

Structural Changes of Bulk Polyethylene by Stress Impact as Studied by Solid-State NMR

HIDENORI SATOH,¹ SHIGEKI KUROKI,² ISAO ANDO²

¹ Nissan Arc, Limited, Natsushima-cho, Yokosuka-shi, Kanagawa, Japan 237

² Department of Chemistry and Materials Science, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo, Japan 152

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ABSTRACT: Solid-state ¹³C- and ¹H-NMR spectra of bulk high-density polyethylene samples, cylindrical in form, to which stress impacts were applied with a home-made stress-impact apparatus, were measured. The fraction of the noncrystalline component increases with an increase in the stress-impact strength. In the crystalline region, the monoclinic crystalline component appear with the stress impact, in addition to the major orthorhombic crystalline component. Furthermore, dynamic characterization was carried out on the basis of the observed values of the relaxation parameters ¹H T_2 and T_{CH} of the ¹H and ¹³C nuclei. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2268–2272, 2001

Key words: structure; dynamics; stress impact; solid-state NMR; polyethylene

INTRODUCTION

Polymers are almost always used as solids. The properties of such materials are closely related to the microscopic structure and dynamics. Polyethylene, considered here, is a typical polymer. Despite a simple chemical structure, polyethylene exhibits a variety of structures under various conditions.¹ For example, the polymer consists of crystalline and noncrystalline regions, the fraction of which is changed by the conditions of crystallization. In the crystalline region, the polymer presents orthorhombic and monoclinic forms as crystal structures.² In the noncrystalline region, the methylene carbons undergo fast exchange between trans and gauche conformations, even at room temperature.³

Polyethylene has been used in various fields because of its excellent mechanical properties. We often have been concerned with problems that arise in the polymer's mechanical properties when it is exposed to strong stress impacts. Naturally, on the microscopic scale, the structure of polyethylene is expected to change with changes in its mechanical properties under strong stress strain. Thus, a highly accurate structural characterization of the polymer is needed.

Solid-state NMR is a powerful means for obtaining detailed information about the structures and dynamics of solid polymers.⁴ In particular, the structure and dynamics of polyethylene prepared under various conditions and/or crystallization conditions have been elucidated with solid-state ¹³C-NMR.^{3–13}

With this as a background, we aim to characterize the structure and dynamics of bulk polyethylene samples, cylindrical in form, to which stress impacts were applied with a home-made

Correspondence to: I. Ando (iando@polymer.titech.ac.jp).

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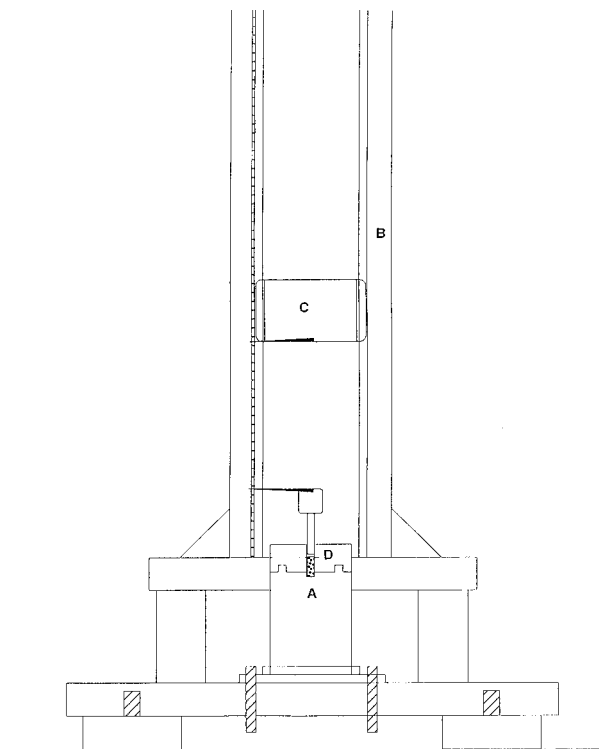


Figure 1 Diagram of the stress-impact apparatus designed in this work: (A) stress-impact cell and (B) support. (C) A 500-g weight is dropped from heights of 5–100 cm along the support, and (D) the polymer sample, 3 mm in diameter, in the cell experiences various stress-impact strengths.

stress-impact apparatus, with high-resolution solid-state ^{13}C -NMR and solid-state ^1H -NMR.

EXPERIMENTAL

Polymer Sample Preparation

High-density polyethylene pellets (weight-average molecular weight = 125,000) were purchased from Aldrich Co., Ltd. Polyethylene cylinders 3 mm in diameter and 15 mm high were prepared with a hot-press machine.

