

Experimental and Modeling Study of the Solid State Polymerization of Poly(ethylene terephthalate) over a Wide Range of Temperatures and Particle Sizes

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ABSTRACT: The solid state polymerization (SSP) of poly(ethylene terephthalate) was studied experimentally over a wide range of pellet sizes and temperatures. A comprehensive model was developed. It considered polycondensation, degradation and polycondensation of vinyl end groups together with diffusion. The reaction rate constants, diffusivities and the corresponding activation energies were obtained through parameter identification using experimental data. The effects of the reaction temperature and pellet size on the SSP time were also investigated. A decrease in the particle size decreases the concentration of the vinyl end groups and narrows the concentration distribution of end groups inside poly(ethylene terephthalate) particles. A decrease in the size of pellets also favors diffusion. Nevertheless it is preferable that the size of pellets be between 1 and 2 mm because too small pellets bring about difficulties with preparation and handling. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: poly(ethylene terephthalate); solid-state polymerization; polycondensation; diffusion; modeling

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INTRODUCTION

Applications such as bottles, industrial fibers, sheets, and packing string require high molecular weight poly(ethylene terephthalate) (PET). The latter is generally produced by solid state polymerization (SSP) with a long reaction time, 10–40 h. Unlike melt phase polycondensation (MPP), SSP operates at temperatures between the glass transition and the onset of the melting of PET. Although SSP exhibits reaction characteristics similar to MPP, the diffusion of volatile byproducts takes place within semicrystalline polymer pellets, which is very different from that in the polymer melt of MPP.

It is generally believed that the SSP of PET consists of four steps: (1) diffusion and collision of end groups in the solid phase, (2) reaction of end groups, (3) diffusion of reaction byproducts from the interiors to the surfaces of the polymer particles, and (4) diffusion of reaction byproducts from the surfaces of the polymer particles into the bulk of the gas phase (nitrogen).^{1,2} The fourth step can be considered to be negligible with a sufficiently high nitrogen flow rate in the laboratory because the interfacial diffusion is instantaneous. However, it

can become rate-limiting in an industrial process because a high flow rate of nitrogen can be very costly. The complexity of the SSP process, i.e., coupling between diffusion and reaction, makes the study of the reaction mechanism and kinetics more difficult.

Much attention has been paid to the effect of reaction temperature on SSP and little to the effect of the particle size.^{3–7} Some researchers investigated the effect of the diffusion of byproducts in a narrow particle size range^{5–7} and found that the diffusion effect could be neglected when PET particles were smaller than a critical threshold.^{1,8}

It is difficult to measure the diffusivity of byproducts. They are generally obtained by parameter identification using experimental data. Those reported in the literature are scattered.⁹ Recently, researchers^{2,10} attempted to predict diffusivities based on the free volume theory. However the free volume theory can only be used to predict diffusivity of SSP near the glass transition temperature and is not applicable at the temperatures close to the melting temperature.¹¹ SSP models can be divided into three categories: (1) reaction models which assume that

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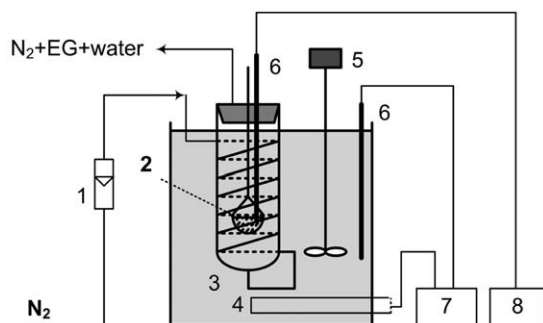


Figure 1. A scheme of the experimental setup. (1) flow meter, (2) hanging basket, (3) oil bath, (4) heater, (5) agitator, (6) thermometer, (7) controller, (8) temperature indicator.

chemical reaction is the rate-controlling step,^{3–5} (2) diffusion models which assume that chemical reaction is so fast that diffusion is the rate-controlling step,^{4,5,12} and (3) comprehensive models which take into account both chemical reactions and diffusion.^{2,6,7,10,11}

The objective of this work is to experimentally study the SSP of poly(ethylene terephthalate) over a wide range of pellet sizes and temperatures. A comprehensive model is then developed. It takes into account the polycondensation, degradation, and diffusion process. The diffusion and reaction rate constants as well as their activation energies are obtained by parameter identification using experimental data. The influences of the pellet size and reaction temperature on the SSP time and the concentrations of end groups are discussed.

EXPERIMENTAL

SSP Setup

Figure 1 shows the experimental setup of the SPP of the PET. PET powder was placed in a basket made of metal mesh, in which a thermocouple thermometer was inserted. Nitrogen was supplied with a controlled rate and monitored by a flow meter. It was heated up to the reaction temperature by passing through a heated coil before entering the reactor from the bottom with an inner diameter of 40 mm. The gas exhausted from the top of the reactor. The reactor temperature was controlled within $\pm 1^\circ\text{C}$ by an oil bath.

