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Polymer 40 (1999) 5623–5629

polymer

Solvent induced crystallization behavior of poly(ethylene 2,6-naphthalate) film

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Received 1 July 1998; received in revised form 28 September 1998; accepted 28 October 1998

Abstract

The relationship between the diffusion behavior and the solvent induced crystallization (SINC) was investigated. We have also studied the crystalline structures of PEN crystallized by solvent and compared them with those of thermally crystallized PEN. The diffusion behavior of dioxane at 40°C and 60°C is not pure Fickian but apparent Fickian where diffusion is controlled by crystallization. The diffusion behavior at 25°C is also not pure Case II. The diffusion behavior in DMF is similar to that in dioxane. The samples treated in dioxane above 40°C, which show the Fickian diffusion behavior, exhibit α-crystal and spherulitic texture. The sample treated in dioxane at 25°C, which show the Case II diffusion behavior, mainly exhibits β-crystal and the amoebae structure. The samples treated with DMF mainly show the α-crystal, irrespective of treatment temperature. The change of diffusion behavior by varying the treatment temperature affects the crystallization conditions, and crystalline form in SINC is changed by the characteristic of solvent.

Keywords: SINC; Diffusion; Crystalline form

1. Introduction

Solvent induced crystallization (SINC) provides a vehicle for the morphological manipulation of semi-crystalline polymers [1–5]. It was known that in the presence of certain interactive liquids, crystallization of amorphous polymers could take place at temperatures well below the glass transition temperature (T_g) of the polymer. The interaction of the polymer with the solvent lowers the effective T_g of the material, and the polymer chains will rearrange themselves onto a lower free energy state. In practice, solvent induced modifications are achieved via a sorption behavior.

Previous studies devoted to the sorption of polymers have primarily focused on poly(ethylene terephthalate) (PET) [6,7]. Weight uptake kinetics of various interactive solvents for PET was investigated in the sorption studies. It was reported that sorption behavior is separated to Fickian and non-Fickian (Case II and anomalous) diffusion [8–12].

Poly(ethylene 2,6-naphthalate) (PEN), which contains a naphthalene ring instead of the benzene ring in PET, is a well-known polymer used for engineering purposes. Most research on PEN has concentrated on photochemical properties, such as absorption, fluorescence, and chemiluminescence. The crystal structure of PEN by thermal crystallization is known to have two different triclinic forms. The most common and well-studied form is α-crystal [13]. The formation of β-crystal was first reported by Zachmann et al. [14,15], and it occurs during crystallization at temperatures above 245°C. Some limited studies concerning the SINC of initially amorphous PEN have indicated that this polymer can also be readily crystallized in certain liquids such as dioxane, aniline, and methylene chloride, resulting in a particularly distinct spherulitic texture [1,2]. Not much work was carried out on the interaction between PEN and organic solvent, and on the crystallization behavior according to the difference of diffusion behavior.

In this article, the relationship between the diffusion behavior and the SINC are investigated by the solvent interaction with PEN. We have also studied the crystalline structures of PEN films crystallized by solvent and compared them with those of thermally crystallized ones.

2. Experimental

Samples of 2×4 cm^2 cut from 170 μm thick films of an unoriented amorphous PEN were supplied by the KOLON. The amorphous films have the crystallinity lower than 1%.

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0032-3861/99/$ - see front matter
PII: S0032-3861(98)00783-6

Table 1
Physical constants of PEN and solvents

	PEN	Dioxane	Dimethyl formamide (DMF)
δ (cal/cm^3)$^{1/2}$[a]	11.02[b]	10.01	12.14
T_g° (°C)[a]	121.3[c]	− 38.2	− 111
ρ (g/cm^3)[a]	1.34	1.035	0.945
α (°C^{-1})[a]	0.365×10^{-3}[d]	1.2×10^{-3}	12×10^{-3}

[a] δ: solubility parameter, T_g: glass transition temperature, ρ: density, α: thermal expansion coefficient.
[b] Solubility parameter is calculated by Hoy's method.
[c] Glass transition temperature is obtained by DSC experimental.
[d] $\Delta\alpha$ is calculated by the molar termal expansivity.

1,4-Dioxane and DMF used in the sorption experiments were reagent grade (Junsei Chemical) and were not further purified.

