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Modification of crystallization properties of poly(ethylene terephthalate) by copolymerization with arylate-units: 2. Hydroquinone-containing copolymers

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Crystallization kinetics of the copolymers of poly(ethylene terephthalate) (PET) containing 2–11 mol% of hydroquinone unit were investigated by time-resolved light scattering method. The copolyesters were prepared from PET, terephthalic acid and hydroquinone diacetate by acidolysis reaction and following polycondensation. The copolymer with 2 mol% of hydroquinone showed a spherulite growth similar to PET with a decreased crystallization rate. On the other hand, increase in the nucleation density was observed for the 6 and 8 mol% copolymers at lower crystallization temperatures and for the 11 mol% copolymer at whole range of the crystallization temperatures. The increase in the nucleation density was accompanied with reduction of the induction time and increase in the crystallization rate. As a result, the 11 mol% copolymer had a maximum crystallization rate of *ca.* three times as fast as that of PET. In this system, wide angle X-ray diffraction peaks of the crystal were similar to those of PET crystal. Another ordered domain was observed in the 11 mol% copolymer. However, it seems to have no direct influence on the crystallization and melting cycle. © 1997 Elsevier Science Ltd.

(Keywords: poly(ethylene terephthalate); hydroquinone-containing copolymer; isothermal crystallization)

INTRODUCTION

Crystallizability of polymers usually decreases by copolymerization. This is because the regular chain packing for crystallization is inhibited by the presence of comonomer segments. In a previous paper[1], however, an arylate-unit-containing PET copolymer was found to show higher crystallizability than PET homopolymer. The paper dealt with the crystallization properties of PET copolymers containing 2, 4 and 8 mol% of 4,4′-biphenylene terephthalate unit. In this system, wide angle X-ray diffraction peaks which appeared with crystallization were similar to those of PET crystal. The 2 mol% copolymer showed spherulite growth similar to PET, though the crystallization rate was slower. In the case of 4 mol% and 8 mol% copolymers, crystal nucleation density was higher and smaller and irregular spherulites appeared. In particular, the 8 mol% copolymer showed the maximum crystallization rate, *ca.* twice as fast as that of PET.

A mechanism of the accelerated nucleation was proposed: rigid biphenylene terephthalate units form a four consecutive para-phenylene moiety which may induce a local orientation of the molecular chains on the molecular level and contribute to an effective crystal nucleation. Longer consecutive para-phenylene unit is expected to be favourable for the orientation of molecular chains. There should exist a limit, however, unfavourable for the melt processability. In order to consider the structural effect on the improvement of the crystallizability in arylate-unit-containing PET copolymers, a series of PET copolymers comprised of hydroquinone unit instead of 4,4′-biphenol were prepared, and their crystallization behaviours were investigated.

EXPERIMENTAL

Materials

Poly(ethylene terephthalate) (Toyobo, RE530), hydroquinone diacetate (Konan Kako), terephthalic acid (Mitsui Petrochemical Ind.), and chlorobenzene (Nacalai Tesque, GR) were used without further purification.

Preparation of copolymers

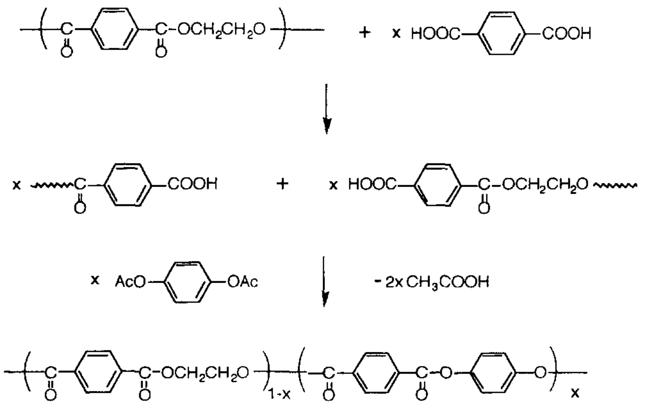
The hydroquinone-containing copolymers were prepared by the procedure described in the previous paper[1].

Characterization

Reduced viscosities were measured at a concentration of $0.4\,\mathrm{g\,dl^{-1}}$ in a mixed solvent of *p*-chlorophenol and 1,1,2,2-tetrachloroethane (3/1 : vol/vol) at 30°C. ^{1}H n.m.r. 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 (d.s.c.) (Perkin–Elmer DSC-7) at a heating rate of $20°\mathrm{C\,min^{-1}}$ and a cooling rate of $10°\mathrm{C\,min^{-1}}$ under flowing nitrogen for quenched samples from the melt. Thermogravimetric analysis (t.g.a.) was conducted at a heating rate of $10°\mathrm{C\,min^{-1}}$ under flowing air or nitrogen, using a thermogravimetric analyser (Shimadzu TGA-50). Wide angle X-ray diffraction (WAXD) measurement was conducted on a Rigaku rotating-anode generator (RV-200) and a scintillation counter with Nickel-filtered 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 by time-resolved light scattering

Time-resolved light scattering was carried out with a light scattering apparatus similar to that described in the literature[1,2]. 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 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 at an azimuthal angle of 45° under cross-polarized (H_V) optical alignment with time was recorded.



