

Crystallization Behavior and Magnetic Orientation of Polyesterether

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The crystallization behavior and magnetic orientation of poly(ethylene-1,2-diphenoxyethane-*p,p'*-dicarboxylate) (PEBC) was studied by means of DSC and WAXD. The isothermal crystallization at 210°C with various maximum melting temperatures T_{max} s was studied by means of WAXD. In the case of $T_{max} > 240^\circ\text{C}$, the β form crystal was formed during crystallization, while in the case of $T_{max} < 235^\circ\text{C}$, the α form or a mixture of the α and β form crystals was formed. This behavior was explained in terms of the existence of the local order domain in a molten state and the difference of the crystallization rate between the α and β forms. Crystallization of the sample in a magnetic field led to the crystal orientation, which was confirmed by WAXD azimuthal analyses. Both the α and β forms underwent magnetic orientation. The direction of the c axis of the β form was parallel to the magnetic field. In the case of the α form, the c axis was not aligned parallel to the magnetic field though the detail has not been clarified yet because the orientation of the α form was very weak.

Key words: Magnetic orientation / poly(ethylene-1,2-diphenoxyethane-*p,p'*-dicarboxylate) / melt structure / crystal polymorphism

1. INTRODUCTION

With the recent advance in superconducting magnets, the use of high magnetic fields has become possible not only for physicists but also for chemists and materials scientists. As a result, many researches for the processing of non-magnetic materials, including diamagnetic and paramagnetic materials, in high magnetic fields have been reported recently⁽¹⁾.

We have reported the magnetic orientation of crystalline polymers, including poly(ethylene-2,6-naphthalate) (PEN)^{(2),(3)}, isotactic polystyrene (iPS)⁽⁴⁾, and poly(ethylene terephthalate) (PET)⁽⁵⁾. These polymers exhibit the magnetic orientation during the induction period of the isothermal crystallization from melt. We have, however, recently reported that isotactic polypropylene (iPP)⁽⁶⁾ undergoes magnetic orientation above the melting point T_m . Also, we have found that PET⁽⁷⁾, which has previously been reported to exhibit the magnetic orientation in the induction period, undergoes orientation even in the molten state.

In this study, we report the magnetic orientation of poly(ethylene-1,2-diphenoxyethane-*p,p'*-dicarboxylate) (PEBC) whose chemical structure is similar to PET. Since PEBC has a large intrinsic birefringence⁽⁸⁾, the control of the alignment of this polymer by means of magnetic fields would be of use to explore the possibility of this polymer for the optical use.

2. EXPERIMENTAL

Pellets of PEBC used in this study were supplied by Asahi Chemical with nominal molecular weight of ca. 20,000. The glass transition temperature (T_g) and the melting point of PEBC were 70°C and 227°C,

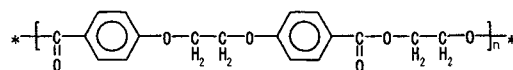


Fig.1 Chemical structure of PEBC

respectively. The pellets were dried at 70°C in a vacuum oven for 12 h. The dried pellets were hot-pressed at 270°C for 3 minutes, then allowed to quench in ice water to obtain a 100 μm thick film. The obtained film showed amorphous halo on X-ray diffraction measurements.

Thermal treatment of the sample was carried out using a home-built heating cell in an HF10 cryocooler-cooled superconducting magnet (Sumitomo Heavy Industries, Ltd.) generating 8 T. The scheme of the thermal treatment is shown in Fig. 2. The film was heated at 5°C/min in the sample cell placed in the magnet from room temperature to the various maximum melting temperatures T_{max} s, which were above the melting point ($T_m = 227^\circ\text{C}$) and held at this

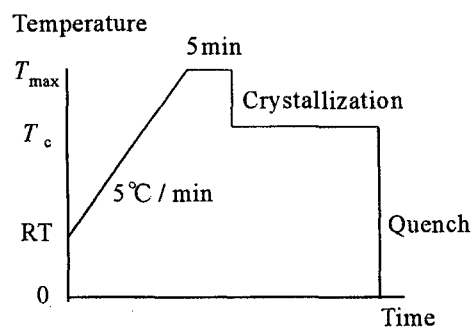


Fig.2 Scheme of the thermal treatment.

temperature for 5 min, followed by cooling at 5°C/min to the isothermal crystallization temperature ($T_c=210^\circ\text{C}$).

The kinetics of crystallization was studied using the differential scanning calorimeter (DSC). The measurements were carried out in a nitrogen gas atmosphere on a Seiko Instruments Inc. DSC200 system equipped with an SSC5200H analysis system. The films were heated at 5°C/min from the room temperature to various T_{max} s and held at this temperature for 5 min, followed by cooling at 5°C/min to the room temperature.

Wide-angle X-ray diffraction measurements were carried out with a MAC Science M18XHF²²-SRA equipped with an imaging plate.

