

# Fast Crystallization of Liquid Crystalline Copolyesters Based on Poly(ethylene terephthalate)

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**ABSTRACT:** Crystallization of a series of liquid crystalline copolyesters prepared from *p*-hydroxybenzoic acid (HBA), hydroquinone (HQ), terephthalic acid (TA), and poly(ethylene terephthalate) (PET) was investigated by using differential scanning calorimetry (DSC). It was found that these copolyesters are more crystalline than copolyesters prepared from PET and HBA. Insertion of HQ–TA disrupts longer rigid-rod sequences formed by HBA and thus enhances molecular motion and increases the crystallization rate. The effects of additives on the crystallization of the copolyesters were also studied. Sodium benzoate (SB) and sodium acetate (SA) increase the crystallization rate of the copolyesters at low temperature, but not at high temperature. It is most likely that liquid crystalline copolyesters do not need nucleating agents, and small aggregates of local-oriented rodlike segments in nematic phase could act as primary nuclei. Chain scission of the copolyesters caused by the reaction with the nucleating agents was proved by the determination of intrinsic viscosity and by the IR spectra. Diphenylketone (DPK) was shown to effectively promote molecular motion of chains, leading to an increase in the crystallization rate at low temperature, but it decreased the crystallization rate at high temperature. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 497–503, 2001

**Key words:** poly(ethylene terephthalate); liquid crystalline polymer; crystallization; melting; nucleation

## INTRODUCTION

The copolyesters of *p*-hydroxybenzoic acid (HBA) and PET was first synthesized by Jackson and Kuhfuss.<sup>1</sup> Their initial study was followed by investigations of the thermal properties,<sup>2–5</sup> crystal structure,<sup>2,6,7</sup> phase separation and morphol-

ogy,<sup>2–4,6,8</sup> and sequence distribution<sup>1,9–14</sup> of the copolyesters.

In our previous work<sup>15</sup> we copolymerized PET with more comonomers, including hydroquinone (HQ) and terephthalic acid (TA), in addition to HBA, and obtained a new copolyester type of PET/HBA/HQ/TA. These liquid crystalline copolyesters were found to be more crystalline than PET–HBA copolyesters. The insertion of TA–HQ into PET–HBA chains may enhance molecular motion by reducing rigid-rod sequence lengths of HBA and thus accelerating the crystallization rate.

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**Table I** Composition and Intrinsic Viscosity of Copolyesters Used in This Research

| Copolyester | Monomer        |     |      |      | Polymer                      |      |            |                |
|-------------|----------------|-----|------|------|------------------------------|------|------------|----------------|
|             | Feed Ratio (%) |     |      |      | Composition (%) <sup>a</sup> |      |            |                |
|             | PET            | HBA | HQ   | TA   | HBA                          | HQ   | [ $\eta$ ] | LC             |
| I           | 40             | 60  | 0    | 0    | 60                           | 0    | 0.65       | N <sup>b</sup> |
| II          | 50             | 50  | 0    | 0    | 50                           | 0    | 0.63       | N              |
| III         | 50             | 40  | 5    | 5    | 40                           | 5    | 0.63       | N              |
| IV          | 50             | 25  | 12.5 | 12.5 | 25                           | 12.5 | 0.64       | N              |
| V           | 50             | 15  | 17.5 | 17.5 | 15                           | 17.5 | 0.64       | N              |
| VI          | 50             | 10  | 20   | 20   | —                            | —    | 0.60       | N              |

<sup>a</sup> Determined by <sup>1</sup>H-NMR.<sup>b</sup> Nematic.

Further improvement of the crystallization rate of copolyesters would be desirable for manufacturing by conventional injection-molding processes and for raising the heat-deflection temperature (HDT) of the molding parts. In recent years various nucleating agents and nucleating promoters have been synthesized in our laboratory, and a detailed study of their effects on the crystallization behavior of PET was carried out.<sup>16,17</sup> We attempted to extend our knowledge and experience in fast crystallization of PET to liquid crystalline polymers (LCP). The effects of nucleating agents and nucleation promoters on the crystallization of PET/HBA/HQ/TA copolyesters are presented in this article and compared with the crystallization behavior of the copolyesters without additives.

## EXPERIMENTAL

### Materials

PET/HBA/HQ/TA copolyesters were prepared by melting polycondensation. The polymerization procedure and characterization of the copolyesters were described previously.<sup>15</sup> Table I lists the copolyesters used in this research and their compositions. Reagent-grade additives including sodium benzoate (SB), sodium acetate (SA), and diphenylketone (DPK) were used as received for the study of their effects on the crystallization behavior of the copolyesters.