Scheme 1

RESULTS AND DISCUSSION

General properties of copolymers

Copolymers were synthesized from PET and equimolar combinations of terephthalic acid and hydroquinone diacetate. In the copolymerization, first, acidolysis reaction of PET by the terephthalic acid occurs, then polycondensation of the carboxylic chain ends and the hydroquinone diacetate proceeds (*Scheme 1*). No catalyst was added for the copolymerization to minimize influence of residual catalyst on the crystallization properties of the resultant copolymers. As a result, the copolymers as-polymerized showed relatively low solution viscosities (η_{sp}/C) around 0.3–0.4. Therefore, solid state polymerization was carried out to increase their molecular weights up to the same level of η_{sp}/C as the original PET. The polymer compositions were determined by ^{1}H n.m.r. The results showed about half of the comonomers fed sublimed during the copolymerization. When the copolymerization was carried out at a comonomer feed ratio below 17 mol%, the polymerization proceeded as a homogeneous and transparent melt. On the other hand, further increase in the feed ratio such as 19 mol% resulted in an appearance of turbidity during

Table 1 Preparation and properties of TA–HQ copolymers

	Monomer feed ratio		Polymer composition[a]		D.s.c.[c]				T.g.a. (5%)[d]	
Polymer	TA(%)	HQ(%)	HQ(%)	η_{sp}/C[b] (dl g^{-1})	T_g (°C)	T_{ch} (°C)	T_m (°C)	T_{cc} (°C)	In air (°C)	In N$_2$ (°C)
PET	0	0	0	0.84	81	148	257	208	352	402
TA–HQ–2	5	5	2	0.88	80	151	248	202	393	404
TA–HQ–6	10	10	6	0.86	83	126	244	191	361	400
TA–HQ–8	15	15	8	0.88	84	114	244	195	395	406
TA–HQ–11	17	17	11	0.89	83	111	244	206	390	410

[a] Molar content of 4,4′-biphenol unit determined by ^{1}H n.m.r.

[b] Reduced viscosity measured at a concentration of 0.4 g dl^{-1} in *p*-cholorophenol/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

[d] 5% weight loss temperature determined at a heating rate of 10°C min^{-1}

Table 2 Sequence distributions in TA-HQ copolymers

	Proportion of signals			Composition						
Polymer	EG–TA–EG	EG–TA–HQ	HQ–TA–HQ	EG	HQ	$P^a_{EG\ HQ}$	$P^b_{HQ\ EG}$	$\overline{Ln}^c_{EG}$	$\overline{Ln}^d_{HQ}$	B^e
TA–HQ–2	0.953	0.046	0.001	0.976	0.024	0.024	0.958	41.7	1.04	0.98
TA–HQ–6	0.876	0.120	0.004	0.936	0.064	0.064	0.938	15.6	1.07	1.00
TA–HQ–8	0.851	0.143	0.006	0.922	0.078	0.078	0.917	12.8	1.09	1.00
TA–HQ–11	0.795	0.195	0.010	0.892	0.108	0.109	0.903	9.2	1.11	1.01

[a] Probability of finding a HQ unit next to an EG unit given by EG–TA–HQ/2EG

[b] Probability of finding an EG unit next to a HQ unit given by EG–TA–HQ/2HQ

[c] Number-average sequence length of EG unit given by $1/P_{EG\ HQ}$

[d] Number-average sequence length of HQ unit given by $1/P_{HQ\ EG}$

[e] Degree of randomness (B) given by $P_{EG\ HQ} + P_{HQ\ EG}$. $B = 1$ when the distribution is random, and B decreases with an increase in the block length, and finally $B = 0$ for a homopolymer mixture

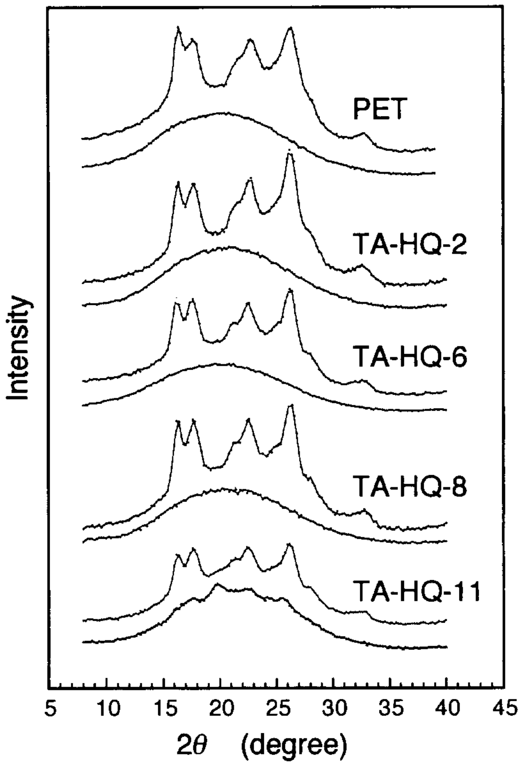


Figure 1 Wide angle X-ray diffractograms of crystallized (upper) and quenched (lower) samples for PET and TA–HQ copolymers

