Modification of Crystallization Properties of Poly(ethylene terephthalate) by Copolymerization with Arylate-Units III. Bisphenol-A- and Bisphenol-S-Containing Copolymers

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(Received March 25, 1996)

ABSTRACT: Crystallization properties of the copolymers of poly(ethylene terephthalate) (PET) comprising small amount of 4,4'-isopropylidenediphenol (bisphenol-A) and bis(4-hydroxyphenyl)sulfone (bisphenol-S) units were compared by isothermal crystallization with the time-resolved light scattering method. These copolyesters were prepared from PET, terephthalic acid and diol diacetates by acidolysis reaction and following polycondensation. The copolymers showed a spherulite growth like PET homopolymer, though their crystallization rates decreased and induction times increased with increase in comonomer content. An accelerated nucleation, which was observed in the case of some rigid arylate units-containing copolyesters, was not detected in these copolymers. The bisphenol-S-containing copolymers showed lower crystallizability than the corresponding bisphenol-A-containing copolymers.

KEY WORDS Poly(ethylene terephthalate) / Bisphenol-A / Bisphenol-S / Copolymers / Crystallization Rate / Isothermal Crystallization /

Crystallizability of polymers is usually decreased by copolymerization. This is because the regular chain packing for crystallization is inhibited by the introduction of comonomer segments. In previous papers,^{1,2} however, it was found that certain arylate-unit-containing poly(ethylene terephthalate) (PET) copolymers showed increased crystallizability compared to PET homopolymer.

The papers described about the crystallization properties of PET copolymers comprising 4,4'-biphenylene terephthalate unit or paraphenylene terephthalate unit. In these systems, the copolymers with very low level of the comonomer content such as 2 mol% showed the crystallization rate slower than that of PET. When the comonomer content increased, increased nucleation density and appearance of smaller and irregular spherulites were observed. As a result, at first, an increase in the crystallization rate was observed at lower region of the crystallization temperature, then more higher content of the comonomers around 10 mol% gave the crystallization rates higher than those of PET at a whole range of the crystallization temperature. These two copolymer systems showed similar crystallization tendency, however, the copolymers containing paraphenylene terephthalate unit needed higher comonomer content to display a remarkable increase in the crystallization rate than the copolymers containing 4,4'-biphenylene terephthalate unit.

The biphenylene terephthalate and paraphenylene terephthalate units form four and three consecutive paraphenylene moieties, respectively. The rigid characteristics of these segments may lead to a local orientation of the molecular chains on the molecular level and resulted in accelerated nucleation. In this article, in order to consider the structural effect on improvement of the crystallizability in arylate-unit-containing PET copolymers, series of PET copolymers comprising 4,4'-isopropylidenediphenol (bisphenol-A) unit and bis(4-hydroxyphenyl)sulfone (bisphenol-S) unit as aromatic diols were prepared, and their crystallization properties

were investigated.

EXPERIMENTAL

Materials

Poly(ethylene terephthalate) (Toyobo, RE530), terephthalic acid (Mitsui Petrochemical Industry), bisphenol-A (Nacalai Tesque, EP), bisphenol-S (Konishi Chemical Industry) and chlorobenzene (Nacalai Tesque, GR) were used without further purification.

Preparation of Diol Diacetates³

Bisphenol-A (50.0 g, 0.219 mol), acetic anhydride (150 ml) and 1 ml of sulfuric acid were stirred at 100°C for 30 min. After cooled to room temperature, the reaction mixture was poured into ice water. A white crystal obtained was collected and washed with 1 liter of 3% sodium hydroxide aqueous solution and pure water, and then dried. Recrystallization was carried out by using toluene/petroleum ether as a solvent. Yield 89%. mp 96°C.

Bisphenol-S diacetate was prepared with the same manner; Yield 66%. mp 171°C.

Preparation of Copolymers

Copolymers were synthesized from PET and equimolar combinations of terephthalic acid and the diacetate of bisphenol-A or bisphenol-S; first, acidolysis reaction of PET by the terephthalic acid occurs, then polycondensation of the carboxylic chain ends and the diol diacetate proceeds as illustrated in Scheme 1. No catalyst was added for the copolymerization to minimize influence of the residual catalyst on the crystallization properties of the resultant copolymers. As an example, preparation of the bisphenol-A-containing copolymer with a feed ratio of 10 mol% is described below.