### Preparation of Samples

Copolyester-additive mixtures were prepared by adding an adequate amount of solution of the

additives in alcohol into powder of the copolyesters to attain a predetermined content of the additives. This was followed by evaporation of the alcohol at 50–60°C while stirring the mixture, and finally drying the mixtures at 100°C in a vacuum oven for 72 h.

### Viscosity Determination of Copolyesters

Intrinsic viscosity [ $\eta$ ] of the copolyesters was used as a relative indication of molar mass. The intrinsic viscosity was measured at a concentration of 0.25 g/dl in a mixed solvent of phenol-tetrachloroethane (vol ratio 60:40) at 30°C.

### IR Spectroscopy

Copolyesters were mixed with SB in a Brabender plastograph at 290°C for 3.5 min. Thin films of the mixtures were obtained by pressing samples at 275°C and quenching in methyl alcohol at 0°C. A Nicolet (Madison, WI) FTIR-5DX infrared spectrophotometer was used for the IR determination.

### Crystallization

The crystallization of copolyesters and additive-containing copolyesters was studied using a Du Pont (Wilmington, DE) 2000-910 differential scanning calorimeter (DSC) in a nitrogen atmosphere. The sample weight was about 5 mg, with an empty aluminum pan as a reference. Calibration was conducted with standard indium. Before performing crystallization, the samples were melted at  $290 \pm 0.5^\circ\text{C}$  for 3.5 min to remove thermal history and then quenched to 0°C to obtain amorphous specimens.

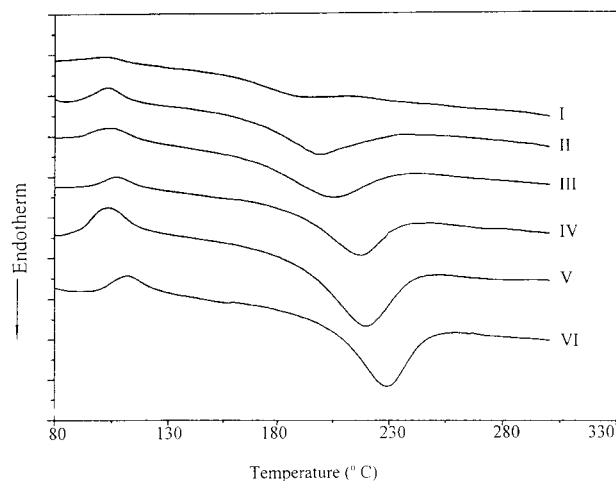
Nonisothermal crystallization of the amorphous specimens was carried out in the DSC cell at a heating rate of 20°C/min, and cold crystallization temperature ( $T_{ch}$ ) was obtained from the DSC heating traces. For hot crystallization temperature ( $T_{cc}$ ), the samples were first melted in the DSC cell and held at 290°C for 3.5 min and then cooled from the melt at a cooling rate of 5°C/min.  $T_{cc}$  was obtained from the DSC cooling traces.

Isothermal crystallization in the low-temperature region was performed by placing the amorphous samples into the DSC cell at a selected temperature and holding at this temperature until the completion of crystallization. For isothermal crystallization in the high-temperature region, the sample was directly melted in the DSC cell at 290°C for 3.5 min and then cooled quickly to a selected temperature and held until the crystallization was completed. The DSC registered the enthalpy change rate ( $\delta H/\delta t$ ) of the samples as a function of time ( $t$ ) at a prefixed crystallization temperature. From these curves  $\delta H/\delta t$  was integrated against  $t$  to obtain the half-time of crystallization ( $t_{1/2}$ ), defined as the time required for half the final crystallinity to develop.

