

POLYMETHYLMETHACRYLATE FILMS IN THE STATE OF HIGH GLOBAL CHAIN ORIENTATION BUT NEARLY RANDOM SEGMENTAL ORIENTATION*

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Abstract PMMA films in the high global chain orientation and nearly random segmental orientation (GOLR) state were prepared by uni-axially drawing at temperatures 20 ~ 30°C above its glass transition temperature, T_g , and their isotropic and anisotropic properties were studied. Experimental results show that this kind of amorphous state, the GOLR state, is nearly isotropic in optical birefringence, IR-dichroism and X-ray diffraction patterns, but is very anisotropic in behaviors of thermal expansion, solvent-swelling and stress-strain.

Keywords Orientation, Uniaxial stretching, Polymethylmethacrylate, Optical birefringence, WAXD, Infrared spectroscopy

INTRODUCTION

The concept of an 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.* in the uniaxial stretching of amorphous films of polyethylene terephthalate (PET) at temperatures ~15 to 25°C above its T_g and the subsequent quenching to freeze into the glass state^[3]. 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 . In an attempt to resolve the difficulties in the understanding of stress-orientation-strain behavior of rubber and thermoplastic under uniaxial stretching, Windle *et al.* put forward a two-component model, that is an *orientational deformation*, and an *extensional deformation*^[4]. This model is regarded by Heymans^[5] as currently one of the most convincing models to describe the orientation behavior of glassy polymers; however one drawback of this model is that it ignores the fact that the orienting units are joined into chains.

On the basis of our study of PET in the GOLR state, we have obtained a portrait of this kind of state, i.e. some physical properties are anisotropic, such as thermal conduction and stress-strain behavior under large deformation, while other properties, i.e. optical birefringence, IR dichroism and WAXD pattern, are nearly isotropic^[3, 6]. Our recently published result reveals that by drawing at temperatures up to ~30°C higher than its T_g , we can acquire oriented atactic polystyrene (a-PS) films which present nearly the same GOLR characteristics as that of PET films^[7]. In the present paper, as one part of our systematic studies, we report the experimental results of our study on

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atactic polymethylmethacrylate (a-PMMA) films in the GOLR state. The subsequent tests give us information on anisotropy or isotropy on a molecular or segmental scale. This thorough observation may suggest that, under proper drawing conditions, the GOLR state can be realized in nearly all amorphous polymeric materials, in addition to noncrystalline PET and a-PS.

EXPERIMENTAL

Sample Preparation

The a-polymethylmethacrylate ($M_n = 753\,000$ g/mol, $M_w = 1\,848\,000$ g/mol, determined by GPC-210, Polymer Laboratory, U.K., with polystyrene as standard sample) used in this research was kindly supplied by Prof. Jing-shu Shen of Institute of Chemistry, Chinese Academy of Sciences. The glass transition temperature (T_g) was measured at $\sim 105^\circ\text{C}$ by using a TA Instrument DSC-2910 at a heating rate of $10^\circ\text{C}/\text{min}$, after calibration with pure indium. Films, with a thickness of $30\ \mu\text{m}$ (used for i. r. dichroism measurement) and $120\ \mu\text{m}$ (used for the other tests) were achieved by casting *ca.* 2 wt% and 4.68 wt% dichloromethane solutions onto glass plates, respectively. Subsequent treatment was carried out at 60°C in a vacuum oven for at least 72 h to remove any traces of solvent and also to relieve internal stress. PMMA films in GOLR state were generated with the aid of a small stretching machine operating at variable strain rates ($33\%\sim 97\%$ / min) and with a special oven to maintain a fairly constant temperature ($140 \pm 0.5^\circ\text{C}$) for all the samples. Draw ratios ($2.32 \sim 2.46$) were determined by measuring the distance between ink marks on the samples. After stretching, the finished films were quenched to room temperature.

Infrared Measurements

The polarized spectra were recorded using 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 co-added interferograms were scanned at $2\ \text{cm}^{-1}$ 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 drawing and transversal directions, respectively. In this work, the $1388\ \text{cm}^{-1}$ absorption band was selected to calculate the orientation function.

$$\langle P_2(\cos\theta) \rangle_{\text{av}} = \frac{(R_0 + 2)(R - 1)}{(R_0 - 1)(R + 2)}$$

where $R_0 = 2\cot^2\alpha$, α is the angle between the chain axis and the dipole moment vector of the vibration being considered, and θ is the angle between the chain axis and the stretching direction.