PET (19.2 g, 0.100 mol), terephthalic acid (1.84 g, 0.0111 mol), bisphenol-A diacetate (3.47 g, 0.0111 mol) and 10 ml of chlorobenzene were placed in a glass vessel

Scheme 1.

at 150°C under nitrogen flow. The mixture was heated to 280°C and kept at the temperature for 30 min with stirring to proceed acidolysis reaction. Then, vacuum was applied gradually to reach 0.3 mmHg in 30 min, and the polymerization was continued for 3 hours.

Other copolymers were prepared by the same procedure except changing the comonomer feed ratio.

Characterization

Reduced viscosities were measured at a concentration of 0.4 g dl⁻¹ in a mixed solvent of *p*-chlorophenol and 1,1,2,2-tetrachloroethane (3:1, vol/vol) at 30°C. GPC measurement was performed on a Shodex GPC system-21 with Tosoh columns GMH_{XL}-GMH_{XL}-G2000H_{XL} (calibrated by polystyrene standards). The working temperature was 40°C, the solvent was a 98/2 mixture of chloroform and hexafluoroisopropanol and the detection was absorption at 254 nm. ¹H NMR spectra were obtained in a mixed solvent of dichloromethane-*d*₂ and deuterated trifluoroacetic acid with a Varian Gemini-200 spectrometer. Thermal transition temperatures were determined by using a differential scanning calorimeter (DSC) (Perkin-Elmer DSC-7) at a heating rate of 20°C min⁻¹ and a cooling rate of 10°C min⁻¹ under flowing nitrogen for quenched samples from the melt. When equilibrium melting temperatures were determined, each polymer was isothermally crystallized at several temperatures for 1 hour before DSC measurement. Thermogravimetric analysis (TGA) was conducted at a heating rate of 10°C min⁻¹ under flowing air or nitrogen using a thermogravimetric analyzer (Shimadzu TGA-50). Wide angle X-ray diffraction (WAXD) was conducted on a Rigaku rotating-anode generator (RV-200) and a scintillation counter with Nickel-filtered Cu-K_α radiation (40 kV, 100 mA). Optical microscopic observation was carried out on a Nikon Type OPTIPHOT2-POL polarized-light transmission microscope.

Isothermal Crystallization with Time-Resolved Light Scattering

Time-resolved light scattering was carried out with a light scattering apparatus described in the previous paper.¹ 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) of the light scattering apparatus set at a crystallization temperature. Change of the angular distribution of scattering intensity under cross-polarized (*H_v*) optical alignment with time was recorded.

RESULTS AND DISCUSSION

Characterization of Copolymers

As no catalyst was added for the copolymerization, the copolymers obtained showed relatively low solution viscosities (η_{sp}/c) around 0.3. The polymer compositions were determined by ¹H NMR. As small amount of the comonomers sublimed during the copolymerization, each copolymer contained *ca.* 80 mol% of the comonomers fed. All the polymerization proceeded as a homogeneous and transparent melt. Table I summarizes the results of preparation of four copolymers with the comonomer feed ratio of 10 and 20 mol% for each diol component: They are abbreviated as TA-BA-8, TA-BA-16, TA-BS-8, and TA-BS-16 by using the content of aromatic diol unit in the copolymers determined by ¹H NMR.

As shown in Table I, the melting temperature decreased with increase in comonomer content. This tendency was also seen in equilibrium melting points (T_m^0) for the copolymers, which were evaluated by the Hoffman-Weeks treatment⁴: T_m^0 is determined as an intersection of the extrapolation of the plots for T_m versus crystallization temperature (T_c) and the line for $T_m = T_c$. The results are shown in Figure 1. Compared to $T_m^0 = 280^\circ\text{C}$ for PET, the copolymers showed lower T_m^0 s: TA-BA-8, 260°C; TA-BA-16, 236°C; TA-BS-8, 248°C;

