Crystallization of a Thermoplastic Polyimide

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INTRODUCTION

Some aromatic polyimides exhibit outstanding heat resistance mechanical properties and are of commercial interest.[1–3] Typical commercial polyimides, such as Kapton and Vespel (both supplied by E. I. Du Pont, Wilmington, DE) and Upilex (supplied by Ube Industries), are infusible and difficult to process. Attempts have been made to develop polyimides that are melt processible,[4–13] and some melt processible polyamide-related resins such as Ultem polyetherimide (G. E. Plastics), Torlon polyamide-imide (Amoco), and Aurum thermoplastic polyimide (Mitsui Chemical, Inc., Tokyo, Japan) have been introduced to the market.

The Aurum thermoplastic polyimide, derived from pyromellitic anhydride and 4,4′-bis(3-aminophenoxy)biphenyl, has been claimed as a crystalline polyimide with excellent heat resistance and injection moldability, and can be used to produce high-performance parts.[13,14] Various properties and the crystalline properties of the Aurum thermoplastic polyimide have been characterized to some extent in the literature.[15–24] The temperature resistance of Aurum is significantly dependent on its crystallinity. Although Aurum is crystalline, it often solidifies in an amorphous form in a practical processing cycle. Thus, an annealing procedure at high temperature is often necessary for the Aurum to develop enough crystallinity if higher temperature resistance is required. Of course, the annealing procedure increases the manufacturing cost. If the crystallization behavior of Aurum is sufficiently understood, it will be helpful for the determination of the molding condition or annealing condition, and may lower the cost. However, systematic studies on the crystallization of Aurum from a practical viewpoint have been scarce. In this study, the crystallization of a pure Aurum thermoplastic polyimide is investigated.

EXPERIMENTAL

A pure Aurum thermoplastic polyimide, PL450, derived from pyromellitic anhydride and 4,4′-bis(3-aminophenoxy)biphenyl, was supplied by Mitsui Chemical, Inc. (Japan). The DSC heating and cooling curves of PL450 at a scanning rate of 20°C/min were determined by a Perkin–Elmer DSC7 (Perkin Elmer Cetus Instruments, Norwalk, CT). The sample was heated in the DSC to 400°C to ensure complete melting, then it was cooled to a given crystallization temperature at a cooling rate of 400°C/min and held at that temperature for a given period. Afterward, a heating thermotherm from the crystallization temperature to 400°C was monitored.

RESULTS AND DISCUSSION

The DSC heating and cooling curves of PL450 at a scanning rate of 20°C/min are shown in Figure 1. Within the temperature range of 100 to 400°C, the DSC heating curve of PL450 exhibits an inflection and an endotherm. The midpoint of the inflection is taken as the glass-transition temperature (T_g) and the peak temperature of the endotherm is taken as the melting point (T_m). PL450 shows a T_g of 248°C and a T_m of 381°C with a heat of fusion (ΔH_m) of 31.0 J/g. The DSC cooling curve of PL450 exhibits a crystallization exotherm (T_c) at 302°C with a crystallization heat of 28.1 J/g.

The successive DSC heating curves after crystallization at 220°C for various periods are shown in Figure 2. It can seen that these successive DSC heating curves exhibit a step inflection corresponding to the T_g (~ 248°C), a cold crystallization exotherm (T_{cc}), and a melting endotherm (T_m). The T_{cc} and T_m peaks separate sufficiently, and the crystallization heat can be estimated as $\Delta H_c = \Delta H_m - \Delta H_{cc}$, where ΔH_m is the peak area (in J/g) of the T_m peak and ΔH_{cc} is the peak area of the T_{cc} peak. The observed T_{cc}, T_m, and ΔH_c are summarized in Table I. The ΔH_c values of PL450 after
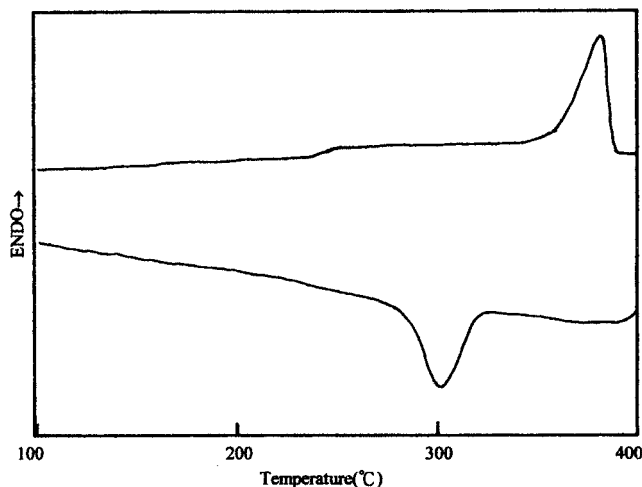
Figure 1 DSC heating and cooling curves of PL450.

crystallization at 220°C for various periods are all almost equal to zero. In other words, no significant crystallization has occurred at an isothermal crystallization temperature of 220°C.

