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The relaxation behavior of amorphous PET in global chain orientation but nearly random segmental orientation (GOLR) state

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Summary

In this report, the relaxation behavior of amorphous poly(ethylene terephthalate) (PET) in global chain orientation but nearly random segmental orientation (GOLR) state is studied by infrared dichroism, optical birefringence and hot shrinkage measurements at temperatures below or up PET's glass transition temperature, Tg. The results indicate that the difference in the relaxing rate between global chains and segments is at least in ~ 10^2 times order above PET's Tg (~ 84 °C), with a rough approximation; while the sudden decrease of small Δn of the sample (~ 10^{-4}) upon being treated at about 85 ~ 90 °C, implies us that the small Δn is closely related with the orientation of global chains.

Introduction

The deformations of polymeric materials, such as melt flow, high elastic deformation and orientation of segment and side chain, etc., are all accomplished by the combination of internal-rotation of **C-C** bond of molecular chain. Here, a molecular chain means the same with a global chain. The relaxation behavior of polymers upon being thermal-treated is a rather complicated process for the global chain owing to the interactions existing in the system, such as van der Waals' force, hydrogen bond and chain entanglement, et al.. However, it's relatively easy for local segments relaxation because of their stronger mobility. So, the relaxation of polymeric materials can be catalogued into two components, the orientation relaxation of coil as whole and that of local segment of molecular chains. Owing to the tremendous difference between these two scales of motions, they must follow different relaxation regulations. How to realize this problem in depth is a task that deserves much work.

The concept of high global chain orientation but nearly random segmental orientation of amorphous state, i.e. the GOLR state of flexible-chain polymers was first pointed out by Slonimsky[1] and experimentally demonstrated by Qian et al[2]. The details about this state of amorphous polymer can be found in Ref.[3]. According to Qian [3], the segmental relaxation time is perhaps in the order of seconds or even much shorter depending on how long the local segment is involved in the molecular motion, while the global chain relaxation time is in the order of minutes or longer at the drawing temperature above Tg. Unfortunately, there are not yet any reliable experimental data to illustrate the difference of relaxation states concerning to these two relaxation modes. Recently, the published results on the relaxation behavior of polycarbonate (PC) samples indicate that the segmental orientation relaxes almost totally at 170°C (Tg = 148°C) before the chain extension even starts to relax[4]. A molecular dynamics

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simulation of the relaxation of a fully extended polyethylene (PE) chains (Molecular Weight ~ 10^4) at 300K, which is 155K above its T_g (145K), shows the state of high global chain orientation but nearly random segmental orientation of single-chain PE[5]. However, direct experimental data, which can quantitatively signify the difference between these two relaxing modes, are not yet available.

In this paper, the relaxation behaviors of amorphous poly(ethylene terephthalate) (PET) film in GOLR state are studied by optical birefringence (Δn), infrared dichroism as well as heat shrinkage.

Experimental

Original PET films (undrawn) were supplied by Chenguang Institute of Chemical Engineering, Chengdu, P.R. China. (Molecular weight: Mn ~ 19,000 g/mol, [η]=0.92 dL/ g, measured in a 60/40 phenol/tetrachloroethane solvent at 25 °C, thickness:~ 0.160 mm, ρ=1.3358 g cm^{-3}.)

Amorphous PET films of *ca.* 10 μm thickness were prepared by casting 2.5 % solution of PET in $CHCl_3$-CF_3COOH (10:1 V / V) onto glass plates at 60 °C. The films were air dried and then dried in vacuum at 40 °C for 96 h prior to drawing. The film was put into drawing chamber at ~ 100 °C of a small stretcher. After 3 min it was drawn in one direction at speed of 56% / min to a draw ratio of 1.14 ~ 1.20, while the other direction was free to contract. After stretching, the film was air-quenched immediately.

The polarized spectra were recorded by using a Perkin-Elmer 2000 Fourier transform infrared spectrometer. A gold wire-grid polarizer, set at a maximum transmission position, was used and the polarizer rather than the samples was rotated 90° in order to obtain the two polarization measurements. A total of 32 coadded inerferograms were scanned at 2 cm^{-1} resolution. Infrared dichroism was calculated as $R=A_{\parallel}/A_{\perp}$ for the peak absorbencies of $A_{\parallel}$ and $A_{\perp}$, in which $A_{\parallel}$ and $A_{\perp}$ were the integrated intensities of the peaks in the parallel and perpendicular to draw directions, respectively.

The orientation of the hot drawn samples was characterized by using optical anisotropy measurements by the method of Samuels[6]. The refractive indexes (Δn) parallel and perpendicular to the draw direction were measured by using an Abbe refractometer (Model WZS-1, Shanghai, P. R. China) conjunction with a specially-built polarizing glasses, illuminated by monochromatic light (λ=589.3 nm) from sodium-vapor lamp. To avoid scattering of light from the surface, 1-bromonaphthalene (of refractive index n_D^{20} 1.657-1.659 at 20 °C) was used as immersion fluid. All the measurements were performed at room temperature (*ca.*16 °C).

