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Magnetic and Viscoelastic Study on Molten State of Low Molecular Weight Isotactic Polypropylene

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ABSTRACT: The molten state of a low molecular weight isotactic polypropylene was studied by means of the viscoelastic method as well as the observation of magnetic orientation. The melt viscosity remained at a higher level in the temperature ranging between the melting point (ca. 170 °C) and the temperature up to 70 °C higher than the melting point, depending on the heating rate. The melt viscosity measured at constant temperatures in this temperature range decreased with time. The rate of decrease depended on the temperature. These observations strongly suggested that some ordered structures exist even above the melting point. Magnetic orientation was observed for the samples melted in the magnet (6 T) at temperatures above the melting point. This observation implied the existence of anisotropic structures, supporting the observation made in viscoelastic measurements.

1. Introduction

Materials with diamagnetic anisotropy can undergo alignment under external magnetic fields.[1] A single chemical bond itself possesses a diamagnetic anisotropy, but it cannot align because its magnetic energy is so small compared to the thermal energy. Only a weak birefringence due to the Cotton−Mouton effect is observed. However, if many bonds are assembled together to form an anisotropic domain with some critical size so as to exceed the thermal energy, then the macroscopic orientation of the domain becomes possible. The condition of the magnetic orientation of a domain strongly depends on the critical size and the strength of the anisotropic diamagnetic susceptibility of the domain. This means that the observation of magnetic alignment is an excellent means to detect and analyze the ordered domains appearing during the phase transition of polymeric systems.

We have reported that crystalline polymers including poly(ethylene-2,6-naphthalate) (PEN),[2,3] isotactic polystyrene (iPS),[4,5] and poly(ethylene terephthalate) (PET)[6] undergo magnetic orientation during crystallization from melt. We have assumed that some ordered structure appearing during the phase transition, especially during the induction period of the crystallization, is responsible for the magnetic orientation. On the other hand, a low molecular weight isotactic polypropylene (iPP) underwent magnetic alignment above its melting point.[7] This suggests that some ordered domain exists in its melt. Incidentally, our recent study shows that molten PET also exhibits some ordered structure above the melting point depending on thermal history.[8]

In this paper, the molten state of iPP is studied through rheological and magnetic measurements. The effect of thermal history on the rheological and magnetic behavior is explained in terms of the ordered structure in the melt. Discussion is made about the size of the ordered structure on the basis of the critical size necessary for the magnetic orientation.

2. Experimental Section

2.1 Material. Isotactic polypropylene (SA002V, M_n = 35 800, M_w = 123 000, supplied by Japan Polychem, Co. Ltd.) was used. This is the same sample that we reported magnetic alignment in the molten state under the magnetic field of 6 T.[7]

2.2. Viscoelastic Measurement. Pellets of the isotactic polypropylene (iPP) sample were heated at 180 °C for 10 min between 25 mm diameter parallel plates with a gap of 1 mm on an ARES rheometry system of Rheometric Inc. and then allowed to cool at 60 °C/min to room temperature. Then measurements were carried out on the storage and loss moduli, G' and G'', and the viscosity η^* at various heating rates ranging from 1 to 20 °C/min at 1 Hz under small shear amplitudes ($\gamma < 0.05$). Also, the temporal change of G' at various constant temperatures was measured by heating the sample at 5 °C/min from room temperature to a given temperature. The time lag in temperature between the plates and the sample center was estimated to be negligibly small according to the calculation of the heat diffusion and the experimental data supplied by the manufacturer.

2.3. Preparation of Samples Heat-Treated in a Magnetic Field. Pellets of the iPP were hot-pressed at 200 °C for 10 min followed by quenching in ice water to obtain a 200 μm thick film. A piece of the quenched film was set in a heating apparatus[7] and subjected to the heat treatment in an Oxford superconducting magnet (6 T). For the study of the effect of heating rate, the sample was heated at 1 and 5 °C/min up to the various maximum melting temperatures (T_{max}'s) and then quenched immediately. For the study of the effect of melting time, the sample was heated to various T_{max}'s and then held for 0−60 min at T_{max}, followed by quenching.

2.4. Polarizing Optical Microscopy. Optical azimuthal scans on the films heat-treated in the magnet were carried out using an Olympus BH-2 microscope system under crossed polars. The transmitting light intensity observed under this setup is expressed as

$$I^2 \sim \sin^2 2\phi \, \sin^2(\pi d \Delta n/\lambda) \qquad (1)$$

where ϕ is the azimuthal angle, d the film thickness, and Δn the birefringence. In the present apparatus, the light is not monochromic, and hence we need integration over the wavelength, λ, for a quantitative comparison between the samples with different Δn values. However, this is beyond the scope of the present study and was not carried out.

