Thermodynamic Properties and Crystallization Behavior of Poly(*p*-phenylene succinate)

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ABSTRACT: The equilibrium thermodynamic properties and crystallization behavior of poly(*p*-phenylene succinate) (PPSc) were examined using differential scanning calorimetry (DSC) and a wide-angle X-ray diffractometer. When PPSc quenched into liquid nitrogen, the PPSc still showed 60 J/g of the heat of fusion, indicating that PPSc crystallizes too fast to be quenched to a glassy state. The equilibrium heat of fusion (ΔH°) of PPSc and its equilibrium entropy of fusion (ΔS°) were estimated to be 28 and 48 J/mol K, respectively. The effect of the molecular weight and undercooling on PPSc rystallization was analyzed by the Avrami expression. The crystallization rate of PPSc was highest at about 276°C, regardless of molecular weight when the sample was isothermally crystallized. This temperature was higher than that of poly(ethylene terephthalate) (PET) by 100°C. The crystallization rate was highest when the number average molecular weight of PPSc was about 20,000 g/mol. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 801–806, 1999

Key words: poly(*p*-phenylene succinate); thermodynamic properties; isothermal crystallization

INTRODUCTION

Poly(phenylene succinate) (PPSc) $[-OC(CH_2)_2$ COO-Ph-O-] is isomeric with PET by inversion of the ester groups. PPSc has higher melting temperature (310°C) than PET (265°C). This may be ascribed to the steric hindrance to the rotation of the -OCO- group around the C₆H₄-O axis because of the steric volume of the ortho hydrogen atom.¹ Recently, we have examined the crystallization behavior of various poly(*p*-phenylene alkylene dicarboxylates) (PPADs) as a function of the length of the alkylene unit and found that PPADs crystallize more readily than poly(alkylene terephthalate) (PATs), which have the same chemical composition

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as its corresponding PPAD but the reversed direction of the ester group.²

It is well known that most of the parameters involved in crystallization of polymers depend on the crystallization temperature and their molecular weight. In PET, the crystallization behavior has been extensively studied as a function of molecular weight, crystallization temperature, and the amount of catalyst in the polymer, because the final physical properties of the fabricated PET largely depend on the crystallization condition.^{3–9} However, the equilibrium thermodynamic properties and crystallization behavior of PPSc have not been thoroughly studied.

In this study we have synthesized several PPScs with different molecular weights and measured their equilibrium thermodynamic properties. The effects of the molecular weight and undercooling on the crystallization of PPSc are also examined. Fi-

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nally, these properties of PPSc are compared with those of PET.

EXPERIMENTAL

PPSc was synthesized by reacting equimolar parts of hydroquinone with succinyl dichloride for 2 h at 140°C in an inert solvent, 1,1,2,2,-tetrachloroethane (TCE). Hydroquinone was purified by recrystallizing twice from acetone, and succinyl dichloride was fractionally distilled under a reduced pressure at 140°C. During polymerization, PPSc was precipitated from the solution. The precipitate as a white solid powder was filtered off, washed repeatedly with acetone, and then dried under vacuum at 80°C for 3 days.

To obtain higher molecular weight PPSc, solidstate polymerization was carried out. As-polymerized PPSc (10 g) and hydrogenated terphenyl (500 mL) as a swelling solvent were introduced into a three-necked 1000-mL flask equipped with a mechanical stirrer and purged with dry nitrogen. The temperature was then raised to 280°C and held at that temperature with nitrogen bubbling (2 L/min) for a predetermined period of time. Intrinsic viscosity of PPSc was measured in phenol (Ph)/TCE (6/4 w/w) at 25 \pm 0.01°C by use of an Ubbehlode viscometer. The intrinsic viscosity $([\eta])$ of as-polymerized PPSc was 0.32 dL/g, and the viscosity was increased to 0.46 and 0.63 dL/g by solid-state polymerization for 2 and 10 h, respectively. When the number-average molecular weight of PPSc was calculated from the intrinsic viscosity using the relation $[\eta] = 1.66 \times 10^{-3}$ $[M_n]^{0.58}$,¹⁰ the molecular weights of three PPScs were 9100, 16200, and 27900 g/mol, respectively.

A Perkin-Elmer differential scanning calorimeter (DSC-7) was used to study the crystallization behavior. Isothermal crystallization was observed by keeping the molten samples at the temperature 20°C above its melting temperatures for 3 min to destroy residual crystallites, and then by rapidly cooling down to the predetermined isothermal crystallization temperature (T_c) at a rate of 200°C/min. The exotherm due to crystallization was recorded as a function of time.

Crystallinity and crystal thickness of PPSc were determined using a wide-angle X-ray diffractometer (Rigaku 12-KW). WAXS patterns are obtained from nickel filtered CuK α radiation.



Figure 1 Heat of crystallization of PPSc as a function of reciprocal cooling rate.

