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Solid-phase polymerization mechanism of poly(ethylene terephthalate) affected by gas flow velocity and particle size

Bin Huang* and John J. Walsh
Hosokawa Bepex Corporation, 333 N.E. Taft Street, Minneapolis, MN 55413, USA
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Experimental studies on the solid-phase polymerization (SPP) of poly(ethylene terephthalate) (PET) for different particle sizes at temperatures of 190–220°C were carried out at different gas flow velocities. The SPP mechanism of PET changes under different operating conditions. At a given gas flow velocity, the SPP reaction mechanism for a large-sized sample changes from chemical reaction control to interior diffusion control with increasing temperature. At a given reaction temperature, the SPP reaction control mechanism for a small-sized sample changes from surface diffusion control to chemical reaction control with increasing gas flow velocity. At a given reaction temperature and gas flow velocity, the SPP reaction mechanism changes from interior diffusion control to surface diffusion control with decreasing particle size. The SPP reaction rate is not determined by a single control mechanism but by both diffusion and chemical reactions in the temperature range of 200–220°C. The primary control mechanism can be discerned based on the operating parameters. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(ethylene terephthalate); solid-state polymerization; reaction mechanism)

INTRODUCTION

Poly(ethylene terephthalate) (PET) is extensively used in the form of a staple, filament, fibre, film, etc. Recently, PET has found widespread acceptance for soft drink and beverage bottles, tyre cord filament and industrial fibres. However, these products required a higher molecular weight than commercial PET chips to enhance their mechanical properties, such as tenacity, modulus, etc. Very high tenacity (18 g d^{-1}) and modulus (240 g d^{-1}) PET materials have been made by using high-molecular-weight PET[1–3]. For preparing PET, which has a molecular weight greater than 20 000, solid-phase polymerization (SPP) is generally preferred. The SPP is carried out by heating the solid low-molecular-weight PET below its melting point but above its glass transition temperature. The process is carried out at approximately 200–240°C. Under these conditions, the polymer end-groups are sufficiently mobilized for reaction to take place. The reaction by-products are removed by allowing a flow of inert gas or by maintaining reduced pressure. The main polycondensation reaction is an equilibrium reaction and the by-product ethylene glycol (EG) is removed so that the forward reaction will be favoured:

The polycondensation rate depends on both chemical and physical processes, and the possible rate-determining steps are:

(a) Chemical Reaction Control:	A reversible chemical reaction
(b) Interior Diffusion Control:	Diffusion of the volatile reaction products in the solid polymer
(c) Surface Diffusion Control:	Diffusion of the volatile reaction product from the surface of the polymer to the inert gas

Depending on the process and operating variables, the polycondensation rate is controlled by one or more of these steps. It is important to examine the control mechanism of the SPP process not only for optimizing the process parameters but also for improving the product quality.

Kinetics of the SPP of PET has been extensively investigated by many researchers. In 1970, Chang[4] interpreted his data on the SPP process by using a diffusion controlled model. Schaff and Zimmermann[5] and Chen *et al.*[6] proposed purely kinetic models. Chen and Chen[7] later analysed the SPP process by taking into account the diffusion of the end-group in their kinetic model. Mashelkar and co-workers[8,9] comprehensively analysed the previous models and brought out some of the limitations that those models had in them. They developed a model considering both diffusion and generation of ethylene glycol during the reaction. However, the control step is changed with changing the operating variables and the SPP reaction rate is controlled by one or more of the steps mentioned above. This paper will discuss the effects of particle size and gas flow velocity on the mechanism of solid-phase polymerization.

EXPERIMENTAL

Materials

Commercial PET pellets were supplied by Hoechst Celanese Corporation. The pellets were extruded at 290°C and cooled in water to repelletize two kinds of samples with different sizes. Both amorphous samples have an initial intrinsic viscosity (IV) of 0.63 dl g^{-1}.

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* To whom correspondence should be addressed

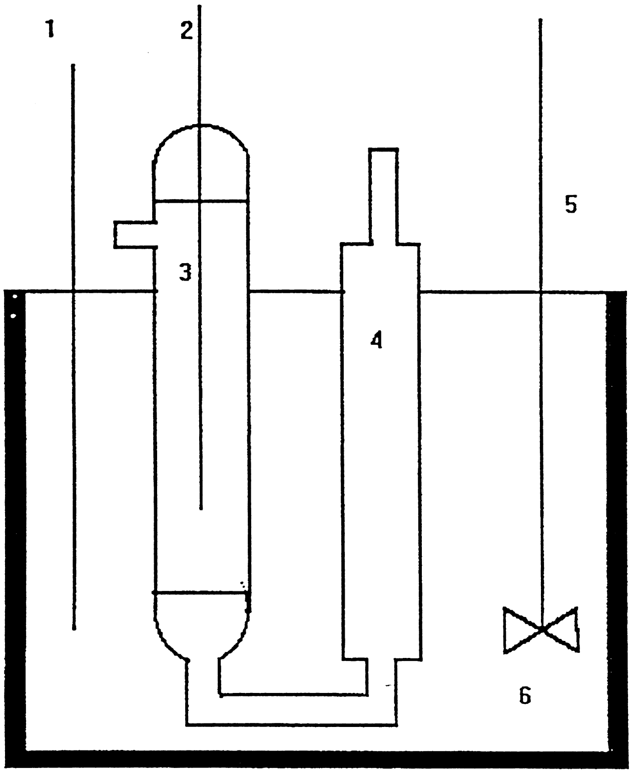

Figure 1 Tube reactor of solid-phase polymerization. 1, TC-1; 2, TC-2; 3, reactor; 4, heating coil; 5, stirring; 6, oil bath

Solid-phase polymerization (SPP)

The SPP test was carried out in the PolyQuest Center at Hosokawa Bepex Corporation (H-Bepex). A tube reactor is shown in *Figure 1*, which is simply equipped and easy to operate. Nitrogen gas was heated by passing through the heating coil before entering the reactor. The reactor and heating coil were heated in an oil bath. Thermocouple TC-1 was used to control the temperature of the oil bath. Thermocouple TC-2 was located 1 cm above the support disc to measure the temperature of the chips. The nitrogen flow velocity was controlled by a gas flow meter and was changed from 0.09 to 6.4 m min^{-1}.