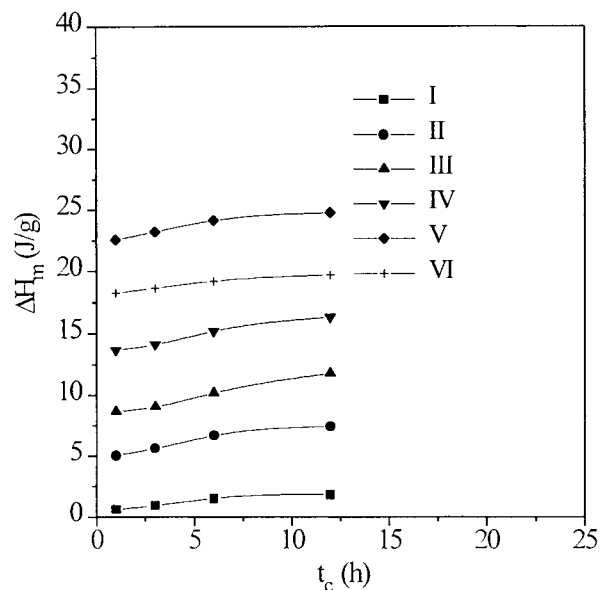
## RESULTS AND DISCUSSION

### Crystallization of PET/HBA/HQ/TA Copolyesters

Figure 1 illustrates the DSC heating traces of the as-prepared copolyesters, indicating crystalliza-



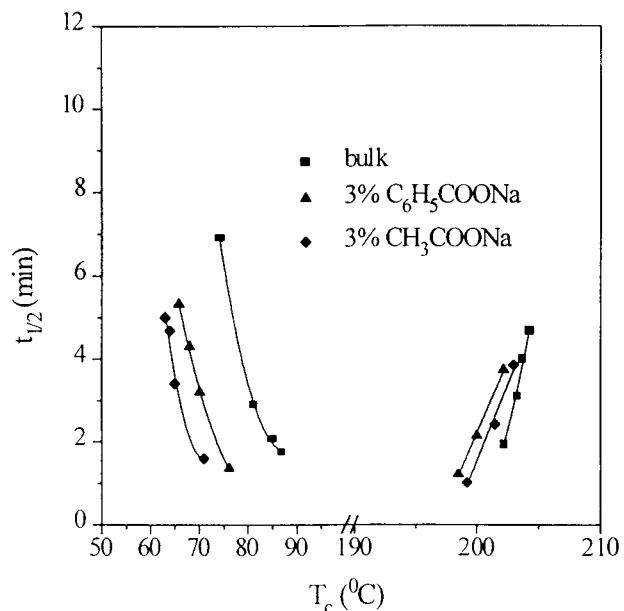
**Figure 1** DSC heating traces for the as-prepared copolyesters. I, II, III, IV, V, and VI represent copolyester I, copolyester II, copolyester III, copolyester IV, copolyester V and copolyester VI, respectively.



**Figure 2** A plot of the heat of fusion versus crystallization time for copolyesters I–VI after crystallization at 150°C. I, II, III, IV, V, and VI represent copolyester I, copolyester II, copolyester III, copolyester IV, copolyester V and copolyester VI, respectively.

tion behavior to be significantly affected by chain structure. There are no apparent crystallization and melting peaks in the DSC curve for copolyester I, while cold crystallization peaks are clearly observed in the DSC curves for copolyester II and copolyesters III–VI, containing HQ/TA. This indicates that copolyester I is hard to crystallize, but the crystallization of copolyesters II–VI is relatively easier and faster. Figure 2 shows a comparison of the heat of fusion ( $\Delta H_m$ ) of the copolyesters after isothermal crystallization at 150°C for various times; obviously, the  $\Delta H_m$  increases when copolyesters contain HQ/TA. This observation shows that the copolyesters prepared from PET, HBA, HQ, and TA are more crystalline than the copolyesters obtained from PET and HBA. Copolyester V reaches a larger  $\Delta H_m$ ; therefore, it has a larger crystallization rate and crystallinity compared with the others.

For copolyester II, the increase in crystallization rate is due to a higher ratio of flexible groups in the chains compared to copolyester I. For copolyesters III–VI, the increase in crystallization rate and crystallinity could be explained as follows: the insertion of HQ–TA into PET–HBA chains reduces rigid-rod sequence lengths of HBA and thus enhances the molecular motion of the chains. Either longer HBA sequences at a higher



**Figure 3** Influences of nucleating agents on crystallization of copolyester V.

HBA mole fraction or longer HQ–TA sequences at a higher HQ/TA mole fraction could inhibit molecular motion; equimolar combinations of HBA, HQ, and TA units would be the best case for the acceleration of the crystallization rate, which is quite close to the composition of copolyester V. On the other hand, the influence of the order within the copolyester chain on the crystallization behavior is also significant. Oxybenzoate units are asymmetrical; hence, they can be inserted into one polymer chain with different directions (AB or BA). This should decrease the probability of the formation of ordered crystals. A detailed discussion on the crystallization behavior of these copolyesters was published elsewhere.<sup>15</sup>