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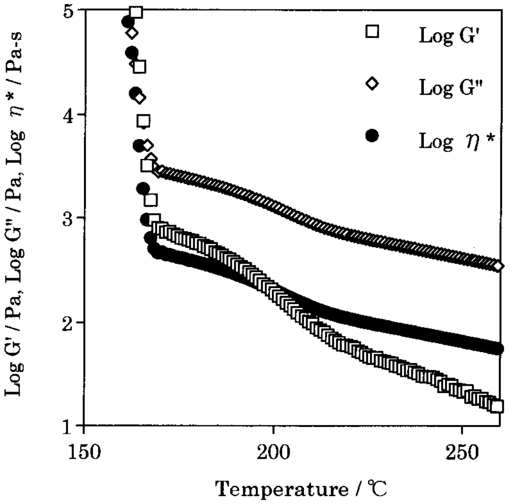

Figure 1. Change in rheological properties upon heating iPP sample at 5 °C/min.

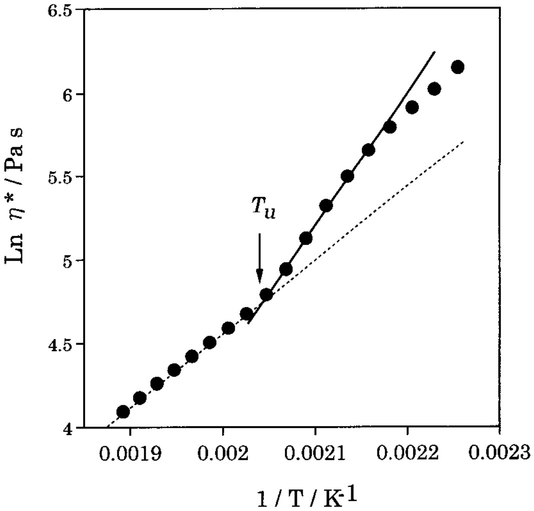

Figure 2. Logarithmic plot of the viscosity against the inverse of the temperature.

3. Results and Discussion

3.1. Viscoelastic Measurements. 3.1.1. Evidence of Ordered Structure.

Figure 1 shows the results of G', G'', and η^* obtained at the heating rate of 5 °C/min. Above the melting point (170 °C), the behavior of these properties could be divided into two regions: one between 170 and 220 °C and the other above 220 °C. In the former region, all these properties are in a higher level than expected by the extrapolation from the high-temperature region. This observation indicates that the melt state between 170 and 220 °C is not simply the low-temperature correspondence of the melt structure above 220 °C. A higher modulus in the former region seems to suggest the existence of some residual ordered structure probably originating from the crystal structure before the melting point. It is reported[9-11] that the G', G'', and η^* of a liquid crystalline polymer remain in a higher level in the liquid crystalline phase before the isotropic phase appears upon further heating. A similar tendency observed in the present study could suggest that liquid-crystalline-like structures may exist in molten iPP above the melting point.

The temperature dependence of the melt viscosity is described as

$$\eta^* = C \exp(E/kT) \tag{2}$$

if the viscous process is governed by a single activation energy E. In Figure 2, an Arrhenius type plot is made for η^*. Two regions are clearly observed, separated by the transition temperature T_u (=218 °C). This temperature is close to the temperature separating two distinct regions discussed above in Figure 1. Above T_u, the plot exhibits a straight line indicating that eq 1 is applied in this region. On the other hand, below T_u, the plot deviates from linearity. This implies that the polymer solid starts to lose its crystalline structure upon reaching the melting point and then passes through a transient phase at temperatures between 170 °C and T_u before finally reaching a "simple" molten state described by a single activation energy. A similar rheological behavior was reported for the melts of normal paraffins $C_{24}H_{50}$ and $C_{36}H_{74}$ by Kruger et al.[12,13] They attributed the phenomenon to the formation of an "intermediate local nematic phase".

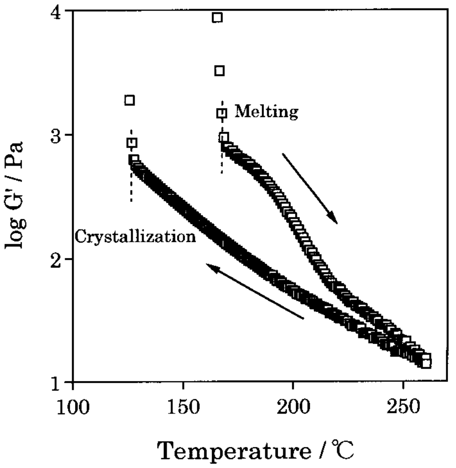

Figure 3. Hysteresis of G' upon heating and cooling at 5 °C/min.