Determination of the intrinsic viscosity

The viscosity measurements were conducted at 25°C in a Cannon–Ubbelohde viscometer on a solution in 50/50% w/w trifluoroacetic acid/dichloromethane (TFA/DM).

Determination of acetaldehyde content

Samples were ground to 20 mesh after quenching in liquid nitrogen. Samples (1 g) were weighed into 15 ml venoject tubes, sealed with rubber serum caps, and heated for 90 min at 160°C in an oven. After completion of the heating cycle, headspace samples of acetaldehyde were removed and injected into a Perkin-Elmer auto-system gas chromatography at H-Bepex, equipped with a flame ionization detector and a stainless steel column (length 6 ft, OD 1/8 in) packed with 80/100 mesh porapak QS.

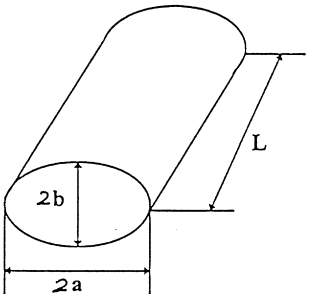

Figure 2 PET particle geometry

Determination of pellet size

Thirty pellets of each sample were measured by a micrometer in order to obtain the average chip size. The chip geometry was assumed to be a cylinder with an elliptical cross-section (shown in *Figure 2*). The surface area (*S*) and volume (*V*) of the PET chips were calculated by equations (2) and (3).

$$S = 2\pi ab + L\pi(2(a^2 + b^2))^{1/2} \tag{2}$$

$$V = \pi abL \tag{3}$$

Thus, the specific surface area (SSA) of the chip can be calculated from equation (4).

$$\text{SSA} = S/V \tag{4}$$

RESULTS AND DISCUSSION

Chemical reaction rate

A one-dimensional unsteady state diffusion process can be described by the following[10,11];

$$\frac{\partial g}{\partial t} = D\frac{\partial^2 g}{\partial^2 x} + \frac{\lambda \partial g}{x \partial x} + k\left(e^2 - \frac{4gz}{K}\right) \tag{5}$$

In this equation, the mass transfer process is assumed to be isothermal and the diffusion process of ethylene glycol (EG) is a Fick type. It is further assumed that the partial specific volumes are independent of composition so that there is no volume change on mixing. Here *g* and *e* are the concentrations of ethylene glycol and the hydroxyl end-group respectively. *D*, *k* and *K* are the ethylene glycol diffusivity, the polycondensation rate constant and the equilibrium constant respectively. *t* and *x* are the reaction time and the distance in the direction of diffusion respectively. λ is the geometry parameter and depends on the shape of the particles. In equation (5), the first section on the right side is related to interior diffusion and surface diffusion. The second section on the right side is related to the chemical reaction rate.

The mass density of the polymer is uniform throughout the particle. However, the concentration of the polymer end-group changes due to the polycondensation reaction and the rate of change can be represented as

$$\frac{\partial e}{\partial t} = -2k\left(e^2 - \frac{4gz}{K}\right) \tag{6}$$

and

$$z = z_0 + (e_0 - e)/2 = 1 - e/2 \tag{7}$$

Here, z and z_0 are the concentration of the diester group at time t and the initial concentration of the diester group respectively. If the diffusion of EG is rapid compared to the rate of chemical reaction, then the concentration of

Table 1 Characteristics of samples

	Initial IV (dl g^{-1})	AA content (PPM)	Chip size (mm)			Specific surface area (cm^{-1})
			L	*a*	*b*	
Small particle	0.631	16.54	1.82	1.14	1.14	44.70
Large particle	0.628	15.29	3.21	2.69	2.82	20.75

EG can be assumed to be nearly zero throughout the particle. Then equation (6) reduces to

$$de/dt = -2ke^2 \quad (8)$$

Integrating equation (8) and expressing e in terms of degree of polymerization (DP), we get

$$P_n = P_{n0} + 4kt \quad (9)$$

where $P_n = 2/e$ and P_{n0} is the initial DP. Therefore, the plots of DP *versus* reaction time should be linear and DP should be independent of particle size in a chemical reaction control process. Two kinds of fibres with different specific surface areas were polymerized at the temperature of 180°C for 3 h[12]. Fibre I was an O-shaped in cross-section and fibre II was Y-shaped in cross-section. The ratio of the specific surface areas of fibres II and I is 1.2. However, the same product IV of 0.775 dl g^{-1} was achieved for both fibres I and II. Since small-diameter fibre was used in this test, the diffusion of EG from the solid polymer to the surface of the fibres was easy. Also, the effect of surface diffusion on reaction rate is denied because the different specific surface area fibres have the same molecular weight at the given reaction temperature and reaction time. Therefore, this is not a diffusion controlled process but a chemical reaction controlled process. Ravindranath and Mashelkar[8] also proved that the SPP reaction rate of PET pellets was controlled by chemical reaction at temperatures lower than 160°C. Thus, the chemical reaction plays a key part in control of the SPP reaction of PET at low reaction temperatures.