The polymer samples were immersed in culture tubes containing the solvents maintained at constant temperature (25°C, 40°C and 60°C). At determined times, the samples were rapidly removed, blotted, and then weighed using an electronic balance (sartorius ISO 9001) with an accuracy of ±0.0001 g. After the swollen samples were dried in ambient atmosphere at room temperature for 8 h, residual solvents were leached from the films by immersion in methanol at the same temperature of the sorption experiment for 24 h. The samples were then dried under high vacuum at room temperature for 48 h.

Samples were immersed in the solvent, removed before equilibrium, and then sectioned for optical measurements (Nicon HFX-II A) of the advancement of the swelling front. To make a sharp front readily visible, the solvent was colored by the addition of iodine (4 g/100 ml penetrant). Cross-sections, approximately 15 μm thick, were microtomed (Broma LKB) from samples.

In order to observe the morphology of sample, the amorphous films of 12–20 μm thick were pressed at 300°C and then quenched. This film was immersed in the solvent at 25°C and 40°C, and then observed by optical microscope.

Thermal property of amorphous sample was measured by a Mettler DSC 30 at a heating rate of 10°C/min.

Wide angles X-ray diffraction (WAXD) of samples treated with solvents were obtained by transmission method using a Rigaku Denki RAD-C at a power of 40 kV and 40 mA. The CuKα-radiation was used in the 2θ angular range 5°–35°.

3. Results and discussion

3.1. Diffusion behavior and SINC

Data on the physical properties of PEN and the two solvents are presented in Table 1. According to the solubility parameter of PEN calculated by Hoy's method [16,17], it is shown that the mutual compatibility between PEN and solvents is good.

The weight uptake curves for the amorphous PEN films in the dioxane at various temperatures as a function of the square root of time are shown in Fig. 1. The weight uptake is expressed in terms of the weight of liquid absorbed per weight of dry polymer. In the case of both 40°C and 60°C, the weight uptakes are directly proportional to the square root of time in the early stage and then weight uptake grows increasingly concave to the abscissa. This situation is common to a number of highly interactive Solvent–polymer systems showing Fickian behavior [12,18,19].

In the case of 25°C, the weight uptake curve exhibits the positive curvature with square-root time. This curve shows the induction period up to about 9 min. After that, the slope of tangential line increases gradually to the equilibrium level. The weight uptake curve is plotted as a function of the time is also reported in the reduced figure. The weight uptake is proportional to the time. It means that the diffusion behavior at 25°C shows Case II, i.e., weight uptake is proportional to time [8,20].

In the interactive Solvent–polymer systems, when the crystallizable polymer absorbs a critical amount of solvent, this polymer will be now swollen and crystallized.

Figs. 2 and 3 show the sequence of the WAXD of PEN films treated with dioxane at various treatment times at 40°C and 25°C, respectively. In the case of 25°C, the crystallization

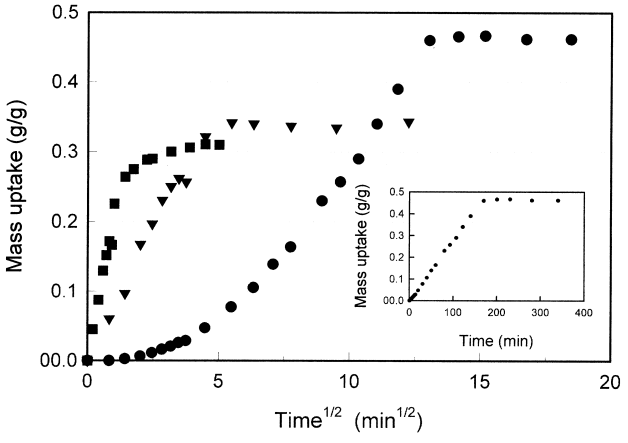

Fig. 1. Mass uptake per mass of dry polymer versus $t^{1/2}$ for dioxane sorption in amorphous PEN films at 25°C (●) 40°C (▼) and 60°C (■).

