

Crystallization Behavior of Poly(ethylene terephthalate) Copolymers Containing *p, p'*-Quaterphenyldicarboxylic Acid or 4,4'-Diphenyldicarboxylic Acid

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ABSTRACT: Copolymers of poly(ethylene terephthalate) (PET) containing small amounts of 4,4'-diphenyldicarboxylic acid (DP) and *p, p'*-quaterphenyldicarboxylic acid (QP) were prepared and their crystallization behavior was characterized by isothermal crystallization with the time-resolved light scattering method. The DP-containing copolymers showed spherulitic growth like PET homopolymer. The crystallization rate for DP-containing copolymers decreased and the induction time increased with comonomer content, which showed that DP unit disturbed the crystallization of PET segments. In the case of QP-containing copolymers, accelerated crystal nucleation was observed for 5–7.5 mol% copolymers. However, their crystallization rates were the same order as that of PET. Remarkable increase in crystallization rate, observed for some rigid arylate units-containing copolyesters in previous works, was not detected in these copolymers. The rigidity of QP is high enough to induce the aggregation of QP-rich segments, but the following orientation of ethylene terephthalate chains seems not to be accelerated in the course of crystallization.

KEY WORDS Poly(ethylene terephthalate) / 4,4'-Diphenyldicarboxylic Acid / *p, p'*-Quaterphenyldicarboxylic Acid / Isothermal Crystallization /

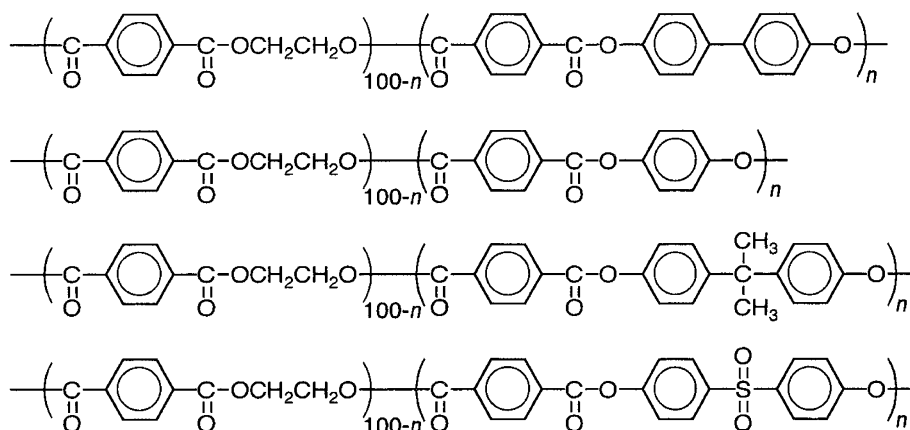
Crystallizability of polymers usually decreases by copolymerization. This is because the regular chain packing for crystallization is inhibited by the introduction of comonomer segments. For example, Poly(ethylene terephthalate) (PET) copolymers containing relatively flexible arylate-units such as 4,4'-isopropylidenediphenol (Bisphenol A) and bis(4-hydroxyphenyl)sulfone (Bisphenol S) as aromatic diols (Scheme 1) showed monotonous decrease in crystallizability with increase in comonomer content.¹

Certain arylate-unit-containing PET copolymers showed increased crystallizability compared to PET homopolymer in previous papers.^{2,3} The papers described the crystallization behavior of PET copolymers comprising 4,4'-biphenylene terephthalate unit or paraphenylene terephthalate unit (Scheme 1). In the isothermal crystallization for these systems, when comonomer content increased, the crystal nucleation density increased, the crystal size became smaller and shape became more irregular. As the first result of increase in the comonomer content, higher crystallization rate than that of PET was observed at lower crystallization temperatures, where crystal nucleation was dominant in the crystallization. Further increase in the comonomer content around 10 mol% gave the crystallization rate higher than that of PET independent of crystallization temperature. These two copolymer systems showed similar crystallization characteristics. However, the copolymers containing parapheny-

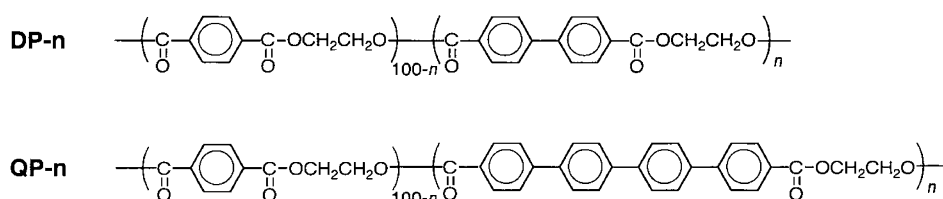
lene terephthalate unit needed higher comonomer content to display remarkable increase in the crystallization rate than the copolymers containing 4,4'-biphenylene terephthalate unit. Structural differences in comonomer sensitively thus affect the crystallization behavior of copolymers.

