Phase Transformation of Polymeric Materials in High Magnetic Field

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A model to describe a non-rotation type magnetic alignment of crystalline polymers during crystallization from melts is presented. The model is based on the presence of mesophase existing between the melt phase and the crystalline phase, with an extremely small transformation enthalpy and a resultant large shift of melting point in the presence of a magnetic field. A calculation of the magnetic effect on the nucleation and growth rates of mesophase is carried out. It is shown that these rates are enhanced for the mesophase with a specific orientation with respect to the applied field, resulting in alignment.

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1. Introduction

Recently, attention has been paid to materials processing of feeble magnetic materials in high magnetic fields thanks to the development of superconducting magnet technology.1) Because the magnetic response of the feeble magnetic materials is very small and slow compared to that of ferromagnetic materials, the magnetic effects on these materials are hardly observed under moderate field strengths supplied by permanent magnets and electromagnets. However, the effects become visible if we work on higher field strengths such as 10 T generated by superconducting magnets, because the magnetic effect is proportional to the square of the applied field strength: a phenomenon occurring under 1 T (electromagnet) is magnified by 100 times in terms of size and time if the observation is conducted under 10 T (superconducting magnet).

It is known that particles with diamagnetic anisotropy undergo magnetic alignment. Examples are the alignment of a short fiber,2) a fine crystallite, etc. suspended in a liquid medium. Because the suspended particle does not change in size and magnetic anisotropy, its alignment mechanism is easily described in terms of the rotation by magnetic torque. We have reported that crystalline polymers undergo magnetic alignment during crystallization from melts. The anisotropic structures responsible for the alignment of crystalline polymers are much more complicated than a particle in a suspension because they may change their size, shape, and structural order during the crystallization process. We have described the magnetic alignment in terms of the rotation of the anisotropic structure (mesophase) occurring during phase transformation. But we cannot rule out the possibility of another mechanism that does not need rotation mechanism, i.e., a mechanism of formation and growth of mesophase in association with preferential alignment with respect to the applied field, resulting in crystal alignment. In this paper, a model for the mechanism of preferential alignment is presented.

2. Preferential Alignment Model

Figure 1 shows a typical thermal history applied to attain magnetic alignment. The field is applied throughout the process. Some important points to successfully lead to alignment, following the scheme shown in Fig. 1, are summarized as follows. (i) The initial film is prepared by quenching or crystallizing from a melt. Namely, it may be glass or semi-crystalline. (ii) During the heating process, glass films could develop crystallites due to cold crystallization. Crystallites formation at this stage is important because the crystallites formed would encourage the formation of mesophase in the subsequent process. (iii) Melting temperature $T_{\text{max}}$ should be between the melting point $T_m$ (defined by the top of the endothermic peak at a thermal measurement) and the equilibrium melting point, $T^{0}_m$. If the sample is heated at high temperatures for a prolonged time, residual mesophase originating from the solid state disappear completely. (iv) Crystallization temperature $T_c$ should not be too high or too low. If $T_c$ is too low, crystallization is completed before alignment develops. If $T_c$ is high, spherulites develop to obscure the alignment.

The conditions above strongly suggest that mesophase is responsible for the magnetic alignment. The mesophase formation and growth could be summarized as follows: The mesophase has its origin in the solid state before melting. The initial crystal phase melts at $T_m$, but a part of crystal order...
(mesophase) could remain, possibly up to the equilibrium melting point $T_{m}^0$, which is defined as the melting point of the crystal with infinite thickness. Our observation\cite{5} for poly(ethylene terephthalate) (PET) and low molecular weight isotactic poly(propylene) (iPP) shows that the mesophase exists in the melt at temperatures above $T_m$. The mesophase disappears if the melt is heated at temperatures high above $T_m$. Upon cooling down to the crystallization temperature $T_e (< T_m)$, crystallization starts but no crystals form during the initial stage of crystallization (induction period). Spectroscopic studies on isotactic polystyrene (iPS)\cite{6} and poly(ethylene-2,6-terephthalate) (PEN)\cite{7} indicate that mesophase forms and/or develops in the induction period. In-situ magnetic birefringence observation and the X-ray diffraction measurement for quenched samples of PEN,\cite{6} iPS,\cite{7} and PET\cite{8} indicate that the magnetic alignment of the mesophase occurs during the induction period.