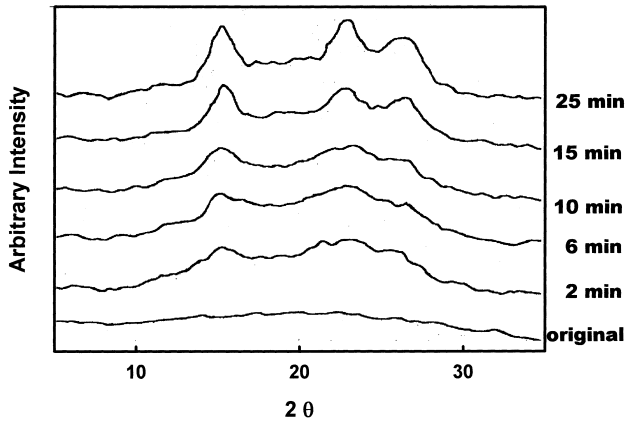

Fig. 2. X-ray diffraction curves of PEN films treated with dioxane at 40°C.

is not occurred until 50 min, while at 40°C, crystallization is occurred from the early stage of treatment time, 2 min. This suggests that as the compatibility between PEN and dioxane increases with temperature, the diffusion and the crystallization are simultaneously occurred. It is well known that the amount of solvent absorbed depends on the volume of amorphous domains and on the degree of interaction between the polymer and solvent. As shown in Fig. 1, the decrease of the equilibrium sorption level with treatment temperature suggests that the amorphous region of polymer treated at 40°C is reduced more than that of polymer treated at 25°C, i.e. the SINC occurred at higher treatment temperature. The WAXD patterns of PEN treated with dioxane are also different according to treatment temperature. This is discussed in detail in the following section.

The immersion of polymer into the interactive solvent depresses the glass transition temperature (effective T_g) of polymer with the diffusion of solvent. The depression of effective T_g can be used as a meaning of compatibility of the solvent. The difference in compatibility affects the diffusion behavior. In the crystallizable polymer, the crystallization behavior will be changed by diffusion of solvent. Hence, Effective T_g of the Solvent–induced crystallized PEN calculated (data in Table 1) is listed in Table 2.

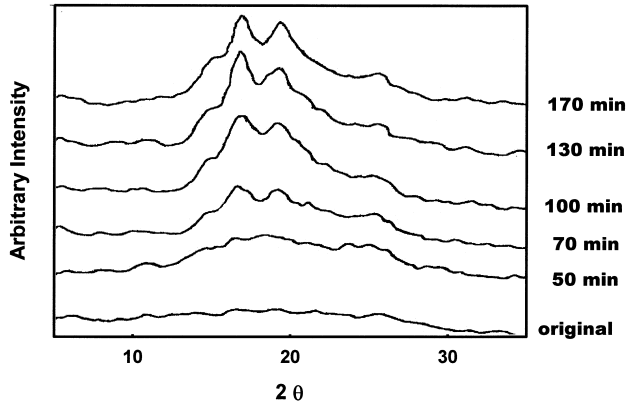

Fig. 3. X-ray diffraction curves of PEN films treated with dioxane at 25°C.

Table 2
Physical data of PEN immersed dioxane and DMF

		Saturation concentration, M_∞ (g/g polymer)	Critical volume fraction of solvent C*	Effective T_g (°C)
Dioxane	25°C	0.47	0.32	15
	40°C	0.36	0.24	25
	60°C	0.31	0.16	31
DMF	10°C	0.37	0.22	− 26
	25°C	0.29	0.18	− 12
	40°C	0.27	0.14	− 8
	60°C	0.23	0.10	1

The effective T_g of PEN is calculated by following Eqs. [6,21,22]:

$$T_g = \frac{(\Delta\alpha_p T_{g,p}^{\circ}(1-\psi_s) + \alpha_s T_{g,s}^{\circ}\psi_s)}{(\Delta\alpha_p(1-\psi_s) + \alpha_s\psi_s)}, \quad (1)$$

$$\psi_s = \frac{M_\infty}{\rho_s/\rho_p + M_\infty}, \quad (2)$$

where $T_{g,p}^{\circ}$ and $T_{g,s}^{\circ}$ are the glass transition temperatures of the pure polymer and solvent, respectively. ϑ_s are the solvent volume fractions. $\Delta\alpha_p$ is the change in the polymer thermal expansion coefficient at T_g, and α_s is the solvent expansion coefficient. M_∞ is the liquid concentration in the saturated polymer, and ρ_p and ρ_s are the pure polymer and solvent densities.