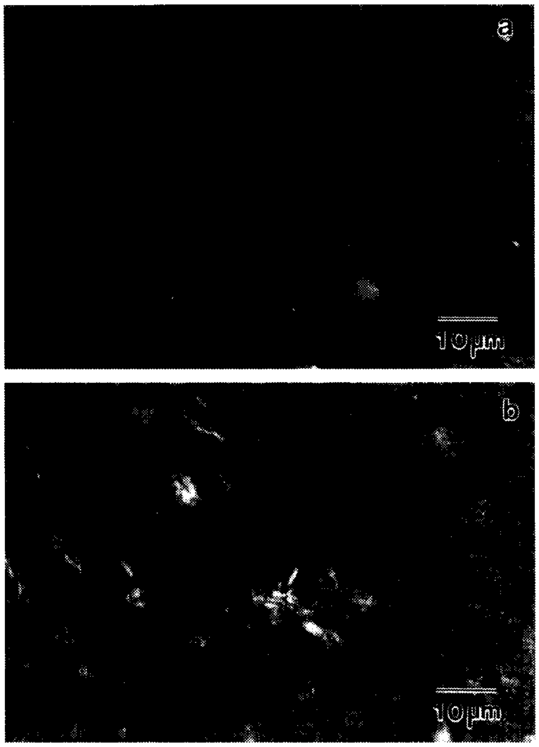


Figure 2 Polarized micrographs of TA–HQ–11: (a) at the melt state at 300°C; (b) after crystallization at 180°C

the polymerization. Therefore, the copolymers obtained by the homogeneous polymerization were selected to study the crystallization properties. *Table 1* summarizes the results of preparation of four copolymers: they are abbreviated as TA–HQ–2, TA–HW–6, TA–HQ–8 and TA–HQ–11 by using the content of hydroquinone unit in the copolymers determined by ^{1}H n.m.r.

Three types of signals in ^{1}H n.m.r. were observed for the terephthaloyl protons distinguished by the monomer unit sequence: EG–TA–EG, EG–TA–HQ (or HQ–TA–EG), and HQ–TA–HQ. Sequence distribution of the copolymers was evaluated according to the treatment of Yamadera and Murano[3] as described in the previous paper[1]. The number average sequence length and the degree of randomness (B) revealed that the para-phenylene terephthalate unit did not form consecutive blocks as shown in *Table 2*. It was concluded that these copolymers were random copolymers.

Crystalline structure of copolymers

TA–HQ–2, TA–HQ–6 and TA–HQ–8 showed the same WAXD pattern as that of PET with peaks at $2\theta = 16.2$, 17.8, 22.5 and 26.1° (*Figure 1*). Although it cannot be concluded only by these data that para-phenylene terephthalate segments were segregated from the crystal domain, it is confirmed 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.

In TA–HQ–11, on the other hand, quenched samples showed not only amorphous halo but also extra peaks caused by the existence of some ordered structure. Optical microscopic observation also showed remaining birefringence in the melt state as shown in *Figure 2a*. As shown later in *Figure 6*, the light scattering measurement indicated that the ordered structure was randomly dispersed and the size is smaller than the wavelength of light (633 nm). The polymerization of TA–HQ–11 proceeded as a homogeneous melt. The ordered domains were observed only after solid state polymerization, and did not melt even above 300°C once they were formed. It is considered that the formation of ordered phase was induced by an aggregation of the chain segments containing the para-phenylene terephthalate unit. Although the ordered domains exist in TA–HQ–11, the diffraction peaks which increased with the crystallization were similar to those of PET as found in the other copolymers. As the microscopic observation showed that the crystal nucleation occurred randomly in the melt, not from the surface of the ordered domains (*Figure 2b*), the ordered domains themselves seem to have no direct influence on the melting and crystallization cycle of TA–HQ–11.

Isothermal crystallization with time-resolved light scattering

Isothermal crystallization from the melt was carried out for the four copolymers at various crystallization temperatures. *Figures 3–6* show the time dependence of H_V light scattering profile for the polymers at three different crystallization temperatures, respectively.

In the case of TA–HQ–2, as seen in *Figure 3*, there was a scattering peak, which shifted to lower angle with time. The four-leaf clover pattern was clearly observed in the two-dimensional scattering pattern and the spherulite growth was confirmed. When the crystallization was performed at higher temperature, growth of a larger spherulite was observed; the scattering peak appeared at lower angle and also larger spherulites were directly detected on the microscopic observation. This behaviour is similar to that of PET[1], though the size of spherulites were slightly smaller and the shape was deformed to some extent.

