Magnetic-field Induced Orientation of Paraffin

Tsunehisa Kimura,* Masafumi Yamato, Wataru Koshimizu, and Takahiko Kawai
Department of Applied Chemistry, Tokyo Metropolitan University, Minami-ohsawa, Hachioji, Tokyo 192-0397

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Paraffin aligns in the magnetic field (9T) during crystallization from melt, forming crystallites oriented with respect to the magnetic field. Discussion is made about the anisotropic structure responsible for the magnetic orientation.

Materials with diamagnetic anisotropy have a potential ability to align under magnetic fields.[1] The origin of their magnetic orientation is traced back to anisotropy of constituent molecules. An anisotropic molecule is energetically stable if it takes a specific orientation with respect to the magnetic field. However, the reduction in magnetic energy due to the orientation is far smaller than the thermal energy, and hence a single molecule can hardly align in the magnetic field. Only the magnetic birefringence due to Cotton-Mouton effect is observed.

However, if an anisotropic domain is formed, then the reduction in the magnetic energy of the domain becomes sufficiently large so as to overcome the thermal energy, resulting in macroscopic orientation of the domain. Typical examples are solids with anisotropic structure, such as fibers[2,3] in liquid suspension and crystals suspended in liquid[4] or crystallized from solutions.[5-7] Other examples are liquid crystals, in which molecules assume anisotropic domains. In addition to these examples, anisotropic structures, occurring transiently during phase transition from an isotropic phase to an anisotropic phase, could also respond to the magnetic fields. Unlike solids and liquid crystals, the transient anisotropic structure changes its diamagnetic property in the course of phase transition. This might complicate the behavior of the magnetic orientation, but could otherwise serve to monitor the development of the transition. Typical examples of this category are crystalline polymers undergoing crystallization from melts.[8-11]

A few studies have been reported on the magnetic orientation of polyethylene crystal[4] and polyethylene fiber[3] suspended in liquid, as well as structure ordering of polyethylene melts in a magnetic field.[12] However, little is known about the possibility of magnetic orientation of paraffin which might be one of organic materials with the smallest diamagnetic anisotropy. This letter reports a new finding of magnetic orientation of paraffin during crystallization from melt. The orientation of crystallite is discussed in relation to conformation change during crystallization.

Paraffin (Kanto Chemical) with nominal melting point of 68~70°C was used. Differential scanning calorimetry exhibited a broad endothermic peak at 69°C and a broad shoulder peak at 52°C. GC/MS measurement showed a high polydispersity ranging between C25 and C45 centered at C36. The shoulder peak is probably due to solid-solid phase transition of larger components and due to melting of samller components.

Melt of the paraffin was poured into an aluminum pan (one usually used for differential scanning calorimetry) and solidified. Then, the pan was put on a copper plate suspended in the middle of a heating unit made of a coil heater. This heating unit was located in a thermally insulating chamber which was placed inside or outside the vertical magnetic field (9T) produced by an HF10-100VHT-3 cryocooler cooled super conducting magnet (Sumitomo Heavy Industries, Ltd.).

The sample was heated from room temperature up to 80°C at 5°C/min and held for 5 min and then allowed slow cooling at ca. 1°C/min down to room temperature. This heat treatment was carried out inside as well as outside the magnet. The aluminum pan was then dissolved in hydrochloric acid. Obtained paraffin sample was subjected to wide angle X-ray diffraction measurement (MAC Science MXP system operating at 40 kV and 250 mA to generate Ni-filtered CuKα X-ray beam).

Paraffin crystallizes in different modifications depending on the chain length, the temperature, and the presence of impurities.[13] Though the crystal type of the sample used in this study was not determined, the comparison with the polyethylene diffraction pattern leads to the assignment that the peaks at 2θ=21.2°, 23.5°, and 35.7° are the diffraction of the (110), (200), and (020) planes, respectively, of the subcell of the orthorhombic type.[14]

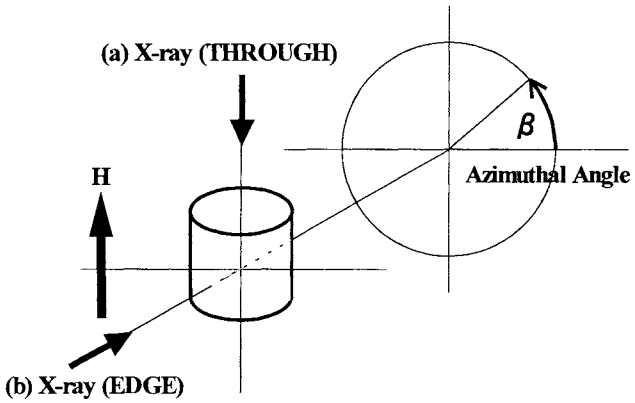

Figure 1. Geometry of X-ray azimuthal scans: (a) through-view and (b) edge-view. Definition of the azimuthal angle β in the case of edge-view is shown. H indicates the magnetic field applied during heat-treatment.

