Magnetic-field induced alignment of low molecular weight polyethylene

Naofumi Naga [a,*], Gaku Ishikawa [a], Keiichi Noguchi [b], Kohki Takahashi [c], Kazuo Watanabe [c], Masafumi Yamato [d,*]

[a] Department of Applied Chemistry, Materials Science Course, College of Engineering, Shibaura Institute of Technology, 3-7-5 Toyosu, Koto-ku, Tokyo 135-8548, Japan
[b] Instrumentation Analysis Center, Tokyo University of Agriculture and Technology, 2-24-16, Naka-cho, Koganei, Tokyo 184-8588, Japan
[c] Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba, Sendai, Miyagi 980-8577, Japan
[d] Graduate School of Urban Environmental of Science, Tokyo Metropolitan University, 1-1 Minami-ohsawa, Hachioji, Tokyo 192-0397, Japan

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ABSTRACT

Magnetic-field induced alignment of polyethylene is firstly reported. Isothermal crystallization of low molecular weight polyethylene samples, high density polyethylene (HDPE) and linear low density polyethylene (LLDPE), from melting state was conducted under the magnetic-field of 2 or 10 T. Isothermal crystallization at the temperatures which induced effective self-seeding achieved alignment of polymer chains. The b axis of polyethylene unit cell was aligned parallel to the magnetic-field. Low viscosity and low crystallization rate of the polyethylene samples were favorable for high degree of the magnetic-field alignment.

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1. Introduction

Polyethylene is one of the most widely used and studied polymers. Various processing methods are applied to form polyethylene products with high performance. Mechanical orientation of polyethylene is a conventional process to produce high strength fibers or films. Melt spinning and gel spinning of polyethylene yield super drown fiber with extremely high strength. The high mechanical property is derived from highly-ordered alignment of polymer chains.

Mechanical orientation is a widely used method to obtain film or fiber with high ordered polymer chains. Alignment of polymer chains by magnetic- or electric-field is also developed to obtain ordered polymer products. The magnetic-induced alignment of kinds of polymers, such as conventional crystalline polymers poly(ethylene terephthalate) [1], poly(ethylene-2,6-naphthalate) [2,3], polycarbonate [4], isotactic-polystyrene [5–7], functionalized block copolymers having liquid crystalline or semicrystalline blocks [8–14], has been reported. The magnetic-field induced alignment of crystalline polymers was conducted during the melt-crystallization process. The essential for the alignment is

existence of some ordered domains having critical size with anisotropic diamagnetic susceptibility in a relatively low viscosity environment [15]. The large diamagnetic anisotropy is one of the important driving forces for the magnetic-field induced alignment of polymer chains. The crystalline polymers listed above have diamagnetic anisotropy in the repeating unit derived from aromatic phenyl group. Polyethylene is composed by only methylene units, which have small diamagnetic anisotropy. Polyethylene has been considered to be an unfavorable polymer to align by melt-crystallization under magnetic-field. Whereas, magnetic-field orientation of small crystals [16] or short fibers [17] of polyethylene suspended in liquids was observed. Magnetic-field orientation of paraffin was also attained, and the c axis of the paraffin lied on the plane normal to the magnetic-field [18,19]. Furthermore, magnetic-field induced alignment of isotactic-polypropylene, which does not contain the repeating units with large diamagnetic anisotropy, has been reported [20]. These reports may suggest possibility of magnetic-filed induced alignment of polyethylene.

We tried the magnetic-field induced alignment of commercial polyethylene, and were confronted with two difficulties. The first is high crystallization rate of polyethylene. The crystallization rate of polyethylene is much higher than that of isotactic-polypropylene (iPP), and the crystallization of polyethylene completes too fast to induce alignment of polymer chains during the crystallization

* Corresponding authors.
E-mail address: nnaga@sic.shibaura-it.ac.jp (N. Naga).

under the magnetic-field. The second is high melt viscosity of polyethylene due to the entanglement of the flexible polymer chains. The high melt viscosity decreases mobility of polymer chains in the melting state. In this experiment, low molecular weight polyethylene samples are used to decrease the melt viscosity, and the conducting temperatures are precisely controlled to optimize the conditions of melt-crystallization. This article firstly reports magnetic-field induced alignment of low molecular weight polyethylene samples, high density polyethylene (HDPE) and linear low density polyethylene (LLDPE).

2. Experimental section

2.1. Materials

HDPE or LLDPE samples were synthesized by polymerization of ethylene (PE-1, PE-2) or copolymerization of ethylene and α-olefin, 1-hexene (PE-H1, H2, H3, H4) or 1-decene (PE-D1), with a zirconocene catalyst, diphenylmethylene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride, using methylaluminoxane as a cocatalyst in toluene at 40 °C. Triethylaluminum was used as a chain transfer reagent to decrease the molecular weight of HDPE and LLDPE samples. The samples were melted at 200 °C and pressed under 10 MPa pressure in a mold of 5.5 mm radius with 0.1 mm thickness, followed by quenching in a water of room temperature. Isothermal crystallization of the polyethylene samples was conducted inside of a magnetic field of 2 T or 10 T generated by a cryocooler cooled super conducting magnet (Sumitomo Heavy Industries, Ltd.) in the atmosphere.