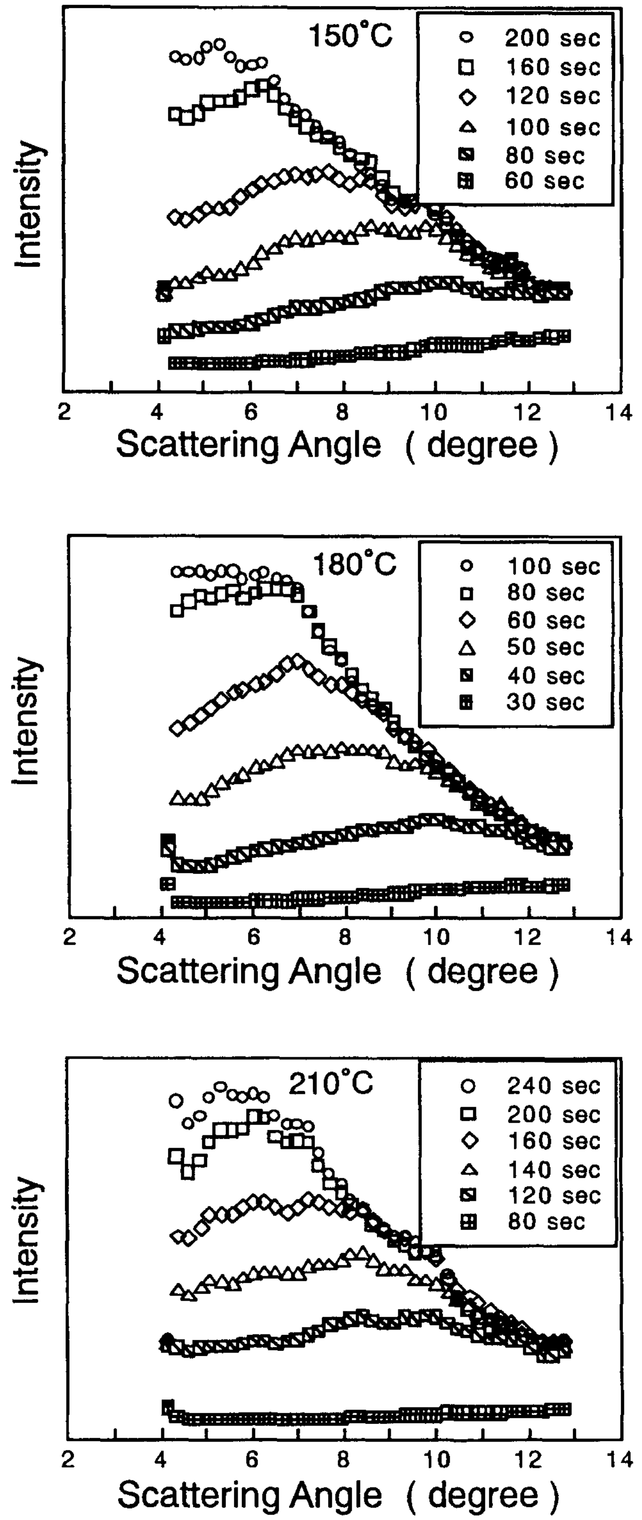


Figure 3 Time dependence of light scattering profile of TA–HQ–2 under isothermal crystallization at 150, 180 and 210°C

