Magnetic Alignment of Poly(ethylene terephthalate) in Molten State

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Abstract. The magnetic alignment of poly(ethylene terephthalate) in molten state was studied by in-situ birefringence measurement in a magnetic field. The melting point of the sample determined by DSC was 253°C. We observed the increase of birefringence in a molten state at temperatures between 254°C and 260°C in the magnetic filed (10T). The dependence of the apparent rate of orientation on the annealing time was attributed to the increase in the viscosity due to the structure formation under the lower supercooling condition. The time at which the transmitting light became a maximum increased with the increase in the melting temperature. These results suggested that the residual structure of crystal, which can be aligned magnetically, existed in the molten state and the volume fraction of the residual structure was reduced with increase in the melting temperature.

1. Introduction

The physical properties of polymeric materials depend greatly on not only their chemical structure, but also their higher order structures. In particular, various physical properties depend on both the crystallinity and the degree of orientation in the case of crystalline polymers. It is possible to control the crystallinity by controlling the temperature conditions during the manufacturing molding process. However, controlling the orientation is not easy. The use of an external magnetic field is a technique that can be used to control the orientation of these materials [1]. Magnetic alignment can achieve unique orientations (such as graded orientations [2]) that cannot be realized by conventional methods.

In a series of studies [3-8], we have discovered that many crystalline polymers can align under a magnetic field. However, we have not reached a fully clear understanding about the factors that determine the magnetic alignment of crystalline polymers. One of the proposed mechanisms is the alignment of some anisotropic structure that might exist in the molten state [5, 6]. However, the magnetic alignment in the melt of polymers has not been observed directly. Moreover, it is reported that the magnetic alignment does not occur in the molten state of isotactic polystyrene [9]. In this study, we report the magnetic alignment of poly(ethylene terephthalate) (PET) in the melt by using an in-situ birefringence measurement in the magnetic field of 10T.
2. Experimental

2.1. Sample preparation
Pellet of poly(ethylene terephthalate) purchased from Scientific polymer products, inc. was used. Amorphous films of 150 μm thickness were prepared by cooling a melted sample in iced water rapidly after hot pressing. The sample (5 mm diameter) cut from the film were used in this study.

2.2. DSC measurement
DSC measurements were carried out using a SEIKO DSC200 equipped with a thermal analysis system SSC5200H under a dry nitrogen atmosphere. The melting point of the sample was measured at a scanning rate of 10 K/min.

2.3. Birefringence measurement
In-situ birefringence measurement was carried out with a home-built apparatus. The block diagram of the apparatus was shown in figure 1. A polarizer and an analyzer were set under the cross-Nicole condition, each making an angle of 45° with respect to the vertical magnetic field. The sample were set to the birefringence apparatus and allowed to melt inside and outside of the magnetic field. The change of the transmitting light intensity was measured under the cross-Nicole condition, which corresponds to the change of the birefringence.

![Figure 1. Block diagram of the optical apparatus used to measure birefringence in a magnetic field.](image)

3. Results and discussions
The temporal change of the transmitting light intensity was measured both inside and outside of the applied magnetic field at an isothermal annealing temperature that is slightly higher than melting point of 253 °C determined by DSC measurement. Under the cross-Nicole condition, the transmitting light intensity is proportional to \(\sin^2\left(\frac{\pi d \Delta n}{\lambda}\right)\), where \(d\) is the film thickness, \(\Delta n\) is the birefringence, and \(\lambda\) is the wavelength (670 nm) of the impinging light. The quantity \(d \Delta n\) is referred to as retardation, denoted by \(Re\). If the increase in \(\Delta n\) due to the magnetic alignment of the polymer chain is large, the intensity would even oscillate.

Figure 2 shows the change of the transmitting light intensity under the cross-Nicole condition during the isothermal annealing at 255 °C. No change in the transmitting light intensity was observed when the magnetic field was not applied, indicating that there was not a change in the birefringence. On the other hand, the transmitting light intensity oscillated as a function of the annealing time in the case of the measurement at 10 T, suggesting the increase in birefringence. This result indicates that some anisotropic structure appeared in polymer melt. We succeeded in detecting the magnetic
alignment in the polymer melt. The structure aligned in the magnetic field is considered as some residual structure of crystal that existed before melting [5, 6]. In addition, the cycle of the oscillation increases as time progresses. This result suggests that the rate of orientation decreases with time. Possible reasons for the decrease of the orientation rate under the constant magnetic field would be the decrease in the anisotropy of magnetic susceptibility of the aligned material or the increase in the viscosity of the surrounding media.