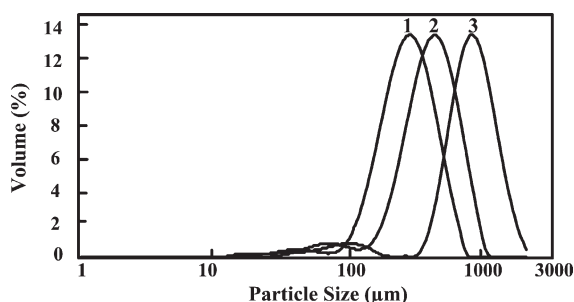


Figure 2. Particle size distributions of the PET powders. (1) 60–80 mesh; (2) 40–60 mesh; (3) 20–40 mesh.

Table I. Components Considered

Abbreviation	Description	Molecular structure
tEG	EG end group	
tTPA	TPA end group	
bEG	EG repeat unit	
bTPA	TPA repeat unit	
tVIN	Vinyl end group	$\text{H}_2\text{C}=\text{CHO}\sim$
EG	EG	$\text{HOCH}_2\text{CH}_2\text{OH}$
AA	Acetaldehyde	CH_3CHO

SSP Experiments

Amorphous PET prepolymer chips with dimensions of $2 \times 3 \times 3 \text{ mm}^3$ (YiZheng Chemical Fibre, Sinopec) were used. The concentration of the catalyst (Sb) in the chips was about 240 ppm and no other additives were added. The equivalent diameter of the chips, r_e , was 2.52 mm calculated by eq. (1)².

$$r_e = \sqrt{\frac{3}{\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2}}} \quad (1)$$

where a , b , c are the length, width, and height of powder, respectively.

PET particles with different dimensions were obtained by grinding and screening of the industrial chips under liquid nitrogen in order to avoid further crystallization and sticking. Before grinding, the industrial chips were predried under vacuum and at 110°C for 6 h. The resulting crystallinity was 32.5%. The industrial chips and screened powders with an average diameter of 0.795 (20–40 mesh), 0.418 mm (40–60 mesh), and 0.283 (60–80 mesh) were used in SSP experiments at 180, 190, 200, 210, 220, and 230°C , respectively. The average diameters of the screened powders were measured with a laser particle size analyzer (Coulter LS230) and their particle size distributions are shown in Figure 2.

The SSP experiments followed the procedure reported in the literature.¹³ The effect of the nitrogen flow rate on the intrinsic viscosity of the PET was preliminarily studied using powders with

Table II. Equations for the Rates of Generation of Components

$G_{\text{EG}} = k_p C_{\text{tEG}}^2 - 4 \frac{k_p}{K} C_{\text{EG}} C_{\text{bEG}}$
$G_{\text{tEG}} = -2 \left(k_p C_{\text{tEG}}^2 - 4 \frac{k_p}{K} C_{\text{EG}} C_{\text{bEG}} \right) + k_d C_{\text{bEG}} - k_t C_{\text{tEG}} C_{\text{tVIN}}$
$G_{\text{bEG}} = k_p C_{\text{tEG}}^2 - 4 \frac{k_p}{K} C_{\text{EG}} C_{\text{bEG}} - k_d C_{\text{bEG}} + k_t C_{\text{tEG}} C_{\text{tVIN}}$
$G_{\text{tVIN}} = k_d C_{\text{bEG}} - k_t C_{\text{tEG}} C_{\text{tVIN}}$
$G_{\text{AA}} = k_t C_{\text{tVIN}} C_{\text{tEG}}$

an average diameter of 0.283 mm. It could be ignored when the flow rate was higher than about 8 L/min (6.4 m/min). It was reported to be around 6.4 L/min (5.1 m/min) for industrial chips.⁷ In the subsequent experiments the nitrogen flow rate was chosen to be 10 L/min (7.96 m/min). An oil bath was used to heat up the reactor to a prescribed temperature. The basket loaded with the powders was then placed in the reactor and the SSP was formally started. At the end of the experiment, the powers were taken out of the reactor for further characterization.

Characterization

The intrinsic viscosity (η) of the PET was measured with dilute solutions at 25°C. The solvent was a mixture of phenol/tetrachloroethane (1/1 by volume) and the PET concentration was 0.005 g/mL. The intrinsic viscosity of the industrial chip was 0.62 dL/g.

The intrinsic viscosity can be converted to the number average molecular weight (M_n) and end-group concentration (C_{tEND}) according to eqs. (2) and (3), respectively.^{4,7}

$$M_n = \left(\frac{\eta}{2.1 \times 10^{-4}} \right)^{\frac{1}{0.82}} \quad (2)$$

$$C_{tEND} = \frac{2 \times 10^3}{M_n} \quad (3)$$

SSP MODELING

Chemical Reaction

Most researchers believe that the following three types of reaction are involved in the SPP: polycondensation, degradation, and side reactions.^{2,6,9,10,11}

Two polycondensation reactions cause an increase in molecular weight. One is the transesterification reaction in which two hydroxyl end groups condense and release a glycol. The other one is the esterification reaction between a hydroxyl end group and a carboxyl end group which releases a water molecule.

The thermal degradation plays a significant role at high temperature and under anaerobic conditions. The cleavage of an ester bond in the PET main chain generates a vinyl ester end group

(tVIN) and a carboxyl end group (tTPA). In addition, tVIN can further react with a hydroxyl end group (tEG) resulting in an increase in molecular weight and the release of acetaldehyde (AA). As the SSP proceeds, the ratio of carboxyl to hydroxyl end group (tTPA/tEG) increases and the reaction slows down, while the tVIN accumulates. Thermo-oxidative degradation can be neglected because the oxygen concentration in the SSP nitrogen atmosphere is low.