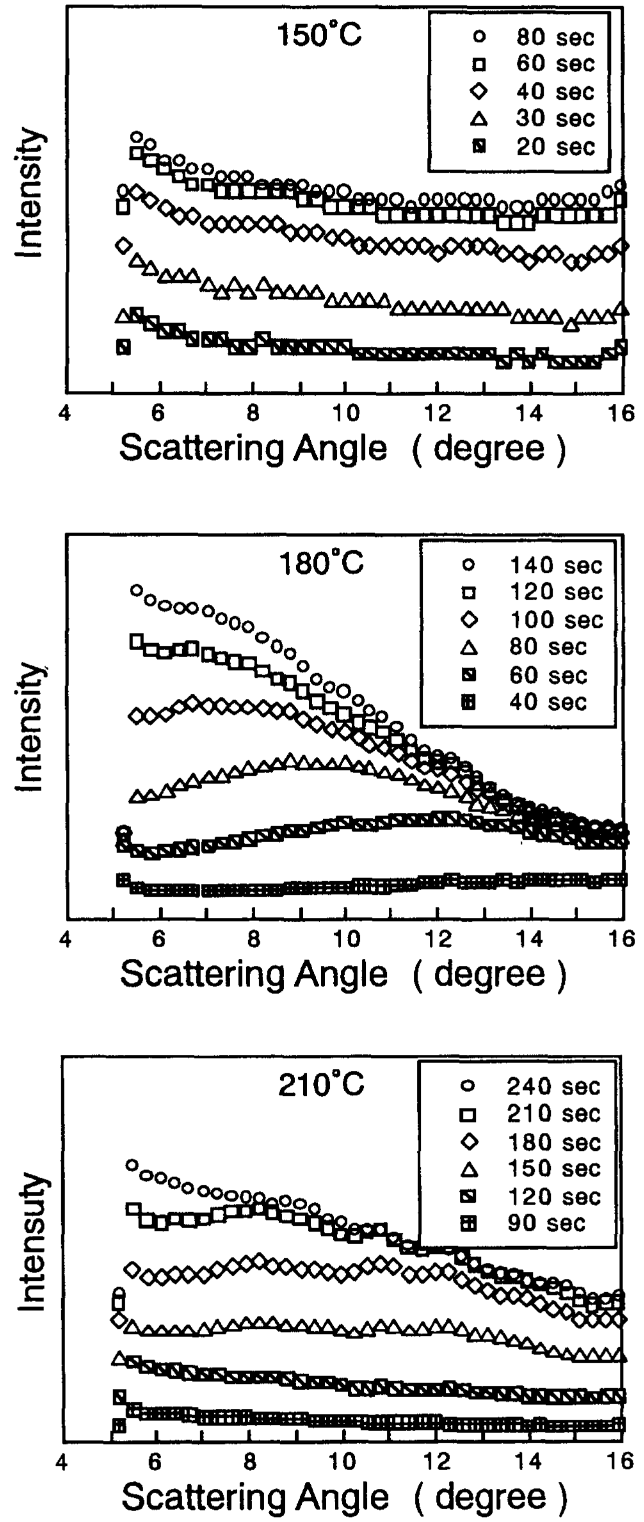


Figure 4 Time dependence of light scattering profile of TA–HQ–6 under isothermal crystallization at 150, 180 and 210°C

The scattering profile of TA–HQ–6 showed a similar tendency to PET and TA–HQ–2 at the crystallization temperatures of 180 and 210°C. When the crystallization was carried out at 150°C, no apparent peak was observed and the scattering intensity increased similarly at any angle with time (*Figure 4*). It is considered that size and shape of the spherulites were more irregular in this system, and the randomness of optical anistropy increased.

In TA–HQ–8, typical spherulite growth was observed at the crystallization temperature of 210°C. No apparent peak was observed at 180°C, and more randomness of optical anisotropy was observed at 150°C (*Figure 5*)

As TA–HQ–11 had the ordered phase even in the melt state, intense scatterings were observed at low angle region from the beginning of the crystallization (*Figure 6*). When the crystallization proceeded, slight increase in the intensity was observed. Although the increase of the

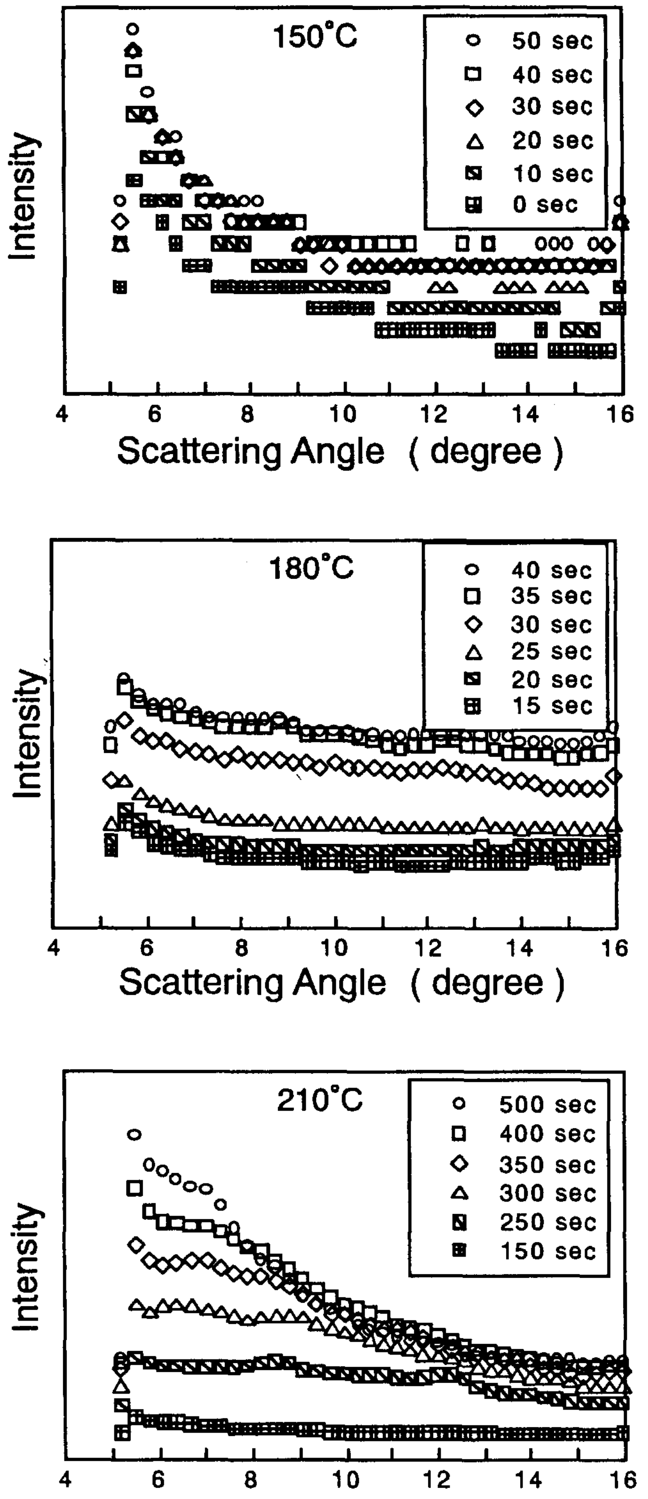


Figure 5 Time dependence of light scattering profile of TA–HQ–8 under isothermal crystallization at 150, 180 and 210°C

