Transactions of the Materials Research Society of Japan 27 [1] 133-136 (2002)

Magnetic Alignment of Poly(ethylene oxide)

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Magnetic birefringence of 60 and 20 wt% mixtures of poly(ethylene oxide) (PEO) with water was observed at 5 T for PEOs with various molecular weights (Mn=4,600, Mn=10,000, and Mv=200,000). Films cast from the 60% PEO (Mn=4,600 and 10,000) mixture prepared at 22.5℃ in the magnet (5 T) exhibited alignment. X-ray diffraction measurements of the cast films (Mn=4,600 and 10,000) indicated that the *c*-axis (chain axis) is aligned perpendicular to the magnetic field. This orientation of the cast film (Mn=4,600) was confirmed by polarized FT-IR spectroscopy. The film (Mn=4,600) cast in the magnetic field exhibited higher transmittance of the polarized light (at 632.8 nm) in the direction parallel to the applied magnetic field than in the direction perpendicular to the field. No magnetic orientation was observed for the film cast from a 20% PEO (Mv=200,000) mixture.

Key words: poly(ethylene oxide), magnetic orientation, X-ray diffraction, polarized FT-IR spectroscopy, polarized optical microscopy

1. INTRODUCTION

The conditions required for the diamagnetic alignment are: (1) existence of the ordered structures with sizes larger than a critical size so that the magnetic torque can overcome the thermal disturbance, and (2) the environmental viscosity is low enough for a quick rotation. Crystal orientation during the solution crystallization[1-5] and orientation of fibers[6,7] in liquid suspension are good examples that satisfy the above conditions. We have reported that crystalline polymers including poly(ethylene-2,6-naphthalate)[8,9], isotactic polystyrene[10], isotactic poly(propylene)[11], and poly(ethylene terephthalate)[12,13] undergo magnetic orientation during crystallization from melts. We believe that some anisotropic ordered structures forming during the induction period of melt crystallization or even existing in the melt[14,15] is responsible for the magnetic orientation.

Poly(ethylene oxide) (PEO) is widely used in cosmetic and medical fields, because of its low toxicity. PEO is also used as a polymer matrix put between the electrodes in lithium polymer batteries. The orientation of PEO molecules might be useful, for example, for the improvement of the battery performance. In this study, we report the magnetic orientation of the PEO/water mixture and the PEO cast from the water mixture under high magnetic fields.

2. Experimental

2.1 Sample preparation

PEO samples (Mn=4,600, 10,000 and Mv=200,000) were purchased from Aldrich Chemical Company, Inc. The PEO samples (Mn=4,600, 10,000 and 200,000) were dissolved into ion-exchanged water to make mixtures of 60% PEO (Mn=4,600, 10,000) and 20% PEO (Mv=200,000).

The mixture obtained were poured into a cell of 10 x 50 x 0.5 mm in size, and then put in the center of a horizontal magnetic field (5 T) generated by a Sumitomo Heavy Industry crycooler-cooled superconducting magnet for 1 h. The direction of the applied magnetic field was parallel to the longest axis of the cell. The temperature inside the bore was maintained at 22.5℃. No evaporation was allowed during the cell was in the magnet. Microscope observations were performed immediately after the cell was taken out from the magnet.

For the optical measurements, the wide angle X-ray diffraction, and the polarized FT-IR transmission measurements, solid samples were prepared. The mixture prepared was poured onto slide glasses or into boxes of 5 x 10 x 8 mm in size made of plastic film, put in the center of a horizontal magnetic field (5 T) for 24 to 52 h, the evaporation was allowed. The temperature inside the bore was maintained at 22.5℃. For some samples, the evaporation was not completed. These samples were allowed a further evaporation outside the magnet at 22.5℃.

2.2 Polarized optical microscopy

An Olympus BH-2 microscope equipped with two polarizers (cross polars) was used to examine the anisotropy of the sample mixture prepared in the magnet.