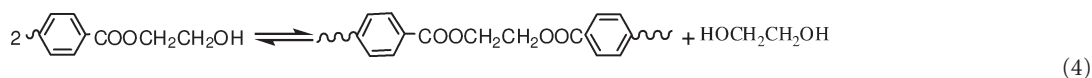
In addition to the polycondensation and degradation reactions in SSP process, there are also side reactions. Two tEGs can be condensed to form a diethylene glycol bond upon releasing a water molecule. Since its reaction rate is low, it can be ignored.^{9,14} The esterification reaction between the ethylene glycol (EG) generated in SSP and the residual terephthalic acid (TPA) generated from the melt phase polycondensation yields the corresponding ester (bEG) and water. Because both the concentration of EG and TPA (4×10^{-5} mol/L)¹⁵ are very low, this reaction contributes little to the SSP.

Tomita developed a kinetic model which was correlated with experimental data for the melt phase polymerization.¹⁶ It assumed that tVIN produced by thermal degradation does not have reactivity and its accumulative concentration increases the molecular weight of PET. However, this assumption is inconsistent with the mechanism of acetaldehyde formation. In addition, the Tomita's model did not take diffusion into account.

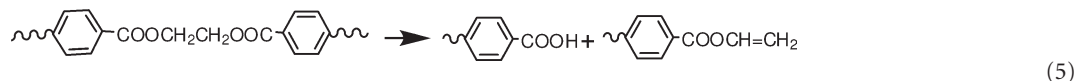
If more reactions are to be considered, more reaction equations and parameters are needed. As a result, it is more difficult to solve equations and measure the concentrations of intermediate species. In order to solve nine reaction rate equations and unsteady-state diffusion equations in a comprehensive model, Kim and Jabarin² had to use the same kinetic constants for four reaction rate equations, and adopt the activation energy data for MPP reported in the literature, which may bring greater error.

In this work, the Tomita's reaction model¹⁶ is modified in order to take into account diffusion in the polycondensation of vinyl end groups. The corresponding comprehensive model considers the following three reactions.

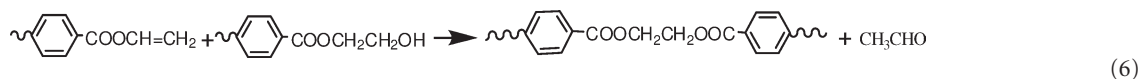
Polycondensation-Transesterification



Thermal degradation



Polycondensation of Vinyl End Groups

**Table III.** Initial and Boundary Conditions for Components

Component	Initial condition	Boundary condition
C_{EG} (mol/kg PET)	0	0 ($r = R$)
C_{tEG} (mol/kg PET)	As received	-
C_{bEG} (mol/kg PET)	5.4	-
C_{tVIN} (mol/kg PET)	0	0
$\frac{\partial C_{\text{EG}}}{\partial r}$		0 ($t > 0, r = 0$)

Table I shows the abbreviations of the corresponding components, where “t” and “b” denote terminal end groups and backbone repeat units within the chain, respectively.

Mass Transfer Equation and Component Rate Equation

The transesterification for the main chain growth is an equilibrium reaction. In order to promote the forward reaction, by-product EG should be timely discharged. During SSP, the unsteady diffusion of the by-product is coupled with the chemical reactions. PET particles can be treated as an equivalent spheroid and the unsteady mass transfer diffusion equation of the volatile component EG can be given in eq. (7).

$$\frac{\partial C_{\text{EG}}}{\partial t} = D_{\text{EG}} \left[\frac{\partial^2 C_{\text{EG}}}{\partial r^2} + \frac{2}{r} \frac{\partial C_{\text{EG}}}{\partial r} \right] + G_{\text{EG}} \quad (7)$$

where C_{EG} and G_{EG} are the concentration of EG in the powder and the rate of formation of EG, respectively; t is the SSP time; D_{EG} is the diffusion coefficient of EG; an r is the distance from the center of the spherical particle.

The mass balance equations of the nondiffusion components follow the equation:

$$\frac{dC_j}{dt} = G_j(t) \quad (8)$$

where j is tEG, tVIN or bEG. Table II shows the equations for the rate of formation of component, $G_j(t)$. Since the comprehensive model developed in this work only considers the transesterification, the concentration of tTPA resulting from the degradation is integrated into that of tEG.