Figure 3 shows the change in G' during heating followed by cooling. The cooling process does not trace the heating process. Upon cooling from 260 °C, G' increases monotonically, indicating that nothing peculiar is happening. Though it is not shown, the cooling process is described by eq 2. The structure existing during the heating process may not be fully recovered during the cooling process.

3.1.2. Heating Rate Dependence.

The heating rate dependence of the rheological behavior is shown in Figure 4a. The transition shifts to higher temperatures with increasing heating rate. This situation is better demonstrated in Figure 4b, where G' is normalized by the values at 170 and 250 °C. The transition temperature T_u is 198, 218, and 237 °C respectively for the heating rate of 1, 5, and 20 °C/min. This heating rate dependence indicates a kinetic nature of this transition to a simple melt.

3.1.3. Annealing Time Dependence.

Figure 5 shows the temporal change in G' measured at various constant temperatures. The heating rate at which the sample is heated to these temperatures is 5 °C/min. It should be remembered that the transition temperature at this heating rate was ca. 220 °C. For the measurements at 180 and 200 °C, the G' decreases in time with the relaxation times of 41 and 7 min, respectively. The relaxation times become shorter with the increase in

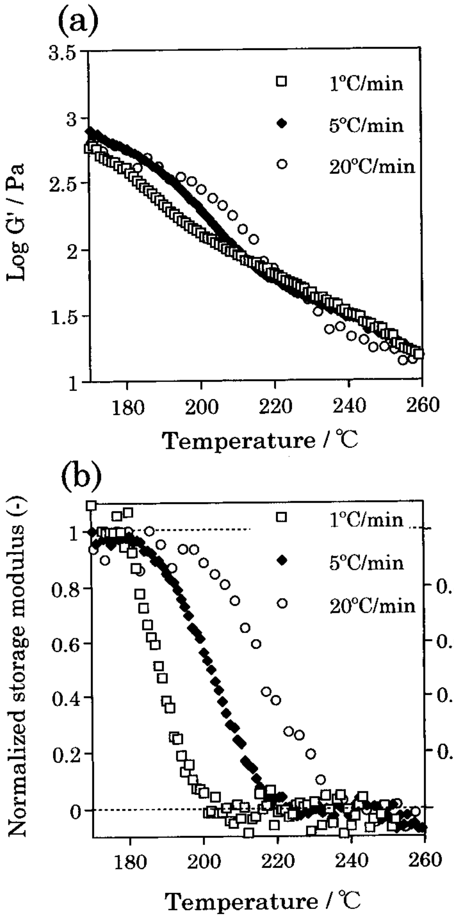

Figure 4. Heating rate dependence of G' (a). The same plot with G' normalized by the values at 170 and 250 °C (b).

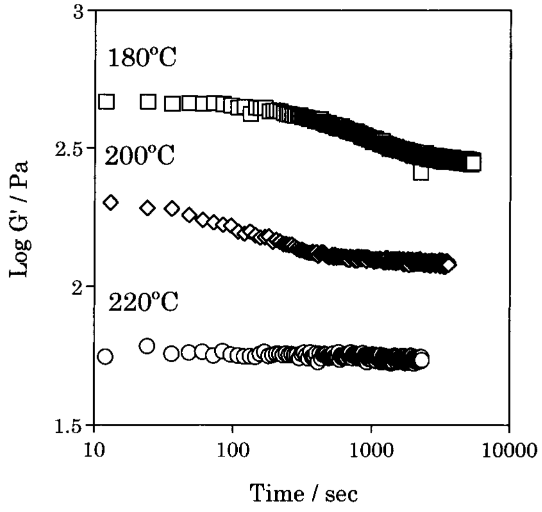

Figure 5. Temporal change in G' upon heating at a constant temperature indicated in the figure.

annealing temperature. The measurement with the annealing temperature at 220 °C does not exhibit the decrease in G' because the transition is completed before the temperature reaches this annealing temperature. As will be shown in the following sections, the relaxation in the rheological measurement occurs at lower temperatures than that in the magnetic measurement. The reason is not clear yet, but possible explanations are (1) the sensitivity to the ordered structure differs between these two methods, that is, magnetic measurements are more sensitive, and (2) rheological measurements distort the ordered structure.