#### Influence of Nucleating Agents on Crystallization of Copolyester V

Some metal salts of aromatic acid or aliphatic carboxylic acid, such as sodium benzoate (SB) and sodium acetate (SA), are typical nucleating agents for the crystallization of PET.<sup>17–22</sup> The effects of SB and SA on the crystallization of copolyester V were investigated and are shown in Figure 3. Compared to the crystallization of the copolyesters without additives, the curves of half time of crystallization ( $t_{1/2}$ ) versus crystallization temperature ( $T_c$ ) for copolyesters containing SB or SA apparently shift to lower temperature in the low-temperature region (Fig. 3), meaning a

substantial increase in the crystallization rate. In the high-temperature region, the curves of  $t_{1/2}$  versus  $T_c$  remain almost unshifted, indicating there is no increase in crystallization rate.

The  $t_{1/2}$  represents the overall crystallization rate and is determined both by rates of nucleation and by linear growth. According to the classical theory of polymer crystallization,<sup>23</sup> the nucleation rate of primary nuclei is controlled by the free enthalpy ( $\Delta G^*$ ) of crystallization of a nucleus of critical size and the free energy of activation ( $\Delta G_\mu$ ), which governs diffusion of polymer segments across the phase boundary. In the high-temperature region,  $\Delta G^*$  is the dominant factor controlling the nucleation rate, while  $\Delta G_\mu$  is the main influence on the nucleation rate in the low-temperature region because of greater supercooling.

In the low-temperature region the addition of small organic molecules, such as SB or SA, can improve the molecular motion of chains and therefore leads to a reduction of  $\Delta G_\mu$  and an increase in the crystallization rate. In the high-temperature region, the crystallization behavior of the copolyesters in the presence of SB or SA is in contrast to that of PET, in which both SB and SA accelerate its crystallization rate. This observation could be explained according to the structural features of LCP. In our opinion liquid crystalline polymers do not need nucleating agents. Small aggregates of local-oriented rodlike segments in nematic phase could act as primary nuclei and could even be added to the surface of the growing crystal as secondary nuclei during the growth process. Therefore, the addition of nucleating agents may not affect the crystallization of the copolyesters. What is needed for fast crystallization of LCP is improvement of molecular motion. However, the melting points of the copolyesters are shown to decrease considerably after the addition of SB or SA (Fig. 8). Assuming a parallel decrease in equilibrium melting temperatures, the plots of  $t_{1/2}$  against supercooling  $T$  may display a shifting of  $t_{1/2}$ -versus- $T$  curves toward higher temperature in the high-temperature region. Accordingly, further study is needed to be able to illustrate the effects of nucleating agents on the crystallization of liquid crystalline copolyesters.

On the other hand, such organic agents do not behave as inert heterogeneous substrates but dissolve into polymer melt and react with chains, accompanied by chain scission. In the case of PET, such reaction has been verified by Legras et

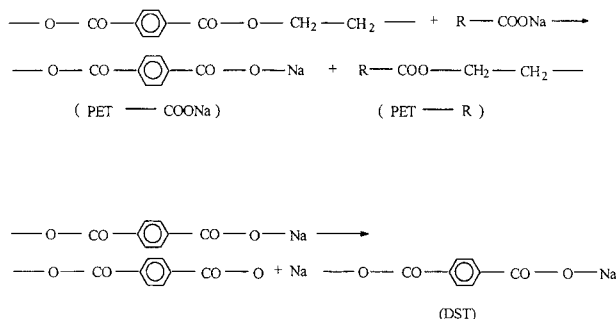


Figure 4 Reaction scheme.

al.<sup>19,22</sup> and by Bu et al.<sup>17</sup>; the reaction scheme is shown in Figure 4. For the mixtures of copolyesters and SA or SB, chain scission of the copolyesters was also observed after heat treatment at 290°C for 3.5 min, as indicated by determination of the intrinsic viscosity,  $[\eta]$ . The decrease of  $[\eta]$  that accompanied the addition of 3 wt % SB and SA was 20.2% and 28.3%, respectively. Moreover, we have confirmed the formation of PET-COONa (see Fig. 5) through IR analysis. A 50/50 (wt %) mixture of SB and copolyester V was made at 290°C for 3.5 min in a Brabender plastograph, and it was dissolved in phenol/tetrachloroethane. The solution was filtered to remove insoluble SB and subsequently precipitated by the addition of a methyl-water mixture (4:1 ratio). The precipitation procedure was accompanied by the elimination of DST (Fig. 4) because it was still soluble. The IR spectra of the resulting precipitate is