WAXD Measurements

X-ray diffraction data were recorded on a Rigaku D/max- γ A rotating anode generator functioning at 40 kV and 25 mA, using $\text{CuK}\alpha$ -Ni filtered radiation. Scattered X-rays were measured using a scintillation counter. Scans were taken along the equator and meridian in the θ geometry, with the drawing direction of the sample placed vertically. The slits were made $0.5^\circ/0.15\ \text{mm}/0.5^\circ$, and orientation scans were taken by fixing the 2θ angle at which the maximum diffraction peak was displayed. During this process, scanning was at $4^\circ/\text{min}$ speed and the PMMA sample was rotated over 180° . Air scattering was subtracted after recording a blank diffractogram, and the constant intensity level at high azimuthal angles was taken as the material's background scattering and subtracted from the intensity profile.

Optical Birefringence

Birefringence could reflect the extent of segmental orientation in the polymer system. The oriented samples were characterized for orientation using optical anisotropy measurements *via* the method

introduced by Samuels^[8]. The refractive indices of the samples in the drawing and transversal direction were measured by using an Abbe refractometer (model WZS-1, Shanghai, China) in conjunction with a specially-built polarizing plate, illuminated by monochromatic light supplied by sodium-vapor lamp with wave length $\lambda = 589.3$ nm. To avoid scattering by the surface, dibutyl terephthalate (refractive index = 1.485 ~ 1.500 at 20°C) was used as immersion fluid. All the measurements were performed at room temperature (*ca.* 16°C).

Shrinkage Measurement

The uniform part of films were cut into 5×70 mm² strips and were put into a heater at pre-determined temperatures. The temperature of the heater was kept constant within $\pm 1^\circ\text{C}$. Using a cathetometer, the dimensional change of PMMA films could be detected by observing the position of the fine nickel wire (coefficient of linear expansion was $\sim 12.5 \times 10^{-6}/\text{K}$) fixed to the end of samples. With the original length L_0 and the length after being subjected to thermal shrinkage, L_s , the shrinkage ratios can be calculated.

Anisotropy of Swelling Behaviors

After being taken out from the swelling agent, the dimensional changes of the immersed GOLR samples in the drawing and transversal directions were measured by a measuring microscope at room temperature, a mixture of diethyl ether/petroleum ether ($v/v = 8:100$) was selected as the swelling solution.

Stress-strain Behavior

Anisotropy of stress-strain behavior was tested with an Instron 1122 tensile tester at *ca.* 17.5°C. The film dimensions held between the clamps were $28 \times 4 \times 0.03$ mm³, and the draw rate and strain rate were ~ 2 mm/min and $\sim 7\%$ /min, respectively.

RESULT AND DISCUSSION

Experimental Realization of PMMA Films in GOLR State

The characteristic parameters of the PMMA stretched under some drawing conditions are tabulated in Table 1. The most direct proof of global chain orientation (GCO) is the large shrinkage (β) of the films in drawing direction on being heated to temperatures above its T_g . The β values indicate that the degrees of GCO are rather high; meanwhile β values less than 100% indicate some rubbery flow during drawing. On the other hand, the small optical birefringences ($\sim \times 10^{-4}$) and IR dichroisms ($\sim 10^{-3}$) indicate that the local segment orientation is in a nearly random state.

Table 1. Experimental realization of GOLR state of PMMA films

Sample code	Draw rate (% / min)	Draw ratio	β (%)	$\Delta n (10^{-4})$	$\langle P_2(\cos\theta) \rangle$
PMMA-1	33	2.32	87.5	-7.0	0.006
					(1388 cm ⁻¹ , $\alpha_v \cong 90^\circ$)
PMMA-2	97	2.46	86.5	-9.0	0.006
					(1388 cm ⁻¹ , $\alpha_v \cong 90^\circ$)

* $\beta = (l_1 - l_2)/(l_1 - l_1/\lambda) = (1 - l_2/l_1)(1 - 1/\lambda)$, where l_1 and l_2 are the length of the GOLR film in the drawing direction before heating and after complete relaxation of GCO on being heated to temperature above T_g .

The Anisotropic Characteristics of PMMA Film in GOLR State

The anisotropic characteristics manifest themselves in some physical properties of these oriented PMMA films. Figure 1 exhibits the discrepancy of thermal expansion behaviors in the drawing and transversal directions of PMMA films in GOLR state. In the drawing direction, the negative expansion ratio actually means that the film is contracted, and this contraction becomes more evident near and above its glass transition temperature, T_g . On the contrary, the positive expansion ratios suggest that, in the transversal direction the sample is elongated when treated at elevated

temperatures. For example, when the film was treated at ~130°C for one hour, the expansion ratio can rise to ~21.94%. In the drawing direction, the contraction is due to the disorientation process which is initiated by enhanced motion of molecules, especially when being treated at temperatures above T_g . On the other hand, the constrained molecules in the transversal direction would elongate when relaxation starts.