The rigid characteristics of the biphenylene terephthalate and paraphenylene terephthalate units may lead to local orientation of molecular chains on a molecular level and resulted in accelerated crystallization. Recently, similar effect was reported in PET or poly(butylene terephthalate) copolymers containing small amount of butylene terephthalamide unit. The amide segments associate in the melt first to form crystal nuclei, and then followed by ordering of the ester segments.⁴

In this article, in order to consider the structural effects on improvement of crystallizability in PET copolymers containing rigid segments, two series of PET copolymers comprising 4,4'-diphenyldicarboxylic acid (DP) and *p, p'*-quaterphenyldicarboxylic acid (QP) as rigid dicarboxylic acid comonomers were prepared (Scheme 2), and crystallization behavior was investigated. The rigidity introduced by *para* oriented dicarboxylic acids in this work instead of *para* oriented diols used in the previous works^{2,3} may result in different characteristics.



Scheme 1.



Scheme 2.

EXPERIMENTAL

Materials

Dimethyl terephthalate (DMT) (Mitsubishi Kasei), dimethyl 4,4'-diphenyldicarboxylate (DMDP) (Ihara Chemical), diisopropyl *p,p'*-quaterphenyldicarboxylate (DIQP) (Sumikin Kako), ethylene glycol (Mitsui Toatsu), antimony trioxide (Nacalai Tesque, GR) and zinc acetate dihydrate (Nacalai Tesque, GR) were used without further purification.

Preparation of Copolymers

Copolymers of poly(ethylene terephthalate) (PET) containing small amounts of 4,4'-diphenyldicarboxylic acid (DP) and *p,p'*-quaterphenyldicarboxylic acid (QP) were prepared by transesterification using dimethyl terephthalate, dimethyl 4,4'-diphenyldicarboxylate and diisopropyl *p,p'*-quaterphenyldicarboxylate as dicarboxylic acid monomers.

As an example, preparation of a copolymer containing 5 mol% of *p,p'*-quaterphenyldicarboxylic acid is described below. DMT (18.45 g, 0.095 mol), DIQP (2.53 g, 0.005 mol), ethylene glycol (24.83 g, 0.400 mol), zinc acetate dihydrate (5×10^{-5} mol) and antimony trioxide (2×10^{-5} mol) placed in a polymerization vessel were heated to 185°C and kept at this temperature for 75 min under nitrogen atmosphere. The reaction mixture was heated to 230°C at a heating rate of 20°C h⁻¹ and kept at this temperature for

30 min. Vacuum was applied and the temperature was raised to 280°C. The polymerization was continued until the reaction mixture became viscous enough under *ca.* 0.2 mmHg.

Other copolymers were prepared by the same procedure except changing the comonomer feed ratio and polymerization time. In order to get copolymers having the same level of molecular weights with the PET homopolymer, solid state polymerization was carried out at 240°C for QP-containing copolymers and 170°C for DP-containing copolymers under reduced pressure for appropriate time.

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: v/v) at 30°C. ¹H NMR spectra were obtained in a mixed solvent of chloroform-*d* and trifluoroacetic acid with a Varian Unity-500 spectrometer. Three types of signals were observed for ethylene glycol units distinguished by the monomer unit sequence in the both copolymers: TA-EG-TA (4.76 ppm), TA-EG-DP (or DP-EG-TA) (4.78 ppm), and DP-EG-DP (4.80 ppm) for DP-containing copolymers; TA-EG-TA (4.75 ppm), TA-EG-QP (or QP-EG-TA) (4.78 ppm), and QP-EG-QP (4.81 ppm) for QP-containing copolymers. Sequence distribution of the copolymers was evaluated according to the treatment of Yamadera and Murano⁵ as described in the previous paper.² Thermal transition temperatures were determined using a differen-

tial scanning calorimeter (DSC) (Perkin–Elmer DSC-7) at a heating rate of $20^{\circ}\text{C min}^{-1}$ and cooling rate of $10^{\circ}\text{C min}^{-1}$ under flowing nitrogen for quenched samples from the melt. Thermogravimetric analysis (TGA) was conducted at a heating rate of $10^{\circ}\text{C min}^{-1}$ 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 scintillation counter with Nickel-filtered $\text{Cu-K}\alpha$ 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.² A sample was kept at 300°C for 2 min between two pieces of cover glass to form a completely melt film (thickness: *ca.* $30\ \mu\text{m}$), and quickly transferred onto a hot stage (Linkam TH-600PH) of the light scattering apparatus set at a crystallization temperature. Change in angular distribution of scattering intensity under cross-polarized (H_v) optical alignment with time was recorded.