Effect of gas flow velocity on SPP reaction mechanism

The characteristics of the amorphous feed chips are shown in *Table 1*. Both small and large particle samples have the same initial IV and were crystallized at 160°C for

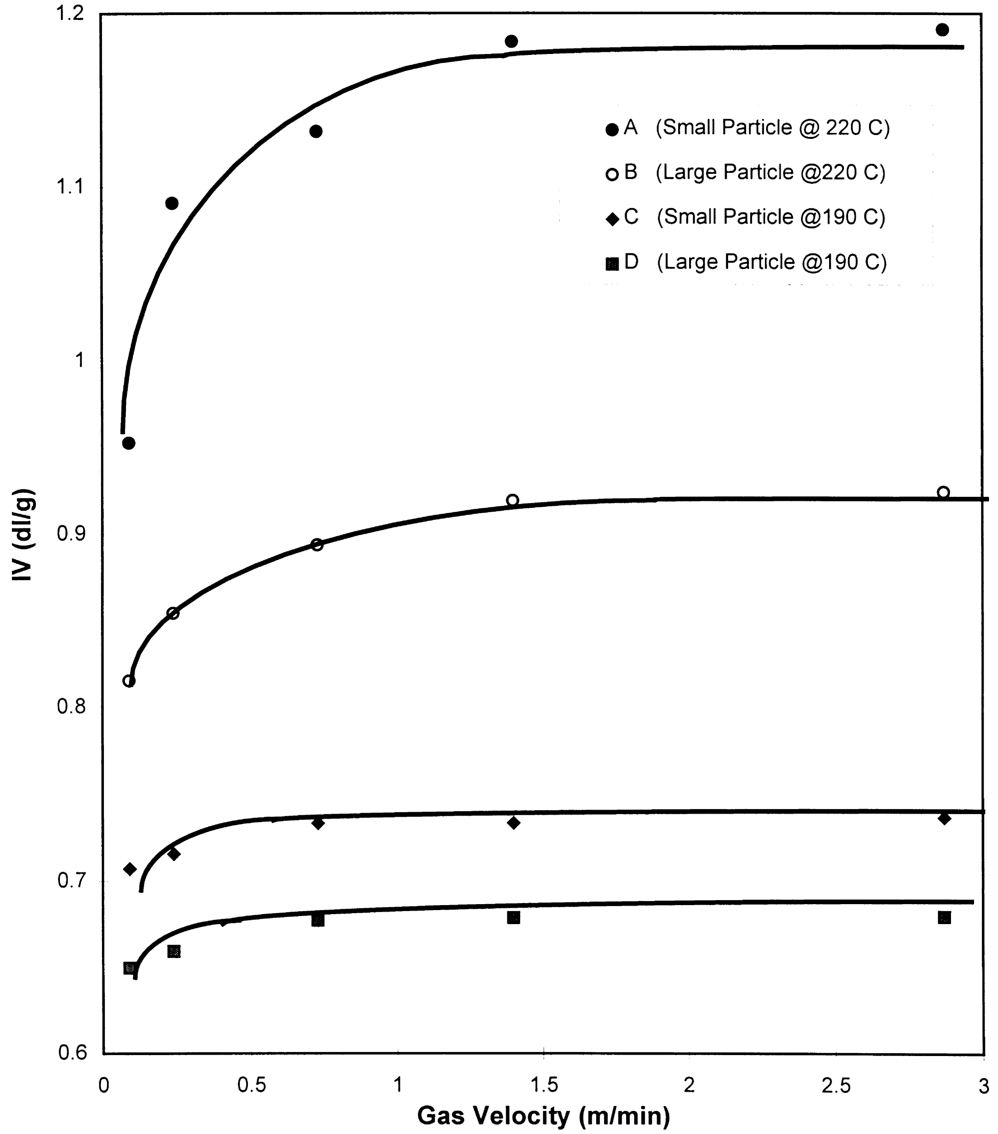

Figure 3 Effect of gas velocity on SPP reaction rate at reaction temperatures of 190 and 220°C

Table 2 IV difference between small- and large-sized chips

Gas flow velocity (m min^{-1})	ΔIV (dl g^{-1})		
	190°C	200°C	220°C
0.24	0.056	0.063	0.236
0.73	0.056	0.067	0.245
1.40	0.055	0.064	0.265
2.87	0.057	0.066	0.267

30 min. Then, crystallized chips were polymerized from 190 to 220°C for a given reaction time.

Figure 3 shows the effect of gas flow velocity on the SPP reaction rate at 190 and 220°C. Curves A and C represent small-sized chips and curves B and D represent large-sized chips. With increasing gas flow velocity, the product IV increases at the range of low gas flow velocity. This indicates that the SPP reaction rate at 190°C is not only controlled by the chemical reaction rate but also by EG diffusion at the low gas flow rate. The diffusion rate of the volatile reaction product (EG) from the surface of the polymer to the inert gas can be determined by the gas side resistance[8]. The gas side resistance (Φ) is affected by three factors: particle size (x_0), diffusivity (D) in the solid polymer and the gas side transfer coefficient (k_g). The gas side resistance is given by:

$$\Phi = k_g x_0 / D \tag{10}$$

The large value of Φ means that there is low gas side resistance. The EG diffusivity in the solid polymer (D) is dependent on the particle morphology and reaction temperature. In this test, the crystal morphology was similar because the chips were crystallized at the same temperature for the same time. It has also been reported[8] that EG diffusivity in PET is independent of the particle size. Therefore, the diffusivity of PET is constant at a given reaction temperature if the same sample size is used in the test. The gas side transfer coefficient (k_g) is affected by the gas flow velocity and the diffusivity of EG in the inert gas. As long as the carried gas is selected, k_g will be proportional to the gas flow velocity. Clearly, the value of Φ in *Figure 3* is only determined by the reaction temperature and the gas side transfer coefficient. At a given temperature, k_g only increases with increasing gas flow velocity, which results in a large Φ value. The large Φ value means that there is low gas side resistance in the particle surface, which results in a high SPP reaction rate. Therefore, the gas side resistance plays an important role at low gas velocity and a given reaction temperature.

