

Crystallization of Poly(ethylene terephthalate) from Oriented Amorphous Film

Dedicated to the Memory of the late Professor Ichiro Sakurada

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ABSTRACT: Solution cast amorphous poly(ethylene terephthalate) (PET) films were hot drawn uni-axially at 80—130% min^{-1} to a draw ratio of 4—5 at 85—94°C to give amorphous films of high chain orientation in the global sense while the segmental orientation was entirely random. These films were isothermally crystallized at 110°C with film ends clamped tight. The kinetics of crystallization was followed by FTIR based on a computer resolution of the 1020 cm^{-1} band into *trans*-conformations in crystalline and in amorphous regions and *gauche* conformation. An induction period of 5—6 min was observed for the crystallization of the oriented film, while undrawn film did not show an induction period longer than 45 s. Comparison with stress relaxation data of these oriented amorphous films at 82—112°C indicates that the thermal relaxation of the global chain orientation by dis-entanglement and rubbery flow which precedes crystallization is responsible for the induction period.

KEY WORDS Crystallization Kinetics / Poly(ethylene terephthalate) / Uni-axially Drawn Film / Stress Relaxation /

When an amorphous poly(ethylene terephthalate) (PET) film is drawn above its glass transition temperature (T_g) the film will undergo strain-induced crystallization or not depending on the drawing rate and temperature as a consequence of the rivalling processes of chain orientation and its thermal relaxation.^{1,2} By drawing at lower rates to a certain draw ratio in the temperature range of 80—105°C the drawn film may appear amorphous by wide angle X-ray diffraction (WAXD), dynamic mechanical spectrometry (DMS) and the chain segments remain un-oriented as judged from results of WAXD, infra-red dichroism, sound velocity and optical birefringence measurements.³⁻⁷ However, in such hot drawn amorphous PET films the macromolecular chains are in fact highly

oriented in the global sense, which is shown by thermal shrinkage, anisotropy in thermal conductivity and elongational stress-strain behavior and also by scanning electron microscopy (SEM).⁷ The term of oriented amorphous film is suggested by the authors⁷ to describe such drawn amorphous PET film, where the molecular chains in global sense are highly oriented while the local segments have random orientation as a result of the enormous difference in the relaxation times of chain segments and global chains. In the present paper the effect of such global chain orientation on the thermal crystallization of the oriented amorphous PET film is studied by Fourier transform infra-red spectrometry (FTIR) in an attempt to elucidate the detailed processes involved.

The methods commonly used to study crystallization rate of polymers include density, microscopy, X-ray diffraction, differential scanning calorimetry (DSC), depolarized light intensity etc. However, fast crystallization process can not be followed by most of the methods mentioned. For the investigation of the isothermal crystallization of oriented amorphous PET films fast response to the process is necessary and thermal shrinkage of the specimen during crystallization is to be avoided. Shen *et al.*^{8,9} found that the IR band near 1020 cm^{-1} assigned to the in-plane bending vibration mode of phenyl C–H in PET is a band sensitive to the conformation of the $-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-$ moiety in the chain and the bands at 1024 , 1021.5 and 1018 cm^{-1} have been assigned to *trans* in the crystalline region (T_c), *trans* in the amorphous region (T_a), and *gauche* (G) conformations respectively. The origin of the effect of $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$ conformation on the in-plane bending frequency of phenyl C–H is not clear at present, very probably in the amorphous region two carboxyl groups of the terephthalate being non-coplanar. The relative contents of T_c , T_a , and G can thus be directly obtained by means of computer resolution of these overlapping bands of the IR spectrum of PET film between 1040 and 990 cm^{-1} . This analysis of the 1020 cm^{-1} band was used in the following isothermal crystallization of oriented amorphous PET films.

EXPERIMENTAL

Air-quenched melt-extruded PET films of 1 mm thickness were amorphous and isotropic by WAXD, birefringence and DMS measurements. Viscosity average mol mass was 1.63×10^4 . Its T_g was 76°C as determined by DMS (3.3 Hz , 2 K min^{-1}) and by DSC (20 K min^{-1}). The half-time of crystallization at 229 and 119°C determined by depolarized light intensity method¹⁰ were 5.3 and 4.5 min , respectively.

