Influence of $^{60}$Co $\gamma$-Ray irradiation on the morphology of crystalline polyethylene studied by high-resolution solid-state $^{13}$C NMR

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The relationship and influence of varying $^{60}$Co $\gamma$-ray irradiation doses, in the range 0.77–5.2 MGy, on the morphology of polyethylene have been investigated using high-resolution solid-state $^{13}$C nuclear magnetic resonance analyses through variation of different phase components, $T_1c$, $T_2e$ relaxation parameters, and line width. The cross-linking in the irradiated polyethylene takes place mainly in the non-crystalline regions. However, distortion and damage to the folded chain of the crystal lattice are observed in the crystalline regions. For the interfacial phase, both cross-linking and distortion could occur. As a result, part of the crystalline component transformed into a non-crystalline one. It was also found that the orthorhombic crystalline lattice transformed into a monoclinic one within the crystalline phase in polyethylene under higher doses of irradiation.

1. Introduction
Having applied cross-polarization (CP), magic-angle sample spinning (MAS) combined with dipolar decoupling (DD) to study the morphology and various kinds of molecular motion in different phases of crystalline polymers having less molecular motion, some mathematical methods have been created to obtain high-resolution solid-state nuclear magnetic resonance (NMR) spectra similar to that in a liquid [1–4]. Being different from solid broad-line NMR, the method is able to obtain information such as chemical shifts of every carbon in the molecular chain, relaxations $T_1$, $T_2$ and NOE, etc., and, therefore, to discuss the chemical structure of solid-state polymer, chain conformation and configuration, morphology and dynamic properties, in detail. Compared with X-ray diffraction studies, the method is also able to obtain information on structure in the non-crystalline region for a part-crystalline polymer.

To date, the mechanism of irradiation cross-linking and its influence on morphology and phase structure are not clear, although studies on irradiation effect of crystalline polyethylene have been under way for a long time. Some results obtained with several methods have been reported in recent literatures [5–7], but they are not consistent with each other. There is, to our knowledge, still no report concerning the problems relating to studies with high-resolution solid-state $^{13}$C NMR.

We have studied the phase structure of the crystalline polyethylene, analysed and characterized in detail by means of high-resolution solid-state $^{13}$C NMR CP/MAS for polyethylene solid samples crystallized from the melt and dilute solution [3, 4], and reported that H-type cross-links and Y-type long branches were found to be significantly formed during the $^{60}$Co $\gamma$-ray irradiation by solution-state $^{13}$C NMR spectroscopy [8, 9]. The work also showed the G-values of the H-links and Y-branches were 0.74 and 0.27, respectively, indicating that H-links are more effectively produced in the molten state than Y-branches for linear polyethylene.

The present paper reports our experimental results on the different phase structures obtained with high-resolution solid-state $^{13}$C NMR for polyethylene crystallized from a dilute solution, and blow-moulded film before $^{60}$Co $\gamma$-ray irradiation above their gelation-forming doses. The relaxation behaviour of $^{13}$C NMR and change of phase component with increasing irradiation dose in crystalline, crystalline-amorphous interphase and rubber-like amorphous phases are also reported, and the effect of irradiation on crystalline polyethylene is discussed.

2. Experimental procedure
2.1. Samples
Sample 1 is a polyethylene with molecular weight (MW) of $M_n = 1.29 \times 10^4$, $M_w/M_n = 1.5$ supplied by Showadenko Company, Japan. Having been prepared into a solution with concentration of 0.17 wt% in
xylene, the sample was crystallized isothermally in a bath of temperature 85 ± 0.1 °C in nitrogen for 30 h. The crystal powder was filtered and washed with acetone several times, then dried at 50 °C in vacuum for 50 h. The sample prepared in this way is denoted SC0.

Sample II is a blow-moulded polyethylene film with molecular weight of \( M_n = 0.84 \times 10^4 \) made by the same Japanese company. After extraction by methanol, the sample film, denoted F0, was dried in a vacuum for 72 h, then cut into pieces of 15 mm x 4 mm.

2.2. \( \gamma \)-ray irradiation

After degassing in a glass tube of 10 mm diameter in a vacuum of \( 10^{-5} \) mm Hg for 24 h, the samples were sealed in the tube. The irradiation rate of the cobalt source was 17.4 kGy h\(^{-1}\). The irradiation doses were 0.77 (SC75, F75), 2.39 (SC240, F240) and 5.20 (SC520, F520) MGy, respectively.

2.3. Measurement of high-resolution solid-state \( ^{13}\text{C} \) NMR

The measurements were carried out using a JNM-FX200 NMR apparatus with a solid magic rotating detector at room temperature. The field intensity, \( B_0 \), was 4.7 T, the resonant frequencies of \( ^1\text{H} \) and \( ^{13}\text{C} \) were 199.5 and 50.1 MHz, respectively, and the observed magnetic field strength, \( \gamma B/2\pi \) was 69.4 kHz (\( B_{1z} = 6.5 \text{ mT}, B_{1H} = 1.6 \text{ mT} \)). In order to avoid discharge from the sample, the \( \gamma B_{1H}/2\pi = 54.3 \text{ kHz} \) (\( B_{1H} = 1.3 \text{ mT} \)) during dipolar decoupling (DD), it is necessary to adjust \( B_{1H} \) and \( B_{1c} \) each time to meet the Hartmann–Hahn condition \( \gamma B_{1H} = \gamma c B_{1c} \). MAS experiments were carried out at a rate of 4.0–4.2 kHz with a cylinder-type rotator made of \( \text{Al}_2\text{O}_3 \) and poly(amide-imide) resins, with a sample weight of about 0.1–0.2 g. The chemical shifts relative to tetramethylsilane were determined from the CH line (29.50 p.p.m.) of solid adamantane used as an external standard [10].

2.4. Computer analysis method

The data from the computer in the JNM-FX200 set were transformed into the IBM computer system in a standard form. The component separation of the spectrum and analysis of \( T_{1c} \) were performed on a FACOM 180 macrocomputer, assuming all spectra were Lorentzian. Having chosen suitable component spectra as a start value, the non-linear least squares method was performed to analog the data.

3. Results and discussion

3.1. High-resolution solid-state spectrum before and after irradiation

Fig. 1 shows CP/MAS and DD/MAS \( ^{13}\text{C} \) spectra of blow-moulded film F0 at various doses of \( ^{60}\text{Co} \) \( \gamma \)-ray irradiation. The contact time was \( t_{CP} = 2 \text{ ms} \) in CP.