

AMORPHOUS POLY(ETHYLENE TEREPHTHALATE) FILMS IN THE STATE OF HIGH GLOBAL CHAIN ORIENTATION BUT NEARLY RANDOM SEGMENTAL ORIENTATION

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ABSTRACT

The isotropy or anisotropy in some physical properties of the amorphous poly(ethylene terephthalate) films uniaxially drawn at temperatures above its T_g and then quenched to room temperature have been studied. Experimental results here presented show that this amorphous state of high global chain orientation but nearly random segmental orientation, the GOLR state, is nearly isotropic in refractive indices and Young's modulus for small deformation, while it is very probably anisotropic in thermal conduction and microwave dielectric properties.

INTRODUCTION

The concept of amorphous state of high global chain orientation but nearly random segmental orientation, the GOLR state, of flexible-chain polymers was first envisaged by Slonimsky^[1,2] and was experimentally demonstrated by Qian et al.^[3] in the uniaxial stretching of amorphous films of poly(ethylene terephthalate) (PET) at temperatures 15 to 25°C above its T_g and subsequent quenching to freeze into the glass state. They interpreted the experimental results as the consequence of large difference in the relaxation rate of global chain orientation and local segmental orientation at temperatures above T_g . An attempt to resolve the difficulties in the understanding of stress-orientation-strain behavior of rubber and thermoplastics under uniaxial stretching, Windle et al.^[4] put forward a two-component

model, that is an orientational deformation, and an extensional deformation and presented a schematical picture of these two modes of deformation shown in Fig. 1 taken from Ref. [4]. Recently a molecular dynamics simulation of the relaxation of a fully extended polyethylene (PE) chain at 300 K (Y. Chen et al. to be published), which is 155 K above its T_g (145 K^[5]), showed the state of high global chain orientation but nearly random segmental orientation of a single-chain PE as presented in Fig. 2. These two figures give us an very vivid and illustrative picture of the GOLR state of a single chain. As the Rouse model^[6] of chain dynamics does not include the fast local segmental relaxation, a clear and quantitative understanding of the rates of local chain segmental relaxation, which will obviously depend on the size of the segment, is lacking. It has been shown that in GOLR state some physical properties are anisotropic such as stress-strain behavior under large deformation and thermal conduction, while other properties are nearly isotropic such as optical birefringence, IR dichroism and WAXD pattern etc.^[3,7] It is interesting to re-examine the isotropy or anisotropy in physical properties of amorphous PET film in GOLR state. In this paper measurements on the modulus at ultrasonic frequency, on thermal conductivity and on microwave dielectrical properties are presented and discussed.

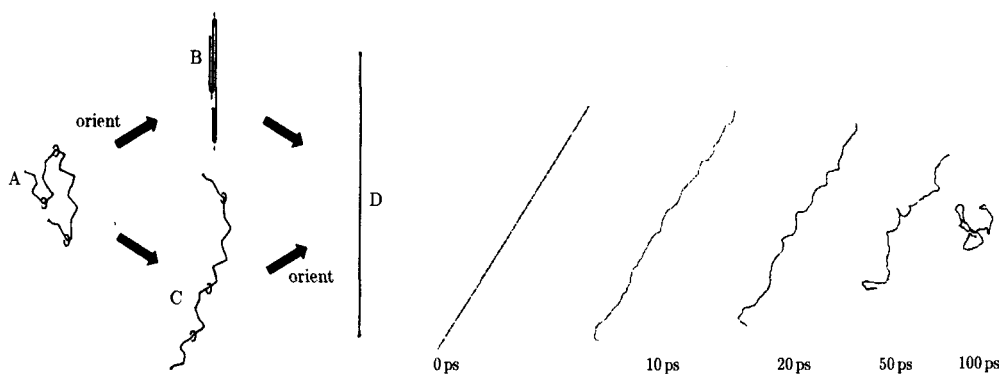


Fig. 1 Schematic showing the two possible modes of deformation on stretching a polymer coil: A-undeformed coil; B-orientational deformation; C-extensional deformation; D-fully extended chain after both modes have operated

Fig. 2 Molecular dynamics simulation of the relaxation of a fully extended PE chain at 300 K. The figures show the morphology of the PE chain after 10 to 100 picoseconds