Hot drawing of amorphous PET films was performed uni-axially with the other direction free to contract on a laboratory stretching set-up constructed in this laboratory. After drawing the films were quenched to room temperature by air immediately. Stress relaxation of the stretched amorphous films was measured on the same machine at various temperatures between 82 and 112°C . A Si semiconductor transducer was used to read the force. During stretching an increase of specimen temperature amounting to $2-3^\circ\text{C}$ was observed due to heat developed in the specimen.

DMS in the draw direction of the specimen was conducted at 3.3 Hz on an Iwamoto Viscoelastic Spectrometer with a servo-controlled pre-stress at a heating rate of 2 K min^{-1} . Dynamic mechanical loss tangent, $tg\delta$, values were recorded during the first temperature scan from room temperature to 130°C .

Thermal shrinkage of drawn PET films was determined by immersing strip specimen in hot water at 80°C for 1 h. The recovery of deformation R was calculated according to

$$R = \frac{l_1 - l_2}{l_1 - l_1/\lambda} \times 100\%$$

where l_1 , l_2 are lengths of the specimen before and after hot water treatment, respectively, and λ is the draw ratio.

Isothermal crystallization of amorphous PET films was measured by FTIR on a Bruker Model IFS-113 V spectrometer with a cumulation of 30 scans in approximately 45 s. The amorphous PET films used were cast from 2.5% solution of PET in chloroform-trifluoroacetic acid (9:1 v/v) at $60-70^\circ\text{C}$. Some of the films were uni-axially drawn to λ 4–5 at a draw rate of $80-130\% \text{ min}^{-1}$ in the temperature range of $85-94^\circ\text{C}$ to get the oriented amorphous films. The oriented amorphous film was fixed at both ends on a metal frame tightly to prevent the film from shrinkage during crystallization, while the undrawn amorphous film was held between two

Table I. Parameters for the re-construction of IR spectrum in 990–1040 cm⁻¹ region

	T_c	T_a	G
Band position/cm ⁻¹	1024.2	1021.5	1017.8
Band width/cm ⁻¹	5.4	6.4	6.8
Relative absorptivity	2.26	1.91	1

Table II. Conformation break down in PET films, % content

	T_c	T_a	G
Undrawn amorphous film	1.5	0.4	98.1
Oriented amorphous film ^a	0.3	5.3	94.4

^a Drawn at 130% min⁻¹ to $\lambda=5$ at 86°C.

pieces of cardboard so that the film could contract freely during crystallization at elevated temperatures. The samples under crystallization were kept in an oven at desired temperatures. IR band resolution to obtain the relative content of T_c , T_a , and G was based on the computer simulation of the spectrum between 1040 and 990 cm⁻¹ with regression analysis, assuming the band shape fits a mixed Lorentz–Gaussian function (8:2). Absorption peak positions, widths and relative absorptivities of the three bands (Table I) were evaluated from solution cast films on NaCl plates annealed at 95, 125, 140, 160, 180, 200, 220, 230, and 240°C to give different crystallinities.⁸ Another band appearing in the spectrum region peaked at 1043 cm⁻¹ with a band width of 24 cm⁻¹ was taken into account during the reconstruction of the spectrum.

RESULTS AND DISCUSSION

Isothermal Crystallization

Relative contents of T_c , T_a , and G conformations of undrawn and oriented amorphous PET films measured at room temperature are shown in Table II. It is interesting to note that T_c in the oriented amorphous film, 0.3%, is even smaller than the value 1.5% found in the undrawn film. This is in accord, however, with the finding that the dynamic mechanical $tg \delta_{max}$ around T_g of the former is higher than that of the latter.⁷ T_a in the oriented amorphous film, 5.3%, is much larger than that in the undrawn film, 0.4%. This indicates a disruption of crystalline region and a G to T_a conformational

change in the amorphous region during hot drawing. The kinetics of T_c , T_a , and G conformation changes during isothermal crystallization at 110°C for the undrawn and oriented amorphous films are shown in Figure 1. For the undrawn film the content of T_c increased rapidly as soon as the specimen was put into the oven and the increase levelled off after 30 min, the total increase being 7%. In contrast to this, for the oriented amorphous film T_c content remained less than 0.5% for 5–6 min which means an induction period for crystallization. After 6 min T_c content increased rapidly and levelled off beyond 50 min, the total increase being 6%. At the same time the T_a contents in both films showed a sharp decrease at the start of crystallization and then increased rapidly after 3–5 min, levelling off to a net increase of ca. 14% from the minimum. Parallel to the decrease of T_a content an increase of G content was observed during the initial stage of crystallization and then decreased rapidly, levelling off to a G content of ca. 77% in both cases.