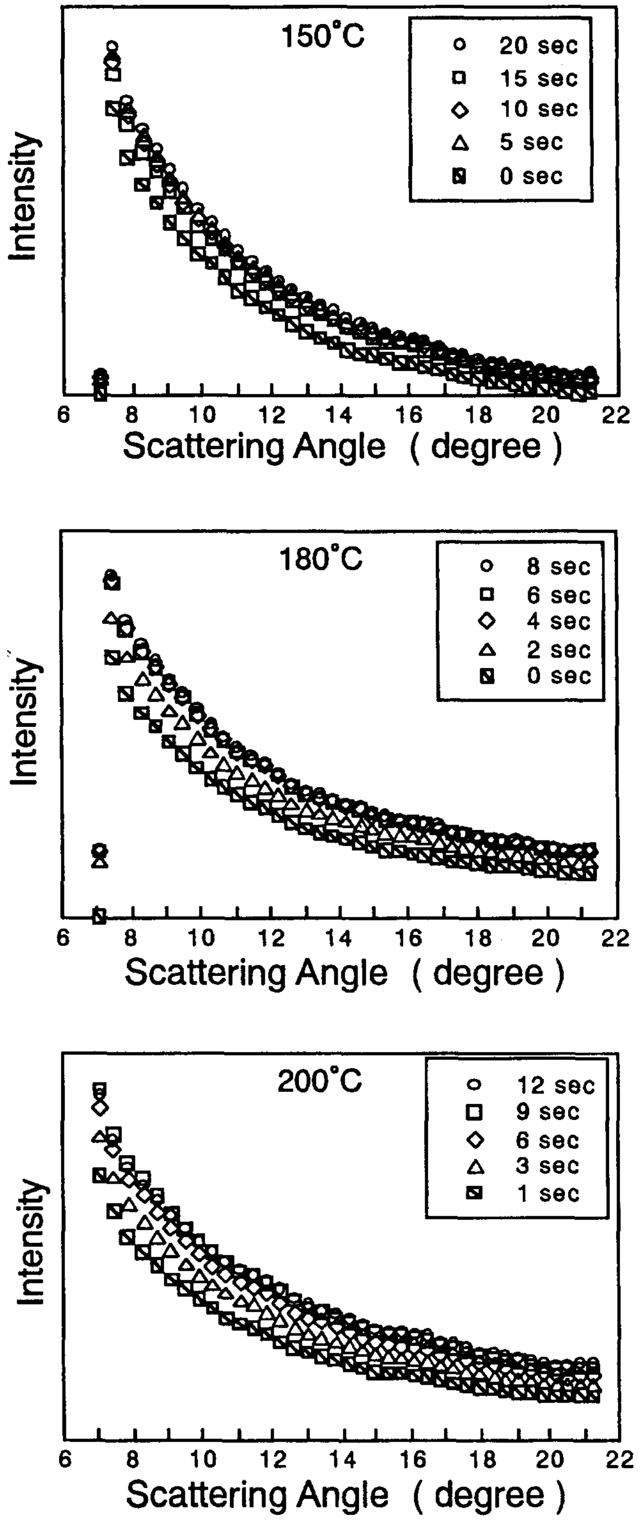


Figure 6 Time dependence of light scattering profile of TA–HQ–11 under isothermal crystallization at 150, 180 and 200°C

scattering intensity was small, the heat of crystallization obtained by d.s.c. under the corresponding isothermal conditions was about 70% of that of PET.

As described above, the copolymers crystallized differently depending on the polymer composition and the crystallization temperature. When the comonomer content was small, the spherulite growth of ethylene terephthalate segments was disturbed to some extent by an irregularity in the chain sequence induced by a para-phenylene terephthalate unit. As the hydroquinone content increased, the nucleation density increased especially at lower crystallization temperature. It was also observed by the polarized microscopic observation. In this case, it seems that an interaction among the segments containing para-phenylene terephthalate unit became dominant to determine the crystalline structure in spite of the increased chain irregularity.