However, on further increasing the gas flow velocity, the IV of the sample reacted at 190°C is independent of gas flow

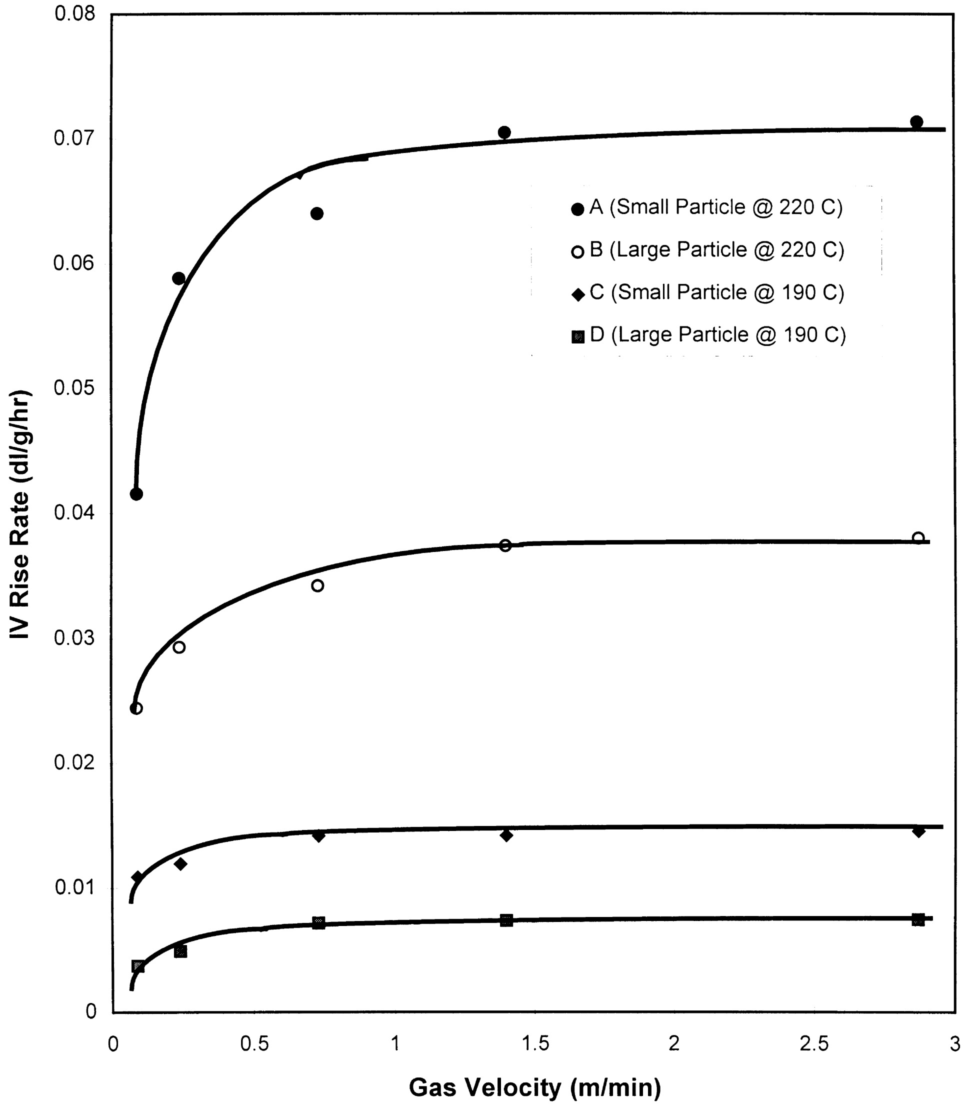

Figure 4 Effect of gas velocity on IV rise rate of SPP product at various temperatures

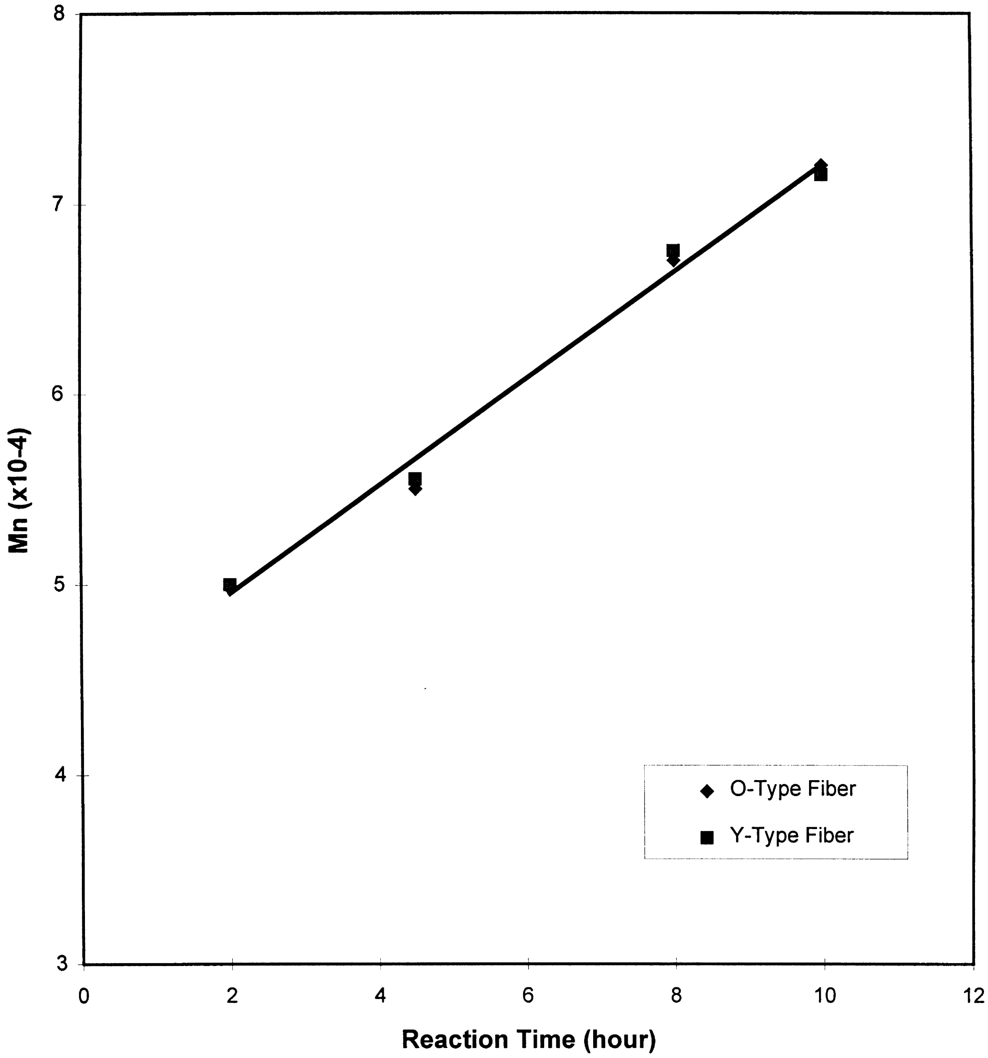

Figure 5 Relationship between molecular weight and SPP reaction time at gas velocity of 640 cm min^{-1} (reaction temperature 235°C)