![Figure 2. Change in the transmitting light intensity under cross-Nicole condition during annealing at 255 °C.](image)

It is well known that the melting point determined by DSC measurement is an apparent melting point for crystalline polymers[10]. The equilibrium melting point of crystalline polymers is higher than that of the apparent melting point. It was reported that the equilibrium melting point of PET is 280 °C [11]. That is, the magnetic alignment occurring at 255 °C is regarded as occurring at a supercooling condition. In this situation, a structure formation such as a crystalline growth should progress. Though the viscosity increases with the structure formation, it is not considered that the anisotropy of the magnetic susceptibility is decreased. Hence, the decrease of the orientation rate originates from the increase of the viscosity due to the structure formation in a condition of lower supercooling.

We estimated the orientation rate to clarify the dependence of the orientation rate on the intensity of the magnetic flux density. If the retardation \( Re \) becomes 355 nm, the transmitting light intensity reaches the first maximum. We defined the time \( \tau_{Re=335} \) as the time at which the intensity reaches the first maximum. The reciprocal of \( \tau_{Re=335} \) is proportional to the orientation rate which is expressed as \( \tau^{-1} = F \chi_a B^2 / 6 \mu_0 \eta \), where \( F \) is the shape factor, \( \chi_a \) is the anisotropic diamagnetic susceptibility of the material, \( B \) is the magnetic flux density, \( \mu_0 \) is the magnetic permeability of vacuum, \( \eta \) is the viscosity of the surrounding media [1]. If the parameters governing the magnetic alignment are unchanged during the alignment, the orientation rate should be proportional to the square of the magnetic flux density. Figure 3 shows the relationship between the orientation rate and the square of the magnetic flux density. The orientation rate is estimated from the measurements of 2 or 3 times and the error bar is shown in the figure. The data points at lower magnetic fields greatly deviate from the straight line. This indicates that the orientation rate decreases at low magnetic fields in which the time...
for $Re$ to reach 355 nm becomes longer. That is, the increasing in viscosity due to the structure formation should be remarkably responsible at lower magnetic fields. The effect of the increase in viscosity can not be ignored.

![Figure 3](image1.png)

**Figure 3.** Relationship between the orientation rate and the square of the magnetic flux density.

Figure 4 shows the change in the transmitting light intensity under the cross-Nicole condition at different melting temperatures. With the increase of the melting temperature, the location of the intensity maximum shifts to longer annealing time and the transmitted light intensity disappeared at 260 °C. As mentioned above, the transmitting light intensity depends on $\Delta n$. Therefore, this result

![Figure 4](image2.png)

**Figure 4.** Change in the transmitting light intensity under cross-Nicole condition during annealing in a magnetic field (10T) at various annealing temperatures shown in the figure.
suggests that the annealing at higher temperatures causes the decrease of the increase rate of $\Delta n$.

Melting at higher temperature below the equilibrium melting point, the followings are expected.

1: The viscosity of polymer melt generally decreases with increase in the melting temperature.
2: The growth rate of the structure such as a crystal structure greatly decreases in the lower supercooling condition.
3: The number and size of the residual structure of crystallite decrease because the residual structure becomes more unstable.

If the viscosity decreases, the orientation rate should increase to result in the increase of the increase rate of $\Delta n$. Therefore, the decrease in the increase rate of $\Delta n$ at higher melting temperatures is not attributed to the decrease of the orientation rate but to the decrease of the volume fraction of the ordered structures that can orient. The amount of the ordered structures is determined by two factors: the decrease of the residual ordered structures and the increase of newly grown ordered structures. At present time, it is difficult to distinguish which factor is dominant. This is our future work.

### 4. Conclusion

The magnetic alignment of poly(ethylene terephthalate) in molten state was studied by in-situ birefringence measurement in the magnetic field. We succeeded for the first time in detecting the magnetic alignment in the polymer melt by the in-situ observation of birefringence in a molten state at temperatures between 254 °C and 260 °C in the magnetic field (10 T). Information of the structure formation in a low supercooling was obtained from the discussions about the change of the apparent orientation rate.

The dependence of the apparent orientation rate was due to the increase in the viscosity with the structure formation and the dependence of the apparent orientation rate on the melting temperature was due to the decrease of the volume fraction of the aligned structure accompanied with the decrease of the residual crystalline structure and/or the decrease in the growth rate of the structure.

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