All of the effective T_g is lower than treatment temperature. It means that crystallization can be occurred at all treatment temperature. However, because the value of effective T_g depends on the value of saturation concentrations, the effective T_g increases with increase of treatment temperature. This is opposite to the result of the Solvent–polymer system which crystallization did not occur in this polymer. As shown in WAXD, this unusualness is caused by the decrease of chain mobility because of severe crystallization.

The critical volume fraction of solvent (C*) [9,10] is the minimum volume fraction of solvent that polymer segments can be relaxed (i.e. the volume fraction of solvent at which the T_g of the polymer–solvent system is lower than the treatment temperature). The C* was obtained by inserting treatment temperature into T_g in Eq. (1). C* is the characteristic value which depends upon the nature of polymer and solvent at treatment temperature. It is assumed that C* is the minimum volume fraction of solvent that can change the microstructure of polymer.

The values of C* for dioxane are 0.24 and 0.16 at 40°C and 60°C, respectively. As shown in Figs. 1 and 2, the SINC is occurred at initial stage of sorption. It means that weight uptake in the surface layer of polymer, which is in contact with solvent, may be reached to above C* as soon as sample is immersed into solvent, i.e. no sooner had the crystallization occurred than solvent diffused into dry polymer. It is

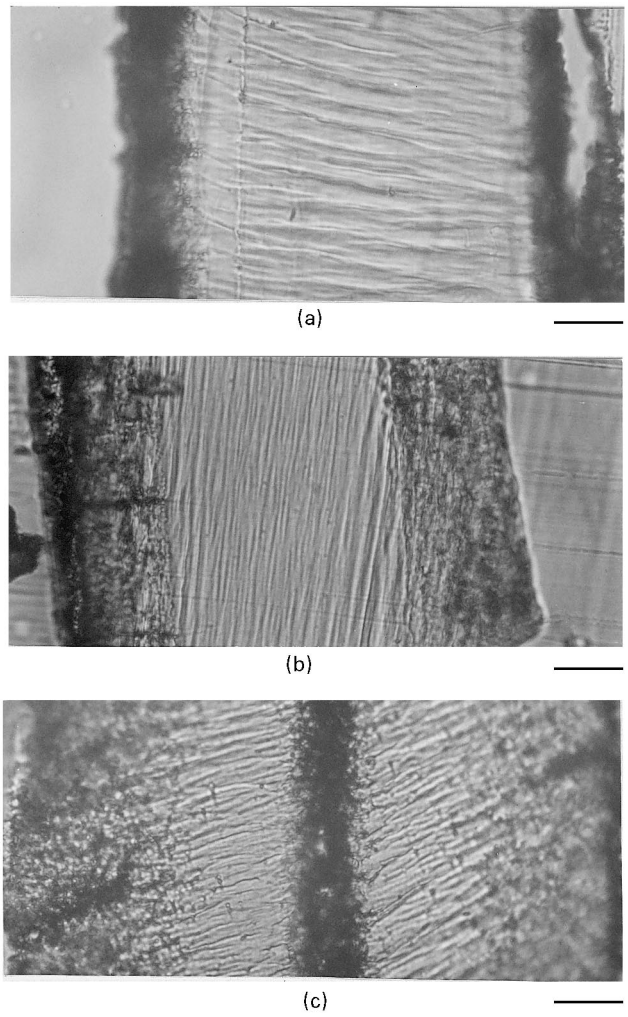

Fig. 4. Optical micrographs of microtomed cross-section of PEN films immersed at 40°C in dioxane coloured with iodine. (a) 2 min, (b) 6 min and (c) 25 min. bar: 25 μm.

also expected that crystallization is completed before the saturation.

These suggest that the crystallization occurred by solvent diffusion at initial stage, the crystallized layer interrupts the sorption of solvent which diffuses into polymer behind crystallized layer, and the rate of interruption is accelerated, and then the rate of diffusion is controlled by crystallization at the final stage. With above assumption in mind, it seems to be possible to explain the concave behaviors in sorption curves at 40°C and 60°C. The diffusion behavior, which occurred between the compatible solvent and the polymer crystallized by solvent, results from competition between the diffusion rate and crystallization. Therefore, the diffusion behaviors at these temperatures are not pure Fickian but apparent Fickian where diffusion is controlled by crystallization.