velocity when the velocity reaches a certain value (0.5 m min^{-1}). As is known, the gas side resistance is caused by forming a concentration gradient of EG in the gas phase during the SPP reaction. When the inert gas velocity is high enough to remove volatile reaction by-products immediately, there will be no EG concentration gradients in the gas phase. The effect of surface diffusion on the SPP reaction rate disappears. The SPP reaction mechanism from both diffusion control and chemical reaction control changes to only chemical reaction control at a high gas flow velocity for a given particle size.

The same situation can be observed at the reaction temperature of 220°C in *Figure 3*. That is, the SPP reaction mechanism changes from both chemical reaction control and diffusion control to only chemical control with increasing gas velocity. However, the turning point, when the SPP reaction rate is independent of gas velocity, moves to a higher velocity at a temperature of 220°C compared to a lower reaction temperature. As mentioned before, the EG diffusivity increases with increasing reaction temperature. There exists a high EG concentration on the particle surface due to rapid EG diffusion from solid polymer to the surface at a given gas flow velocity. Both factors lead to a large gas side resistance. The result suggests that the effect of surface diffusion on the SPP reaction rate tends to increase with increasing temperature. The effect is more significant at low gas flow velocity due to a low k_g value. The temperature effects will be discussed in more detail later.

Effect of particle size on the SPP reaction mechanism

In *Figure 3*, we can see that small-sized PET chips have a higher SPP reaction rate at 190°C for a given reaction time. However, in *Table 2*, it can be found that the IV difference between small- and large-sized particles does not change with increasing gas flow velocity at the reaction temperature of 190°C. This IV difference is mainly related to EG diffusion from the solid polymer to the particle surface since the same reaction temperature and gas flow velocity were used for both small and large particle samples. Although we can see the effect of the gas flow velocity on the SPP reaction rate at the low gas flow velocity in *Figure 3*, the effect is relatively small compared to EG diffusion from solid particle to surface and the chemical reaction rate at the low reaction temperature range. The IV increases by only 0.03 dl g^{-1} for both small and large chips at the reaction temperature of 190°C when the gas flow velocity increases 32 times (from 9 to 287 cm min^{-1}). The increase of product IV, that is due to EG diffusion from solid polymer to particle surface, is about 0.06 dl g^{-1} (see *Table 2*) at the same reaction temperature. This implies that the interior diffusion has more effect on the SPP reaction rate than the surface diffusion when the large particle sample is used. On the

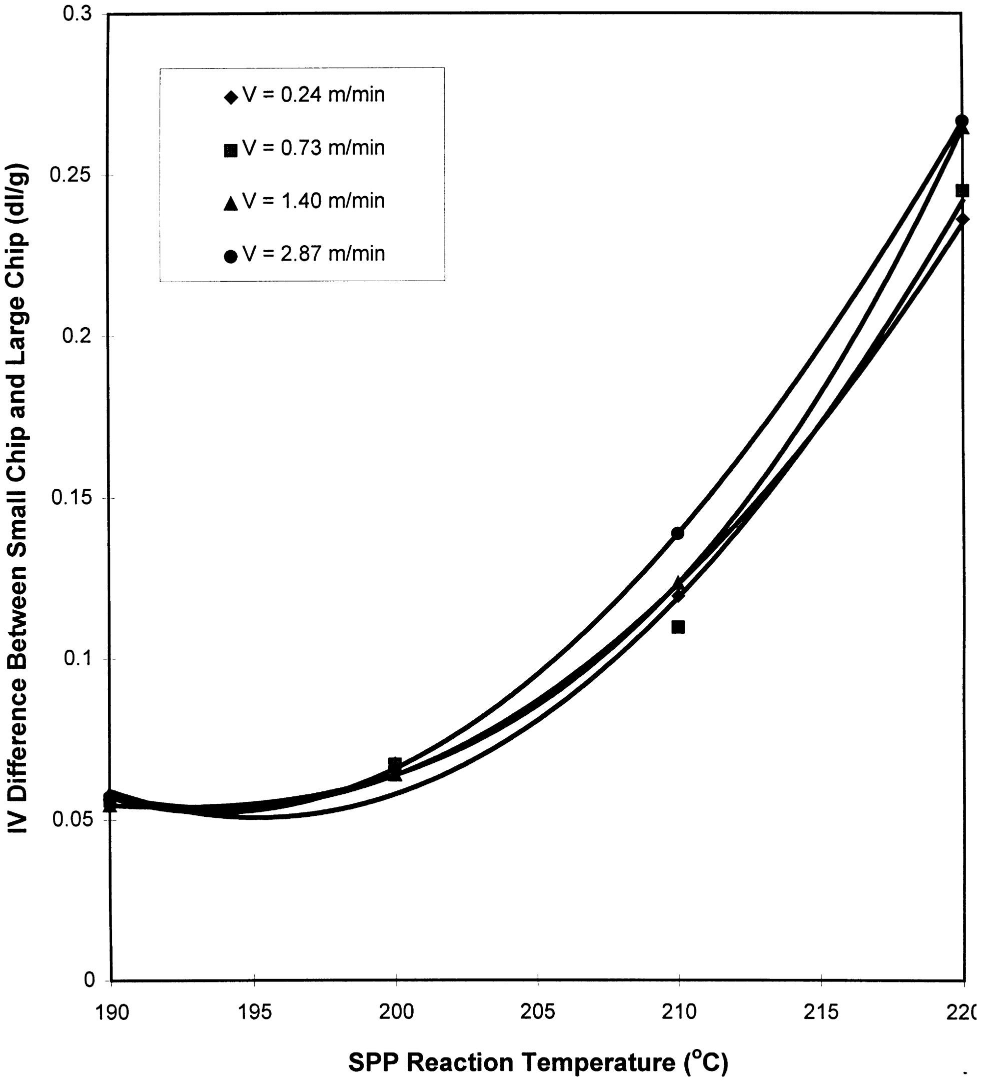

Figure 6 Effect of diffusion on SPP reaction rate at various reaction temperatures