Figure 1 shows the geometry of X-ray measurements. In the case of through-view measurements, all the samples exhibited uniform Debye-Scherrer rings for each diffraction plane irrespective of the presence or absence of the magnetic field.

Figure 2 shows the X-ray azimuthal scans (edge-view) along the peaks corresponding to the (110), (200), and (020) planes for the samples heat-treated outside (a) and inside (b) the magnet. The sample prepared outside the magnet does not exhibit perfect powder pattern but shows a slight and irregular orientation (Figure 2a). Even with other heating methods, orientation was unavoidable. This is probably due to the temperature gradient associated with cooling process and/or specific alignment of the chains on the surface of aluminum pan.

On the other hand, the sample, which is prepared in the

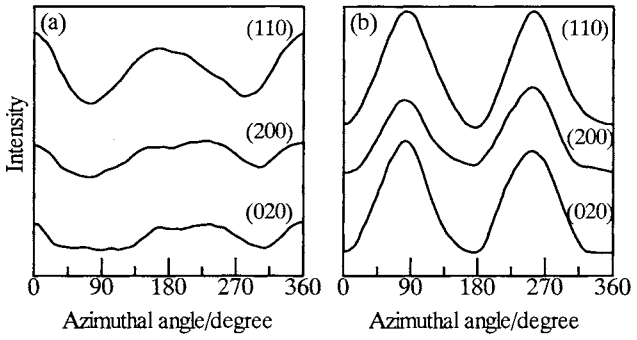

Figure 2. X-ray azimuthal scans (edge-view) for the (110), (200), and (020) planes measured for the samples heat treated (a) outside and (b) inside the magnet (9T). The intensity is normalized at the peak top, and each profile is shifted for clarity.

magnet under exactly the same thermal condition as applied for the sample preparation outside the magnet, exhibited azimuthal profile showing intense peaks at 90° and 270° (Figure 2b). Since this profile is clearly different from that in Figure 2a, it is concluded that the effect of magnetic field overwhelms the effect of temperature gradient and so on, resulting a peculiar orientation.

Now, we discuss about the manner of crystal orientation attained in the magnet. Figure 2b shows that all three diffraction planes exhibit maxima at 90° and 270°. This observation is most likely explained by the orientation distribution of crystals that the *c*-axis lies on the plane normal to the magnetic field but is distributed randomly within the plane. The *a*- and *b*-axes are distributed randomly around the *c*-axis. The orientation of the *c*-axis perpendicular to the magnetic field is reasonable according to the study on polyethylene fiber[3] and crystal.[4] Due to the axial symmetry of the magnetic field, the random distribution of the *c*-axis around the direction of the magnetic field is also reasonable.

A possible reason for the occurrence of the orientation distribution described above would be as follows: The anisotropic structure responsible for the magnetic field is one like a 'rotator phase' in which each chain is allowed to rotate around the chain axis. Due to the axial symmetry of this phase, two of the three principal axes of diamagnetic susceptibility take very similar value to each other in the directions normal to the chain axis, while the other one in the chain direction is negative and the largest. As a result, domains of 'rotator phase' align with the chain direction perpendicular to the magnetic field. With further decrease in temperature, the domains transform from 'rotator phase' to orthorhombic packing, with the chain axis aligned perpendicular to the magnetic field, but the order growth in the direction perpendicular to the chain axis occurs randomly from domain to domain because the initial 'rotator phase' is isotropic with respect to the direction perpendicular to the chain axis. Once the transformation starts, domain orientation becomes difficult because of the increase in viscosity associated with the growth of crystals.

The above scheme describes the main route of magnetic orientation, but there are other possibilities. Behavior of the magnetic orientation is affected by the factors including the size of the domain, the strength of the anisotropic diamagnetic susceptibility of the domain, and the viscosity of the medium surrounding the domain. All these factors would change in time in various ways depending on the thermal history. This situation suggests a possibility that under some thermal history the alignment of orthorhombic crystals occurs rather than the alignment of 'rotator phase'. In addition, it is not ruled out that a selective transformation from 'rotator phase' to orthorhombic phase occurs, where the *a*- or *b*-axis grows selectively perpendicular to the magnetic field, resulting in the orientation of the *a*- or *b*-axis in addition to the *c*-axis orientation.

In conclusion, paraffin undergoes magnetic orientation during melt crystallization. The analysis of the orientation of crystallites suggests that anisotropic structures with axial symmetry around the chain axis are responsible for the magnetic orientation. Further study with the use of monodisperse alkanes is under way.

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