At 25°C, the value of C* is 0.32. The phenomenon of the crystallization and diffusion is not similar to the case of 40°C. The sorption curve plotted as $t^{1/2}$ shows induction period at initial stage, i.e. weight uptake in the surface layer of polymer is below C*. After that, the sorption curve plotted as $t^{1/2}$ also shows the weight uptake which linearly increase to the saturation concentration without concave uptake. The sorption curve plotted as t shows the linear increase of weight uptake. It is known that Case II is characterized by a distinct diffusion front separating the inner glassy core from the outer swollen layer and the front advances with constant velocity. However, the crystallization is actually initiated after 50 min. The above results mean that the concentration, which the front advances, is different from the crystallizable concentration. Hence, the SINC continuously occurred after the concentration reached a critical volume fraction of the solvent, and mildly occurred in comparison with 40°C. Therefore, the diffusion behavior at 25°C is not pure Case II because diffusion is affected by crystallization though its influence is much less severe than that by the case of high treatment temperature.

Once SINC begins, the advancing fronts will appear to have diffused into film. Microtomed cross-sections of films partially swollen in dioxane colored by iodine (4 g/100 ml) at 40°C and 25°C are shown in Figs. 4 and 5, respectively.

In Fig. 4, the front is observed although the it is not sharp. This phenomenon did not occur at Fickian diffusion, which is not crystallized by solvent. It is thought that these occurred owing to the presence of excess iodine, which is absorbed at voids accompanied by crystallization. However, the front shown in Fig. 5 is caused by the moving boundary, which is exhibited at Case II diffusion.

The weight uptake curves for the amorphous PEN films at various DMF treatment temperatures are shown in Fig. 6.

The diffusion behavior at 40°C and 60°C is similar to Fickian of dioxane. In the case of 25°C, weight uptake increased proportionally with the square root of time up to the saturation level. This diffusion behavior is the anomalous. The weight uptake curve at 10°C exhibits the positive curvature with square-root time. This curve shows also the induction period. This weight uptake is proportional to the time as like the case of dioxane at 25°C. It means that the diffusion behavior at 10°C shows Case II. However, the treatment temperature, which occurs in Case II diffusion, is lower by 15°C in comparison with that of dioxane. The saturation concentration in all treatment temperatures is lower in comparison with that of dioxane and the time reached to saturation concentration in the case of DMF is faster than that in the case of dioxane.

As shown in Table 1, the compatibility between the two solvent and PEN is nearly the same by using the total solubility parameter. However, the dissimilar diffusion behavior for the two solvents in PEN was observed at same treatment temperature. This is a reflection of the differences in the degree of compatibility between the polymer and each solvent. The solubility parameter distance, $\Delta\delta$, is used to classify the compatibility of solvent for the polymer. For a good solubility, $\Delta\delta$ must be small (≥ 5). The values of $\Delta\delta$ for dioxane and DMF in PEN have been estimated using the