Avrami plot has been tried for the crystallization kinetics as shown in Figure 2, in which X_c is the crystallinity of the sample at time t and X_∞ is that at which further increase of crystallinity with time is imperceptible, and

$$\frac{X_c}{X_\infty} = \frac{C(t) - C(0)}{C(\infty) - C(0)}$$

where $C(0)$, $C(t)$, and $C(\infty)$ are T_c contents at beginning of crystallization, at time t and at later periods when further increase is imperceptible, respectively. For the undrawn amorphous film the plot is linear with a slope of 2.0.

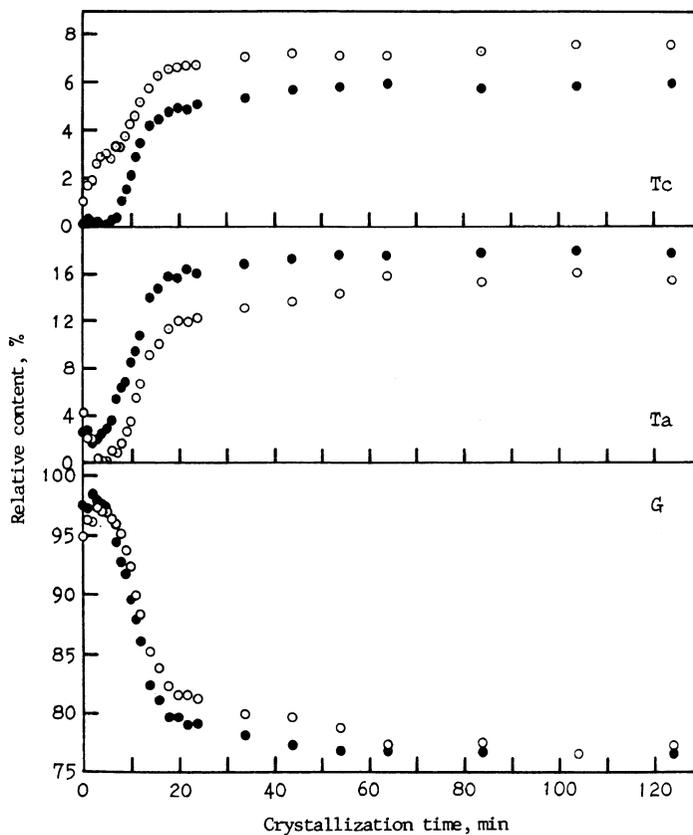


Figure 1. Isothermal crystallization of amorphous PET films at 110°C. O, undrawn film; ●, oriented film drawn at 130% min⁻¹ to $\lambda=5$ at 86°C.

For the oriented amorphous film the plot is linear only in the initial stage of crystallization of 8–14 min with a slope of 3.0. In later times data deviate from the straight line to a much smaller slope.

Thermal Relaxation and the Induction Period of Crystallization

An induction period of 5–6 min exists in the isothermal crystallization of the oriented amorphous PET film at 110°C. The only difference, which may be responsible to this induction period, between the oriented amorphous film and the undrawn amorphous film is the global chain orientation present in the former. It is natural to suppose that thermal relaxation of the global chain orientation is

probably the cause of the crystallization induction period. Thermal stress relaxation experiments were done on oriented amorphous films drawn at 33% min⁻¹ to $\lambda=1.7$ and subsequently relaxed at temperatures between 82 and 112°C. Experimental results are shown in Figure 3. The drawn films relaxed for 1×10^4 s were examined by DMS and the position, height and shape of the α -peak (T_g) of the *tg* δ -*T* curve were used as a probe for the state of macromolecular aggregation in the amorphous regions.⁵ For the specimens relaxed at 82–97°C sharp and high α -peak around 80°C was observed which indicates that the specimen remained amorphous after 10^4 s relaxation. For the specimen relaxed at 105°C a broad and low α -peak shifted to 100°C was observed

indicating crystallization during the relaxation experiment. The results are summarized in Table III. In fact there is a minimum in the