The successive DSC heating curves after crystallization at 240 and 260°C for various periods are similar. A typical curve is shown in Figure 2. Of course, the T_g cannot be found from these successive DSC heating curves. These successive DSC heating curves exhibit a T_{cc} and a T_m similar to those at 220°C, as shown in Figure 2. The ΔH_c values are all almost equal to zero as
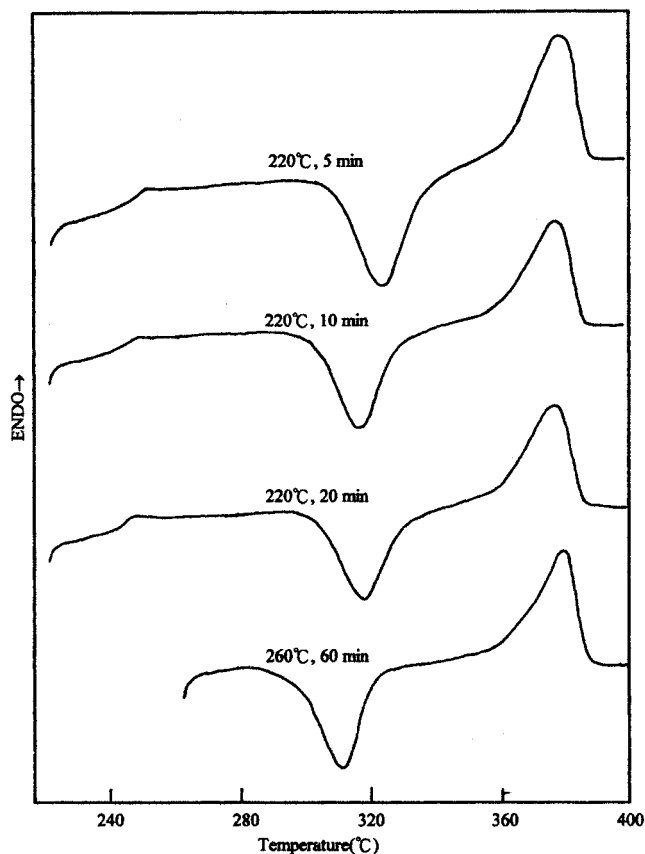

Figure 2 Successive DSC heating curves of PL450 after crystallization at 220°C for various periods and 260°C for 20 min.

TABLE I
T_{cc}, T_m, and ΔH_c Values of the Successive DSC Heating Curves of PL450 After Isothermal Crystallization

Temperature (°C)	Parameter[a]	Time (min)				
		2	5	10	20	60
220	T_{cc}	—	325	318	319	—
	T_m		380	379	378	
	ΔH_c		~ 0	~ 0	~ 0	
240	T_{cc}	—	322	327	320	
	T_m		380	379	378	—
	ΔH_c		~ 0	~ 0	~ 0	
260	T_{cc}	—	322	326	319	313
	T_m		380	378	378	380
	ΔH_c		~ 0	~ 0	~ 0	
280	T_{cc}	318	306	309	NA	NA
	T_m	379	380	380	380	381
	ΔH_c	2.7	8.1[c]	15.3[a]	26.3	28.5
300	T_{cc}	NA	NA	NA	NA	—
	T_m	380	382	380	380	
	ΔH_c	16[c]	28.9	27.6	29.5	
320	T_{cc}	NA	NA	NA	NA	—
	T_m	377	378	375	375	
	ΔH_c	25.3	29.0	27.6	28.2	
340	T_{cc}	NA	NA	NA	NA	NA
	T_m	381	381	380	380	380
	ΔH_c	5.2	28.4	27.0	28.0	28.8
360	T_{cc}	—	NA	NA	NA	NA
	T_m		NA	NA	387	389
	ΔH_c		0	0	7.8[c]	24.0[c]