The initial and boundary conditions are shown in Table III. The Crank-Nicolson finite difference method was used to solve eq. (7).² The distribution of the end group concentration within a particle is obtained as a function of the SSP time. The average

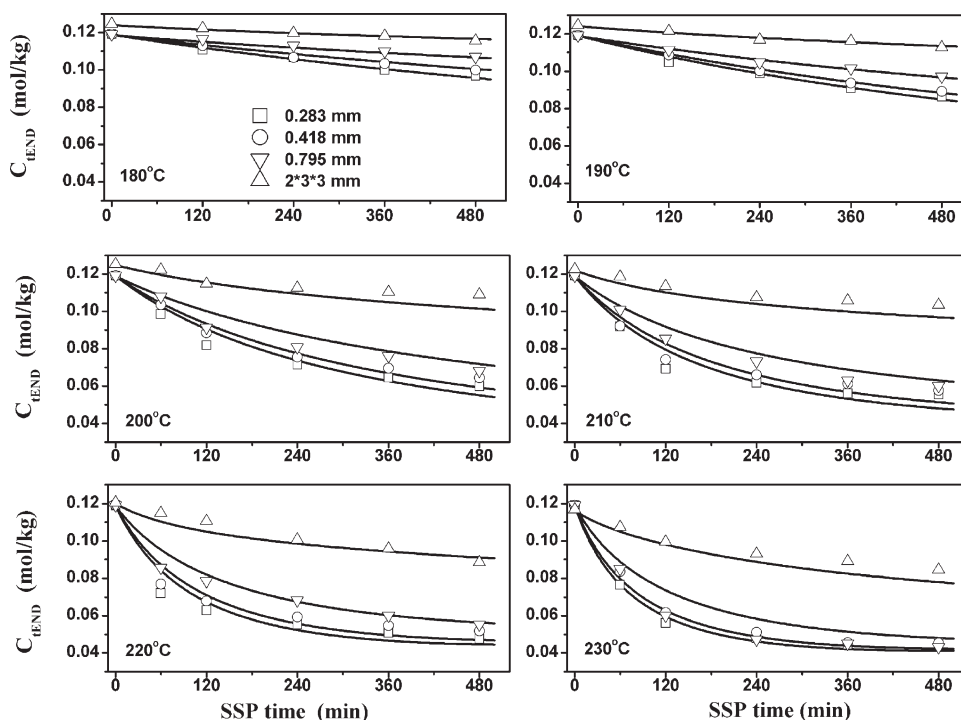
**Figure 3.** Concentrations of the PET end groups as a function of SSP time. Symbols: experimental data; curves: simulations.

Table IV. Polycondensation Rate Constants

Temperature (°C)	Polycondensation rate constant [(kg/mol)/min]	Reference
160	^a 4.6×10^{-4}	^c Ravindranath and Mashelkar ⁵
180	3.7×10^{-3}	This work
180	^b 1.4×10^{-3}	^c Kim and Jabarin ²
230	^b 2.4×10^{-2}	^c Kang ¹⁰
230	4.1×10^{-3}	^c Tang et al. ⁷
230	5.1×10^{-2}	This work
230	^b 4.9×10^{-2}	^c Kim and Jabarin ²

^aEstimated using a kinetic model, ^bCalculated for a polymerization degree of 200, ^cCalculated at a density ρ of 1.4 g/cm³.

end-group concentration, C_{tEND} , within a particle can be calculated using eq. (9):

$$C_{tEND} = \frac{\int_0^R 4\pi r^2 (C_{tEG} + C_{tVIN}) dr}{\frac{4}{3}\pi R^3} \quad (9)$$

where C_{tEG} and C_{tVIN} are concentration of tEG and tVIN, respectively. R denotes the radius of the spherical particle. The calculated average end-group concentration was compared with the experimental data in order to identify the parameters of the equation.

RESULTS AND DISCUSSION

Evolution of the End-Group Concentrations

Figure 3 shows the evolution of the end-group concentration as a function of SSP time for different PET end-groups. The powder size and reaction temperature are varied. The solid curves are the simulated results and symbols are the experimental points. The agreement between them is good.

When the SSP temperature is low, the concentrations of the end groups decrease linearly with the SSP time. Moreover, the

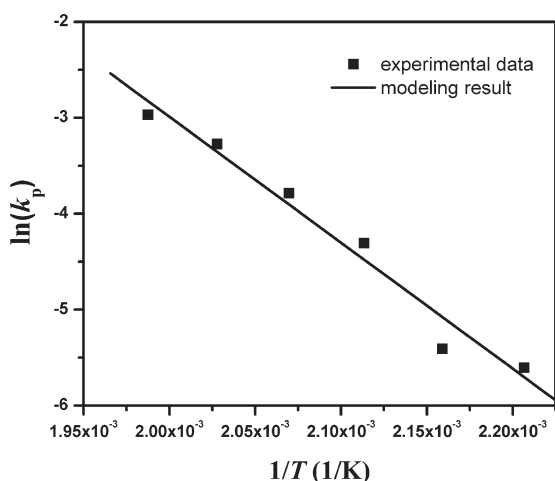


Figure 4. Relationship between polycondensation rate constant and temperature.