2.3 Optical measurements

A home-built optical apparatus was used for the determination of the optical property. The sample was rotated between two parallel polarizers, and the intensity of the transmitting light was measured. The intensity as a function the ratation angle, θ is expressed as

$$I(\theta)^2 = I_0^{\,2}\{\alpha^2\cos^4(\theta-\phi)+\sin^4(\theta-\phi)+1/2\cdot C\cdot\alpha\cdot\sin^2\cdot 2(\theta-\phi)\} \quad \text{-----------(1a)}$$

$$C=\cos(2\pi d\Delta n/\lambda) \quad \text{-----------(1b)}$$

where α and ϕ were determined experimentally. The quantities λ, d, and Δn are the wavelength of He-Ne laser, the film thickness, and the birefringence, respectively. The obtained transmitting light intensity was fitted to the above equation by computer.

2.4 Wide angle X-ray measurements

Wide angle X-ray diffraction (WAXD) measurements for the solidified samples were carried out at room temperature using a MAC Science M18XHF22-SRA system operating at 50kV and 90 mA to generate Ni-filtered CuKα X-ray beam. The X-ray azimuthal scans for these samples were carried out with the geometry shown in Fig. 1.

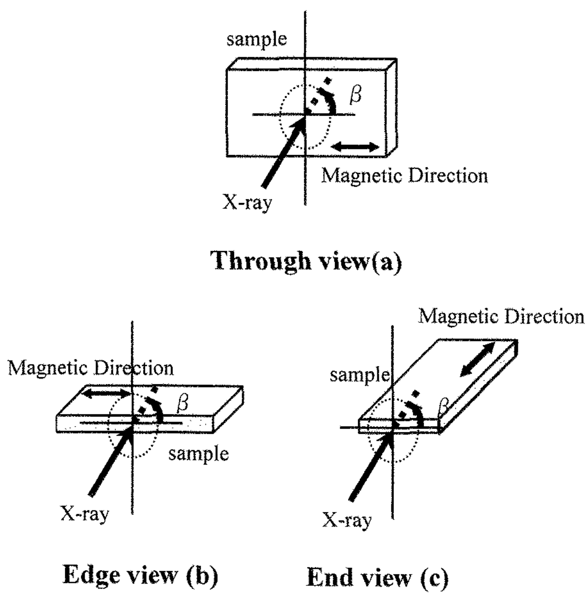

Fig. 1 Geometry of X-ray azimuthal scan: (a) Through view, (b) edge view: the X-ray is perpendicular to the magnetic field, and (c) end view: the X-ray is parallel to the magnetic field.

2.5 Polarized FT-IR transmission measurements

Polarized FT-IR transmission spectra were obtained with 4cm^{-1} resolution and 32 scans, using a Nicolet Nexus 860 FT-IR spectrometer.

3. RESULTS AND DISCUSSION

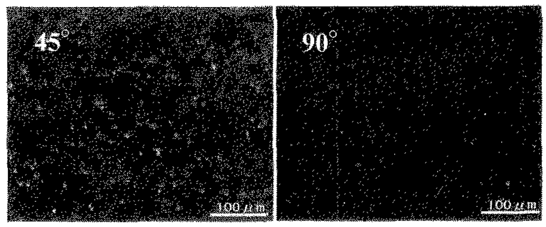

Fig. 2 Optical micrographs of the 20 wt% PEO (Mv=200,000)/water mixture taken between crossed polars after application of 5 T magnetic field. Angles of 45 ° (left) and 90° (right) with respect to the analyzer.

Figure 2 shows the micrographs obtained for the 20% mixture (PEO of Mv=200,000). The micrograph at 45° exhibits a bright image, while that taken at 90° exhibits a dark image, indicating that the sample is aligned in the direction of the magnetic field. The polarized optical microscope observation of 60% (PEO of Mn=4,600, 10,000) mixtures subjected to the magnetic field also clearly exhibited alignment.

Figure 3 shows the result of the optical measurement of the cast film (Mn=4,600). The pattern clearly demonstrates the alignment. The intensity of the transmitting light parallel to the magnetic field is twice stronger than that of the light perpendicular to the magnetic field.