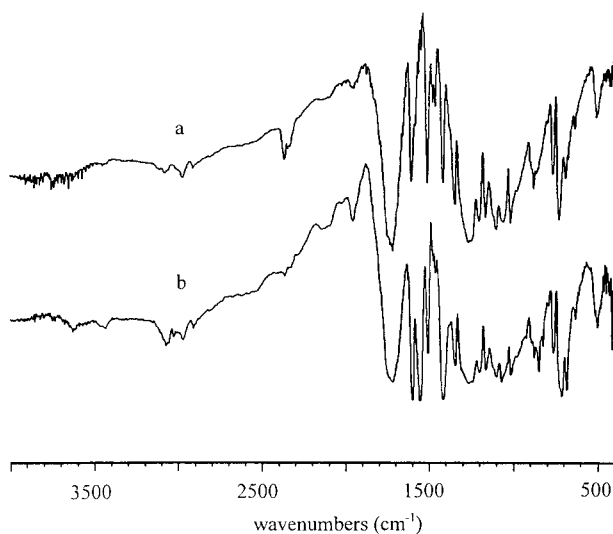


Figure 5 IR spectra of copolyester V (a) before reaction with SB, (b) after reaction with SB.

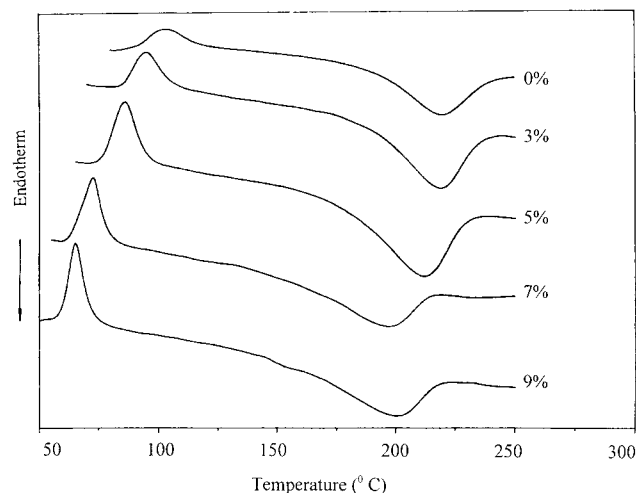


Figure 6 Effects of DPK on cold crystallization of copolyester V.

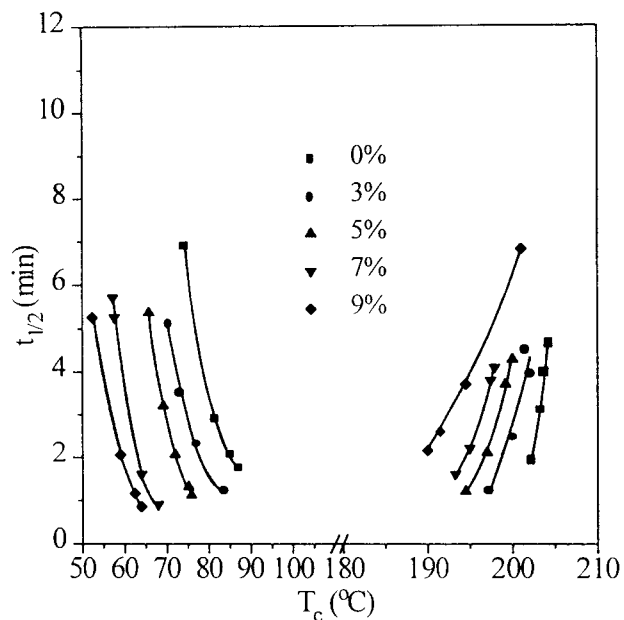
shown in Figure 5(b). Compared with the IR spectra of copolyester V [Fig. 5(a)], this precipitate shows a characteristic absorption at  $1550\text{ cm}^{-1}$ , attributable to the stretch vibration of  $\text{---COONa}$  formed by the reaction between the copolyester and SB.