[a] T_{cc} measured in °C; T_m measured in °C; ΔH_c measured in J/g.
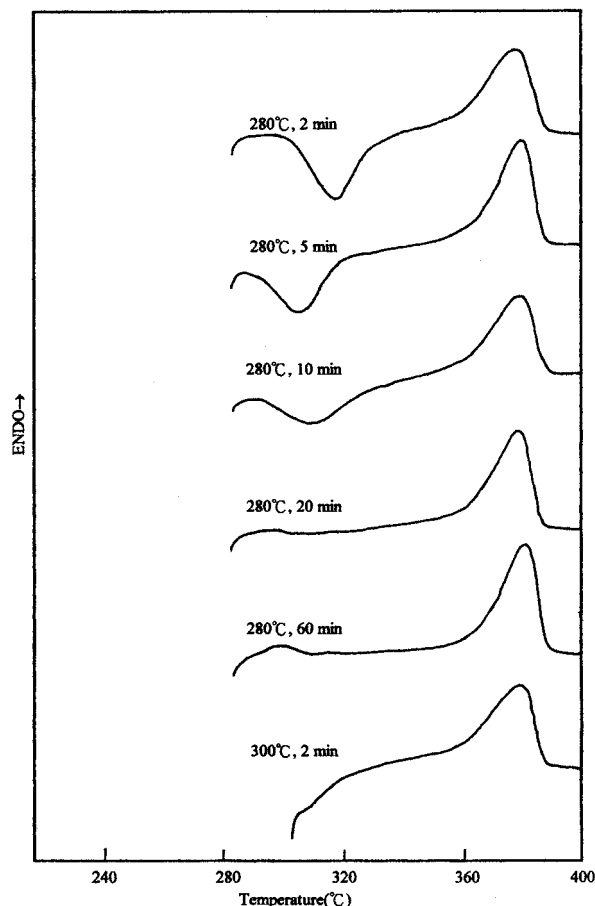[b] NA, not obtained.
[c] Estimated value.

Figure 3 Successive DSC heating curves of PL450 after crystallization at 280°C for various periods and 320°C for 20 min.

shown in Table I. Thus, PL450 cannot crystallize significantly at an isothermal condition of 240–260°C within 60 min.

The successive DSC heating curves of PL450 after crystallization at 280°C for various periods and 300°C for 2 min are shown in Figure 3. The observed T_{cc}, T_m, and ΔH_c of PL450 isothermally crystallized at 280–300°C are summarized in Table I. It can be seen that the ΔH_c of PL450 after crystallization at 280°C increases as the isothermal time increases, and reaches a plateau value of about 28 J/g at times > 20 min. In other words, PL450 can crystallize significantly at 280°C. Because the isothermal crystallization time at 280°C was ≥20 min, the sample crystallized as it could, and thus no T_{cc} is observed in the successive DSC heating curves. Similarly, no T_{cc} is observed in the successive DSC heating curves of PL450 after crystallization at 300°C for ≥5 min, as shown in Table I. This indicates that PL450 can crystallize in a rather fast rate at 300°C. The successive DSC heating curve after crystallization at 300°C for 2 min, as shown in Figure 3, does show a cold

crystallization phenomenon, but the cold crystallization exotherm is disturbed by the thermal imbalance of the DSC. Thus the ΔH_c value is estimated according to the successive DSC heating curves in combination with the ΔH_c values of PL450 after crystallization at other temperatures for 2 min. Clearly, the crystallization rate of PL450 at 300°C is greater than that at 280°C.

The successive DSC heating curves of PL450 after crystallization at 320°C for various periods exhibit a T_m but show no T_{cc}. The ΔH_c value 2-min curve is 25.3 J/g and other ΔH_c values are about 28 J/g, as shown in Table I, indicating that the sample had crystallized to its best under these conditions.

The successive DSC heating curves of PL450 after crystallization at 340 and 360°C for different periods are shown in Figure 4. The observed T_m and ΔH_c data are listed in Table I. The ΔH_c value of PL450 after crystallization at 340°C for 2 min is 5.2 J/g and then reaches a plateau of about 28 J/g for an isothermal time of ≥5 min. Thus PL450 can crystallize as it can at a temperature of 340°C for more than 5 min. More interesting, the melting peaks of the successive DSC heating curves of PL450 after crystallization at 340°C
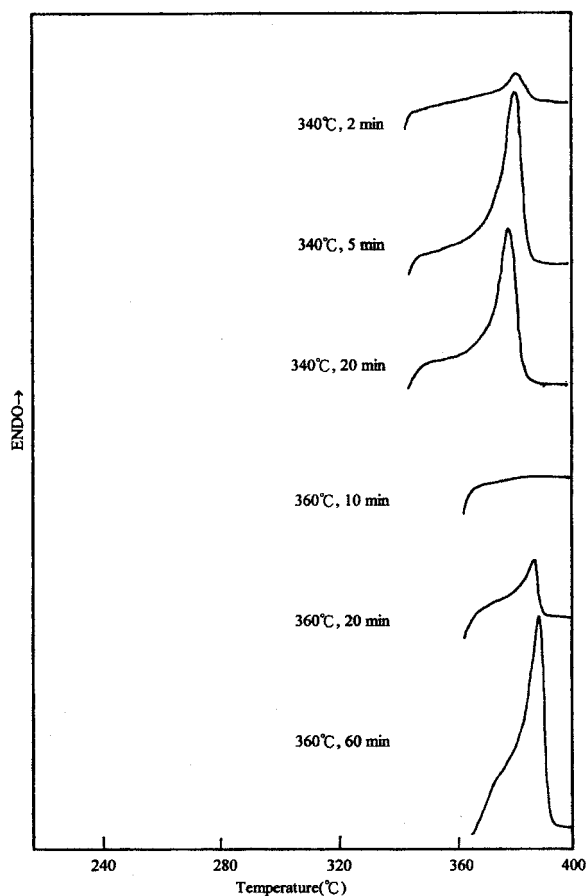