Stress impacts were applied to the polyethylene samples with a home-made stress-impact apparatus, which was a modified DuPont-type apparatus, as shown in Figure 1. The apparatus consisted of a stress-impact cell and a support. A 500-g weight was dropped from a height of 5–100 cm along the support, and the polymer sample, 3 mm in diameter, in the cell experienced various stress-impact strengths with changes in the height from which the weight was dropped.

Measurements

^{13}C cross-polarization/magic-angle spinning (CP-MAS) NMR spectra^{14,15} of the polyethylene samples were measured with a Bruker MSL300 NMR spectrometer operating at 75.45 MHz and room temperature. The MAS rate was about 3 kHz, and the ^1H decoupling field was about 200 kHz. The cross relaxation time between ^{13}C and ^1H nuclei (T_{CH}) was determined with changes in the contact time. Chemical shifts were determined from the higher signal (29.5 ppm) of solid adamantane relative to tetramethylsilane.

Solid echo ^1H -NMR spectra of the polymer samples were measured with a Bruker Minispec PC-20 NMR spectrometer operating at 20 MHz and room temperature. The spin-spin relaxation time (T_2) for ^1H was determined with the obtained solid echo spectra.

RESULTS AND DISCUSSION

^{13}C CP-MAS NMR Spectra and Structural Analysis

^{13}C CP-MAS NMR spectra of polyethylene samples with stress impacts from a 500-g weight be-

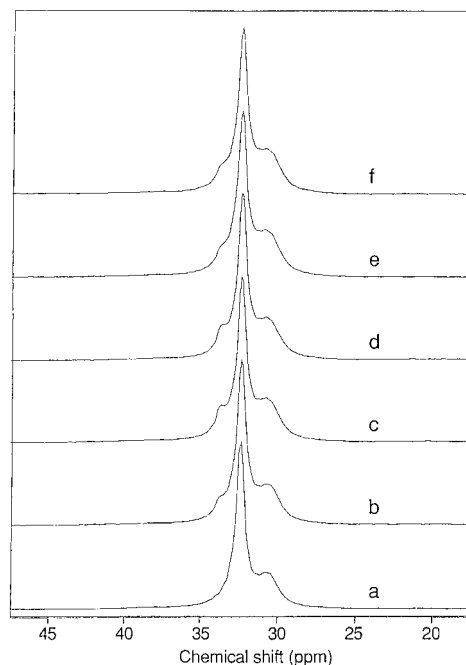


Figure 2 ^{13}C CP-MAS NMR spectra of polyethylene samples that experienced stress impacts by a 500-g weight being dropped from heights of (a) 0, (b) 10, (c) 20, (d) 30, (e) 40, and (f) 50 cm.

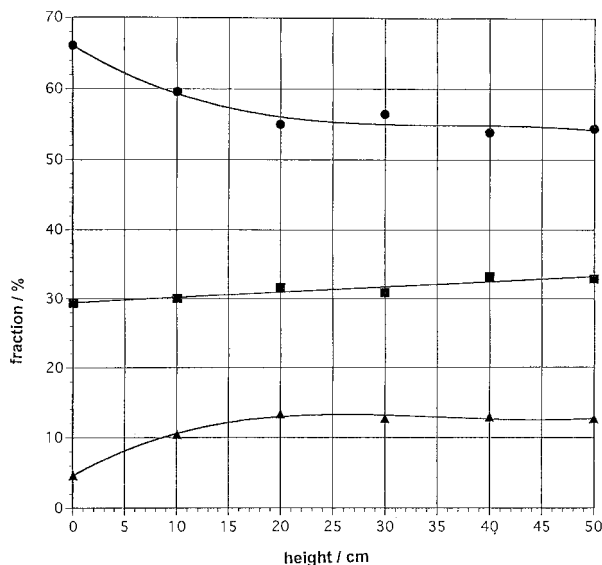


Figure 3 Fractions of (●) noncrystalline, (■) orthorhombic, and (▲) monoclinic components plotted against the height from which a weight was dropped.

ing dropped at heights of 0, 10, 20, 30, 40, and 50 cm are shown in Figure 2. The spectral assignment was made on a straightforward basis with reference data. In Figure 2(a), the ^{13}C CP-MAS NMR spectrum of a polyethylene sample without a stress impact is shown and consists of an intense peak at about 33 ppm and a peak at about 30 ppm. Peaks at about 33 and 30 ppm come from the orthorhombic crystalline and noncrystalline components, respectively, as seen from reference data reported previously.³ In polyethylene samples with stress impacts, another peak appears at about 34 ppm, which comes from the monoclinic crystalline component. In the orthorhombic form, all-trans zigzag planes of polyethylene chains are perpendicular to one another, and in the monoclinic form, all-trans zigzag planes of polyethylene chains are parallel to one another. In the noncrystalline region, the methylene carbons are undergoing a fast exchange between trans and gauche conformations at room temperature. The molecular motion is in the fast motion limit of the Bloembergen–Purcell–Pound theory,¹⁶ $\omega_0\tau_c \ll 1$, where ω_0 is the resonance frequency and τ_c is the correlation time for molecular motion.