It is known that the phase transformation point in the presence of a magnetic field depends on the orientation of the anisotropic phase (liquid crystal\cite{9} or crystal\cite{10}) with respect to the applied field. The melting point of a crystal aligned in a magnetically stable direction has a higher melting point than the opposite one. Then, an appropriate temperature setting could in principle result in a preferential crystal alignment. However, the melting point shift, $\delta T$, evaluated with the phase transformation enthalpy and the anisotropic diamagnetic susceptibility, is less than milli Kelvin. Therefore, it was hard to imagine that there is an appreciable effect of $\delta T$ on the preferred magnetic alignment. Recent DSC experiments under a magnetic field, however, has shown that $\delta T$ is a several orders higher than the evaluated ones. The value of 60 mK for $\delta T$ is reported for n-C$_{31}$H$_{66}$ under 5 T, which is four orders larger than the calculated value.\cite{11} This observation indicates that mesophase exhibiting an extremely small transformation enthalpy is involved in the phase transformation.

Here we present a model of preferential magnetic alignment of mesophase. Theory of the crystal nucleation and growth is well known. It is based on two factors: The first one is thermodynamic one: the difference in chemical potentials between the solid and liquid phases drives the liquid phase to the crystal phase when the liquid phase is supercooled. The second one is related to the polymer chain kinetics, i.e., polymer chain diffusion. A homogeneous field under present consideration does not affect the second one. Both the nucleation and the growth depend on these factors. Although we do not know at present whether the mesophase is a thermodynamically stable phase or just a transient one, the driving force to form and grow the mesophase might be similar to the case for the crystal.

In the present model, the mesophase is assumed to be thermodynamically stable. In addition, it is assumed that the difference in enthalpy between the liquid phase and the mesophase is very small compared to that between the mesophase and the crystal phase. Much smaller difference in enthalpy is assumed here in comparison to the difference between a liquid phase and a liquid-crystalline phase. This means that the slope for the chemical potential of the mesophase is very close to that of the liquid phase. We define the intercepts of the mesophase line with the solid line and with the liquid line as $T_m$ and $T_m^0$, respectively as shown in Fig. 2.

Phase transformation point $T_{m}^0$ depends on the orientation of the mesophase with respect to an applied field $B$. Here we assume that the mesophase has a uniaxial anisotropy, making an angle $\theta$ against the applied field. The value of the shift from $T_{m}^0$ in the presence of the magnetic field is expressed by Magneto-Clapeyron equation:\cite{10}

$$
\delta T = \frac{(\cos^2 \theta - 1/3)\chi_a B^2}{2\mu_0\Delta H} T_{m}^0,
$$

where $\mu_0$ is the magnetic permeability of vacuum, $\Delta H(>0)$ is transformation enthalpy per volume (densities of mesophase and melt are assumed to be equal), and $\chi_a = \chi_1 - \chi_2$ is anisotropic diamagnetic susceptibility, with $\chi_1$ and $\chi_2$ being volumetric diamagnetic susceptibilities in the direction parallel and perpendicular, respectively, to the mesophase axis. If $\chi_a = \chi_1 - \chi_2 > 0$, parallel orientation ($\theta = 0$) is more stable than perpendicular orientation ($\theta = 90^\circ$), resulting in a positive $\delta T$ value for the parallel orientation. It

\[\text{Fig. 2. Chemical potential plotted against the temperature. (a) The}
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\[\text{intercept of crystal and mesophase lines defines the melting point}
\]
\[\text{and the intercept of mesophase and melt lines defines the equilibrium}
\]
\[\text{melting point $T_{m}^0$. The slope of mesophase is very close to the slope}
\]
\[\text{of melt. (b) Enlargement of the area around $T_{m}^0$ when an external}
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\[\text{magnetic field is applied. The mesophase line splits into two lines}
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\[\text{depending on the orientation of mesophase (parallel or perpendicular).}
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\[\text{In this figure, $x_a > 0$ is assumed. The shift $\delta T$ is defined by eq. (1).}
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should be noted that it is assumed here that the average susceptibility of the mesophase is equal to the susceptibility of the melt.

The theory of crystallization is now applied for the description of the nucleation (primary nucleation) and growth (secondary nucleation) of mesophase in the presence of an external magnetic field. Change in free energy necessary to form mesophase of a volume $V$ from a melt (liquid) is expressed

$$\Delta G = A\sigma - V\Delta F$$

(2)

where $A$ is the surface of the mesophase and $\sigma$ is the surface energy per unit surface area of the mesophase. The volumetric free energy term $\Delta F$ is the difference in free energy between a unit volume of melt and mesophase at temperature $T$, and is expressed as

$$\Delta F = \Delta \tilde{H} \Delta T / T_m^0,$$

(3)

where the enthalpy change at $T_m^0$ is used for $\Delta \tilde{H}$ (the same quantity as in eq. (1)) irrespective of the temperature. Here, the equilibrium melting point $T_m^0$ and the supercooling $\Delta T$ for the original expression for the case without the field are modified to be $T_m^0 = T_m^0 + \Delta T$ and $\Delta T' = T_m^0 - T + \Delta T = \Delta T + \Delta T'$, respectively, because of the presence of the magnetic field.