3.2. Magnetic Alignment. 3.2.1. Condition of Magnetic Alignment. The critical size required for the magnetic alignment is given as

$$V > \frac{2kT\mu_0}{|\chi_a|B^2} \qquad (3)$$

where μ_0 is the magnetic permeability of the vacuum, B the magnetic flux density, V the volume of the anisotropic domain, k the Boltzmann constant, and $\chi_a = \chi_{\|} - \chi_{\perp}$ the anisotropic diamagnetic susceptibility of the domain with $\chi_{\|}$ and $\chi_{\perp}$ indicating the diamagnetic susceptibility in the directions parallel and perpendicular, respectively, to the uniaxial anisotropic direction. This equation comes from the requirement that the domain size V should be larger than a critical size in order that the magnetic energy of the domain reduced by taking a specific orientation with respect to the magnetic field should exceed the thermal energy.

The value of χ_a of the iPP crystal is ca. -2.7×10^{-6}.[14] With this value, we estimate the minimum of the domain size in the linear dimension to be ca. 50 nm at 180 °C. Since the χ_a value of a domain in a molten state might be smaller than that of crystal because of less perfect organization of chains within the domain, e.g., 100 times smaller, then the critical size might be as large as 200 nm.

The time required for an anisotropic spherical domain to rotate under magnetic field is given as[15]

$$\tau = \frac{6\mu_0\eta}{\chi_a B^2} \qquad (4)$$

where η is the viscosity. It should be noted that the size of the domain does not come into the equation. With η taken as $10^{2.5}$ Pa s and χ_a as 10^{-6}, the estimation of τ is 100 s. If the anisotropic domain is of prolate shape, the estimation of τ becomes larger.[15] The order of the time scale is in agreement with the experiment with magnetic orientation.

3.2.2. Heating Rate and Melting Temperature Dependence. The ordered structure is also confirmed through the observation of magnetic alignment. Figure 6 shows the optical azimuthal scans of the film samples heated at (a) 1 °C/min and at (b) 5 °C/min (a) up to various maximum melting temperatures (T_{max}'s) followed by immediate quenching. In the case with 1 °C/min, the sinusoidal behavior demonstrates that the orientation retains up to $T_{max} = 200$ °C. This temperature is close to the transition temperature ($T_u = 198$ °C) determined in the rheological experiment. On the other hand, in the case of 5 °C/min, the orientation retains up to $T_{max} = 240$ °C, which is far higher than the rheological transition at $T_u = 218$ °C. The reason is not clear at present, but one possibility is that the ordered structure is less sensitive to rheological measurements. Another possibility is that the transition is so slow that it takes some time for the transition to be completed.

3.2.3. Annealing Time Dependence. In Figure 7, optical azimuthal scans are shown for the films heat-treated in the magnetic field (6 T) for the annealing times of 0, 10, 30, and 60 min at various annealing temperatures (T_{max}'s). Heating was carried out at 5 °C/min. For the annealing temperature of 180 °C, the sample shows the orientation irrespective of the an-

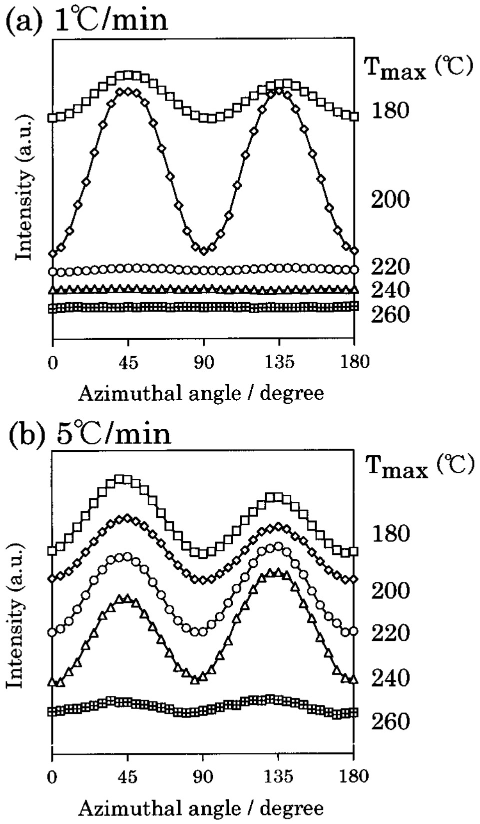

Figure 6. Optical azimuthal scans under crossed polars obtained for the samples quenched at various melting temperatures T_{max}'s indicated in the figure. At zero azimuthal angle, the direction of the applied magnetic field coincides with the direction of the analyzer. The heating rates are (a) 1 and (b) 5 °C/min.