The uniform parts of films were cut into 0.5 X 7 cm^2 strips and were put into the heater, and the temperatures were controlled within ±1 °C. By cathetometer, the dimensional change of PET samples could be detected by observing the position of the fine nickel wire (coefficient of linear expansion at room temperature is ~ 12.5 X 10^{-6} / K) fixed to the end of samples. With the original length L_0 and the length subjected to the above shrinkage Ls, the changed ratios could be calculated.

Results and discussion

1. *Infrared dichroism detection*

The infrared dichroism technique is a powerful tool for studying the orientation and relaxation[7]. In this investigation , the 973 cm^{-1} band is used to monitor the relaxation processes of local segments, and this band is assigned to the stretching vibration of **C-O** bond. Besides this treatment, we select 727 cm^{-1} band as the internal standard band (**ISB**), which is assigned to the **C=O** out-of-plane bending mode coupled with a ring **C-**

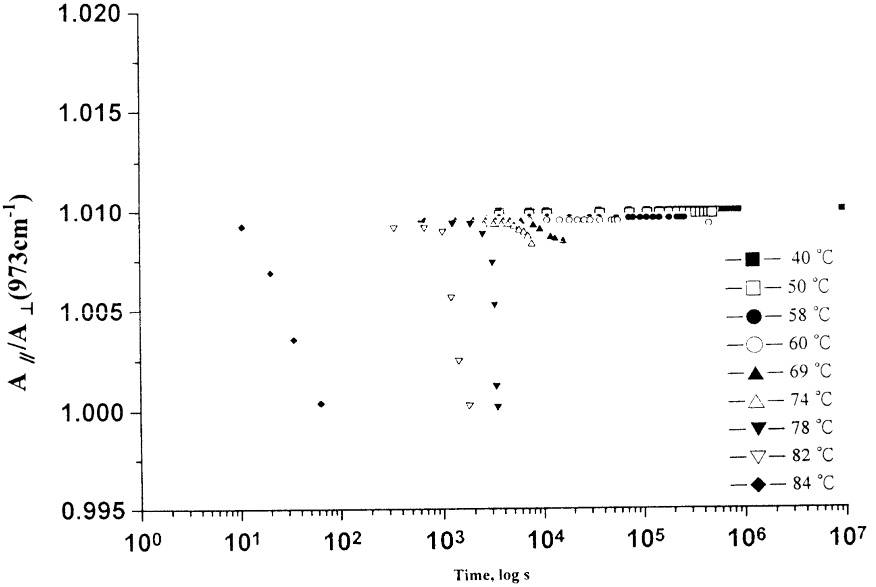

Figure 1 The variation of infrared dichroism (973 cm^{-1} band) was against a function of time at different relaxing temperatures.

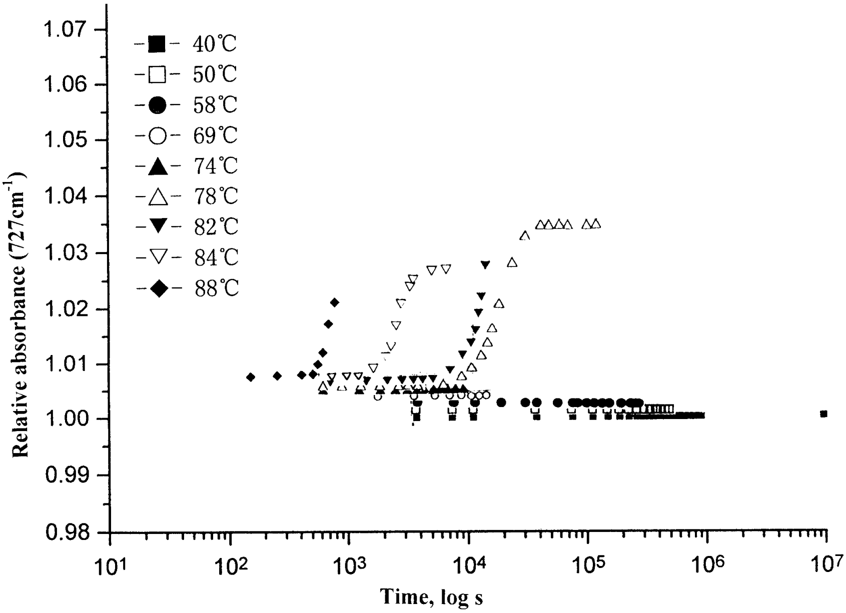

Figure 2 The variation of relative absorbance (727 cm^{-1} band) was against a function of time at different relaxing temperatures.

H out-of-plane bending mode, to follow the change of film thickness during the heating process. In this investigation, the variation of absorbency of **ISB,** 727 cm^{-1}, can be used to give us information on the relaxation behavior of molecular chain, as elucidated in detail in Ref. [8,9].