Equation (3) is expressed as

$$\Delta F = \Delta \tilde{H} \frac{(1 - T_R + \Delta T_R)}{1 + \Delta T_R},$$

(4)

where the quantities $T$ and $\Delta T$ are reduced by $T_m^0$ to define $T_R = T/T_m^0$ and $\Delta T_R = \Delta T/T_m^0$, respectively.

The minimum of $\Delta G$ in eq. (2) with respect to the volume gives the activation energy $\Delta E_a$ necessary to form a stable nucleus. The activation energies for the primary and secondary nucleation are related to $\Delta F$ in a manner as $\Delta E_{a1} = \sigma^2 / (\Delta F^2)$ and $\Delta E_{a2} = \sigma^2 / (\Delta F)$, respectively, where numerical front factors relating to the nucleus shape is ignored. The magnetic effect also comes into the critical size of the nucleus through $\Delta F$. The quantity $\exp(-\Delta E_a/RT)$ is proportional to the nucleation rates. Here the diffusion term $\exp(-\Delta E_{a1}/RT)$, which cause a decrease in nucleation rates at lower temperatures, is not considered. In Fig. 3, $-\Delta \tilde{H}/(\Delta F)$ defined by eq. (4), which corresponds to the logarithm of the secondary nucleation (i.e., growth) rate, is plotted as a function of reduced crystallization temperature $T_R$ for various values of $\Delta T_R$. It should be noted that due to the diffusion term, the actual growth rate decreases at low temperatures, resulting in the maximum rate locating around $T_R = 0.005$. The rate becomes zero at glass transition temperature, $T_R = 2/3$. We find that the magnetic field accelerates preferentially the growth of the mesophase with a parallel orientation to the field (in the case of $\chi_a > 0$), while the growth rate of the mesophase with a perpendicular orientation is suppressed. This tendency is especially enhanced in the vicinity of the equilibrium melting point. In addition, the growth rate for the parallel orientation is larger than that in the absence of the field. Similar statements are also valid for the primary nucleation. Incidentally, magnetic alignment experiments are usually carried out at ca. $T_R = 0.9$ to 0.95.

If the temperature is brought below the melting point $T_m$, the mesophase transforms to crystal. Because both the mesophase and the crystal phase possess the anisotropy, the estimation of $\Delta F$ at a given temperature $T$ ($< T_m$) is complicated. However, it should be noted that in the present model the change in enthalpy from mesophase to crystal is assumed to be far larger than $\Delta \tilde{H}$. Therefore the shift $\Delta T$ is small and $\Delta F$ is large, affecting little regarding alignment and the rates of nucleation. In this temperature range, the mesophase with specific alignment turns out to the crystal phase with its original alignment unchanged, resulting in crystal alignment.

Both the rotation mechanism and the preferential-formation-and-growth mechanism could explain the experimental results of magnetic birefringence and subsequent crystal alignment. However, the acceleration of crystallization is not explained by the rotation mechanism because the assumption is that the field does not affect the phase transformation but it just rotates the mesophase domain. The acceleration of crystallization observed for iPS$^1$ might be explained in terms of preferential alignment mechanism. Of course, we cannot rule out a possibility that both mechanisms work together. Some experiments should be devised for further investigation.

Direct observations for the mesophase have been reported. By means of in-situ Fourier transform infrared spectroscopic measurements, the conformation change before the crystal formation is reported for various crystalline polymers. This change could occur in association with the mesophase formation. Both for iPS$^4$ and PEN$^5$ mesophase formation is observed during the induction period, prior to the formation of crystals. These experimental evidence might support the present model that assumes the mesophase.

3. Conclusions

Preferential alignment model was presented to explore the possibility of the non-rotating mechanism of magnetic alignment. The model assumes (i) a stable mesophase exists...
between the melt and crystalline phases, (ii) the intercepts of the mesophase chemical potential line with those of the crystal and the melt are defined as the melting point $T_m$ (determined by thermal analysis) and the equilibrium melting point $T_0$, respectively, (iii) the transformation enthalpy $\Delta H$ from mesophase to melt is extremely small compared to that from crystal to mesophase, and (iv) the shift of $T_0$ due to the presence of the magnetic field is expressed by Magneto-Clapeyron equation. Infrared spectroscopic study and thermal analysis under a magnetic field recently reported are referred to in order to rationalize the existence of mesophase and an extremely small $\Delta H$.

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REFERENCES