other hand, it has been reported[7] that the effect of temperature on the chemical reaction rate ($E = 19.1$ kcal - mol^{-1}) is larger than that on the EG diffusion rate in the solid polymer ($E_{\mathrm{EG}} = 5.4$ kcal mol^{-1}). Therefore, at low reaction temperatures, the SPP reaction rate for the large particle sample is controlled first by chemical reaction, second by EG diffusion from solid polymer to the surface and then by EG diffusion from the surface to the inert gas.

Comparing curves A and B in *Figure 3*, we find that the SPP reaction rate of the small-sized particle is affected significantly by gas flow velocity at the high reaction temperature. In *Table 2*, the IV difference between small- and large-sized pellets is also affected by the gas flow rate at the temperature of 220°C. This means that the effects of the surface diffusion on the SPP reaction rate increase on reducing the particle size at the high reaction temperature.

This effect can be further seen in *Figure 4*. The product IV rise rate is affected significantly by the gas flow velocity at high temperatures in *Figure 4*, especially for the small-sized particles. As we know, EG diffusivity (D) increases with increasing reaction temperature. Also, the interior diffusion distance is short for small particles. So, EG diffuses very easily from solid polymer to surface when small-sized particles are polymerized at the high temperature. According to equation (10), small x_0 and large D will result in high gas side resistance (small Φ value) which lowers the EG diffusion from the surface to the inert gas phase. In order to increase the Φ value, the high gas flow velocity has to be used to raise the gas side transfer coefficient (k_g). This is the reason why the gas velocity has more effect on the SPP reaction rate when the high temperature was used in the SPP of small-sized chips.

In addition, we know that the chemical reaction rate is more thermally sensitive than EG diffusivity and increases significantly with increasing reaction temperature. When very small-sized particles are polymerized at the high temperature, the diffusion from the solid polymer to the surface could be neglected. With the situation of low gas flow velocity, the control mechanism of the SPP changes from the chemical reaction control at the low temperature ($<$ 180°C) to the surface diffusion control process at the high reaction temperature.

It is also noted in *Figure 4* there exists an equilibrium point of IV rise rate with further increasing gas flow velocity although the small chip was polymerized at high temperature (series A). This illustrates that the effect of the surface diffusion on the SPP reaction rate is limited. In *Figure 4*, same size chips were tested at the temperature of 220°C for a given time. EG diffusion from the solid polymer to the surface should be similar in series A because the samples had similar morphology and the same reaction temperature was used. At the high gas flow velocity, the effect of the gas

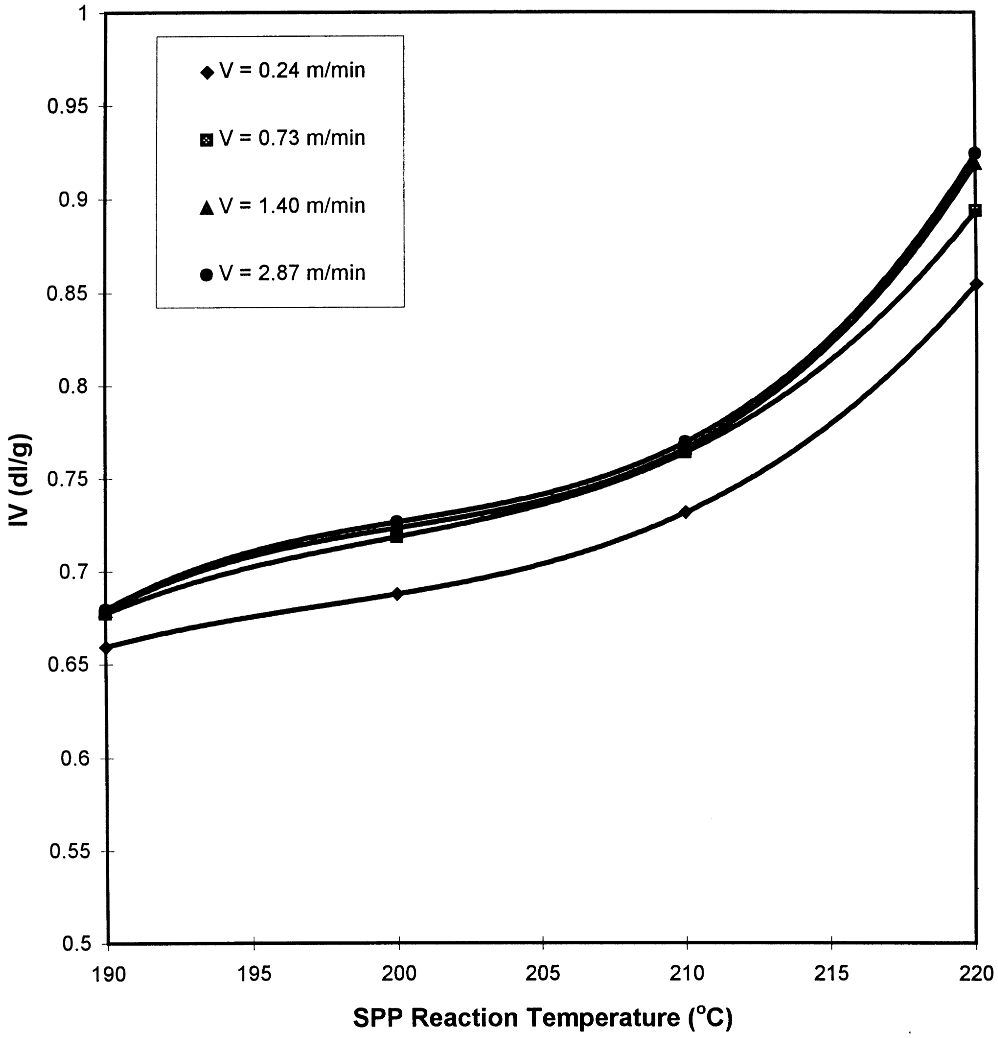

Figure 7 Effect of SPP reaction temperature on SPP reaction rate at various gas flow velocities (large chips)