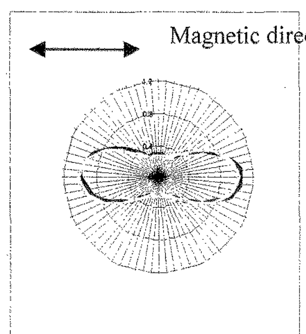

Fig. 3 Transmitting light intensity against sample rotataion angle, θ. Experimental result ▬ for PEO (Mn=4,600) film between two parallel polarizers and simulation result ---- (α =0.5, ϕ =0, R=119 nm).

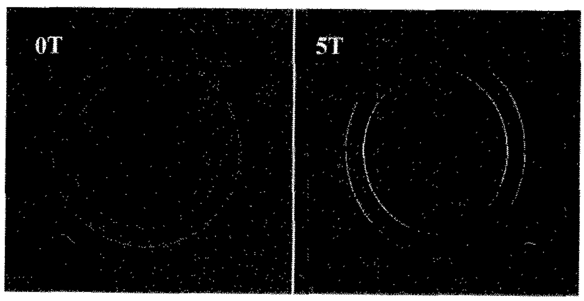

Fig. 4 Through view of the X-ray diffraction of the PEO cast film (Mn=4600) without (left) and with (right) magnetic field (5T). The arrow indicates the field direction.

In order to confirm the alignment, wide angle X-ray measurements were performed. Figure 4 shows the X-ray diffraction photographs obtained for the cast film (PEO with Mn=4,600) with and without the magnetic field. These phtographs clearly indicate that the sample prepared in the magnetic field is aligned. However, the degree of orientation is not very high.

Figure 5 shows the azimuthal scans of through view for the lattice plane (100) of the sample (Mn=4,600) prepared under the magnetic field. The unit cell reported is monoclinic with a=8.05, b=13.04, c (fiber axis)=19.48Å and β=125.4° [16]. For the sample treated inside the magnet, the a^*-axis is parallel to the magnetic field. On the contrary, no orientation was observed for the sample treated without magnetic field.

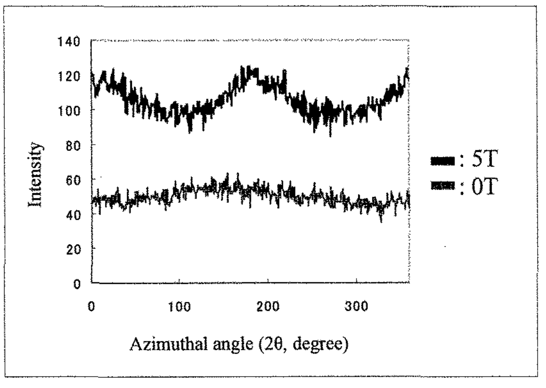

Fig. 5 X-ray azimuthal scans (through view) for the (100) plane measured for PEO film (Mn=4,600) prepared with (5T) and without magnetic field. Field direction corresponds to 0 and 180 degree.

In order to further confirm the orientation of the sample treated inside the magnet, FT-IR measurements were performed. Figure 6 shows the polarized FT-IR transmission spectra of the cast sample (Mn=4,600) prepared under the magnetic field. For comparison, the polarized FT-IR transmission spectra of a stretched PEO film (Mn=4,600) were shown in Fig. 6. The band at 530cm^{-1} is assigned to the OCC antisynmetric bending mode whose transition moment is parallel to the fiber axis (c-axis)[17]. For the sample treated inside the magnet, a stronger intensity was observed for the polarized light with the electric vector perpendicular to the magnetic field, indicating that the c-axis is aligned perpendicular to the magnetic field. This result is in agreement with the X-ray diffraction results.