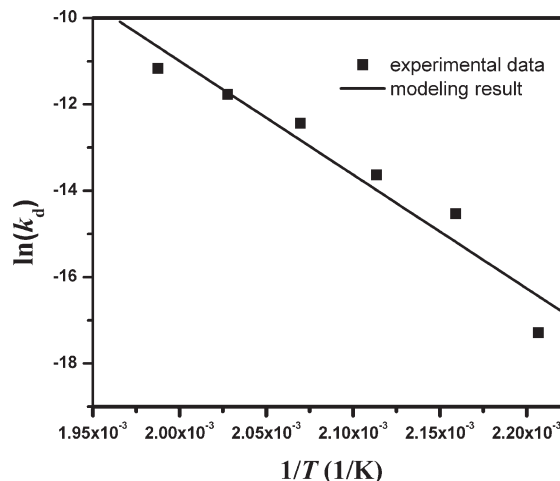


Figure 5. Relationship between degradation rate constant and temperature.

decrease is faster for small particles than for the industrial chips. At 200°C, the end-group concentrations of the industrial chips begin to deviate from the linear relationship, especially for small particles. This trend is even more obvious at higher temperatures. At 220 and 230°C, after 6 h of reaction, the end-group concentrations do not change much with the SSP time for PET particles whose average diameters are 0.418 and 0.283 mm, respectively. In fact, they are very close to each other.

Identification of Reaction Kinetic Parameters

Scheirs and Long¹⁴ summarized published kinetic constants. Like most published works in the literature, this work also chose a value of 0.5 for the polycondensation equilibrium constant K . The value of the EG diffusivity (D_{EG}) and those of the rate constants of the polycondensation (k_p), degradation (k_d), and vinyl end group polycondensation (k_v) were obtained by fitting the above kinetic model to the experimental results. Table

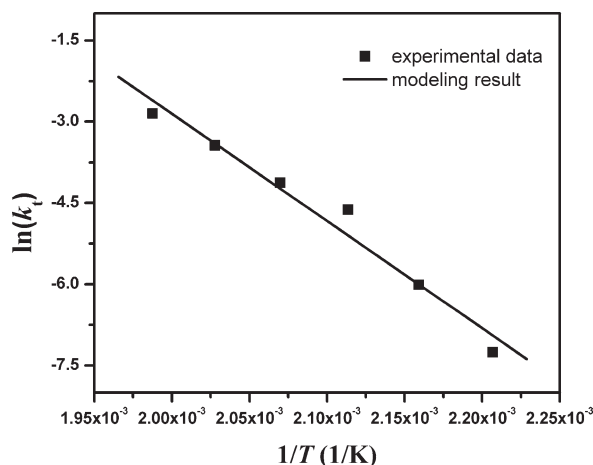


Figure 6. Relationship between vinyl end group polycondensation rate constant and temperature.

Table V. Pre-Exponential Factors and Activation Energies

Reaction rate constant	Frequency factor	Activation energy (kcal/mol)	Polymerization method	Reference
k_p	1.26×10^{11}	26.09	SSP	This work
		14.02	MPP	Stevenson ¹⁷
		18.54	MPP	Yokoyama et al. ¹⁸
		23.73	MPP	Tomita ¹⁶
		18.50	SSP	Kang ¹⁰
		23.60	SSP	Duh ¹
		18.40–22.80	SSP	Jabarin and Lofgren ³
		24.00	SSP	Chen and Chen ⁴
		21.00	Swollen ^a	Tate and Ishimaru ¹⁹
k_d	1.18×10^{18}	52.33	SSP	This work
		37.80	MPP	Yokoyama et al. ¹⁸
		46.65	MPP	Tomita ¹⁶
		40.00	Swollen ^a	Tate and Ishimaru ¹⁹
k_t	8.93×10^{15}	37.80	SSP	Kang ¹⁰
		39.34	SSP	This work
		18.50	SSP	Kang ¹⁰

^aSwollen state polymerization in hydrogenated terphenyl.

IV compares between this work and the literature in terms of the rate constants.

Arrhenius-types of equations were used to fit D_{EG} , k_p , k_d , and k_t at various temperatures. The values of the activation energies and pre-exponential factors for polycondensation (Figure 4), degradation (Figure 5), and vinyl end group polycondensation (Figure 6), were determined from the slopes and intercepts of the Arrhenius plots and are shown in Table V. The values of the activation energies reported in the literature for the MPP and SSP are also listed.

The value of the activation energy of the polycondensation for SSP obtained in this work is about 26 kcal/mol, while the one reported for MPP^{16–18} is between 14 and 24 kcal/mol, and that for SSP ranges from 15 to 24 kcal/mol.

There is no report on the value of the activation energy of degradation for SSP. In this work, it is found to be 52.3 kcal/mol. The value of the activation energy of degradation for MPP is reported to be in the range of 37–47 kcal/mol. Kang¹⁰ used the activation energy of degradation for MPP (37.8 kcal/mol)¹⁸ to study SSP. Tate and Ishimaru¹⁹ studied the swollen state polymerization of PET in hydrogenated terphenyls and obtained a value of 40 kcal/mol for the activation energy of the degradation. They neglected the polycondensation of vinyl end groups. The differences in terms of the activation energy of degradation for the swollen state polymerization, SSP, and MPP may result from those in the rates of diffusion of the end groups and byproducts.