3. RESULTS AND DISCUSSION

Fig.3 shows the result of the DSC measurements for the heating process of amorphous PEBC and PET. The chemical structure of PEBC is similar to that of PET, and hence many physical properties of PEBC are similar to those of PET. As shown in fig.3, the glass transition temperature(T_g) of PEBC was about 70°C, same as the T_g of PET. The melting temperature of PEBC was slightly lower than that of PET, because of the asymmetry introduced by ether bond⁽⁹⁾. Both polymers underwent cold crystallization in the heating process. The onset temperature of the cold crystallization of PEBC was lower than that of PET. This indicates that the crystallization rate of PEBC is higher than that of PET⁽⁹⁾.

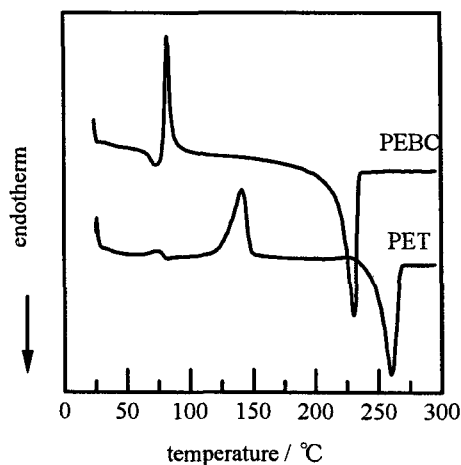


Fig.3 DSC curves: PEBC(top) and PET(bottom).

Crystallization behavior strongly depends on at what temperature the sample is melted prior to the crystallization. If the sample is melted just above its melting point (T_m), local ordered domains remain in the melt, which play an important role in the subsequent process of magnetic orientation^{(6),(7)}. The existence of the local domain was studied by DSC measurements. Fig.4 shows DSC thermograms obtained for PEBC. The PEBC film was heated from room temperature to the melting temperature T_{max} and maintained for 5 min,

followed by cooling at 5°C/min. The onset of exothermic peak shifts to a lower temperature with an increase in T_{max} , reaching a constant temperature for $T_{max} > 240^\circ\text{C}$. It is suggested that the local domain does not exist in a molten state above 240°C. This result suggests that the magnetic orientation of PEBC could be attained by heating at temperatures not exceeding 240°C, followed by a subsequent

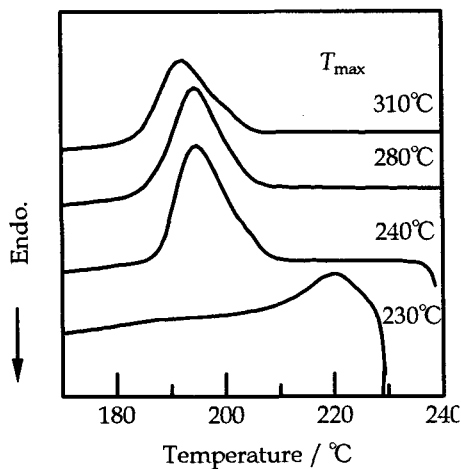


Fig.4 DSC curves for the cooling process of PEBC with different T_{max} values.

crystallization.

Fig.5 shows WAXD patterns obtained for PEBC. The top pattern was obtained for the sample melted at $T_{max}=230^\circ\text{C}$, followed by isothermal crystallization at 210°C for 90 min, while the bottom one was obtained for the sample melted at $T_{max}=280^\circ\text{C}$ followed by isothermal crystallization at the same temperature. The top and the bottom diffraction patterns are assigned to the α and β forms of PEBC, respectively. The α form is monoclinic and the β form is orthorhombic⁽⁸⁾. It has been reported that the α

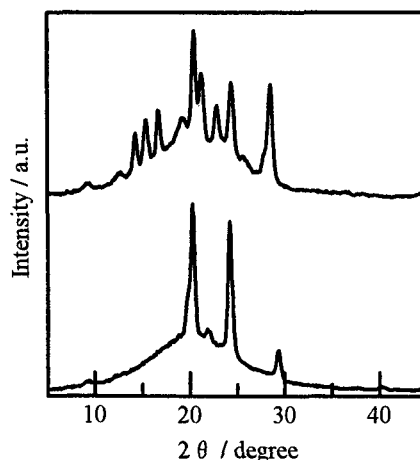


Fig.5 WAXD patterns for PEBC annealed by several thermal histories.

form grows in a low speed spinning and the β form grows in a high speed spinning at a spinning rate higher than 4000m/min⁽⁶⁾. In the present case, however, the difference of T_{\max} has caused the growth of different crystalline forms. In the case of $T_{\max}=235^{\circ}\text{C}$, we observe the formation of an α - and β -form mixture. The β form occurs when $T_{\max}=240^{\circ}\text{C}$. Therefore, we conclude that $T_{\max}=ca. 240^{\circ}\text{C}$ is a critical temperature that determines the crystal form in the subsequent crystallization. The effect of the heating time on the resulting crystal phase was examined by changing the heating time upto 24 h at $T_{\max}=235^{\circ}\text{C}$. The obtained crystal was the mixture of the α - and β -forms, which is same as the result for the heating time of 5 min.