side resistance on the SPP reaction rate is very small. The chemical reaction rate is not affected by the gas side resistance since it is only dependent on the reaction temperature and the concentration of the end-groups. We can expect that the control mechanism of the SPP reaction for small-sized chips changes from diffusion control to chemical reaction control again with increasing gas flow velocity at the high reaction temperature.

A special experiment has been carried out[12]. The O-shaped and Y-shaped cross-section PET fibres with different specific surface areas were polymerized at 235°C at very high gas flow velocity (640 cm min^{-1}). The results are shown in *Figure 5*. With increasing reaction time, the molecular weight increases linearly and the reaction rate is independent of the specific surface area. According to equation (9), it can be concluded that the reaction is controlled by the chemical reaction rate in *Figure 5*. As we know, the EG diffusion path in the fibres is very short. Therefore, the EG diffusion rate from the solid polymer to the surface will be higher than the chemical reaction rate. When a very high gas flow velocity is used, the EG diffusion from the surface to the inert gas will also be very fast. That is the reason why the SPP reaction mechanism changes back to chemical reaction control. This result suggests again that chemical reaction is the main control in the SPP reaction when a very small-sized sample was polymerized at the high temperature and high gas velocity.

As discussed above, we can conclude that the SPP reaction for small-sized chip is mainly controlled by the chemical reaction rate at a temperature less than 180°C. With increasing reaction temperature, the SPP mechanism changes from chemical reaction control to surface diffusion control at the low gas flow velocity. However, it will return to chemical reaction control if the gas flow rate is high enough to remove the by-products immediately.

Effect of temperature on the SPP reaction mechanism

It is clear that the chemical reaction rate, interior diffusion and surface diffusion of by-products have a close relationship with the reaction temperature. It is important to understand the reaction temperature effect on the SPP reaction rate with changes of particle size and gas velocity. As mentioned in Section Section 1, the SPP reaction rate is mainly controlled by the chemical reaction rate at temperatures less than 180°C. In *Figure 4*, we have seen that the turning point, when IV is independent of gas velocity, moves to a higher gas flow velocity with increasing reaction temperature. This implies that the effect of EG diffusion on the SPP reaction rate increases with increasing reaction temperature. In Section Section 3, we have pointed out that the SPP mechanism for very small particles changed from chemical reaction control to surface diffusion control with increasing reaction temperature. However, the effect of temperature on the reaction mechanism is more complicated for large-sized particle.

In *Figure 6*, it was found that the IV difference is

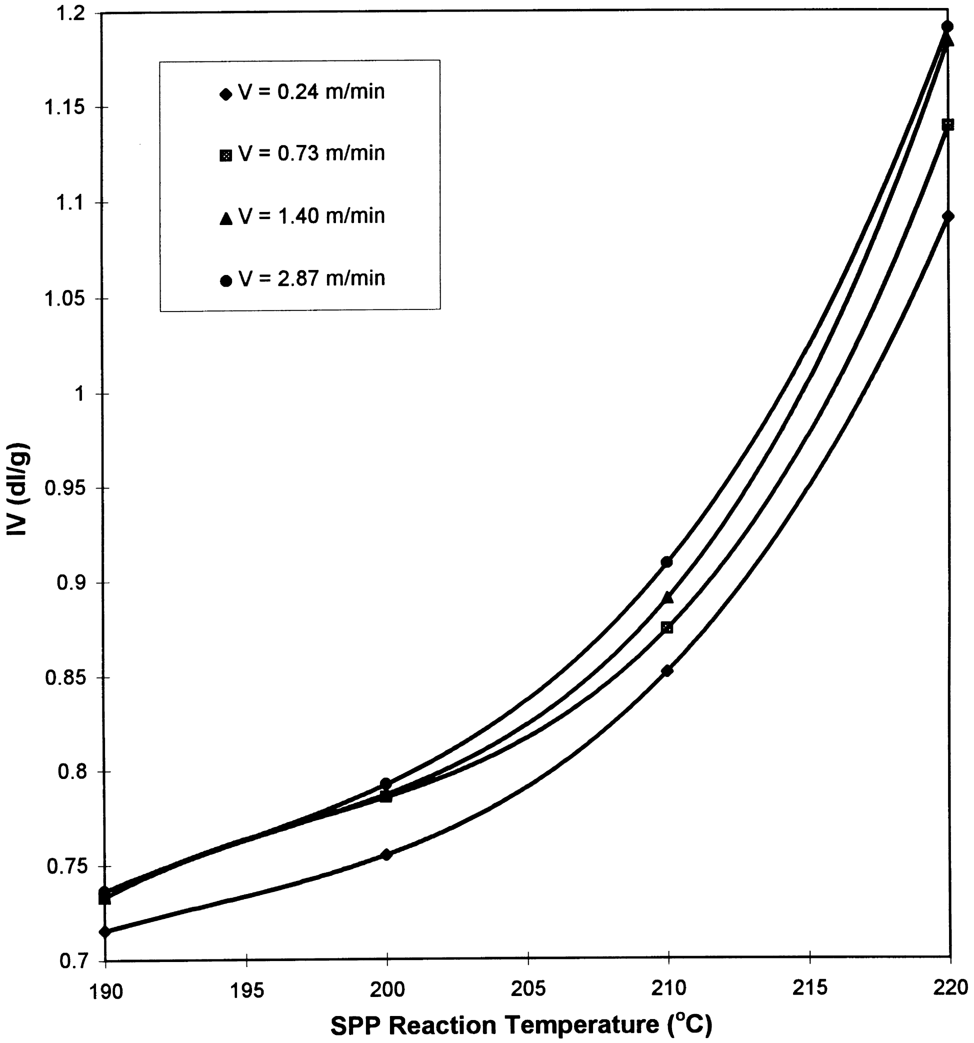

Figure 8 Effect of SPP reaction temperature on SPP reaction rate at various gas flow velocities (small chips)