The activation energy of degradation of SSP is 5–15 kcal/mol higher than that of MPP, due to the different states in which the molecular chains are. For semicrystalline polymers (SSP),

Table VI. Comparison of Diffusivity for EG

Temperature (°C)	Particle size (mm)	D_{EG} ($\times 10^{-6}$ cm ² /s)	Reference
180	0.2–3.0	0.03	This work
180		3.00	Kim and Jabarin ²
190	0.2–3.0	0.19	This work
190		3.05	Kim and Jabarin ²
200	0.2–3.0	0.65	This work
200		3.14	Kim and Jabarin ²
210	0.2–3.0	1.29	This work
210		3.24	Kim and Jabarin ²
210	1.6	0.005	Chang et al. ²¹
210	1.6	0.99	Ravindranath and Mashelkar ⁵
220	0.2–3.0	2.20	This work
220		3.19	Kim and Jabarin ²
220	1.6	1.97	Ravindranath and Mashelkar ⁵
220	3.2	1.9	Ravindranath and Mashelkar ⁵
220	1.6	0.009	Chang et al. ²¹
220	3.2	0.01	Chang et al. ²¹
230	0.2–3	4.12	This work
230		3.14	Kim and Jabarin ²
230	1.6	3.60	Ravindranath and Mashelkar ⁵
230	4.0 \times 4.0 \times 1.5	2.60	Tang et al. ⁷
230	0.97 and 2.13	3.10	Kang ¹⁰

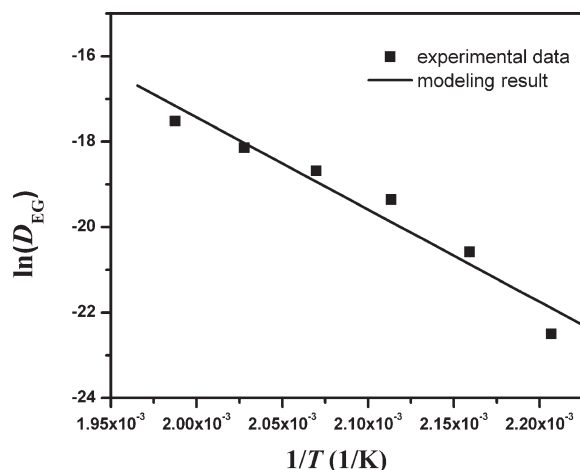


Figure 7. Relationship between diffusivity of EG and temperature.

some chain segments are in the crystalline ordered state and others are in the amorphous state.

The value of the activation energy of the tVIN polycondensation reaction was found to be 39.3 kcal/mol, which is higher than the one reported in the literature for MPP. Previously there were no data available for the activation energy of the tVIN polycondensation reaction for SSP. Therefore those for MPP were used instead.

Identification of Diffusion Coefficients

PET polycondensation is an equilibrium reaction for which the diffusion of the volatile byproduct, EG, in particles may play a key role. Table VI gathers the values of diffusion coefficients obtained in this work and the literature. They are much scattered because some were obtained by calculations based on the free volume theory and others by experiments.

The values of the diffusivity of EG obtained by Kim and Jabarin² based on the free volume theory are in a narrow range

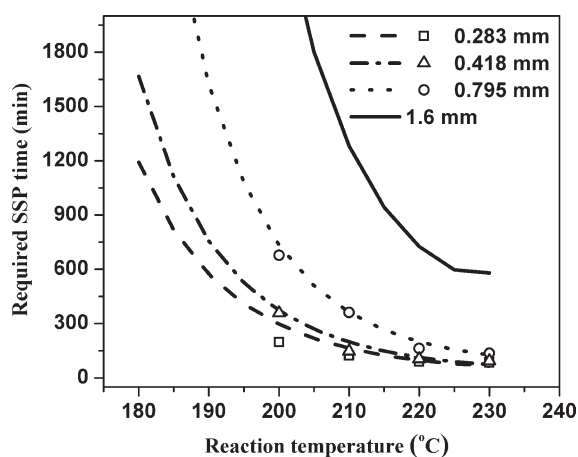


Figure 8. Relationship between reaction temperature and SSP time required for obtaining an increase in intrinsic viscosity from 0.62 to 0.9 dL/g for different particle diameters. Symbols: experimental data; curves: simulations.

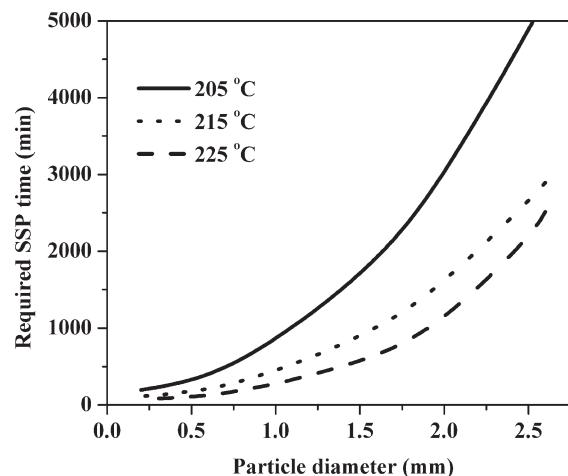


Figure 9. Relationship between particle diameter and SSP time required for obtaining an increase in intrinsic viscosity from 0.62 to 0.9 dL/g at various temperatures.

