondensation by lowering the activation energy. EG (IV) is released in this step. The end group with the catalyst (in polymer chain III) can react with a normal end group to form a diester link (V) and regenerate glycolate, which can continue to participate in the catalytic reaction.

Hovenkamp [2] found that the catalytic activity of Sb is inversely proportional to [OH] in a glycol-rich system. This is probably because the glycol tends to hold back the catalyst. As the glycol is depleted in the later melt polycondensation stage, practically all the catalyst will be attached to the polymer chain ends and the catalytic activity will become independent of [OH].

In SSP, two end groups must diffuse toward each other to effect polycondensation. While an end group containing the catalyst has a higher reactivity (with the capability to lower the activation energy of polycondensation), it has a lower mobility or diffusion rate than a normal end group. Therefore, the frequency factor as well as the activation energy decreases with increasing Sb concentration.

4. Conclusions

The effect of Sb catalyst concentration on the SSP of PET has been successfully evaluated using a kinetic model, which assumes that part of the end groups remain inactive throughout the SSP and the SSP is a second-order reaction with respect to the active end group concentration. In general, the model fits the data very well, indicating the validity of the calculated values for the kinetic parameters. The SSP rate and the rate constant increase with increasing Sb concentration until they reach their respective maximum values at an Sb concentration of about 150 ppm. The activation energy decreases with increasing Sb concentration. Thus the activation energies are 30.7 kcal/mol for uncatalyzed SSP and 23.3 kcal/mol for SSP catalyzed with 210 ppm Sb. The frequency factor decreases with increasing Sb concentration presumably because, during SSP, the catalyst molecules are attached to the polymer chain ends, resulting in bulkier end groups with a lower mobility.

It should be noted that prepolymers with negligible carboxyl concentrations were used in this study to simplify data treatment and that the SSP rate varies with prepolymer molecular weight. Nevertheless, the methodology presented in this article can serve as a basis for the studies of the SSP of prepolymers with substantial carboxyl concentrations and /or different molecular weights.

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Appendix A. Solution to rate equation for SSP of PET

For the reaction-controlled SSP of PET with negligible carboxyl content, the rate equation is given as

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = 2k(C - C_\mathrm{i}) \quad (A1)$$

where C_i is the inactive end group concentration.

Eq. (A1) can be integrated and rearranged to give an equation of the following form:

$$\frac{C_0 - C}{t} = 2k(C_0 - C_\mathrm{i})C - 2k(C_0 - C_\mathrm{i})C_\mathrm{i} \quad (A2)$$

where C_0 is the initial or prepolymer end group concentration. Therefore, if the model fits the experimental data, the

$(C_0 - C)/t$ vs. C plot should be a straight line, and k and C_i can be calculated using the following relationships:

$$\text{Slope} = 2k(C_0 - C_i) \tag{A3}$$

$$C_i = \frac{\text{Intercept}}{\text{Slope}} \tag{A4}$$

Once k and C_i are determined, the C and IV values at any time during the SSP can be calculated using the following two equations:

$$C = \frac{C_0 + 2k(C_0 - C_i)C_i t}{1 + 2k(C_0 - C_i)t} \tag{A5}$$

$$\text{IV} = 14.4465\left[\frac{1 + 2k(C_0 - C_i)t}{C_0 + 2k(C_0 - C_i)C_i t}\right]^{0.68} \tag{A6}$$

These two equations can be used to generate the predicted C and IV curves to check the adequacy of the model.

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