2.2. Analytical procedures

^{1}H NMR spectra of the polyethylene samples were recorded at 120 °C on a JEOL Alpha-300 spectrometer in pulse Fourier transform mode. The sample solution was made up in 1,2,4-trichlorobenzene/C_6D_6 (9/1 *v*/*v*) or 1,1,2,2-tetrachloroethane/1,1,2,2-tetrachloroethane-d_2 (9/1 *v*/*v*) as the solvent and the resonances of C_6D_6 (7.15 ppm) or 1,1,2,2-tetrachloroethane-d_2 (5.88 ppm) were used as internal references. Number−average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the polyethylene samples were measured at 140 °C by means of gel-permeation chromatography (PL-GPC-220) using trichlorobenzene as a solvent and calibrated with standard polystyrene samples. Viscosity of polyethylene was measured with a cone and plate viscometer (Brookfield CAP Viscometer, Model CAP 2000+) at 140 °C under 100 rpm.

Thermal analysis of the polyethylene samples was conducted with a differential scanning calorimetry (DSC) of a Rigaku DSC 8230. Melting temperature was determined at a heating rate of 5 °C/min after previous heating to 200 °C and cooling to room temperature. The top of endothermic peak on the 2nd heating process is defined as melting temperature (T_m). The polarized optical micrographs of the samples were observed using an optical microscope (Olympus BX50) equipped with a hot stage, Mettler Toledo FP90. Crystallization rate was estimated by time evolution of depolarized light intensity detected by the optical microscope equipped with CdS sensor. Wide angle X-ray diffraction (WAXD) patterns of the polyethylene samples were recorded on a Rigaku R-AXIS RAPID using Cu Kα radiation.

3. Results and discussion

3.1. Structure and properties of the polyethylene samples

Structure and properties of the polyethylene samples are summarized in Table 1. Number−average molecular weights of the polyethylene samples are 8200−34,100. The molecular weight and viscosity of the polyethylene samples used in the experiment are much lower than those of commercially produced polyethylene. Comonomer content of LLDPE samples were 4.4−6.7 mol%.

3.2. Optimization of temperature program

A scheme of temperature program of isothermal crystallization under the magnetic-field is illustrated in Scheme 1. The sample is heated from room temperature (RT) to a temperature for melting (T_{max}) at a rate of 5 °C/min, and kept at T_{max} for 10 min. Then the sample is cooled to an isothermal crystallization temperature (T_{itc}) at a rate of 5 °C/min and kept at T_{itc} for 60 min. Optimization of T_{max} is important to achieve effective magnetic-field induced alignment of crystalline polymers [1,6,7,20]. Local ordered domains existing in the melt could be heterogeneous nuclei, and would increase the crystallization temperature (T_c) and crystallization enthalpy (ΔH_c). Effect of the melt structure on T_c and ΔH_c was observed in iPP. Kawai et al. reported relationship between T_{max} and T_c, ΔH_c of iPP [21]. They reported that T_{max} and ΔH_c showed a large change at around 240 °C. This temperature indicates the highest temperature existing local ordered domains. In our experiment, DSC measurement with alternative temperature program was used to optimize T_{max} and T_{itc} of polyethylene samples without magnetic-field, as shown in Scheme 2. The sample is heated from RT to T_{max} at a rate of 5 °C/min and kept for 10 min, and then cooled to RT at a rate of 5 °C/min. Exothermic peaks are detected on the cooling process, and the top

Table 1
Structure, properties and degree of magnetic induced alignment of polyethylene samples.

Sample	Comonomer		T_m[a] °C	T_{max}[b] °C	T_{itc}[c] °C	t_{hc}[d] min	M_n[e] × 10^4	M_w/M_n[e]	Viscosity[f] Pa·s	$f_{\phi 200}$[g]	
		mol%								2 T	10 T
PE-1			132.4	131	128	9.9	2.09	2.13	15.9	−0.179	−0.193
PE-2			130.9	130	127	9.3	1.39	2.06	2.9	−0.189	−0.205
PE-H1	1-hexene	4.4	105.8	112	108	14.7	3.41	2.03	62.0	−0.168	−0.184
PE-H2	1-hexene	4.8	105.7	112	109	11.1	1.70	2.05	8.2	−0.191	−0.222
PE-H3	1-hexene	5.0	106.7	111	109	8.4	0.82	2.13	1.8	−0.154	−0.189
PE-H4	1-hexene	6.7	97.5	110	104	13.9	0.99	1.95	4.0	−0.108	−0.113
PE-D1	1-decene	4.7	111.7	119	114	9.7	1.10	2.37	5.7	−0.181	−0.213

[a] Melting point determined by DSC on the 2nd heating process.
[b] T_{max} which induced maximum T_c on the cooling process.
[c] T_{itc} which achieved most effective magnetic-field induced alignment.
[d] Half crystallization time at T_{itc} after the melting at T_{max}.
[e] Determined by GPC using polystyrene standard samples.
[f] Measured with a cone and plate viscometer at 140 °C.
[g] Degree of magnetic induced alignment determined by (200) azimuthal scans using equations (1) and (2).