of 3.0×10^{-6} to 3.24×10^{-6} cm²/s over a temperature range of 180–230°C. Those reported by Ravindranath and Mashelkar⁵ based on the analysis of experimental data are in the range of 0.99×10^{-6} to 3.60×10^{-6} cm²/s for the temperatures ranging from 210 to 230°C. The values of the diffusivity of EG in this work are obtained by parameter identification using experimental data. They are close to those of Ravindranath and Mashelkar,⁵ Tang et al.,⁷ Kang,¹⁰ Kim and Jabarin,²⁰ but are larger than those of Chang et al.²¹ Differences among those values may be related to different assumptions the models made. Chang et al.²¹ assumed that the reaction in solid phase was always at equilibrium and no degradation reactions were considered. At low temperatures, the values of the diffusivity obtained in this work are lower than those by Kim and Jabarin,² who used a free volume model to express the diffusivity. Their values did not vary much with temperature. The free volume theory is

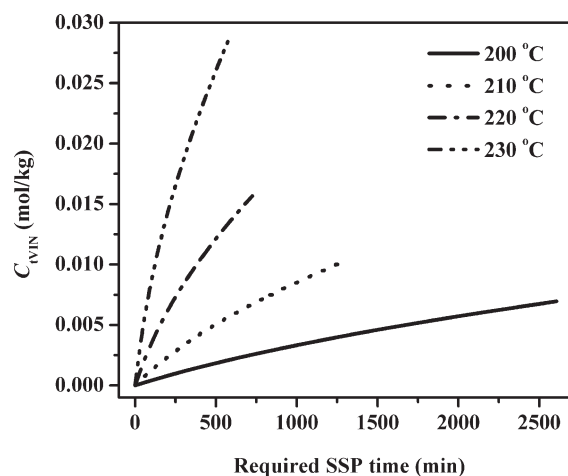


Figure 10. Relationship between the concentration of the vinyl end groups and SSP time required for obtaining an increase in intrinsic viscosity from 0.62 to 0.9 dL/g for PET powders with an average diameter of 1.6 mm at various temperatures.

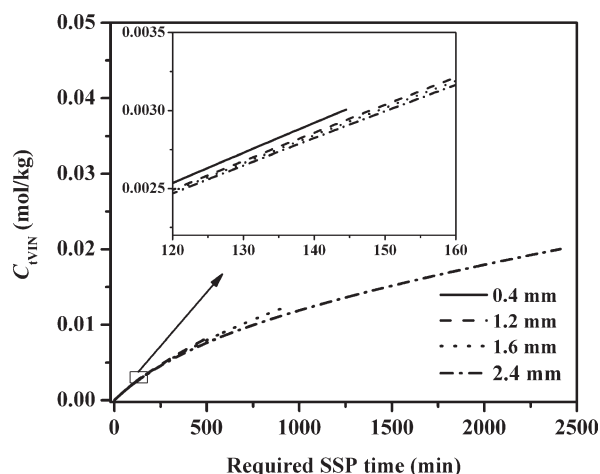


Figure 11. Relationship between vinyl end groups concentration and SSP time required for obtaining an increase in intrinsic viscosity from 0.62 to 0.9 dL/g for various particle sizes at 215°C.

valid when the temperature is not well above the glass transition, say, $T_g + 50^\circ\text{C}$. Solid-state polymerization processes are generally at temperatures well above the glass transition and is close to the melting temperature of the polymer.¹¹

Figure 7 shows the temperature dependence of the diffusivity in the form of Arrhenius equation. The value of the activation energy obtained is 42.9 kcal/mol, which is much higher than 5.4 kcal/mol obtained by Chen and Chen⁴, 30 kcal/mol by Chang et al.²⁰ and 31.3 kcal/mol by Ravindranath and Mashelkar.⁵

SSP Time Simulation

The SSP time required for an increase in intrinsic viscosity from 0.62 to 0.9 dL/g is predicted using the comprehensive model developed in this work for PET particles of different diameters and different reaction temperatures. Figure 8 compares the model predictions with the experimental data. The agreement is good.

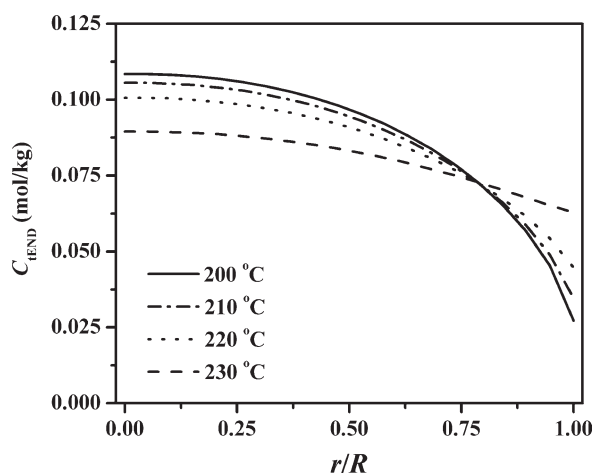


Figure 12. End-group concentration in a particle as a function of its radius at different temperatures. Particle diameter = 1.6 mm, $\eta = 0.9$ dL/g.