RESULTS AND DISCUSSION

General Properties of Copolymers

DP-containing copolymers were prepared by changing the ratio of terephthalic acid unit (TA) and 4,4'-diphenyldicarboxylic acid unit (DP). All polymerizations of DP-containing copolymers proceeded as a homogeneous and transparent melt. The preparation and thermal properties are shown in Table I. From sequence analysis based on $^1\text{H NMR}$, the degree of randomness (B) for DP-containing copolymers was slightly less than 1. As defined in the literature,⁵ $B = 1$ when the sequence distribution is random, and B decreases with increase in block length, and finally $B = 0$ for a homopolymer mixture. The existence of consecutive blocks of DP segments may thus be ignored. Depression of the melting point and disappearance of crystallization peaks on DSC measurements were observed with increase in DP content. These results show that the introduction of DP-unit decreased the crystallizability of copolymers. The glass transition temperature increased with DP content because of the introduction of the rigid component.

In the course of crystallization of copolymers containing 10 and 20 mol% of DP, slow spherulitic growth was observed by polarized microscope. The same wide

angle X-Ray diffraction pattern as that of PET with peaks at 16° ($0\bar{1}0$), 17.5° (010), 22.5° ($\bar{1}10$), and 26° (100), was noted (Figure 1). It is considered that crystal formation by ethylene terephthalate segments is dominant in these copolymers. The copolymer containing 30 mol% of DP did not show crystalline peaks with thermal treatment. Each sample gave a totally amorphous state by quenching with liquid nitrogen from the melt, as the crystallization rate was not so high.

QP-containing copolymers were prepared by changing the ratio of terephthalic acid unit (TA) and *p,p'*-quaterphenyldicarboxylic acid unit (QP). The results of preparation and thermal properties are shown in Table II. In the preparation of QP-containing copolymers, turbidity of the melt polymerization system was observed even in 2.5 mol% of QP content, and it became more distinct with increase in QP content. The sequence distribution was almost random despite some heterogeneity in the polymerization. It was difficult to obtain a high enough molecular weight of copolymers for copolymerization with more than 10 mol% of QP content due to low fusibility under the polymerization conditions. In this copolymer system, depression of the melting point by copolymerization was not remarkable, and crystallization peaks on DSC measurements were detectable. The crystallization temperature with heating from the glass (T_{ch}) decreased with increase in QP content. This suggests that the crystallizability at lower temperature was enhanced by incorporation of QP content.

It is considered that the turbidity observed in the polymerization melt of QP-containing copolymers is caused by the ordered phase as a result of aggregation of QP-rich segments. Figure 2a shows the existence of the unmeltable ordered phase in the melt of QP-5 under polarized microscopic observation. When this sample

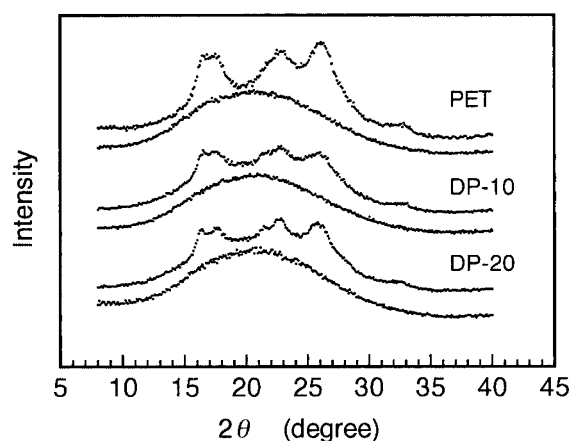


Figure 1. Wide-angle X-Ray diffractograms of crystallized (upper) and quenched (lower) samples for PET and DP copolymers.