Figure 1 and 2 shows the relaxing spectrum of orientation of PET's segments and chains respectively at various relaxing temperatures as the function of time. It should be noted that each curve for specific relaxing temperature in Figure 1 and Figure 2 represents a separate experiment on a new film.

For clarity, the corresponding results in these two figures can be summarized in Table 1. As shown, at temperature below Tg, any trace of relaxation of orientation, either of chain (727 cm^{-1}) or of segment (973 cm^{-1}), can not be detected at least in the duration of relaxing time. At about Tg temperature (~ 78 °C), the fully relaxation of segment can be completed within 1 h, while the relaxation of global chain orientation just initiated after ~ 3 h at this temperature. When the temperature goes up to ~ 84 °C (above PET's Tg), the fully relaxation of chain orientation and that of segment can be completed within ~ 90 min and ~ 60 sec, respectively.

Table 1 The comparison of relaxation time scale between molecular chain and segment of PET in GOLR state

	Molecular chain (727 cm-1)	Segment (973 cm-1)
< Tg (°C)	————	————
Tg (78 °C)	3 h ~ 8 h	0.5 ~ 1 h
> Tg (°C)	30 ~ 90 min	10 ~ 60 sec

2. Optical birefringence and hot shrinkage

In order to go in-depth of this investigation, we detect the recovery of length (which can reflect the relaxation of molecular chain) in the drawing direction and the variation

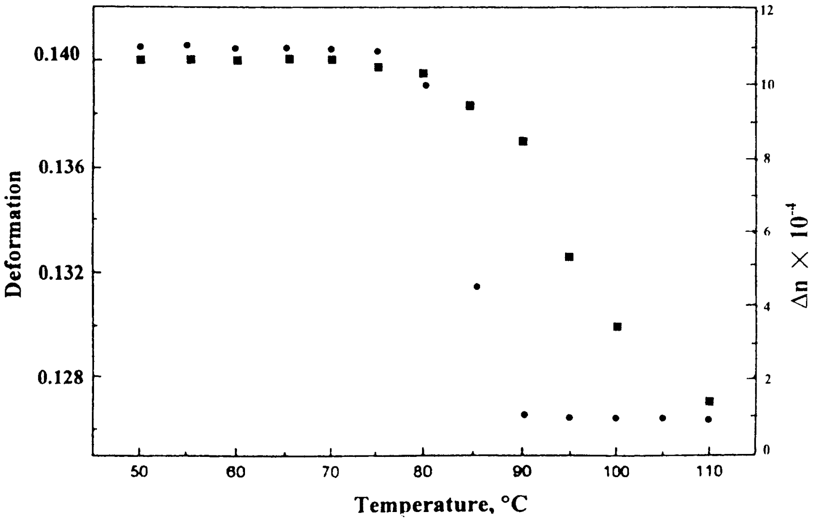

Figure 3 The temperature dependence of recovery of deformation (■) and variation of optical birefringence (●) of PET films in GOLR state

of Δn (which can be used to follow the relaxation of segment orientation) with the elevated temperature and the results are depicted in Figure 3. Each point in this figure corresponds to the sample that is subjected to 2 h relaxation at certain temperature. For the oriented PET sample, no detectable shrinkage can be found when treated in the temperature range of 50-80 °C; meanwhile the optical birefringence (Δn) hardly has any change. In the temperature range of 80-90 °C, the dimension and optical birefringence both change remarkably, the recovery can reach up to ~ 80 % and the Δn abruptly diminishes from ~ 10 X 10^{-4} to 1 X 10^{-4}. So it can be concluded that the abrupt decrease of Δn is followed by the evident shrinkage of PET film when the relaxing temperature is above its Tg.

As a further study, we deliberately select a series of PET films in GOLR state (Δn: 6 ~ 11 X 10^{-4}), then observe the changes of their Δn upon being treated at temperatures above Tg for short time (sec ~ min). The results are tabulated in Table 2.

Table 2. The relaxation time scales assessed by optical birefringence of PET samples in GOLR state

Sample	Δn (10^{-4})	Relaxing temperature (°C)	Time
1#	7	78	~ 60 min
2#	6	80	~ 15 min
3#	11	85	~ 1 min
4#	9	90	~ 20 sec

We can find that the complete relaxation of segment orientation can be finished in ~ 60 min at ~ 78 °C; however, this total relaxation can be completed in seconds at 90 °C. All these results are in well agreement with the observations of infrared dichroism of 973 cm^{-1} band.

Conclusion remarks:

The data of infrared dichroism indicate that at 84 °C, the orientation in segments can be fully relaxed in seconds while the fully relaxation of total molecules need 90 minutes at least. Such tremendous discrepancy in these two relaxation modes suggests us that they must obey different relaxation mechanism. The small value of Δn (~ 10^{-4}) does not decrease until the oriented PET samples begin fast shrinkage at ~ 90 °C (well above PET's Tg, ~ 78 °C), and Δn relaxes rapidly and completely as soon as the recovery in drawing direction is initiated, these results may tell us that the small Δn is intimately associated with the orientation of molecular chains.

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