As seen in Figure 2(a–f), the intensities of the peaks at about 30 and 34 ppm for the polyethylene samples increase with an increase in the magnitude of the stress impact. From these spectra, the fractions of the three components were deter-

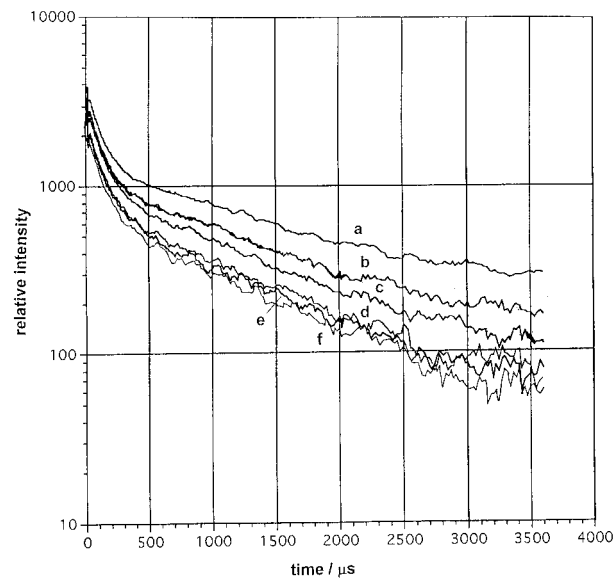


Figure 4 Solid echo ^1H -NMR spectra of polyethylene samples that experienced stress impacts by a 500-g weight being dropped from heights of (a) 0, (b) 10, (c) 20, (d) 30, (e) 40, and (f) 50 cm.

mined by computer fitting, under the assumption of Lorentzian-shape lines for each component. The fractions of these components are plotted against the height from which a 500-g weight was

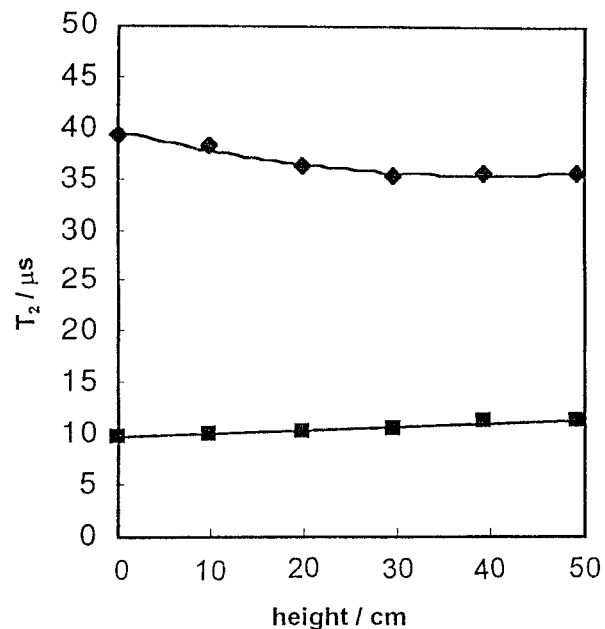


Figure 5 Plots of T_2 values of (◆) noncrystalline and (■) crystalline components against the height from which a 500-g weight was dropped.