Table I. Preparation and properties of DP copolymers

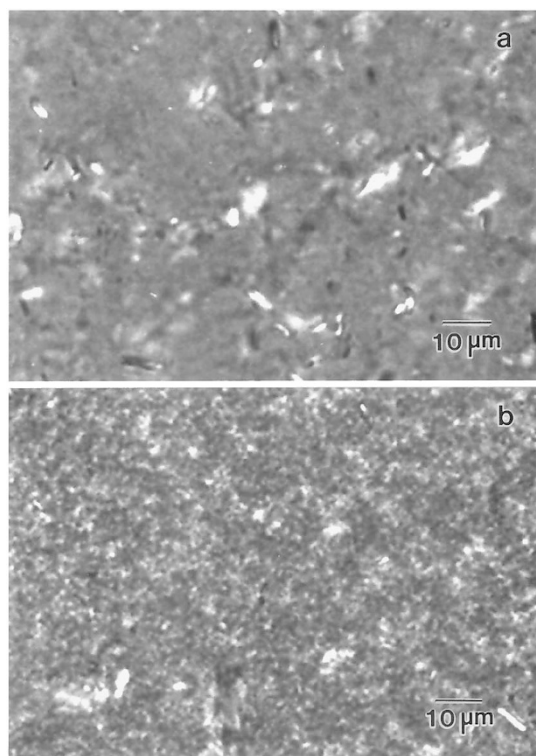
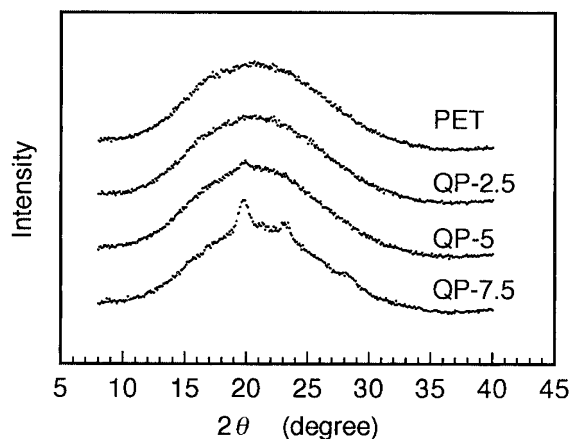
Polymer	Monomer feed ratio		Polymer composition ^a DP/%	B ^b	η_{sp}/C^c dL g ⁻¹	DSC ^d				TGA(5%) ^e	
	TA/%	DP/%				T_g °C	T_{ch} °C	T_m °C	T_{cc} °C	in air °C	in N ₂ °C
	PET	0	0	0		0.99	78	147	249	208	357
DP-10	90	10	10.1	0.94	1.03	84	168	231	—	389	405
DP-20	80	20	21.1	0.96	1.03	88	—	211	—	390	408
DP-30	70	30	30.8	0.97	1.03	91	—	(191)	—	394	411

^aMolar content of 4,4'-diphenyldicarboxylic acid unit determined by ¹H NMR. ^bDegree of randomness. ^cReduced viscosity measured at a concentration of 0.4 g dL⁻¹ in *p*-chlorophenol/1,1,2,2-tetrachloroethane (3/1). ^dMeasured at a heating rate of 20°C min⁻¹ and a cooling rate of 10°C min⁻¹ in nitrogen for quenched samples from the melt; T_{ch} : crystallization temperature with heating from the glass, T_{cc} : crystallization temperature with cooling from the melt. ^eFive percent weight loss temperature determined at a heating rate of 10°C min⁻¹.

Table II. Preparation and properties of QP copolymers

Polymer	Monomer feed ratio		Polymer composition ^a QP/%	B ^b	η_{sp}/C^c dL g ⁻¹	DSC ^d				TGA(5%) ^e	
	TA/%	QP/%				T_g °C	T_{ch} °C	T_m °C	T_{cc} °C	in air °C	in N ₂ °C
	PET	0	0	0		0.99	78	147	249	208	357
QP-2.5	97.5	2.5	2.6	1.00	1.14	81	125	245	201	381	410
QP-5	95.0	5.0	5.0	0.98	1.16	81	112	242	203	391	409
QP-7.5	92.5	7.5	7.2	0.94	1.10	81	111	240	201	404	411

^aMolar content of *p,p'*-quaterphenyldicarboxylic acid unit determined by ¹H NMR. ^bDegree of randomness. ^cReduced viscosity measured at a concentration of 0.4 g dL⁻¹ in *p*-chlorophenol/1,1,2,2-tetrachloroethane (3/1). ^dMeasured at a heating rate of 20°C min⁻¹ and a cooling rate of 10°C min⁻¹ in nitrogen for quenched samples from the melt; T_{ch} : crystallization temperature with heating from the glass, T_{cc} : crystallization temperature with cooling from the melt. ^eFive percent weight loss temperature determined at a heating rate of 10°C min⁻¹.