Similar anisotropy also appears in the variance of solvent swelling response as showed in Fig. 2. The swelling ratio in the drawing direction was rather small and nearly unchanged considering experimental errors; while in the transversal direction, the swelling ratio was successively increased with increasing immersion time.

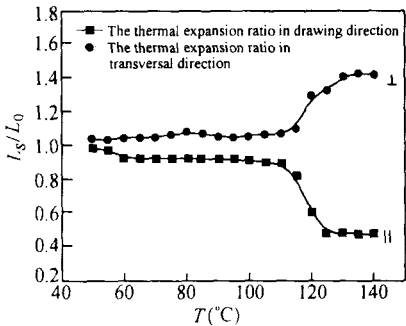


Fig. 1 Anisotropy of thermal expansion behaviors of GOLR PMMA film in the drawing and transversal directions
The film is drawn at 140°C; draw rate and draw ratio are 97%/min and 2.46, respectively.

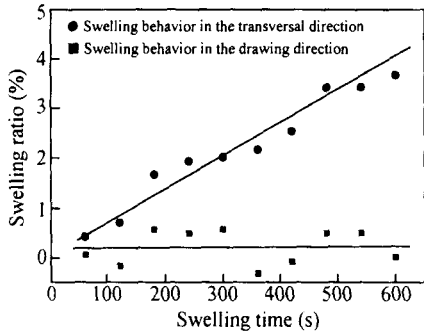


Fig. 2 Anisotropy of solvent swelling behaviors of GOLR PMMA film in a mixture of diethyl ether/petroleum ether ($v/v=8:100$) at room temperature
The GOLR film is drawn at 140°C; draw rate and draw ratio are 97%/min and 2.46, respectively.

Another anisotropy is directly revealed in the stress-strain behaviors in the drawing and transversal directions. At room temperature, the oriented PMMA films are brittle-fractured without yield point but the corresponding values in those two directions vary greatly. For simplicity, the corresponding results are given in Table 2. Each data in this table is the average value of 5 tests.

Table 2. The comparison of σ_b , E_t and ϵ_b in drawing and transversal directions for GOLR PMMA film

	Break strength	Tensile modulus	Elongation at break
	σ_b (MPa)	E_t (GPa)	ϵ_b (%)
Drawing direction	71.09	1.11	16.86
Transversal direction	25.52	0.43	26.25

The Isotropic Characters of PMMA film in GOLR State

Figure 3 shows the polarized infrared spectra of GOLR PMMA film in the drawing and transversal directions (the upper two spectra) and the corresponding difference spectrum (the lower spectrum) of this film sample. Based on the α angle presented in Ref. [9], we can calculate the orientation function value of 1388 cm^{-1} , which is assigned to the symmetric bending mode of the α -methyl (C—CH₃ bond) group, and the transition moment vector of this vibration is taken to be perpendicular to the chain axis ($\alpha = 90^\circ$). The small value (~0.006) implies that the GOLR sample is in a nearly isotropic state in segmental scale.

In the following study, films with a thickness of *ca.*100 μm were subjected to optical birefringence and WAXD tests. Table 3 depicts the result of optical birefringence tests on PMMA films which were stretched at 140°C with different drawing rates and to different draw ratios. In order to depress the experimental errors with respect to the detection of rather low birefringence

($\Delta n, \sim 10^{-4}$) for each sample, at least 5 determinations were carried out and only the average values were listed in Table 3.

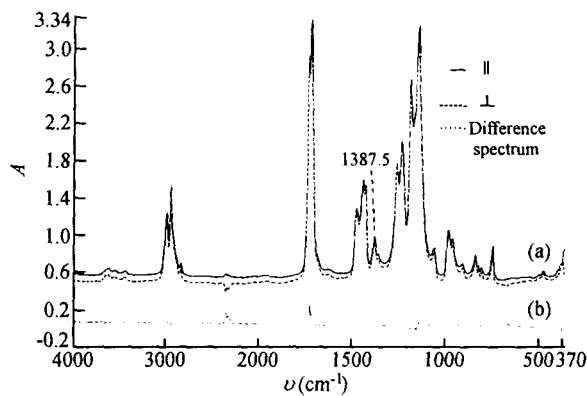


Fig.3 Infrared spectra of GOLR PMMA film stretched at 140°C to a draw ratio ~ 2.46
(a) in the drawing direction (—) and transversal direction (-----),
(b) corresponding difference spectrum (.....)