RESULTS AND DISCUSSION

Effect of Cooling Rate on Crystallization

We have reported that the crystallization rate of PPSc is much faster than that of PET when the crystallization half time of PPSc is compared with that of PET at the same degree of undercooling.² Figure 1 shows the heat of nonisothermal crystallization of PPSc as a function of reciprocal cooling rate, as the temperature is lowered from the temperature 20°C above its melting temperature. The heat of crystallization decreased with increasing the cooling rate. However, when the heat of crystallization was extrapolated to an infinite cooling rate, the value was about 62 J/g, indicating that rapid quenching does not completely suppress the crystallization of PPSc. In fact, when the polymer melt was quenched in liquid nitrogen, the heat of crystallization was about 60 J/g. This result indicates that PPSc crystallizes so fast that molten PPSc cannot be quenched to a glassy state. In the case of PET, although the crystallization rate depends on its molecular weight and the presence of a catalyst, the PET of zero crystallinity can be obtained when the molten polymer is guenched at the rate of 130°C/min for high molecular weight PET and at the rate of 400°C/min for low molecular weight PET, respctively.⁸ Figure 2 shows WAXS patterns of PPSc (a) quenched into liquid nitrogen and (b) molten at 325°C. The crystal thickness (D_{hkl}) perpendicular to a given set of (hkl) planes at $2\theta = 20.5^{\circ}$ was calculated using Scherrer equation:¹¹

$$D_{hkl} = K\lambda/\beta \cos \theta \tag{1}$$



Figure 2 Wide-angle diffractograms of PPSc (a) quenched to liquid nitrogen, and (b) melted at 325°C.

where *K* is the Scherrer shape factor (0.9), λ is the wavelength of the X-ray, and β is the breadth of the diffraction peak associated with the (hkl) planes. The crystal thickness perpendicular to (hkl) planes of as-quenched PPSc was calculated to be 154.8 Å.

Determination of T_g and ΔH°

As-polymerized PPSc was annealed at various temperatures. The relationship between the heat of fusion (ΔH) and annealing time t at different annealing temperatures (T_a) can be described as^{12,13}

$$\Delta H(T_a, t_a) = K(T_a)\log t + B(T_a, t_a) \qquad (2)$$

The slope $K(T_a)$, dependent on the annealing temperature, is a parameter that determines the transformation rate. When ΔHs were plotted against log t at various annealing temperatures as shown in Figure 3, straight lines were observed. From the slopes of straight lines, the values of $K(T_{\alpha})$ were determined. When the value of $K(T_a)$ so determined was plotted as a function of annealing temperature, a straight line is observed, as shown in Figure 4. It is apparent that higher annealing temperature shows a faster rate of increase in ΔH of PPSc. Extrapolation to zero $K(T_a)$ yields the glass transition temperature $(T_g).^{12}$ According to this method, the T_g of PPSc was estimated to be 185°C. In this study we were not able to directly determine the T_g of PPSc from the DSC thermogram due to its higher crystallinity. Considering that the steric hindrance of PPSc is larger than that of PET, it is expected that the T_g of PPSc is higher than that of PET.



Figure 3 Relationship between the heat of fusion ΔH and the logarithm of annealing time *t*: (\oplus) 230°C, (\bigcirc) 240°C, (\Box) 250°C, (\blacksquare) 260°C, (\blacktriangle) 270°C.

We have determined the equilibrium melting temperature (T_m°) of PPSc by the Hoffmann-Weeks plot. The value of T_m° obtained was 308°C. It has been reported that PPADs show higher melting temperatures compared to PATs with an equal length of an aliphatic unit.¹⁵ The crystallinity of polymers can be determined using wideangle X-ray diffraction by subtracting the amorphous halo [Fig. 2(b)] from diffraction peaks of a partially crystalline sample. When the crystallinity determined from WAXS was plotted against ΔH as shown in Figure 5, a linear relationship was obtained. Extrapolation of ΔH to 100% crystallinity yields the heat of fusion of 100% crystallinity ($\Delta H^{\circ} = 145 \text{ J/g}$). By using the value of ΔH° , the entropy of fusion (ΔS°) is calculated using the following equation:



Figure 4 Variation of the rate of transformation $K(T_a)$ as a function of the annealing temperature T_a .



Figure 5 Variation of the crystallinity with the heat of fusion ΔH for different annealed samples.

$$\Delta S^{\circ} = \Delta H^{\circ} / T_{m}^{\circ} \tag{3}$$

The values thus obtained are listed in Table I and compared with the values of PET.¹⁶ T_m° and ΔH° of PPSc are larger than those of PET chain, whereas ΔS° of PPSc is lower than that of PET. This suggests that the PPSc chain is more rigid than PET.