Figure 4 Successive DSC heating curves of PL450 after crystallization at 340 and 360°C for different periods.
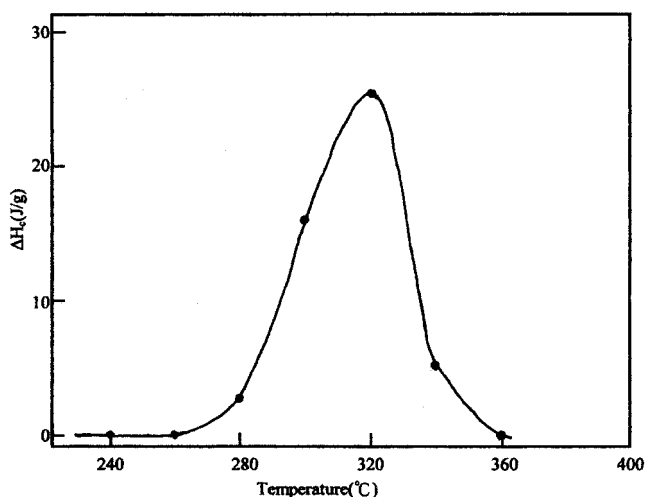
Figure 5 ΔH_c versus temperature curve after crystallization for 2 min.

for ≥ 5 min are somewhat narrower than those at $\leq 320°C$. Possibly, smaller or less perfect crystallites could not be formed at a temperature as high as 340°C, and this allowed the melting endotherm to narrow to some extent.

The ΔH_c value of PL450 after crystallization at 360°C for no more than 10 min is zero, indicating that PL450 cannot crystallize at 360°C within 10 min. However, when the isothermal crystallization time at 360°C is ≥ 20 min, PL450 can crystallize, and the ΔH_c value increases with time as expected. The successive DSC heating curves of PL450 after crystallization at 360°C for a time not less than 20 min exhibit a higher T_m value than that at other temperatures. The T_m and ΔH_c data shown in Table I indicate that an isothermal crystallization temperature of 360°C may have an annealing effect to raise the T_m on PL450.

It can be seen from Table I that the crystallization rate is significantly influenced by temperature. The plot of ΔH_c versus temperature after crystallization for 2 min is shown in Figure 5. This curve is more or less similar to the crystallization rate versus temperature curve. Two major temperature-related factors govern the crystallization rate of PL450 from the molten state. One factor is the mobility of the polymer chains or the polymer segments affected by the T_g. Another factor is the driving force for crystallization, which increases with the supercooling (the difference between the crystallization temperature and the T_m). Below T_g (about 250°C), the polymer segments of PL450 are frozen, the crystallization rate is extremely slow, and it is not unexpected that the ΔH_c after crystallization at 220 or 240°C within 60 min is almost zero. Above T_g, as the crystallization temperature increases, the crystallization rate

first increases, reaching a maximum at about 320°C, and decreases as a balance of the above-mentioned two factors as shown in Figure 5. More interesting, the crystallization rate at a temperature of 300 to 340°C seems to be very fast. PL450 seems to crystallize as it can within this temperature range in 5 min. This is why the T_{cc} is around 320°C for the quenched samples as shown in Table I. From a practical viewpoint, a mold temperature of about 320°C may allow PL450 to develop enough crystallinity in a reasonably short molding cycle. Moreover, a quenched PL450 sample may be annealed at 300–340°C to obtain enough crystallinity within a very short time.

CONCLUSIONS

The effect of temperature on the crystallization rate of PL450 can be described as the balance between the mobility of the polymer segment and the extent of supercooling. Within the temperature range of 300–340°C, the crystallization rate of PL450 is practically fast for the development of enough crystallinity in molding or annealing.

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