This phenomenon could be explained by the existence of the local order domain in the molten state and by the difference in crystallization rates for different crystalline forms. From the DSC measurement, it is suggested that the local order domain exists in a molten state up to 240°C . Crystallites that grow through cold crystallization is of the α form. Therefore, the local ordered domain existing up to 240°C would be of a similar structure to that of the α form crystal. If heated above 240°C , this local ordered domain disappears.

The crystallization rate strongly depends on the crystallization temperature. There is a temperature between T_g and the melting point, at which the crystallization rate becomes the highest. This temperature depends on the crystal form. From the result of the DSC measurement, the cold crystallization was observed at a lower temperature close to T_g . At this temperature, α form occurs, indicating that the crystallization rate of the α form is higher than that of the β form near T_g . On the other hand, it is observed that the β form occurs if the isothermal crystallization is conducted at 210°C after melting above 240°C . This observation is explained as follows: The ordered domains existing in the melt, which subsequently could be the embryo of the α form crystal, disappear if the sample is melted above 240°C . In addition, the crystallization rate of the β form might be higher than that of the α form near the melting point, for example, at 210°C .

Isothermal crystallization was carried out under a magnetic field of 8 T in the condition encouraging the formation of both the α and β forms. The obtained sample exhibited the magnetic orientation of both the α and β forms. The magnetic orientation of the α form could be explained by the existence of the local ordered domain in the molten state^{(6),(7)}. In the case of the β form, the magnetic orientation might be attributed to the ordered structure formed during the induction period of crystallization such as PEN^{(2),(3)} and iPS⁽⁴⁾.

Fig.6 and Fig.7 show the azimuthal scans for various diffraction planes for the α and β forms, respectively. The β form exhibits higher orientation

than the α form. The c axis of the β form aligns parallel to the magnetic field. The tensor of the diamagnetic susceptibility of the α and β forms of this polymer is little known. Hence the prediction of the direction of magnetic alignment of the crystal is difficult at the present time. However, the result obtained for the β form suggests that the absolute value of the diamagnetic susceptibility for the c -axis of the β form is smaller than those for the other axes. On the other hand, the α form does not exhibit the c -axis alignment though a further analysis is necessary to confirm the orientation manner because the orientation of the α form is very weak.

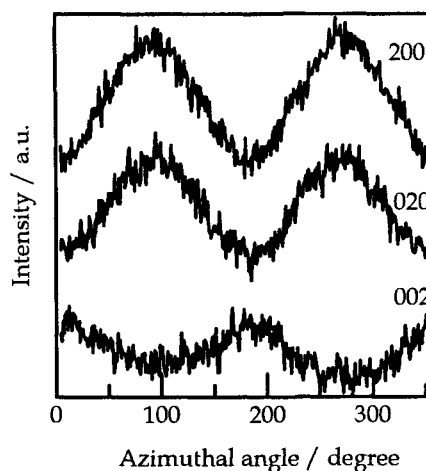


Fig.6 Diffraction intensity distribution for azimuthal angles of various diffraction plane for α form.

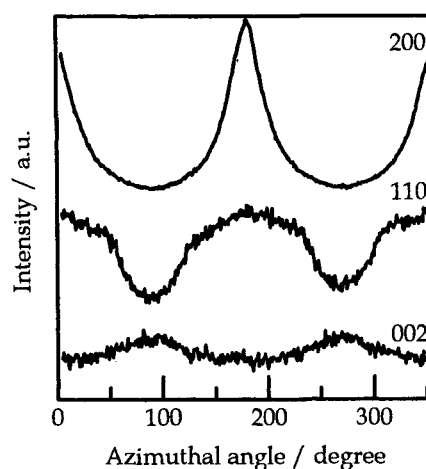


Fig.7 Diffraction intensity distribution for azimuthal angles of various diffraction plane for β form.

4. CONCLUSION

The crystallization behavior and magnetic orientation of PEBC were studied. The X-ray analyses showed that in the case of $T_{\max} > 240^{\circ}\text{C}$, the β form crystal was

formed, while in the case of $T_{\max} < 235^{\circ}\text{C}$, the α form crystal or a mixture of the α and β forms was formed. This phenomenon was explained in terms of the existence of the local order domain in a molten state and the difference in the crystallization rates between the α - and β -form crystals. It was found that both the α - and β -form crystals underwent magnetic alignment. The degree of alignment, however, was different depending on the crystal forms. The β form exhibited higher orientation than the α form. The direction of the c axis of the β form was parallel to the magnetic field, but that of the α form was not.

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