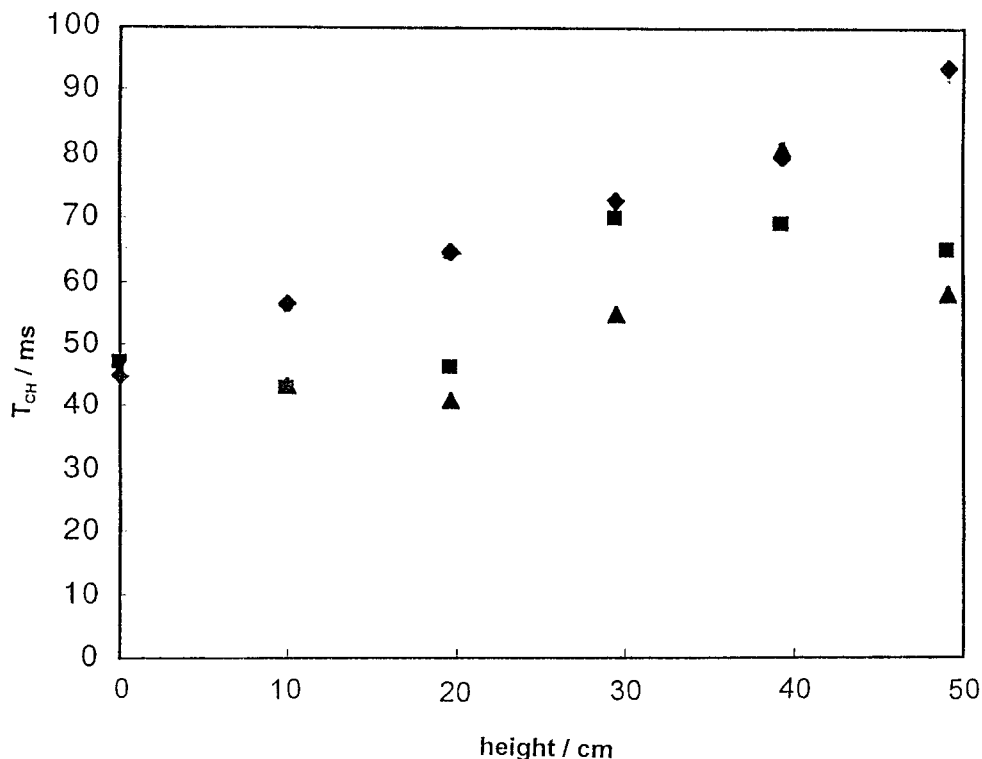


Figure 6 T_{CH} values of the (◆) noncrystalline, (■) orthorhombic, and (◆) monoclinic components plotted against the height from which a weight was dropped.

dropped, as shown in Figure 3. The fraction of the noncrystalline component slowly increases with an increase in the force of impact. That is, an increase in the stress-impact force leads initially to a higher fraction of the monoclinic component. This fraction then becomes constant.

It is known that the stretching of a polyethylene film leads to a change from the orthorhombic form to the monoclinic form, and the crystallization of polyethylene under high pressure leads to the generation of the monoclinic form. We, therefore, conclude that the generation of the monoclinic form by the stress impact as described previously proceeds by a mechanism similar to that induced by the stretching of polyethylene film and by the recrystallization of polyethylene under high pressure.

Dynamic Aspect of Polyethylene Samples with Stress Impact

Figure 4 shows solid echo ^1H -NMR spectra of polyethylene samples as a function of the height from which a 500-g weight was dropped. It is apparent that the solid echo signal consists of two

different decays with different T_2 values. The long T_2 component [Fig. 4(A)] comes from the noncrystalline region, and the shorter T_2 component [Fig. 4(A)] comes from the crystalline region. The slopes of the spin-echo curves depend on the stress-impact strength. From the slope and intercepts of these solid echo curves, the T_2 values of the individual components can be obtained. Plots of T_2 values of the noncrystalline and crystalline components against stress-impact strengths are shown in Figure 5. The T_2 values of the noncrystalline and crystalline components slowly decrease and increase with an increase in the impact strength, respectively. From the decrease of the ^1H T_2 value for the noncrystalline component with an increase in the stress impact, as obtained from the aforementioned experiments, and the slow increase of its fraction with an increase in the stress impact, as obtained from the ^{13}C -CP-MAS NMR experiments, it is suggested that the number of domains of the noncrystalline component decreases with an increase in the stress impact, and molecular mobility accordingly decreases. However, the increase in the T_2 value of the crys-

talline component shows that the domain size of the crystalline component surrounded by the noncrystalline domain decreases with an increase in the stress impact, and so the molecular mobility increases.

The determined T_{CH} values of the noncrystalline, orthorhombic, and monoclinic components, as determined by ^{13}C CP-MAS NMR experiments with changes in the contact time, are plotted in Figure 6 against the height from which a 500-g weight was dropped. Before the application of the stress impact to the sample, the T_{CH} values for the three components are almost the same. They begin to increase with an increase in the stress-impact strength. The T_{CH} values for the noncrystalline component and for the orthorhombic and monoclinic crystalline components increase with an increase in the stress-impact strength. This means that the size of the noncrystalline domain increases, and so the mobility increases; moreover, the size of the orthorhombic and monoclinic crystalline domains become smaller with an increase in the stress-impact strength, and so the mobility increases with influence of the increase of the mobility of the surrounding noncrystalline domain. This shows that the structural changes in the corresponding three components are associated with the cross relaxation time.

Finally, from the solid-state NMR experiments, it can be concluded that the structure and dynamics of polyethylene are noticeably changed under impact stress. The fraction of the noncrystalline component decreases with an increase in the stress-impact strength, and in the crystalline region, the monoclinic crystalline component appears from stress impact in addition to the major orthorhombic crystalline component.

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