EXPERIMENTAL

Amorphous PET films in GOLR state

Amorphous PET films of ca. 0.3 mm and 1 mm thickness taken from the cold drum after melt extrusion of PET in an industrial production line were taken. The film was amorphous as checked by its density, $\rho = 1.3363 \text{ g/cm}^3$ and no X-ray crystallinity was observable and the optical birefringence $< 10^{-4}$. The $90 \times 90 \text{ mm}^2$ sheet film was uni-axially drawn at a temperature above its T_g on a Toyoseki biaxial stretching machine at a specified speed to a draw ratio of λ , while the other direction was free to contract. The drawn film was cold air quenched and test specimens were cut from its central part. The deformation of the drawn film was not uniform along the machine direction, the actual value of λ of the testing specimen was obtained from the change of the spacing between parallel line marks painted on the film before stretching. The nearly random segmental orientation of the GOLR state was checked by measuring the refractive indices of the drawn film in the draw direction and the transversal direction in the film plane by the method of Samuels^[8] using an Abbe refractometer. In some cases the refractive index in the thickness direction was also measured. It was found that the actual segmental orientational state of the drawn film was very sensitive to the actual conditions of drawing and relaxation. As the temperature control of the specimen chamber of the stretching machine and subsequent cold air quenching could not be very precisely reproduced in each drawing operation, some variations in the refractive indices and in the measured physical properties were found to result.

Measurements of physical properties

The measurement of sonic velocities along three directions, the draw direction, the transversal direction and the thickness direction, of the drawn film was performed at an ultrasonic frequency of 10 MHz using an experimental setup described elsewhere^[9]. From the sonic velocity, v , the Young's modulus value $E = \rho v^2$ was calculated.

The measurement of thermal diffusivities, D , along three directions of the film was carried out by the method of pulsed photothermal radiometry^[10]. The value of thermal conductivity, Λ , was calculated from $D = \rho c_p \Lambda$, where c_p is specific heat of the film. Drawn films of $60\text{--}80 \mu\text{m}$ thickness were used for thermal diffusivity measurements.

The measurement of the real part, ϵ' , and the imaginary part, ϵ'' , of the complex dielectric constant at a microwave frequency of 3.98 GHz in the film plane in draw

and transversal directions was carried out by the method of Osaki^[11].

RESULTS AND DISCUSSION

Young's modulus

Mechanical properties at small deformation of a PET film in GOLR state was studied by ultrasonic velocity measurements at 10 MHz. The specimen was drawn at 100°C and 88%/min to a $\lambda = 3$. Hereafter the draw direction and the transversal direction in the film plane are designated as the directions 1 and 2 respectively and the thickness direction is designated as the direction 3. Refractive index and ultrasonic velocity measurements gave the following results:

Refractive indices $n_1 = 1.5747$, $n_2 = 1.5773$, $n_3 = 1.5737$

Young's modulus $E_1 = 3.72$, $E_2 = 3.80$, $E_3 = 3.68$ GPa

Within the experimental error of $\pm 4\%$ the Young's modulus of the specimen could be considered as isotropic. It is to be noted in our previous publication^[3] the sonic velocity at 3 kHz along the draw direction was 3% smaller than that before stretching. The order of E values in the three directions are in parallel to the order of refractive indices in these three directions. This seems to be reasonable. Here $n_2 > n_1$. In other cases usually $n_1 \approx n_2$. According to the publication of Chiu et al.^[12] for an amorphous PET film of $n = 1.571$ uni-axially drawn at 100°C and 100%/min to $\lambda = 1.5 - 5.0$ the refractive indices in the film plane were $n_1 = 1.575$, $n_2 = 1.570$ from Fig. 1 of their paper, being independent of λ , and n_1 was a little bit larger than n_2 . Very small birefringence in the film plane and refractive indices in the film plane being independent of λ could be considered as the characteristics of GOLR state of amorphous polymer films.