Isothermal Crystallization

Isothermal crystallization has been analyzed by the Avrami equation.¹⁷ The weight fraction of crystalline material, X(t), at time t has been calculated by integrating the areas under the exothermic peak as given by

$$X(t) = \int_{0}^{t} (dH/dt) / \int_{0}^{\infty} (dH/dt) dt$$
 (4)

where dH/dt is the rate of heat evolution on the DSC thermogram. According to the Avrami equation, X(t) is expressed as $X(t) = 1 - \exp(-kt^n)$, where k is the kinetic rate constant and n is the Avrami exponent. Values of the exponent n can be obtained from the slope of the double-logarithmic

Table IEnthalpy and Entropy of Fusion ofPET and PPSc

Polymer	$\Delta H^{\circ} (\mathrm{J/g})$	T_m° (K)	$\Delta S^{\circ} (J/gK)$	
PET PPSc	$\begin{array}{c} 140 \\ 145 \end{array}$	$\begin{array}{c} 550 \\ 581 \end{array}$	$\begin{array}{c} 255\\ 250 \end{array}$	

Table IIIsothermal Crystallization Data ofPPSc

M_n (g/mol)	$T_c~(^{\circ}\mathrm{C})$	k	n	$t_{1/2}$ (min)
9,100	270	5.4	0.5	0.13
	275	112.6	2.4	0.12
	280	145.0	3.1	0.18
	285	213.0	4.1	0.25
	287	25.0	3.9	0.40
	290	6.1	3.9	0.57
	292	0.6	2.7	1.03
16,200	275	38.3	0.6	0.09
	280	526.9	3.0	0.11
	282	146.7	2.7	0.14
	285	27.4	2.2	0.19
	287	70.1	2.9	0.21
	290	13.3	2.3	0.27
	292	14.5	3.7	0.44
27,900	275	4.5	0.65	0.06
	280	19.6	1.54	0.11
	282	97.6	2.57	0.15
	285	82.7	2.83	0.18
	287	182.4	3.79	0.23
	290	265.0	5.83	0.36
	292	12.4	3.87	0.48

plot, $\log[-\ln(1-X(t))]$ vs. log t. The kinetic parameters determined from the slope and the intercept are listed in Table II. The crystallization half-time $(t_{1/2})$, defined as the time taken for half of the crystallinity to develop, is instead used as a measure of the crystallization rate. The value of $t_{1/2}$ is easily obtained from the relation, $t_{1/2} = (\ln 2/k)^{1/n}$. It is well known that the crystallization rate depends on the crystallization temperature and the molecular weight of polymer. Van Antwerpen and van Krevelen⁵ reported that the maximum growth rate of PET spherulite occurs at 180°C when the numberaverage molecular weights of samples are in the range of 19,000 to 27,000 g/mol. Lin⁶ also showed that the maximum crystallization rate of PET occurs at about 175°C, regardless of molecular weight. When the values of $t_{1/2}$ are plotted against T_c for three different molecular weight PPScs, as shown in Figure 6, all PPScs show the maximum crystallization rate at 276°C \pm 3°C. Note that the minimum $t_{1/2}$ corresponds to the maximum crystallization rate. The temperature at the maximum crystallization rate for PPSc is higher than that of PET by 100°C, indicating that the crystallization rate of PPSc is much faster than PET. For a given undercooling, the crystallization rate is closely

related to the nucleation free energy and the transport of polymer segment at the liquidcrystal interface. Here, the transport term is directly related to the molecular weight that determines the environmental viscosity. When the crystallization half-time is plotted against the number-average molecular weight as shown in Figure 7, a minimum is observed for all crystallization temperatures examined. For low molecular weights, the viscosity of the medium is low, giving rise to large thermal agitation that opposes the formation of stable nuclei. Thus, this thermal agitation results in high $t_{1/2}$. The medium of high molecular weights becomes viscous, which makes transport of polymer segment to the crystal interface more difficult, resulting in high $t_{1/2}$. Therefore, the two effects by molecular weight compete each other, resulting in the existence of the molecular weight showing the minimum value of $t_{1/2}$. Vilanova et al.⁹ have reported that the PET with the numberaverage molecular weight of about 9200 g/mol shows the maximum crystallization rate. Figure 7 shows that the number-average molecular weight of PPSc showing the minimum value of $t_{1/2}$ is about 20,000 g/mol. This also supports that the crystallization rate of PPSc is faster than PET.

CONCLUSIONS

Equilibrium thermodynamic properties and crystallization behaviors of PPSc were examined. When PPSc was quenched into liquid ni-



Crystallization temperature (°C)

Figure 6 Dependence of crystallization half time of PPSc on the crystallization temperature: (•) $M_n = 8700$, (•) $M_n = 16,200$, (•) $M_n = 27,900$.



Figure 7 Plots of $\log t_{1/2}$ against molecular weight at various crystallization temperatures: (•) 292°C, (\bigcirc) 290°C, (\blacksquare) 287°C, (\square) 280°C.

trogen, the heat of fusion of PPSc was 60 J/g, indicating that PPSc crystallizes too fast to be quenched to a glassy state. The equilibrium heat of fusion and entropy of fusion of PPSc were estimated to be 28 and 48 J/mol K, respectively. The glass transition temperature of PPSc was higher than PET due to larger intermolecular interaction of PPSc. PPSc showed the maximum crystallization rate at about 276 \pm 3°C, and the number-average molecular weight of PPSc showing the maximum crystallization rate was about 20,000 g/mol.

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