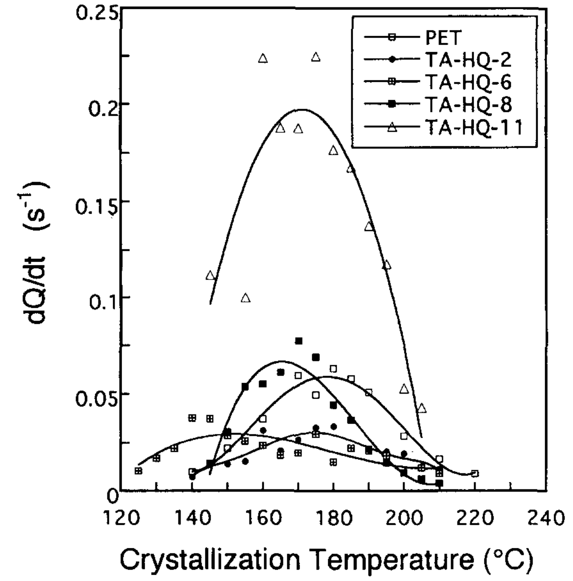


Figure 7 Temperature dependence of the overall crystallization rate (dQ/dt) of PET and TA–HQ copolymers under isothermal conditions

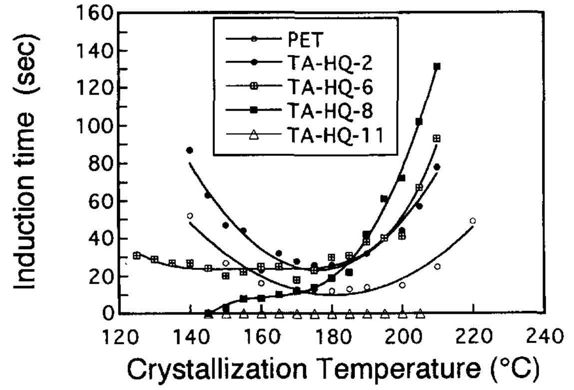


Figure 8 Temperature dependence of the induction time of PET and TA–HQ copolymers under isothermal conditions

Invariant Q_δ of the scattering intensity for H_V (I_{H_V}) is defined as equation (1)[4] and has a relation expressed by equation (2),

$$Q_\delta = \int I_{H_V} q^2 \mathrm{d}q \qquad (1)$$

$$Q_\delta \propto \langle \delta^2 \rangle = \phi_C(\alpha_1 - \alpha_2)^2 \qquad (2)$$

where q is the magnitude of the scattering vector, $\langle \delta^2 \rangle$ is the mean-square anisotropy, ϕ_C is the volume fraction of the crystalline domain, and α_1 and α_2 are the principal polarizabilities of the crystal lamella. Here, ϕ_C at time t is given by equation (3).

$$\phi_C(t) = Q_\delta(t)/Q_\delta(\infty) \qquad (3)$$

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

Overall crystallization rate was determined from the slope of $Q_\delta(t)/Q_\delta(\infty)(\mathrm{d}Q/\mathrm{d}t)$ in the crystallizing region. *Figure 7* compares the overall crystallization rates of the four copolymers and PET at various crystallization temperatures. The crystallization rate of TA–HQ–2 was smaller than that of PET in the whole range of crystallization temperatures due to probably the reduction of regularity in the chain sequence induced by para-phenylene terephthalate unit. TA–HQ–6 showed smaller $\mathrm{d}Q/\mathrm{d}t$ at high crystallization temperatures, however, $\mathrm{d}Q/\mathrm{d}t$ at lower crystallization temperatures was higher than that of PET and TA–HQ–2. TA–HQ–8 showed a similar level of maximum of $\mathrm{d}Q/\mathrm{d}t$ with PET, and superiority in the crystallization rate at lower crystallization temperatures compared to the homopolymer was more significant. Moreover, TA–HQ–11 showed a maximum of $\mathrm{d}Q/\mathrm{d}t$ *ca.* three times as fast as that of PET. In spite of the increase in chain irregularity, increase in the content of para-phenylene terephthalate unit has some effect to accelerate the crystallization of the copolymers.

Changes in the induction time with crystallization temperature are illustrated in *Figure 8*. Inverse relation was observed between the induction time and the crystallization rate when the typical spherulite growth was observed. TA–HQ–6 and TA–HQ–8 at lower crystallization temperatures showed relatively short induction times. TA–HQ–11 showed remarkably short induction times in the whole range of crystallization temperatures. These results support that the increase in the hydroquinone content has some contribution to enhance the nucleation.

Crystallization kinetics for polymers has been approximately described by the Avrami equation[5]

$$\phi_C = 1 - \exp[-k(t - t_0)^n] \qquad (4)$$

where k is the rate constant and n is the Avrami index related to the geometry and mode of crystal growth. The equation for Avrami plot is obtained from equations (3) and (4).

$$\ln\{-\ln[1 - Q_\delta(t)/Q_\delta(\infty)]\} = \ln k + n\ln(t - t_0) \qquad (5)$$

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

Figure 9 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. Although $n = 1.5$ is smaller than the values reported for PET, $n = 2.5$–3.0[6–8], this 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 10*. Dependence of k on the polymer structure and crystallization temperature was consistent with that of the overall crystallization rate determined from $\mathrm{d}Q/\mathrm{d}t$.