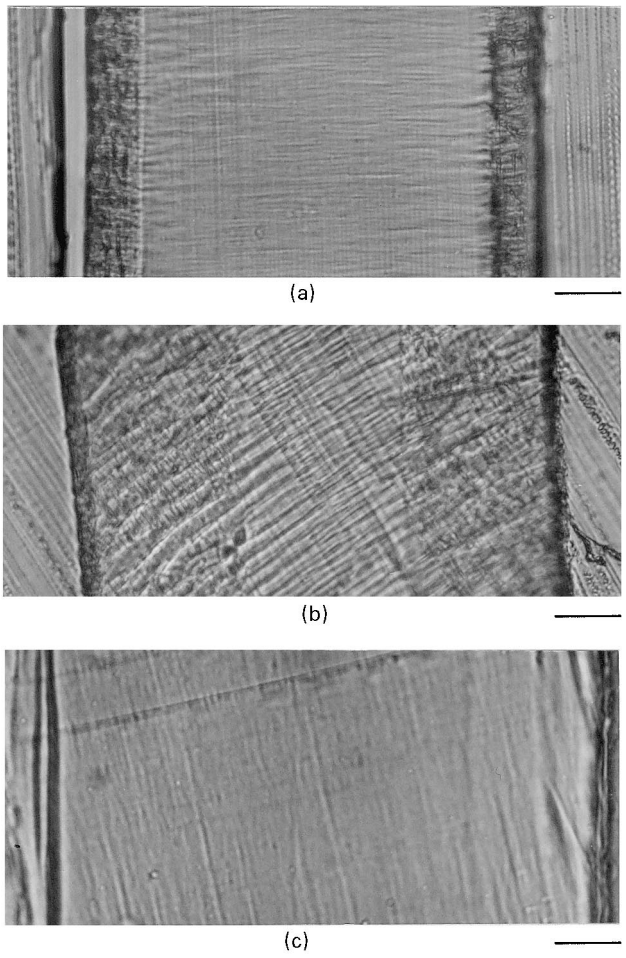

Fig. 5. Optical micrographs of microtomed cross-section of PEN films immersed at 25°C in dioxane coloured with iodine. (a) 50 min, (b) 130 min and (c) 170 min. bar:25 μm.

three component solubility parameter (Hoy's method) [16,17]. The Δδ for DMF and dioxane is calculated to be 1.0 and 5.7, respectively. It suggest that DMF is much better solvents for PEN than dioxane though the compatibility of DMF and dioxane for PEN is similar in the view of the concept of total solubility parameter. The differences of diffusion behavior between dioxane and DMF are caused to the compatibility of solvents for PEN.

Fig. 7 shows the sequence of WAXD of PEN films saturated with DMF at all treatment temperatures. The crystalline reflection of WAXD profiles at all treatment temperatures are similar with those represented in PEN treated with dioxane above 40°C.

4. Morphology of Solvent Induced Crystallized PEN

Several researchers have studied the crystallization behavior of PEN. Makarewicz et al. [1] and Desai et al. [2] studied spherulitic growth behavior by SINC. By the thermal crystallization, Buchner et al. [23] observed the

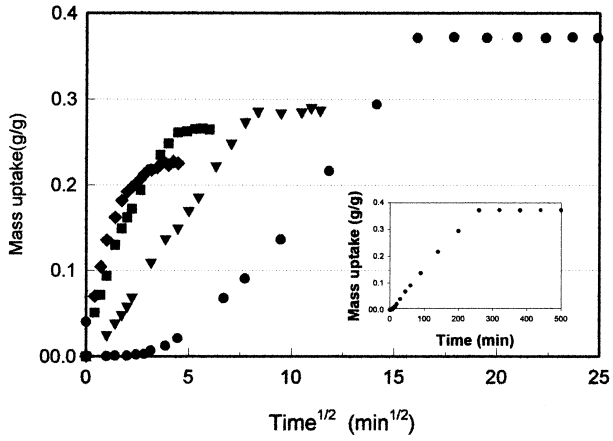

Fig. 6. Mass uptake per mass of dry polymer versus $t^{1/2}$ for DMF sorption in amorphhous PEN films at 10°C (●), 25°C (▼), 40°C ■) and 60°C (◆).

number of fluctuating crystal embryos with assumption that if embryos are larger than the critical nucleus, they may act as crystal nuclei. According to their observation, it is reported that after melting at 300°C, the α-modification is formed at crystallization temperatures below 200°C, while mainly β-modification is formed above this temperature, irrespective of which modification was present before melting. It is also reported that when the melting occurred at 320°C, the α-modification was obtained above 200°C [23].

As shown in Figs. 2 and 3, the WAXD patterns of PEN treated with dioxane are quite different according to treatment temperature. The samples treated in dioxane above 40°C exhibits the diffraction profile based on the typical α-crystal, in which the (010), (100), and (10) reflections occur respectively at $2\theta = 15.63°$, 23.31°, and 26.98° [13]. The sample treated in dioxane at 25°C shows the diffraction profile of the β-crystal, in which (1), (020), and (22) reflections occur at $2\theta = 16.44°$, 18.54°, and 25.52°, respectively [14,15]. Also, the reflection corresponding to the (010) of