Table 3. The degree of segmental orientation assessed by optical birefringence of a-PMMA films

Samples code	$n_{ }$ ($\times 10^{-4}$)	$n_{\perp}$ ($\times 10^{-4}$)	$n_{thickness}$ ($\times 10^{-4}$)	Optical birefringence ($\Delta n, \times 10^{-4}$)
PMMA-1 ^a	1.5054	1.5061	1.5057	-7
PMMA-2 ^b	1.5087	1.5096	1.5094	-9

Note: $n_{||}$, $n_{\perp}$ and $n_{thickness}$ are refractive indices in the drawing, transversal and thickness directions, respectively.

- a) Drawing temperature = 140°C, drawing rate and drawing ratio are 33%/min and 2.32%/min, respectively.
- b) Drawing temperature = 140°C, drawing rate and drawing ratio are 97%/min and 2.46%/min, respectively.

In order to acquire further information on the orientation in segmental scale, the films as that used in refractive indices determination, are subjected to WAXD scanning. Although X-ray diffraction method is a well-established technique for the determination of the crystalline phase orientation, quantitative evaluation of the amorphous polymers is far from being straightforward and has been attempted by many researchers^[11-13]. Figures 4(a) and (b) respectively show the X-ray diffraction equatorial scan and orientation scan of the GOLR PMMA films. In Fig. 4(a), as we anticipated, there is the typical diffused shape of scattering centered at around 14°(13.8°). From the orientation scan appearing in Fig. 4(b), we should realize that the high level of noise observed in this spectrum is directly related to the weak intensity of the amorphous halo at the 2θ position chosen for the experiment. As to this GOLR PMMA sample, the intensity follows a straight line, with no evident variation with the χ angle. Base on the calibrations we have undertaken as described in the experimental part, no noticeable orientation can be detected. As a semi-quantitative result this is acceptable. The results discussed above are in good agreement with i.r. dichroism and optical birefringence investigations, with allowance made for the deviations which may be brought about by different analytical techniques.

For interpretation this pattern of GOLR can be ascribed to the difference in the relaxation rate of global chain orientation and local segmental orientation at a temperature above PMMA's T_g . It is well known that orientation and disorientation are temperature-dependent processes. Drawing at

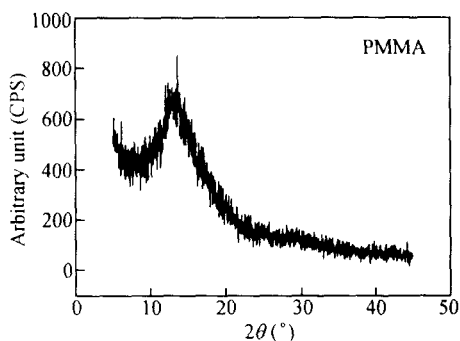


Fig. 4a X-ray diffraction equatorial scan of GOLR PMMA film
The film is stretched at 164°C to $\lambda=2.42$, drawing rate is 53%/min.

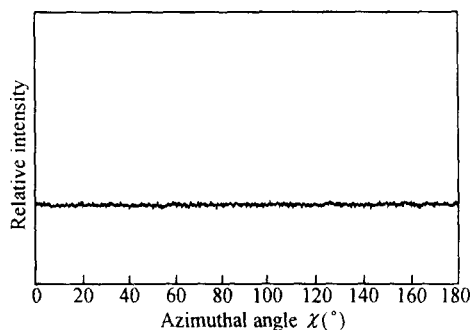


Fig. 4b Orientation scan of the amorphous halo ($2\theta=13.8^\circ$) for a-PMMA film in GOLR state

rubbery state under particular conditions, these two processes will reach an equilibrium in segmental scale. When we try to freeze this state, it is possible to make the amorphous polymer material in GOLR state. Until now there is insufficient reliable experimental data to illustrate the difference of relaxation state concerning these two relaxation modes. Recently, a molecular dynamics simulation of the relaxation of a fully extended polyethylene (PE) chain (molecular weight $M_n \sim 10^4$) at 300 K, which is 155 K above its T_g (145 K) showed the state of high global chain orientation but nearly random segmental orientation of a single chain PE. On the basis of our laboratory's work on amorphous PET by using FT i.r. and the thermal relaxation method, the difference between these two relaxation modes is at least ca. 10^2 times order above its T_g , to a rough approximation^[14]. To sum up, how to understand this unusual behavior of noncrystalline polymers on molecular scale remains a challenge to polymer researchers. As the Rouse model^[15] of chain dynamic 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. More work is needed to pinpoint the exact mechanism behind this unusual relaxation behavior.

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