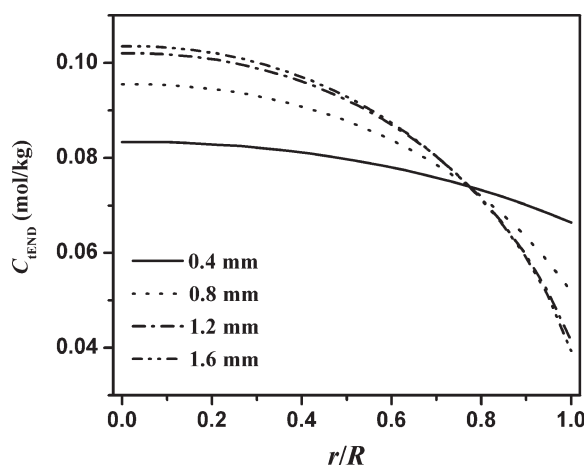


Figure 13. End-group concentration in a particle as a function of its radius for different initial particle diameters. Reaction temperature = 215°C, $\eta = 0.9$ dL/g.

It is seen that the required SSP time decreases exponentially with increasing reaction temperature. It is very sensitive to temperature in the range of 180 to 200°C. Generally, SSP is not carried out in this temperature range due to the slow reaction rate. Above 200°C, the required SSP time does not change much with the reaction temperature. It still lasts almost 10 h at 230°C. Also the reaction temperature cannot be further increased otherwise PET particles would become sticky. Therefore, one should consider other parameters instead of reaction temperature to increase the molecular weight of PET upon shortening the SSP time.

There is also an exponential function between the SSP time and particle size, as shown in Figure 9. When the particle diameter is decreased by a factor of 1.6 from 2.6 to 1.6 mm, the required SSP time is decreased by a factor of 3. However, the effect of the particle size decreases as it becomes smaller. Too small particles bring about difficulties with granulation and handling. As such it is recommended that in practice, the particle diameter be in the range of 1–2 mm. Kim and Jabarin² suggested that an effective diameter of around 2 mm would be optimum for pellets in terms of byproduct diffusion and ease of handling.

Simulation of the End-Group Concentrations

Up to now, there are no effective and accurate experimental methods to determine the tVIN concentration inside the particles.²⁰ Figure 10 shows the relationship between the vinyl end group (tVIN) concentration and the SSP time required for an increase in the intrinsic viscosity from 0.62 to 0.9 dL/g for PET particles with an average diameter of 1.6 mm at different temperatures. It increases considerably with increasing reaction temperature. At 200°C the time to reach the targeted intrinsic viscosity of 0.9 dL/g is long but the ultimate tVIN concentration remains low. At 230°C the reaction rate is not increased much but the tVIN concentration inside particles is increased by a factor of 4 compared with 200°C. The tVIN may further react to form acetaldehyde, which has adverse effects on packaged food. In this regard, a relatively low reaction temperature is preferred for producing PET resins with low acetaldehyde contents.

Figure 11 shows the effect of the particle size on the tVIN concentration at 215°C. As expected, the use of small PET particles shortens the required SSP time and reduces the tVIN concentration.

Figure 12 shows the distributions of the end-group concentration C_{TEND} inside the PET particles for an average diameter of 1.6 mm and an intrinsic viscosity of 0.9 dL/g. As the temperature increases, the profile of C_{TEND} along the radius direction becomes more flat.^{22,23}

Figure 13 shows the distribution of the end-group concentration in a particle for an ultimate intrinsic viscosity of 0.9 dL/g at 215°C. It becomes more flat when the particle diameter is smaller because of reduced effect of diffusion. When the particle diameter is large, say 1.2 or 1.6 mm, the end-group concentration in the center is much higher than near the surface.

CONCLUSIONS

The solid state polymerization (SPP) of PET was studied experimentally over a wide range of particle sizes (0.2–3 mm) and temperatures (180–230°C). A comprehensive model was developed to study the effects of reaction and diffusion on the SPP upon taking into account the polycondensation, degradation, and polycondensation of vinyl end groups. The reaction rate constants, diffusion coefficients and the corresponding activation energies were obtained by parameter identification based on experimental data.

The model was then used to analyze the SSP process of the PET with an initial intrinsic viscosity of 0.62 dL/g to a targeted one of 0.9 dL/g. Two recommendations are proposed: (1) the reaction temperature should be between 200 and 230°C, (2) the particle diameter should be between 1 and 2 mm.

The concentration of vinyl end groups is very sensitive to reaction temperature and particle size. Lower reaction temperature and smaller particle size should be chosen for producing PET with low concentration in vinyl end groups.

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NOMENCLATURE

C_{EG}	EG concentration in the particle (mol/kg)
G_j	generation rate of j component (mol/kg)
C_{TEND}	end group concentration (mol/kg)
C_{tEG}	concentration of tEG (mol/kg)
C_{tVIN}	concentration of tVIN (mol/kg)
D_{EG}	diffusion coefficient of EG (cm ² /s)
G_{EG}	generation rate of EG ((kg/mol)/min)

G_j	generation rate of j component ((kg/mol)/min)
M_n	number average molecular weight (g/mol)
k_p	reaction rate constants of polycondensation ((kg/mol)/min)
k_d	reaction rate constants of degradation (kg/min)
k_t	reaction rate constants of vinyl end group polycondensation [(kg/mol)/min]
r	distance from the center of the spherical particle (m)
R	radius of the spherical particle (m)
t	SSP time (min)
T	reaction temperature (K)
η	intrinsic viscosity (dL/g)

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