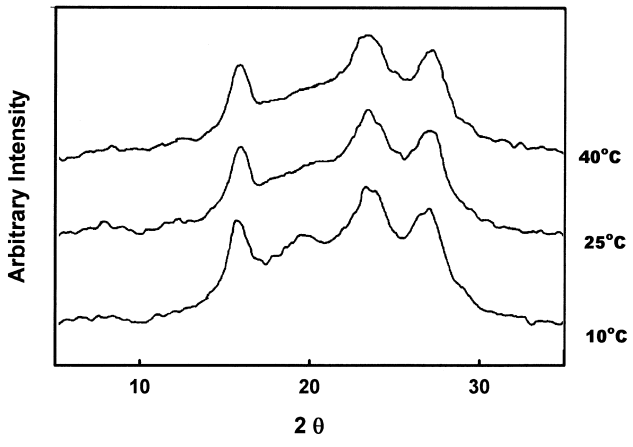

Fig. 7. X-ray diffraction curves of PEN films treated with DMF at 10°C, 25°C and 40°C.

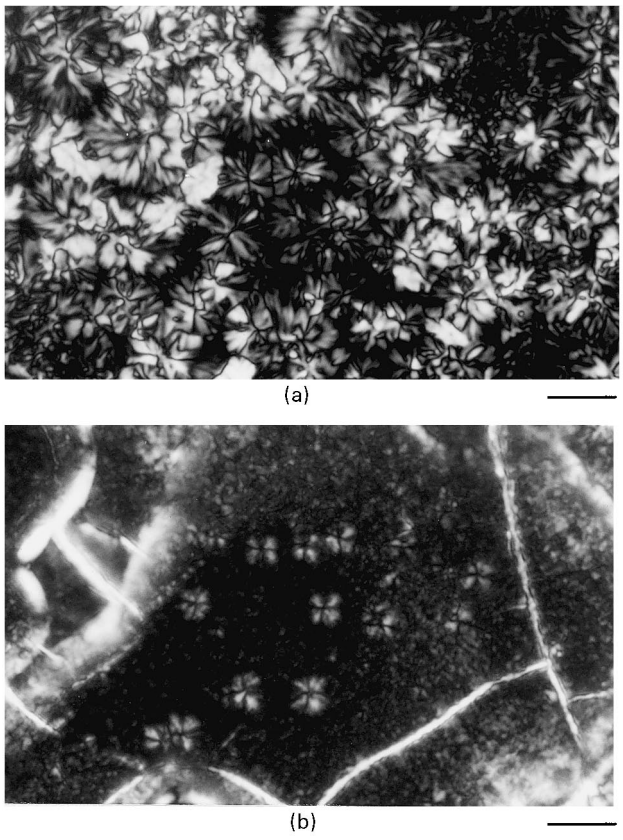

Fig. 8. Morphological change of crystal structure according to the crystallization process. bar: 25 μm. (a) Annealing at 230°C, (b) SINC at 40°C.

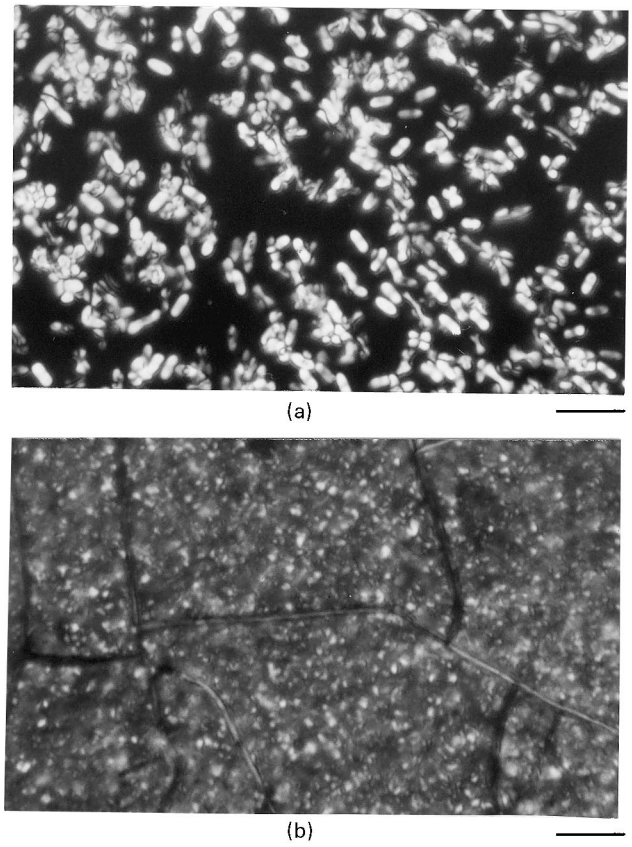

Fig. 9. Morphologial change of crystal structure according to the crystallization process. bar: 25 μm. (a) Annealing at 260°C, (b) SINC at 25°C.