independent of reaction temperature and gas flow velocity at the low temperature range (190–200°C). This illustrates that EG diffusion from the solid polymer to the surface is independent of temperature and is only determined by the diffusion distance at the low temperature. However, in *Figure 7*, we can see that the IV increases when the temperature was raised from 190 to 200°C even if the same size particle and same gas flow velocity were used in those test. Clearly, the IV rise in the temperature range of 190–200°C is mainly due to increase of the chemical reaction rate with increasing temperature shown in *Figure 7*. This verifies again that the SPP reaction rate is mainly controlled by the chemical reaction rate in the temperature range of 190–200°C. However, an IV difference between the large- and small-sized chips has been found in *Figure 6* at this temperature range. So, for large particles, the SPP reaction rate is controlled first by the chemical reaction rate and then by diffusion from the solid polymer to the surface. At the given particle size and gas flow velocity, the effect of EG diffusion increases gradually in the SPP reaction with further increasing.

Figures 7 and 8 show the relationship between the product IV and temperature at a given gas velocity. Clearly, the product IV is affected significantly by the temperature at a given gas flow rate. At the same gas flow velocity, the high reaction temperature results in an increase of the chemical

Table 3 Mechanism of SPP reaction under different conditions

Reaction temp.	Particle size	Gas flow velocity	Mechanism of SPP reaction
$T < 180$°C	Large	Low	Chemical reaction control process
		High	Chemical reaction control process
	Small	Low	Chemical reaction control process
		High	Chemical reaction control process
$T = 190$–200°C	Large	Low	Chemical reaction > interior diffusion > surface diffusion
		High	Chemical reaction and interior diffusion
	Small	Low	Chemical reaction, surface diffusion, interior diffusion
		High	Chemical reaction control process
$T = 210$–220°C	Large	Low	Interior diffusion > surface diffusion > chemical reaction
		High	Interior diffusion > chemical reaction
	Small	Low	Surface diffusion control process
		High	Chemical reaction control process

Table 4 Factors operating on the control mechanism in the SPP reaction

Mechanism of SPP reaction	Particle size	Temp.	Gas velocity	Catalyst
Chemical reaction rate	No	Yes	No	Yes
Interior diffusion	Yes	Yes	Yes	No
Surface diffusion	Yes	Yes	Yes	No
Chemical reaction and diffusion	Yes	Yes	Yes	Yes

reaction rate and an increase of EG diffusivity. However, comparing *Figures 7 and 8*, we find that the effect of temperature on the SPP reaction rate of large-sized particle is much less than the effect on small-sized particle at the high temperature range from 210 to 220°C. It is well known that chemical reaction rate is very fast at the high temperature and is independent of particle size. The EG diffusivity for both small and large particles should be similar at a given temperature. According to equation (10), the gas side resistance will reduce the SPP reaction rate of small-sized particles due to high EG concentration on the surface of the particles. However, the small-sized chip still has a higher SPP reaction rate than the large-sized chip at the SPP reaction temperature of 210–220°C. This result suggests that the SPP reaction rate of the large-sized chip is mainly controlled by EG diffusion from the solid polymer to the surface at the high reaction temperature.

This situation can also be observed in *Figure 6*, which shows that the IV difference between small- and large-sized particles increases significantly with increasing reaction temperature above 200°C and at a given gas flow velocity. As discussed above, the chemical reaction rate is independent of particle size. Therefore, the IV difference between small and large particle sizes is mainly determined by EG diffusion from solid polymer to surface at the given temperature and gas flow velocity. The larger IV difference means that the interior diffusion has more effect on the SPP reaction rate. On the other hand, the gas side resistance has a negative effect on the SPP reaction rate with reducing particle size if the same gas flow velocity is used. The mobility and reactivity of the polymer chain end-groups are much more temperature sensitive than the diffusion process. Thus, the resistance for the polymerization due to chemical reaction is reduced as the reaction temperature is increased. This result indicates again that the large-sized particle is mainly controlled by an interior diffusion process at the high reaction temperature range.

The SPP reaction rate at the temperature range of 200–210°C is expected to be controlled by both the chemical reaction rate and the diffusion process. It needs to be further investigated to determine which mechanism is the main control for the SPP reaction rate at this temperature range. However, we believe that the control mechanism changes from chemical reaction control to interior diffusion control with increasing particle size and changes to surface diffusion control with reducing gas flow velocity.

CONCLUSION

According to the discussions above, it is clear that the SPP reaction is controlled by different mechanisms at the various operating conditions. At the given gas flow velocity, the SPP reaction control mechanism for large-sized particle can change from chemical reaction control to interior diffusion control with increasing temperature. At the given temperature, the SPP reaction control mechanism for small-sized particle changes from surface diffusion control to chemical reaction control with increasing gas flow velocity. At the given reaction temperature and gas flow velocity, the SPP reaction mechanism changes from interior diffusion control to surface diffusion control with decreasing particle size. Some special cases of SPP reaction mechanisms are listed in *Table 3* based on the discussions above. However, the SPP reaction rate is not determined by a single control mechanism but by both diffusion and reaction rate in the temperature range of 200–220°C. *Table 4* presents some factors that may affect the SPP reaction mechanism. By using *Tables 3 and 4*, the primary control mechanism of SPP reaction rate can be discerned based on the operating parameters.

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