**Figure 2.** Polarized microscopic observation for QP-5: (a) in the melt state at 300°C; (b) after crystallization at 180°C.**Figure 3.** Wide angle X-Ray diffractograms of PET and QP copolymers quenched from 300°C.

was cooled slowly on the hot stage of the polarized optical microscope, appearance of small spherulites with crystallization was observed (Figure 2b). The wide angle X-Ray diffractograms of QP-containing copolymers quenched from 300°C are shown in Figure 3. There are diffraction peaks of the unmeltable ordered phase at 20° and 23° in QP-5 and QP-7.5. When the copolymers were crystallized, similar wide angle X-Ray diffraction patterns to that of PET were mainly observed (Figure 4). Overlapping of additional diffrac-

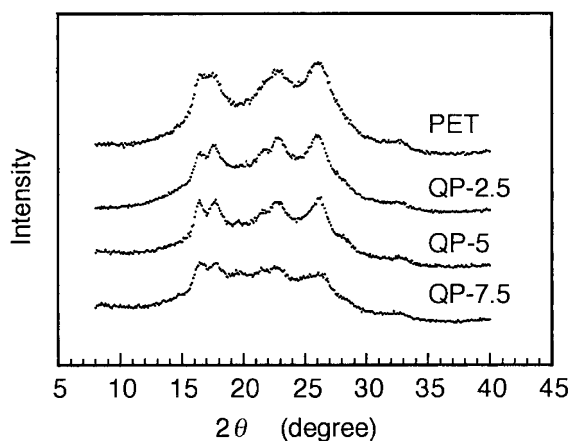


Figure 4. Wide angle X-Ray diffractograms of crystallized samples for PET and QP copolymers.

tion peaks due to the unmeltable ordered phase might occur for copolymers containing more than 5 mol% of QP. It seems that the crystallization of QP-containing copolymers in the heating and cooling cycle is mainly proceeded by rearrangement of PET-rich segments although some influence of QP segment exists.

Isothermal Crystallization with Time-Resolved Light Scattering

Isothermal crystallization from the melt was carried out at various crystallization temperatures. Figure 5 shows the light scattering profiles of isothermal crystallization of DP-10 and DP-20 at 180°C at the azimuthal angle of 45° under H_V optical alignment. In these systems, a four-leaf clover pattern, evidence of spherulite growth, was observed in the two-dimensional scattering pattern.

Invariant Q_d of the scattering intensity for H_V (I_{H_V}) is defined as eq 1⁶ and 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. For calculation of Q_d , I_{H_V} at time = 0 was subtracted from each I_{H_V} at time t . Here, information on the crystallization kinetics can be obtained from the time variation of $C(t)$ defined by eq 3,

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

where $Q_d(\infty)$ is the attainable invariant at a given crystallization condition. Q_d increased gradually with time after a certain induction time (t_0).

Information on the crystallization rate was determined from the slope of $Q_d(t)/Q_d(\infty)$ (dQ/dt) in the

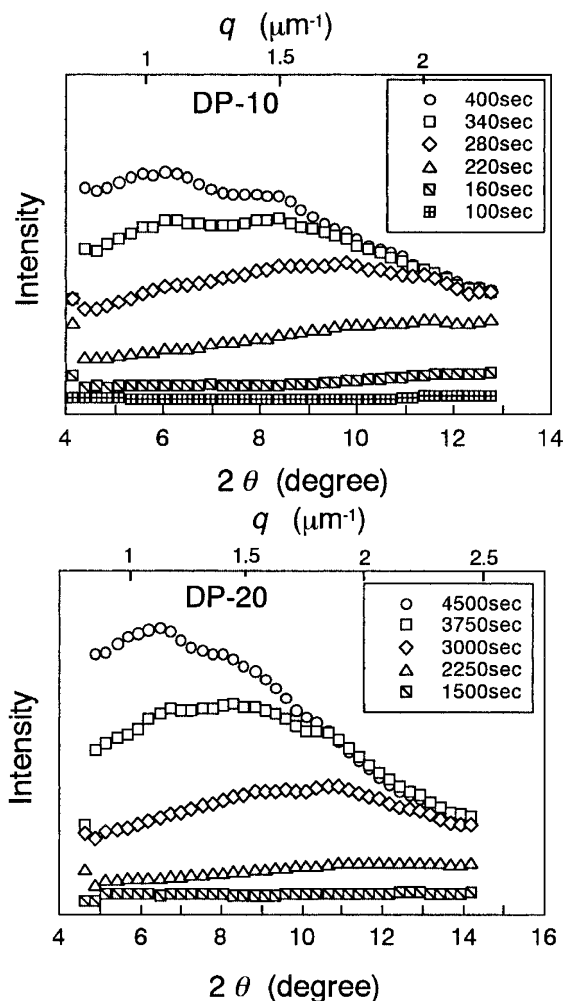


Figure 5. Time dependence of light scattering profiles of DP-10 and DP-20 under isothermal crystallization at 180°C.

