

Influence of Incorporation of 4,4'-Biphenol and Hydroquinone Units into Poly(ethylene terephthalate) on the Crystallization Properties

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A PET copolymer containing small amount of 4,4'-diphenyldicarboxylic acid and 4,4'-biphenol showed higher crystallization rate than PET at the crystallization temperatures below 160 °C. When hydroquinone was incorporated instead of 4,4'-biphenol, the crystallization rate was lower than that of PET at whole range of crystallization temperatures. These results suggest a possibility of increasing the crystallization rate of PET by incorporation of an appropriate arylate-unit.

Poly(ethylene terephthalate) (PET) is used in various industrial fields such as fibers, films, bottles and moldings. In the case of application as moldings, PET has a disadvantage of slow crystallization rate that is sometimes controlled by addition of crystal nucleation agents and/or plasticizers.¹⁻³ The crystallization properties are also changed by the modification of polymer structure. In many cases, however, it is known that nonuniformity in the polymer structure induced by copolymerization reduces the crystallizability of homopolymer. This report will show that incorporation of small amount of a certain arylate-unit into PET resulted in a remarkable change in crystallization behavior of the homopolymer. This finding provides a new approach to widen the industrial field in which PET can be used.

Copolymers were synthesized by the acidolysis reaction and following polycondensation.^{4,5} PET, 4,4'-diphenyldicarboxylic acid (DP), 4,4'-biphenol diacetate (BP) and hydroquinone diacetate (HQ) were used as starting materials (each comonomer was fed by 5 mol%). The structures of copolymers prepared are shown in Scheme 1, and abbreviated as DP-BP and DP-HQ, respectively. In the copolymerization, 20 g of the mixture of PET and the comonomers described above was heated with 10 ml of chlorobenzene up to 280 °C and kept at the temperature for 30 min with stirring to continue acidolysis reaction. Then, vacuum was applied gradually to reach 0.3 mmHg in 30 min, and the polycondensation was continued for 3 hours. As the copolymers as-polymerized showed relatively low solution viscosities (η_{sp}/C) around 0.4, solid state polymerization was carried out to increase their molecular weights up to the same level of η_{sp}/C as the original PET (0.84). Comonomer contents in the copolymers were determined by ¹H-NMR: DP-BP contained 4 mol% of DP and 4 mol% of BP, and DP-HQ contained 5 mol% of DP and 3 mol% of HQ, respectively. The glass transition temperature (T_g) and the equilibrium melting temperature (T_m^0) for the polymers are as follows: DP-BP ($T_g = 86$ °C, $T_m^0 = 271$ °C), DP-HQ ($T_g = 85$ °C, $T_m^0 = 261$ °C), PET ($T_g = 81$ °C, $T_m^0 = 280$ °C).

Wide angle X-ray diffraction was measured to study the

crystalline structure of the copolymers. Both copolymers showed the same diffraction pattern as that of PET with peaks at $2\theta = 16.2, 17.8, 22.5$ and 26.1° . These polymers formed isotropic melt above the melting temperatures and quenching of the melt samples by liquid nitrogen gave totally amorphous samples. Crystallization in these systems is considered that ethylene terephthalate segments form the crystal domain while excluding the comonomer segments from the crystal region.

Time-resolved light scattering was carried out to measure the crystallization rates under isothermal conditions, by using a light scattering apparatus similar to that described in a literature.⁶ A sample was kept at 300 °C for 2 min between two pieces of cover glass to form a completely melt film (thickness: ca. 30 μm), and quickly transferred onto a hot stage (Linkam TH-600PH) in the light scattering apparatus set at a crystallization temperature. Change of the angular distribution of scattering intensity at an azimuthal angle of 45° under cross-polarized (H_V) optical alignment with time was recorded.

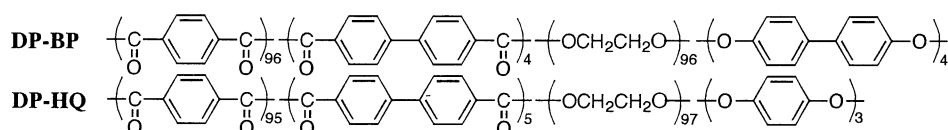
Invariant Q_d of the scattering intensity for H_V (I_{H_V}) is defined by equation 1⁷ and also described by equation 2,

$$Q_d = \int I_{H_V} q^2 dq \quad (1)$$

$$Q_d \propto \langle \delta^2 \rangle = f_c (\alpha_1 - \alpha_2)^2 \quad (2)$$

where q is the magnitude of the scattering vector, $\langle \delta^2 \rangle$ is the mean-square anisotropy, f_c is the volume fraction of the crystalline domain, and α_1 and α_2 are the principal polarizabilities of the crystal lamella. Overall crystallization rates for the copolymers were determined from the slope of $Q_d(t)/Q_d(\infty)$ (dQ/dt) in the crystallizing region. The results are shown in Figure 1. Both copolymers showed smaller maximums of dQ/dt than PET. However, DP-BP showed higher crystallization rates than PET at lower crystallization temperatures. Figure 2 shows the induction time for the crystallization. DP-HQ had longer induction time than PET at every crystallization temperature in accordance to the behavior of crystallization rate. Although DP-BP showed a similar behavior at higher crystallization temperatures, it showed short induction times at crystallization temperatures below 160 °C.