Table I. Preparation and properties of TA-BA and TA-BS copolymers

Polymer	Monomer feed ratio		Polymer composition ^a	η_{sp}/c^b dl g ⁻¹	DSC ^c					TGA/5% ^d	
					T_g	T_{ch}	T_m	T_{cc}	ΔH_m	In air	In N ₂
					°C	°C	°C	°C	J g ⁻¹	°C	°C
PET				0.84	81	148	257	208	42	352	402
TA-BA-8	TA/%	BA/%	BA/%	0.30	77	146	225	164	28	390	404
TA-BA-16	20	20	16	0.27	84	—	209	—	9	367	403
	TA/%	BS/%	BS/%								
TA-BS-8	10	10	8	0.31	84	—	215	156	16	389	404
TA-BS-16	20	20	16	0.32	99	—	—	—	—	368	409

^a Molar content of comonomer unit determined by ¹H NMR. ^b Reduced viscosity measured at a concentration of 0.4 g dl⁻¹ in *p*-chlorophenol/1,1,2,2-tetrachloroethane (3/1). ^c Measured at a heating rate of 20°C min⁻¹ and a cooling rate of 10°C min⁻¹ in nitrogen; T_{ch} , crystallization temperature with heating from the glass, T_{cc} , crystallization temperature with cooling from the melt, ΔH_m , heat of fusion. ^d 5% weight loss temperature determined at a heating rate of 10°C min⁻¹.

Figure 1. Hoffman-Weeks plot of PET and copolymers.**Table II.** Molecular weights of PET and copolymers determined by GPC

Polymer	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
PET	53900	15500	3.5
TA-BA-8	16000	6400	2.5
TA-BA-16	16200	6500	2.5
TA-BS-8	14400	5900	2.4
TA-BS-16	15000	6200	2.4

no melting peak for TA-BS-16. With incorporation of the comonomers, the crystallization temperature from the melt (T_{cc}) decreased or disappeared and the crystallization temperature from the glass (T_{ch}) disappeared. These results reveal that the crystallizability of PET was lowered by copolymerization with these comonomers. As shown in Table II, the molecular weights of the copolymers were lower than that of PET. Therefore, the crystallizability should increase from the view point of the effect of molecular weight. However, the influence of molecular weight was overcome by the structural effect.

Figure 2. Wide angle X-ray diffractograms of PET and copolymers: upper, crystallized at 170°C for 1 hour; lower, quenched from the melt.

Crystallization Properties of Copolymers

Wide angle X-ray diffraction was measured to study the crystalline structure of the copolymers. The measurements were carried out for the samples annealed at 170°C for 1 hour. TA-BA-8, TA-BA-16, and TA-BS-8 showed the same diffraction pattern as that of PET (Figure 2). Although it can not be concluded by these data only that the arylate segments were segregated from the crystal domain, it is considered that the crystal consisted mainly of ethylene terephthalate segments. These polymers showed isotropic melt, and totally amorphous samples were obtained by quenching the melt samples with liquid nitrogen. On the other hand, TA-BS-16 showed no apparent peak to show the existence of crystalline phase even if longer annealing time was applied.

Spherulite growth was detected by polarized microscopic observation and light scattering for the crystallization of each copolymer except for TA-BS-16. Figures 3 and 4 show the light scattering profiles of isothermal crystallization of TA-BA-8 and TA-BS-8, respectively,

Figure 3. Time dependence of light scattering profile of TA-BA-8 under isothermal crystallization at 150, 180, and 200°C, at an azimuthal angle of 45° under H_v optical alignment.

at 150, 180, and 200°C at an azimuthal angle of 45° under H_v optical alignment. Under two dimensional observation, a four-leaf clover pattern was clearly observed at lower crystallization temperatures, and the pattern changed to ring shape at higher crystallization temperatures.

Figure 5 shows the light scattering profiles of isothermal crystallization of TA-BA-16 at 150, 180°C at the azimuthal angle of 90°. In this system, a four-leaf clover pattern was observed at 0 and 90°, while PET and the other copolymers showed it at 45°. A deviation of the optical axis might be induced by increased content of bisphenol-A unit in this copolymer.