the α-crystal is shown as shoulder at $2\theta = 15.63°$. It is thought that this sample is crystallized mainly in the β-crystal. The samples treated with DMF mainly show the α-crystal irrespective of treatment temperature. However, the reflection corresponding to the (020) of the β-crystal shows in the sample treated at 10°C.

The β-crystal occurred at lower treatment temperature in SINC, while the β-crystal occurred at higher crystallization temperature in isothermal crystallization.

According to the results of diffusion behavior and WAXD, it is thought that the change of crystal form in PEN films treated with dioxane and DMF is caused to the difference of diffusion behavior and the characteristics of solvents. The sample treated in dioxane at 25°C showing Case II behavior is crystallized mainly to β-crystal, but the sample treated in dioxane above 25°C showing Fickian behavior does not show β-crystal, i.e. the crystal form of the sample treated in dioxane changes with the diffusion behavior according to the solvent treatment temperature. It suggests that the β-crystal which is thermodynamically more stable [14] is formed because of stable packing of chain segments in PEN, because the crystallization in the Case II occurs continuously and slowly in comparison with the Fickian behavior. However, the sample treated in DMF at 10°C is crystallized mainly in the α-crystal although the diffusion behavior is Case II. The dioxane and DMF are good solvents for the aromatic and aliphatic moiety of PEN as like the case of PET [24], respectively. That is, the interaction of dioxane for aromatic moiety of PEN is larger than that with aliphatic moiety of PEN when dioxane is selected as solvent. That may affect the formation of β-crystal. Therefore, the characteristics of the solvent is yet another factor to affect the crystal form.

Our experimental results concerning the influence of SINC conditions on the formation of β-crystal are as follows. The solvent, which has good compatibility for the aromatic moiety of PEN, may be selected. And then, solvent treatment temperature must be enough low to make Case II diffusion behavior. However, the cause for the formation of β-crystal in SINC warrants further research.

The isothermal crystallization behavior of PEN was studied by Kim [25] who found that the α-crystal was accompanied by spherulitic growth below 230°C and the amoebae structure which is in the β-crystal was formed at 230°C–250°C.

Figs. 8 and 9 show the polarized optical micrographs of the change in the crystal structure of PEN samples.

The sample treated with dioxane at 40°C shows the distinct maltese cross patterns, indicative of optically anisotropic spherulites [1,2]. The amoebae structure is observed

from the PEN film, which was thermally crystallized at 260°C and crystallized in dioxane at 25°C. However, the size of amoebae by SINC is smaller than that by thermal crystallization.

5. Conclusion

The diffusion behavior in dioxane at 40°C and 60°C was not pure Fickian but apparent Fickian where diffusion was controlled by crystallization. The diffusion behavior at 25°C was not pure Case II because diffusion is affected by crystallization though its influence is much less severe than that by the case of high treatment temperature. The diffusion behavior in DMF was similar to that in dioxane. However, the saturation concentration in all treatment temperatures was lower in comparison with that of dioxane, and the time reached to saturation concentration in the case of DMF was faster than that in the case of dioxane. The differences of diffusion behavior between dioxane and DMF are caused to the compatibility of solvents for PEN.

The samples treated in dioxane above 40°C exhibited α-crystal and spherulitic texture, while in the case of 25°C was β-crystal and the amoebae structure. The DMF treated samples mainly showed the α-crystal irrespective of treatment temperature. However, the trace of β-crystal showed in the sample treated at 10°C.

It is manifested that the change of diffusion behavior with treatment temperature affects the crystallization conditions, and the crystalline form in SINC is changed by the characteristics of the solvent.

Acknowledgement

The authors wish to acknowledge the financial and technical support of KOLON Industries Inc.

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