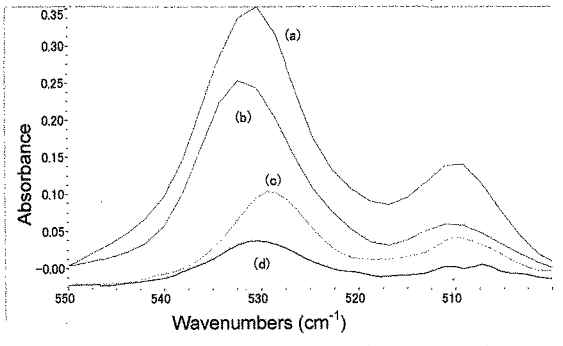

Fig. 6 Polarized FT-IR transmission spectra for the cast film of PEO (Mn=4,600) prepared under the magnetic field ((a), (b)) and by the mechanical stretching ((c), (d)). The polarization is parallel (b) and perpendicular (a) to the magnetic field, and parallel (c) and perpendicular (d) to the stretching direction.

Figure 7 shows the X-ray diffraction phtograph of the cast film (Mn=10,000) prepared under the magnetic field. The degree of orientation of this sample is much higher than that of the sample (Mn=4,600).

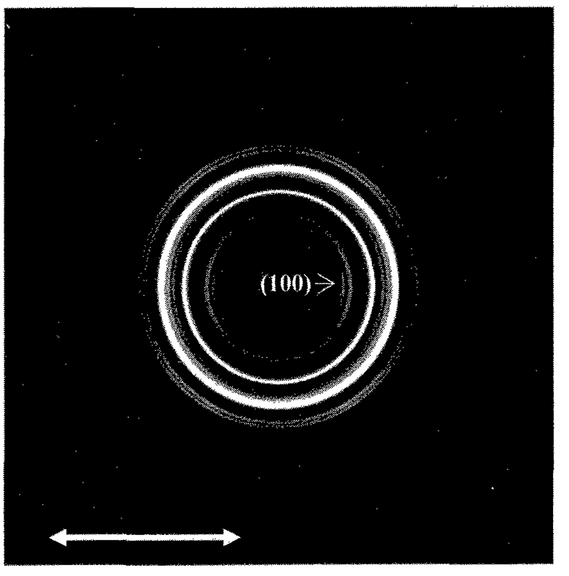

Fig. 7 X-ray through view of the PEO cast film (Mn=10,000) prepared under magnetic field (5T). The arrow indicates the magnetic field direction.

Figure 8 shows X-ray azimuthal scans on through, edge, and end views of the (100) plane measured for the sample (Mn=10,000) treated inside the magnet. The direction of the magnetic field corresponds to 0 and 180 degree. The azimuthal patterns of the through view and the edge view are the same, indicating that the alignment is symmetry along the direction of the magnetic field. The azimuthal pattern of the end view does not show any orientation. These results indicate that the c-axis is aligned parallel to the magnetic field.

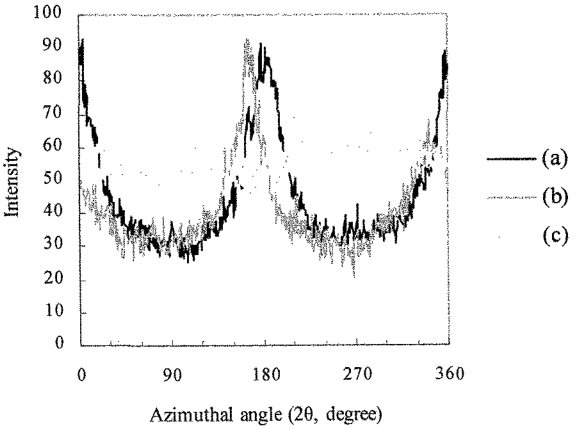

Fig. 8 X-ray azimuthal scans ((a) through, (b) edge, and (c) end views) of the (100) plane measured for the sample with Mn=10,000 treated inside the magnet (5T). Field direction corresponds to 0 and 180 degree.

On the other hand, the X-ray diffraction photograph of PEO cast from 20% PEO (Mv=200,000) mixture shows that no magnetic orientation was observed.

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(Received December 21, 2001; Accepted January 30, 2002)