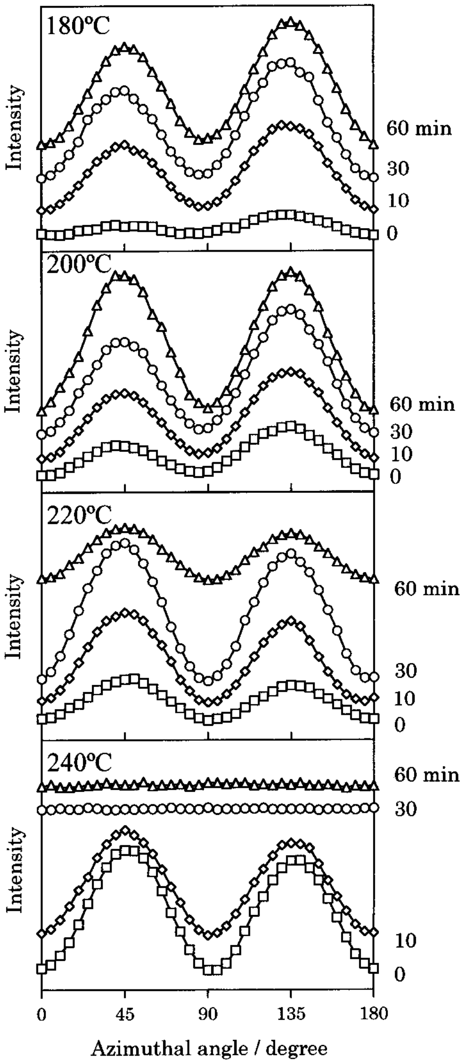

Figure 7. Optical azimuthal scans for the samples heat-treated for 0, 10, 30, and 60 min at the temperatures indicated in the figure.

nealing time. Though a detailed analysis is required for the precise estimation of the birefringence, the amplitude of the sinusoidal curve would be considered to reflect the degree of orientation. Starting with a low orientation degree at annealing time of 0 min, the alignment proceeds with time being. Similar behavior is observed for the annealing treatment at 200 °C. It should be noted that this temperature is close to the rheological transition temperature (T_u = 198 °C) obtained for the same heating rate (1 °C/min).

Heat treatment at 220 °C causes the alignment in the initial stage, but the alignment starts to disappear at a prolonged heating time. Development of the alignment and the transition to the isotropic melt might be competing at this temperature. The time required for the orientation development is of the same order as a liquid crystalline polymer.[16] Heat treatment at 240 °C encourages the alignment in the initial stage, but the alignment disappears completely at heating times longer than 30 min. These observations could suggest the following. As was indicated in the previous section, the transition from the ordered structure to the isotropic melt could be slow. Especially the heating rate of 5 °C/min, used in the experiment in Figure 7, is so fast for the ordered structure to transform itself completely to the isotropic melt. Thus, the orientation remains at short annealing time in the experiments at 220 and 240 °C.

4. Concluding Remarks

Viscoelastic measurements and the observation of magnetic orientation have demonstrated evidence that there are ordered structures above the melting point of iPP. Combining the results of viscometry and magnetic measurements, we draw the following picture regarding the ordered structure in the melt. Above the melting point (170 °C), there is a stable ordered structure or its mixture with the isotropic phase, existing up to 180−200 °C. Because the transition from this ordered structure to the isotropic melt is diffuse and slow, an apparent transition temperature shifts to higher temperatures when working at larger heating rates (≥5 °C/min). At 5 °C/min, the ordered structure remains for a few minutes even upon heating to 240 °C. This observation is consistent with our previous work[7] of the melt crystallization study on the same iPP sample. Once the sample is heated at 5 °C/min up to 260 °C, the onset of the crystallization upon cooling shifts to a lower temperature in comparison to the onset of the crystallization of the melt once heated to 240 °C. This indicates that the ordered structure can survive kinetically up to 240 °C but disappears at 260 °C, if the heating rate is 5 °C/min.

The molecular weight of the iPP used in this study is extremely low. An isotactic polypropylene with a higher molecular weight did not exhibit magnetic orientation.[17] A similar molecular weight dependence is observed for normal alkanes and polyethylene. Normal alkanes can easily align in magnetic fields during solidification from melts,[18,19] while we have not observed magnetic orientation of polyethylene. The condition for polyethylene might be severely limited.[20] A possible reason would be the difference in melt viscosity. Another possibility is that since normal alkanes form various different solid phases, some of them might have a strong susceptibility to the magnetic field, resulting in facilitated orientation. We do not know whether it is also the case for our iPP samples, but this possibility could not be ruled out.

Finally, our finding might be relevant to the liquid crystallinity of iPP studied in the context of blends[21] with liquid crystalline polymers.

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