Thermal conductivity

A qualitative but very convincing conclusion about the anisotropy of thermal conductivity in the film plane of an amorphous PET film uni-axially drawn at 105°C to $\lambda = 3.5$ was given in the previous publication^[3]. The anisotropy estimated from Fig. 2 of Ref. [3] is $A_1/A_2 \sim 1.1$. A more precise determination of the thermal diffusivity D along three directions of the film specimens in GOLR state was attempted by pulsed photothermal radiometry. One measurement on an amorphous PET film drawn at 105°C and 390%/min to $\lambda = 7.3$ showed $\rho = 1.3364$ g/cm³, $n_1 = 1.5279$, $n_2 = 1.5728$, $n_3 = 1.5728$ and $D_1 = 1.46$, $D_2 = 1.32$, $D_3 = 1.32$, all in units of 10^{-3} cm²/s. That is $A_1/A_2 = 1.11$. Other results of measurements on amorphous PET films drawn at 100°C to $\lambda = 4 - 5$ are listed in Table 1.

As the experimental precision was only $\pm 3\%$, the error in D_1/D_2 is $\pm 6\%$ it is difficult to say that the thermal conductivity is anisotropic except the last specimen, which however showed rather large birefringence. Hence it is very important to have more precise determination of thermal diffusivity in order to draw convincing conclusion about its anisotropy. The simple method of observing the melt front to show the anisotropy in thermal conduction seems to be really valuable, as here the thermal conductivities in two directions are compared simultaneously. It is also to be noted that in these films when the draw rate used is small it leads to smaller global chain orientation.

Table 1 Refractive indices, thermal diffusivities, draw ratios, draw rates and densities of uniaxially hot drawn amorphous PET films

λ	draw rate (%/min)	ρ (g/cm ³)	n_1	n_2	n_3	D_1 (10 ⁻³ cm ² /s)	D_2	D_3	D_1/D_2
4.0	75	1.3375	1.5727	1.5721	1.5667	1.39	1.38	1.37	1.01
4.0	98	1.3375	1.5728	1.5718	1.5659	1.36	1.32	1.30	1.03
5.0	75	1.3383	1.5729	1.5727	1.5723	1.39	1.36	1.32	1.02
~ 4.0	378	1.3365	1.5834	1.5702	1.5520	1.60	1.40	1.31	1.14

Hellwege et al.^[13] arrived at a definite conclusion long time ago that the thermal conductivities are anisotropic for amorphous PVC, PC, PMMA and PS films drawn above their T_g and then cooled to 30°C below their T_g to give Λ_1/Λ_2 values 1.38 and 1.10 as estimated from their published Fig. 7^[13] for PMMA and PS respectively, both being drawn to $\lambda = 3.0$. They also showed that thermal expansion coefficients, β , were anisotropic, $\beta_1 < \beta_2$.

Microwave dielectric properties

The method utilizes polarized microwaves in a cavity resonator system and the measurement involves no contact with the specimen film. It is a very convenient method to measure the molecular orientation through the anisotropy in complex dielectric constant $\epsilon^* = \epsilon' - j\epsilon''$ of film samples at microwave frequencies^[11]. The measurement could be performed as short as a half minute. The instrument has been improved^[14] to take narrow strip samples of >2 mm in width.

Amorphous PET films drawn at 100°C and 100%/min to a $\lambda = 4$, $n_1 - n_2 \sim 3 \times 10^{-3}$ were cut to strips along the draw direction to strips of 15–19 mm width, and the strips were 128–155 μ m thick. The average values of ϵ' and ϵ'' at 3.98 GHz measured from three strip specimens found were: $\epsilon'_1 = 3.05_4$, $\epsilon'_2 = 3.14_6$; $\epsilon''_1 = 2.28_5$, $\epsilon''_2 = 2.33_3$. That is $\epsilon'_1/\epsilon'_2 = 0.97$ and $\epsilon''_1/\epsilon''_2 = 0.96$, a rather small but probably

true anisotropy. It is to be noticed that $\epsilon'_2 > \epsilon'_1$ and $\epsilon''_2 < \epsilon''_1$. For uniaxially drawn semicrystalline PET films^[12], $\epsilon'_1 > \epsilon'_2$ and $\epsilon''_2 > \epsilon''_1$.

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Keywords:

Orientation; Uniaxial stretching; Refractive indices; Ultrasonic moduli; Thermal conductivities; Microwave dielectric properties

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