#### Influence of Nucleating Promoter on Crystallization of Copolyester V

As shown in Figure 6, the addition of diphenylketone (DPK) has a pronounced influence on cold crystallization of copolyester V. Cold crystallization peaks become large and shift to low temperature with increasing DPK. Obviously, DPK is not a nucleating agent; it may act as a plasticizer, promoting molecular motion of the copolyesters. A higher content of DPK would improve chain mobility more efficiently and would lead to a lower cold-crystallization temperature,  $T_{ch}$ . The decrease in  $T_{ch}$  is important for fabrication of crystalline polymers because it allows injection molding of the copolyesters at a lower mold temperature.

Figure 7 shows the effect of various contents of DPK on the crystallization rate of copolyester V. In the low-temperature region a considerable increase in the crystallization rate follows the addition of DPK. Since DPK enhances molecular motion of chains and lowers the free energy of activation for the diffusion of segments  $\Delta G_{\mu}$ , the nucleation rate and hence the crystallization rate rise. While in the high-temperature region, the  $t_{1/2}$ -versus- $T_c$  curves for mixtures of copolyester-

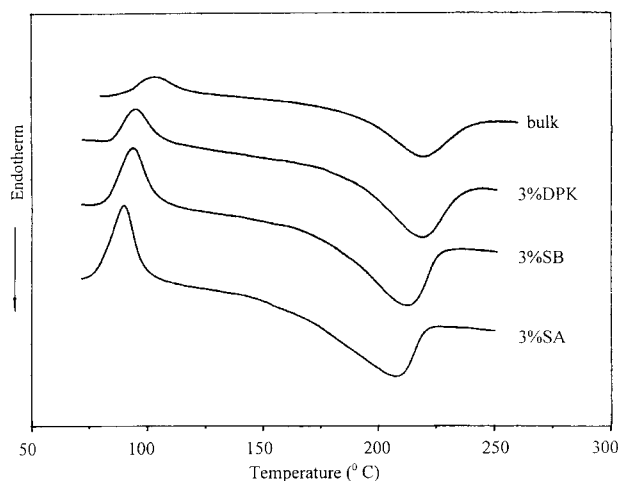




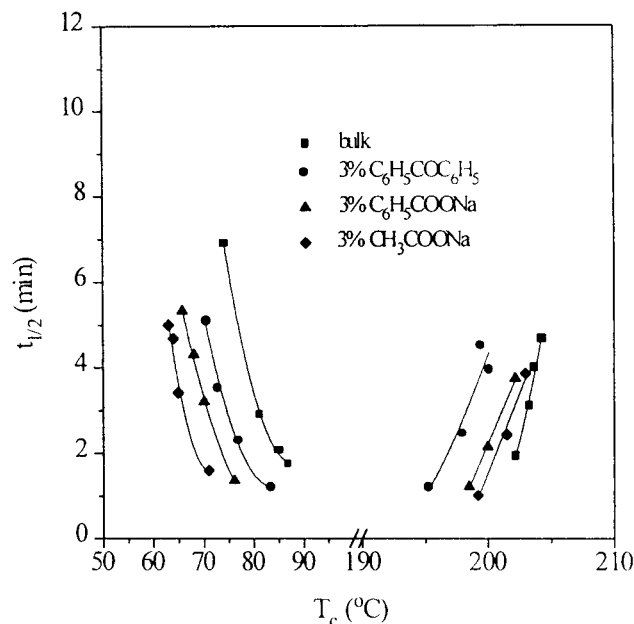
**Figure 7** Effects of DPK on crystallization rate of copolyester V.

DPK shift to lower temperature. It seems that crystallization of the copolyesters is impeded by the addition of DPK. Since DPK has a low melting point (about 50°C), it can be finely dissolved into the melt of the copolyesters; therefore, it may serve as a diluent and hinder the crystallization of copolyesters.

For comparison, the effects of SA, SB, and DPK on the crystallization of copolyester V are collected in Figures 8 and 9. It can be observed that



**Figure 8** Comparison of cold crystallization behavior of copolyester V after mixed with SA, SB, and DPK at a ratio of 3%.



**Figure 9** Comparison of crystallization rate of copolyester V after mixed with SA, SB, and DPK at a ratio of 3%.

both SA and SB are better than DPK for the depression of the cold-crystallization temperature (Fig. 8) and for the acceleration of the crystallization rate (Fig. 9). However, both SA and SB cause a significant decrease in  $[\eta]$ . The decrease in molar mass may contribute to the observed increase in crystallization rate, but it will destroy the mechanical properties of the copolyesters.

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