crystallizing region. Figure 6 compares the crystallization rates of DP-10 and DP-20 at various crystallization temperatures. The crystallization rates of copolymers were slower than that of PET in the whole range of crystallization temperatures due to reduction of regularity in the molecular structure. DP-20 showed much smaller dQ/dt than DP-10.

Change in the induction time with crystallization temperature is illustrated in Figure 7. Inverse relation was observed between induction time and crystallization rate. As reported previously,^{2,3} the copolyesters containing biphenylene terephthalate or paraphenylene terephthalate unit showed remarkably short induction time when crystallization rates were higher than that of PET. This is explained by accelerated crystal nucleation induced by the rigid comonomer segments and following chain alignment of PET segments. Such effect was not observed in DP-containing copolymers. DP-containing segments did not enhance crystal nucleation, because the rigidity of DP was not high enough. Therefore, they only restrict the regular chain alignment of PET segments in the course of crystallization.

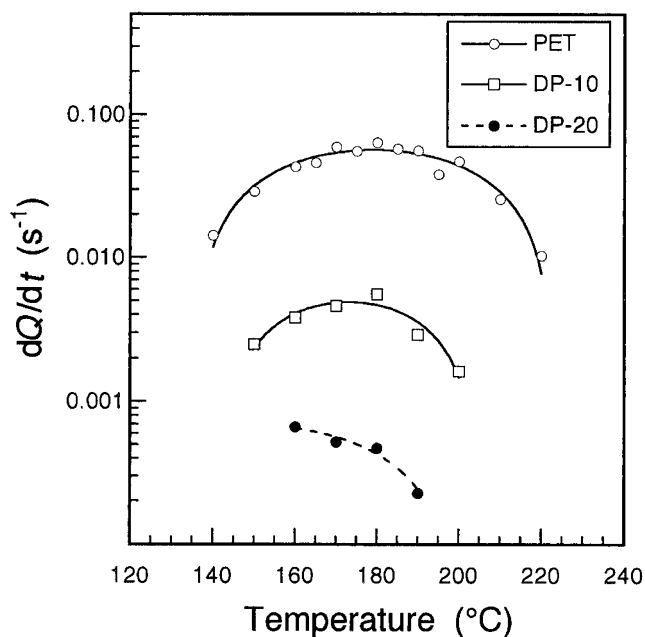


Figure 6. Temperature dependence of crystallization rate (dQ/dt) of PET and DP copolymers under isothermal conditions.

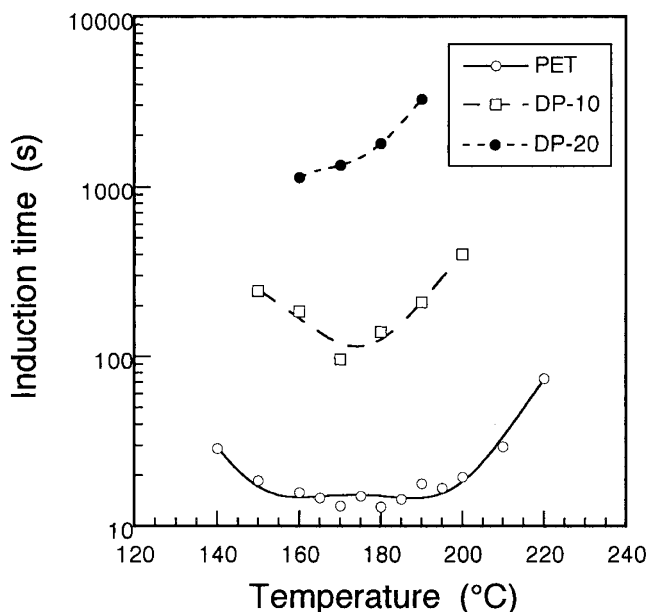


Figure 7. Temperature dependence of induction time of PET and DP copolymers under isothermal conditions.