Characteristic behavior of DP-BP was also seen in the scattering profiles. Figure 3 and 4 show the time dependence of H_V light scattering profile for the copolymers at 200 °C. In the case of DP-HQ, as seen in PET, there was a scattering peak as a result of four-leaf clover pattern, which means the spherulite growth. Increase in diameters of the spherulites is observed with the shift of scattering peak to lower angle with time. The scattering profile of DP-BP showed no apparent peak and the



Scheme 1.

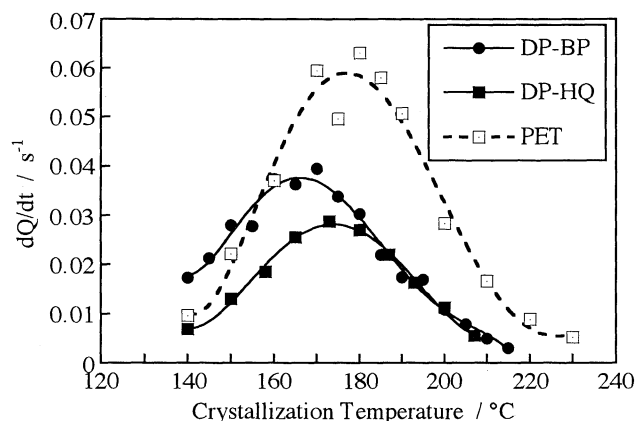


Figure 1. Temperature dependence of overall crystallization rate (dQ/dt) of PET-copolymers under isothermal conditions.

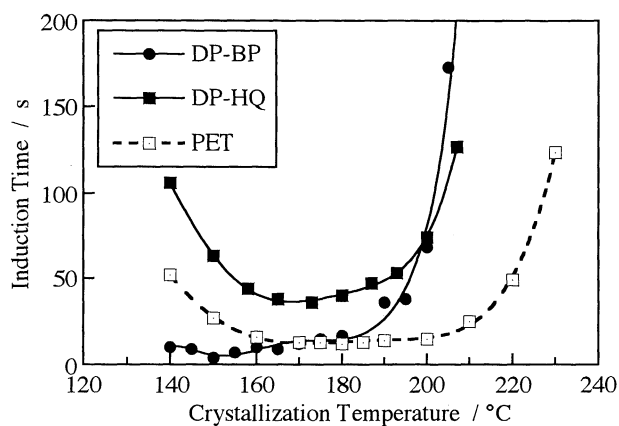


Figure 2. Temperature dependence of induction time of PET-copolymers under isothermal conditions.

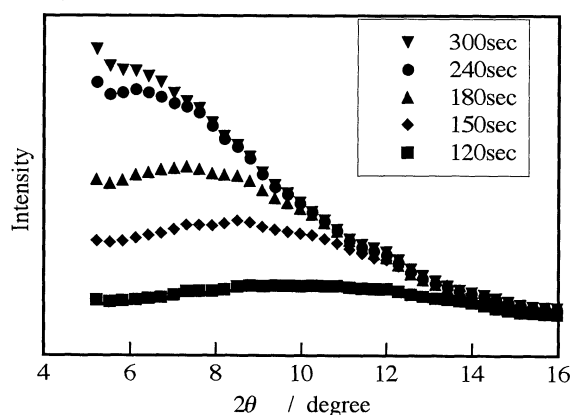


Figure 3. Time dependence of light scattering profile for DP-HQ under isothermal crystallization at 200°C.

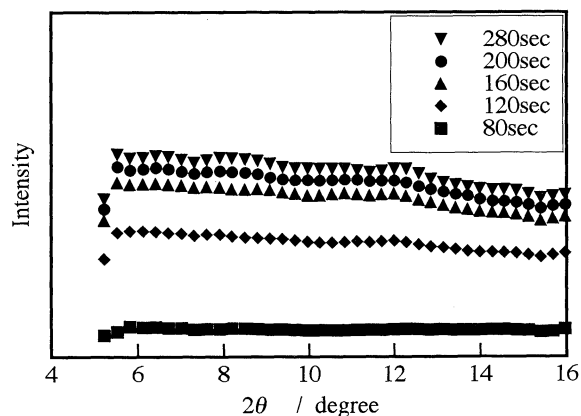


Figure 4. Time dependence of light scattering profile for DP-BP under isothermal crystallization at 200°C.

scattering intensity increased similarly at any angle with time. Much smaller spherulites and higher nucleation density were detected by microscopic observation. These results suggest that size and shape of the spherulites were irregular in this system, and the randomness of optical anisotropy increased.

High nucleation density is a remarkable characteristic of DP-BP. Therefore, it is considered that the crystallization rate became higher than other polymers at the temperature range in which crystal nucleation is dominant to determine the crystallization rate. This is also supported by the extremely short induction times of DP-BP in this temperature region.

It was found that crystallization properties of PET were influenced by incorporation of arylate units. The enhanced crystal nucleation detected in DP-BP suggests that there is a possibility to improve the crystallization properties of PET by copolymerization. Structural effects in details, such as comonomer structure and content, will be reported in following papers.

References and Notes

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