Invariant Q_d of the scattering intensity for H_v (I_{H_v}) is defined as eq 1⁵ and has a relation expressed by eq 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. Here, f_c at time t

Figure 4. Time dependence of light scattering profile of TA-BS-8 under isothermal crystallization at 150, 180, and 200°C, at an azimuthal angle of 45° under H_v optical alignment.

is given by eq 3,

$$f_c(t) = Q_d(t)/Q_d(\infty) \quad (3)$$

where $Q_d(\infty)$ is the attainable crystallinity in the crystalline domain at a given crystallization condition. From these relations, information on the crystallization kinetics in terms of f_c can be obtained from the time variation of Q_d . Q_d increased gradually with time after a certain induction time (t_0).

Overall crystallization rate was determined from the slope of $Q_d(t)/Q_d(\infty)$ (dQ/dt) in the crystallizing region. Figure 6 compares the overall crystallization rates of the four polymers at various crystallization temperatures. The crystallization rate of the copolymers was smaller than that of PET in the whole range of crystallization temperatures due to the reduction of regularity in the chain sequence. TA-BA-16 showed much smaller dQ/dt than TA-BA-8. Although the molecular weights of the copolymers were lower than that of PET, the structural effect induced by the comonomers was dominant to determine the crystallization rate. As TA-BS-8 showed smaller dQ/dt than TA-BA-8, the structural effect was different depending on the comonomer structure.

Figure 5. Time dependence of light scattering profile of TA-BA-16 under isothermal crystallization at 150 and 180°C, at an azimuthal angle of 90° under H_v optical alignment.

Figure 6. Temperature dependence of overall crystallization rate (dQ/dt) of PET and copolymers under isothermal conditions.

Change in the induction time with crystallization temperature is illustrated in Figure 7. Inverse relation was observed between the induction time and the crystallization rate. As reported previously,^{1,2} the copolyesters containing biphenylene terephthalate or paraphenylene terephthalate unit showed remarkably short induction time when they showed the crystallization rate higher than that of PET. Such an effect was not observed in the bisphenol-A and bisphenol-S-containing copolymers. These comonomer segments just restricted the regular chain alignment of PET segments, and had no effect to enhance the crystal nucleation.

Crystallization kinetics for polymers has been approximately described by the Avrami equation⁶ shown below,

$$f_c = 1 - \exp(-k(t - t_0)^n) \quad (4)$$

where k is the rate constant and n is the Avrami index

Figure 7. Temperature dependence of induction time of PET and copolymers under isothermal conditions.

Figure 8. Temperature dependence of the Avrami index for PET and copolymers.

Figure 9. Temperature dependence of the crystallization rate (k) derived from Avrami treatment for PET and copolymers.

related to the geometry and mode of crystal growth. The equation for Avrami plot is obtained from eq 3 and 4.

$$\ln(-\ln(1 - Q_d(t)/Q_d(\infty))) = \ln k + n \ln(t - t_0) \quad (5)$$

The kinetic parameters are obtained by plotting the data according to eq 5; the slope is equal to n and the intercept is equal to $\ln k$.

Figure 8 shows the Avrami index obtained for the polymers. Almost constant n values around 1.5 were obtained for each polymer independent of crystallization temperatures. These results mean the crystallization mechanism for these polymers was the same. The value, $n = 1.5$, is the same with the PET copolymers comprising

4,4'-biphenylene terephthalate unit or paraphenylene terephthalate unit as described in the previous papers.^{1,2} Although this is smaller than the values previously reported for PET, $n = 2.5 - 3.0$,⁷⁻⁹ it is attributed to the selection of $(t - t_0)$ as the measuring time instead of t .

The rate constants (k) obtained by Avrami analysis are illustrated in Figure 9. Dependence of k on the polymer structure and crystallization temperature was nearly consistent with that of the overall crystallization rate determined from dQ/dt .

As a conclusion, the existence of bisphenol-A and bisphenol-S units in PET disturbs the crystallization of the copolymers. These comonomers did not induce any remarkable change in the crystal formation of PET, while an accelerated crystal nucleation was observed when 4,4-biphenol and hydroquinone were incorporated. It is considered that flexibility and bulkiness of bisphenol-A and bisphenol-S has no effect on the local orientation of the molecular chains. From these results, it is clear that the structure of the comonomers is important to modify

the crystallization properties of PET.

Acknowledgments. The author is grateful to Mr. Yoshinori Nakae of Toyobo Co., Ltd. for GPC measurements.

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