Crystallization of polymers is explained in general by crystal nucleation and molecular mobility. The former is dominant at lower crystallization temperature, and the latter is dominant at higher crystallization temperature. Characteristic crystallization behaviour of TA–HQ copolymers appears when 6–8 mol% of para-phenylene terephthalate unit is incorporated. In this region, the changes are observed at lower crystallization temperatures. Therefore, one of the reasons of the increased crystallization rate in the hydroquinone-containing copolymers is attributed to the accelerated nucleation. This is supported by the increased nucleation density

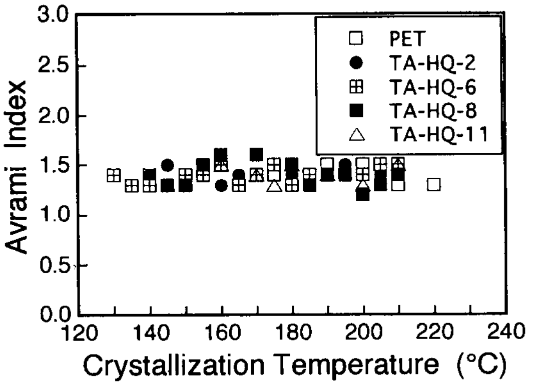


Figure 9 Temperature dependence of the Avrami index for PET and TA–HQ copolymers

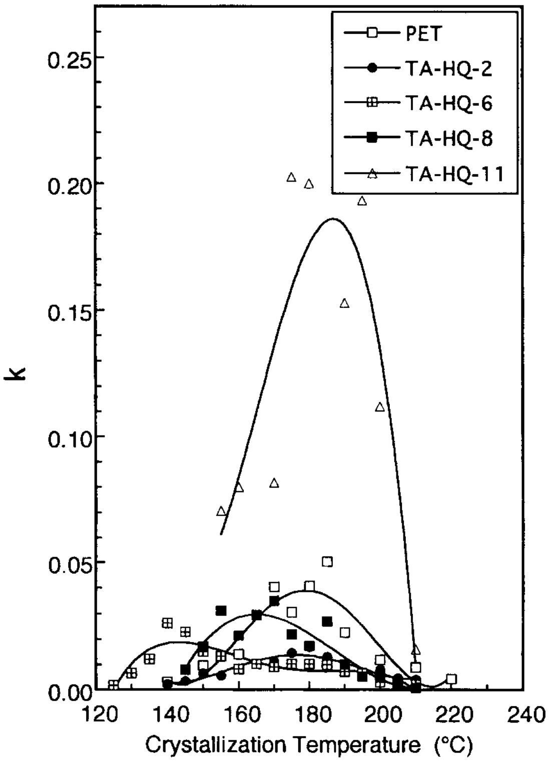


Figure 10 Temperature dependence of the crystallization rate (*k*) derived from Avrami treatment for PET and TA–HQ copolymers

observed on polarized microscopy and the extremely reduced induction time under the isothermal crystallization. When the comonomer content is too small, this effect does not appear. When the comonomer content increases too much, the unmeltable ordered phases, which does not influence the crystallization behaviour directly, is increased. Therefore, it may be considered that the effective formation of the crystal nuclei is induced by a local orientation of the molecular chains containing para-phenylene terephthalate segments in the melt at moderate compositions.

Although crystallization behaviour of the hydroquinone-containing copolymers is similar to that of the PET copolymers comprising biphenylene terephthalate described in the previous paper, characteristic changes in TA–HQ copolymer appears at higher compositions of comonomers. One para-phenylene terephthalate unit forms three consecutive para-phenylene moieties in contrast with the biphenylene terephthalate unit which forms four. Therefore, difference in the rigidity between these segments may create a different effect in local orientation of the molecular chains on the molecular level.

As described above, the crystallization characteristics in these systems were explained by an accelerated nucleation induced by the local orientation effect. However, the fact of the highest crystallization rates of TA–HQ–6 in the polymers at the lower temperature region cannot be explained by this effect only. An effect of chain mobility might be overlapped in this phenomenon. Further study is necessary and planned to clarify the detailed crystallization mechanism in these systems.

CONCLUSION

Crystallization properties of PET copolymers containing 2, 6, 8 and 11 mol% of hydroquinone, TA–HQ–2, TA–HQ–6, TA–HQ–8 and TA–HQ–11, were compared with that of PET. In this system, WAXD peaks were similar to those of PET crystal. In the copolymer with 11 mol% of hydroquinone, there was an additional ordered phase, which seems to have no direct influence on the crystallization and melting cycle. Increased nucleation density and appearance of smaller and irregular spherulites were observed with increase in hydroquinone content. The increase in the nucleation density was accompanied with reduction of the induction time and increase in the crystallization rate. As a result, TA–HQ–11 showed the maximum crystallization rate, *ca.* three times as fast as that of PET for the isothermal crystallization. It is considered that the effective formation of the crystal nuclei was induced by a local orientation of the molecular chains containing para-phenylene terephthalate segments in the melt.

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