Figure 8 shows the light scattering profiles of isothermal crystallization of QP-2.5, QP-5, and QP-7.5 at 200°C at the azimuthal angle of 45° under H_v optical alignment. In this system, no apparent scattering peak was detected. This phenomenon is considered as a result that the size and shape of spherulites appeared were irregular, in addition to the existence of unmeltable ordered phase. The randomness of optical anisotropy is high in this copolymer system.

Figures 9 and 10 compare crystallization rates and induction times of QP-2.5, QP-5, and QP-7.5 at various crystallization temperatures, respectively. The crystal-

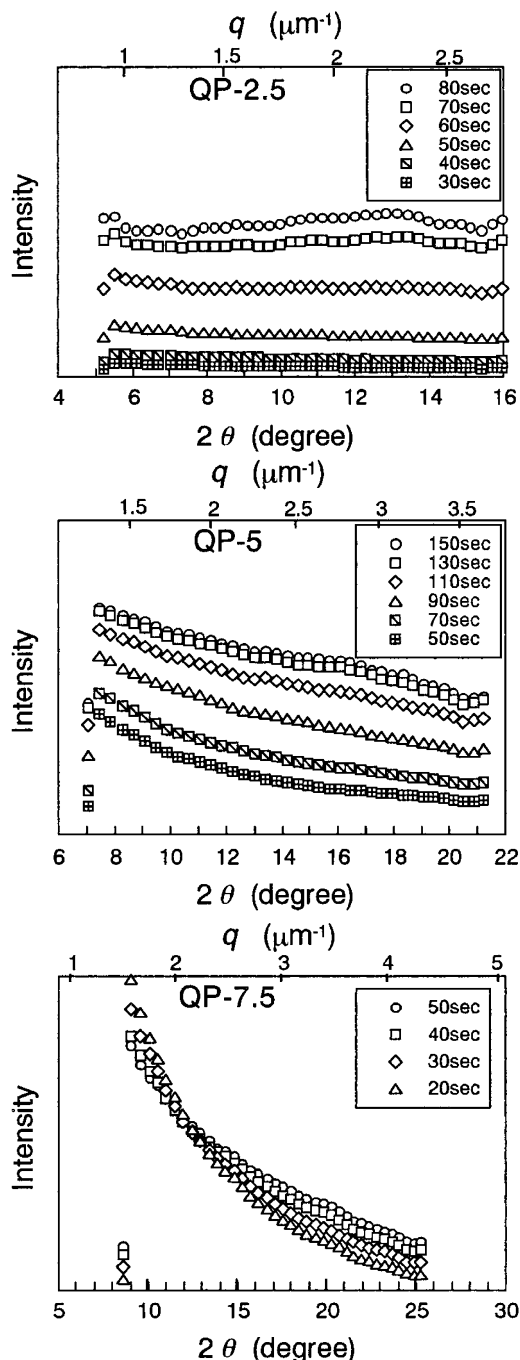


Figure 8. Time dependence of light scattering profiles of QP copolymers under isothermal crystallization at 200°C.

lization rate of QP-2.5 was almost the same as that of PET in the whole range of crystallization temperature, and no apparent influence of the copolymerization was observed. QP-5 showed slightly higher crystallization rate than that of PET at lower crystallization temperature. At these crystallization temperatures, the induction time of QP-5 was very short. Acceleration of the crystal nucleation in QP-5 may contribute to increase in the crystallization rate. In the case of QP-7.5, crystallization was observed only at higher crystallization temperatures, and increase in crystallization rate compared to PET was not detected. Although induction

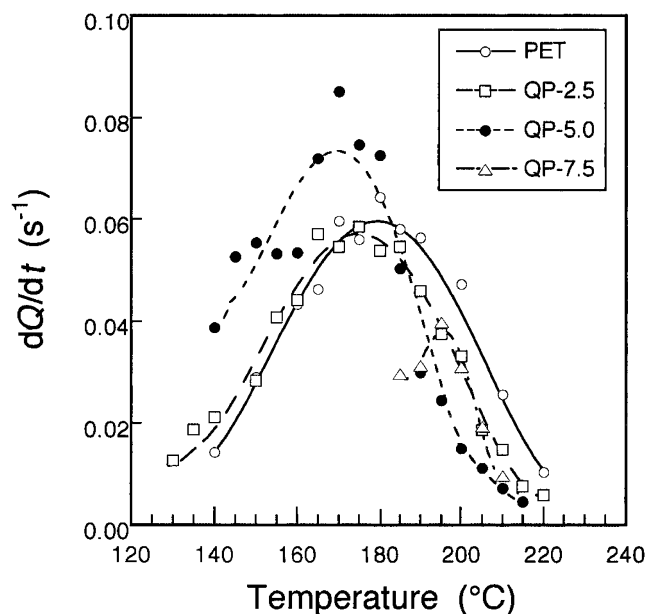


Figure 9. Temperature dependence of crystallization rate (dQ/dt) of PET and QP copolymers under isothermal conditions.