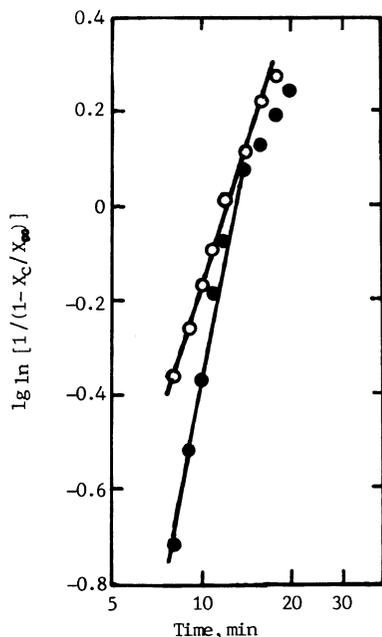


Figure 2. Avrami plots of isothermal crystallization of amorphous PET films at 110°C. ○, undrawn film; ●, oriented film drawn at 130% min⁻¹ to $\lambda=5$ at 86°C.

stress relaxation curve in Figure 3 located around 30 min then followed by a rise of stress values. For the specimen relaxed at 112°C the stress minimum of the stress relaxation curve occurs around 3 min. The stress rise in the relaxation indicates the commencement of crystallization. Comparing these results with the induction period ob-

Table III. DMS data for oriented amorphous PET films after stress relaxation for 10⁴ s. The films has been drawn at 33% min⁻¹ to $\lambda=1.7$

Relaxation temperature/°C	$tg\delta_{max}$	Peak temperature/°C	Peak half-width/°C
83	1.05	81	10
90	0.94	80	13
97	0.74	82	18
105	0.24	100	48

Table IV. Thermal shrinkage at 80°C, 1 h for PET films drawn at 30% min⁻¹ to $\lambda=1.7$ and relaxed at 96°C

Time of relaxation/s	1	10	10 ²	10 ³	10 ⁴
Recovery R/%	60	33	13	5	2

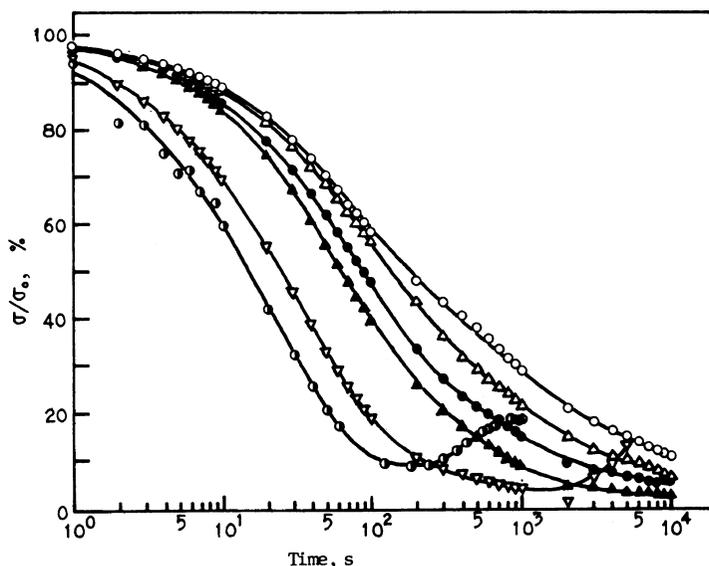


Figure 3. Stress relaxation curves of oriented amorphous PET films drawn at 33% min⁻¹ to $\lambda=1.7$ and relaxed at various temperatures. ○, 82°C; △, 85°C; ●, 90°C; ▲, 97°C; ▽, 105°C; ●, 112°C.

served in isothermal crystallization we believe that the induction period corresponds to the stress decay period in thermal relaxation.

In hot drawing of PET film the deformation process leading to chain orientation in global sense is mainly rubbery deformation with small contribution from rubbery flow as shown by 75% recovery in thermal shrinkage.⁷ Thermal shrinkage at 80°C for 1 h for the above mentioned drawn specimens relaxed at 96°C to various times and then air quenched is shown in Table IV. In this case the film remained amorphous after 10⁴ s of thermal relaxation. As the stress was decaying all the time, the decrease of recovery of deformation during the stress relaxation experiment must be attributed to rubbery flow and chain disentanglement. The fact that in an oriented amorphous film the chain crystallization is to be preceded by rubbery flow and disentanglement is quite understandable. A decrease of chain orientation as revealed by optical birefringence in the initial stage of crystallization at 95–115°C of amorphous pre-oriented PET fiber sample melt spun at 1250 m min⁻¹ was also observed by Wasiak *et al.*^{11,12}

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