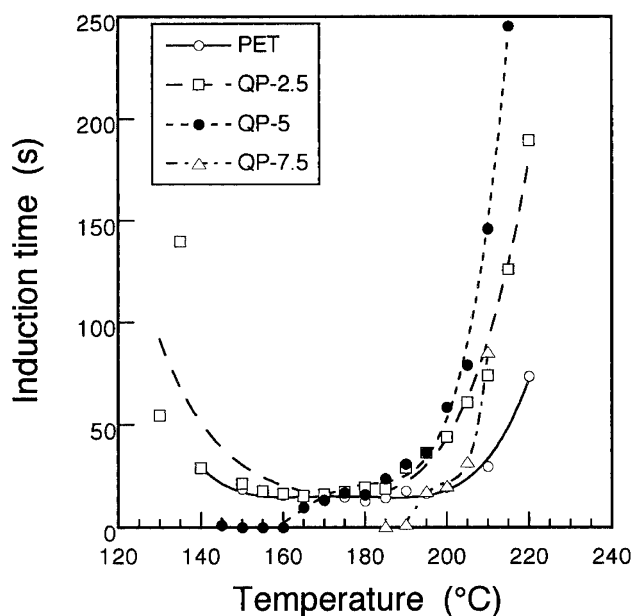


Figure 10. Temperature dependence of induction time of PET and QP copolymers under isothermal conditions.

time was very short when crystallization was carried out around 190°C, the crystallization rate was slower than that of PET even under these conditions. When aggregation of QP-rich segments became evident with increase in QP content, molecular arrangement of ethylene terephthalate segments to the crystalline structure was not accelerated, rather restricted. In QP-containing copolymers, higher crystallization rate than PET was observed in the limited range for polymer composition in which moderate aggregation of QP-rich segments occurred and crystallization temperature at which crystal nucleation became evident. The crystal nucleation induced by strong aggregation of QP-rich segment thus

seems to dominate the crystallization process.

As reported in the previous papers,^{2,3} when certain rigid diol components such as 4,4'-biphenol and hydroquinone were copolymerized in PET, aggregation of arylate unit-rich segment contribute to effective molecular orientation of ethylene terephthalate segments. In this study, rigid components were introduced as the dicarboxylic acid monomers instead of the diols, and such effect found in the previous works^{2,3} was not observed. The rigidity of DP was not high enough to enhance the crystal nucleation of copolymers, and the rigidity of QP was too high to induce a local orientation of ethylene terephthalate segments after the aggregation of QP-rich segments. Consecutive paraphenylene groups formed by copolymerization with diol comonomers have ester linkages, but those with dicarboxylic acid comonomers are bonded directly. Therefore, affinity of QP and ethylene terephthalate segments seems low, and it results in aggregation of QP-rich segments without influence on the orientation of ethylene terephthalate segments.

From the viewpoint of crystallization mechanism based on crystal nucleation and molecular mobility, it is generally considered that the introduction of a rigid segment into the PET molecule shows an effect like a nucleation agent, but decreases the mobility of molecular chain. When the molecular orientation of rigid segment induces the following orientation of PET segments as in the case of liquid crystalline polymers or acceleration of the nucleation is superior to the restriction of chain mobility, effective increase in crystallization rate may become possible. In order to control the crystallization rate of PET by copolymerization, we should recognize that small differences in the structure of comonomers play important roles to determine crystallization behavior.

CONCLUSION

Copolymers of poly(ethylene terephthalate) (PET) containing small amounts of DP and QP were prepared and crystallization behavior was characterized by isothermal crystallization with time-resolved light scattering. The rigidity of DP, which has two consecutive paraphenylene units, was not high enough to accelerate crystal nucleation, and the crystallizability of copolymers decreased monotonously with increase in DP content. DP unit only restricted the regular chain alignment of PET segments in the course of crystallization. In the case of QP, which has four consecutive paraphenylene units, accelerated nucleation was observed in the copolymers. However, a remarkable increase in crystallization rate, observed in the case of

some rigid arylate units-containing copolyesters, was not detected in these copolymers. The aggregation of QP-rich segments seems to induce no molecular orientation of ethylene terephthalate segments because of low affinity between QP unit and ethylene terephthalate segments.

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