

# Notes

## Solid State NMR Study of Solid-Solid Phase Transition in High Density Polyethylene Due to Thermal/Mechanical Treatment

Oc Hee Han\*, Seen Ae Chae, Seongok Han<sup>†</sup>,  
and Sangkuk Woo<sup>†</sup>

*Magnetic Resonance Research Group,  
Korea Basic Science Institute,  
Taejon 305-333, Korea*

<sup>†</sup>*Energy Materials Research Team,  
Korea Institute of Energy Research,  
Taejon 305-343, Korea*

*Received June 21, 1996*

Many physical properties of polymer depend on its morphological state.<sup>1,2</sup> Solid state NMR and X-ray diffraction (XRD) have been used to study the degree of crystallinity as well as identification of individual phases.<sup>3-5</sup> In this work, the phase transformation of high density polyethylene (HDPE) due to mechanical/thermal treatments such as powdering at 77 K or molding at high temperature and pressure, are studied by <sup>13</sup>C solid state NMR techniques.

HDPE has a majority (typically more than 99%) of methylene carbons and minor components such as methyl carbon, tertiary carbon, and functional groups other than alkyl groups.<sup>6,7</sup> Practically, it is impossible to quantitate all these minor components of the HDPE with solid state <sup>13</sup>C magic angle spinning (MAS) NMR<sup>2</sup> due to long carbon T<sub>1</sub> values and required dynamic range. Thus, only methylene carbon signal from each phase was discussed for quantitation study in this work.

### Experimental

**Sample Preparation.** Commercial grade HDPE pellet (product number F120A) from the Samsung General Chemicals was used without further treatment, which was named as PEO-plt. Density and melting index (MI) of PEO-plt were measured as 0.956 g/cm<sup>3</sup> and 0.04 g/10 min, respectively. Melting point and heat of fusion were reported as 124 °C and 38.5 cal/g, respectively.<sup>8</sup> The 1 mm thick sheet made out of this pellet by molding at the high temperature (~200 °C) and pressure (4.0 atm for 6 minutes and 48 atm for 4 minutes consecutively) was named as PEO-sht. This molded HDPE was cooled at atmospheric pressure for several minutes or longer. The PEO-sht was exposed to 9.4 Mrad electron beam irradiation to make PE9-sht. PEXL-sht is a sliced commercial ondol (the Korean under-floor heating system) pipe. Gel contents<sup>9</sup> summarized in Table 1 were determined with the sliced HDPE sheet in ~0.2 mm thickness by the procedure described in the ASTM designation number D 2765-

90. The sample in sheet form were powdered with a freezer/mill (Spex industries Inc.) for ~5 mins. by grinding at liquid nitrogen temperature, 77 K. These powdered samples were designated as PEyy-pwd where yy is 0, 9 or XL.

The notation of the samples can be summarized as following:

PEyy-zzz

where yy is the electron beam irradiation dosage applied to the sample

(excpion: XL for the sample from the ondol pipe)

and zzz is the physical form notation of the sample

(plt for pellet, sht for sheet, and pwd for powder).

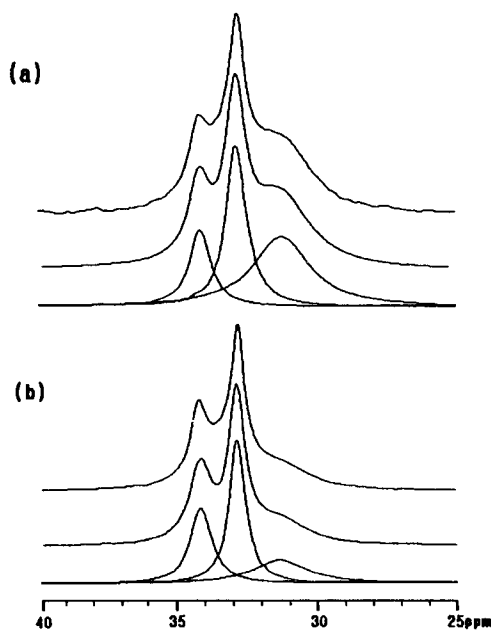
For the NMR experiments of the samples in sheet form, the samples were cut to fit into the rotor with inner diameter and length of 5 mm and 10 mm, respectively. Three or four pieces were optimum to fill up the rotor and to maximize the size of the piece.

**NMR Spectroscopy.** All experiments were carried out with the UNITY plus NMR system (Varian association Inc.) of 7.05 Tesla and a multinuclear cross polarization magic angle spinning (CPMAS)<sup>2</sup> probe (Varian association Inc.) at room temperature. Typical spinning rate employed for MAS and CPMAS experiments was 5 kHz. H<sub>1</sub> field strength for CP and decoupling was 55.6 kHz resulting in 4.5 us 90° pulse length. All spectra were acquired under proton decoupling. Carbon chemical shift was referenced to external tetramethyl silane (TMS). Methyl peak of hexamethyl benzene which was externally set as 17.3 ppm<sup>10</sup> was used as a secondary chemical shift standard. Fine NaCl powder was added to fill up the rotor packed with the samples in pellet or sheet form in order to achieve stable spinning. The basic pulse sequences used in this work are the same with ones in reference 2. The contact time of 200 us and pulse sequence repetition delay (D1) of 5 sec were employed for CPMAS and 4.5 us pulse length and D1=1500 sec were employed for MAS unless stated otherwise. For dipolar dephase experiment,<sup>2</sup> the delay time between CP and the starting point of acquisition was arrayed while decoupling was off. The contact time values were arrayed for the contact time variation experiment.<sup>2</sup> The repetition delay variation experiment<sup>1,2</sup> was demonstrated for MAS instead of exact measurement of spin-lattice relaxation time T<sub>1</sub> since it would take too much time to get the T<sub>1</sub> data.

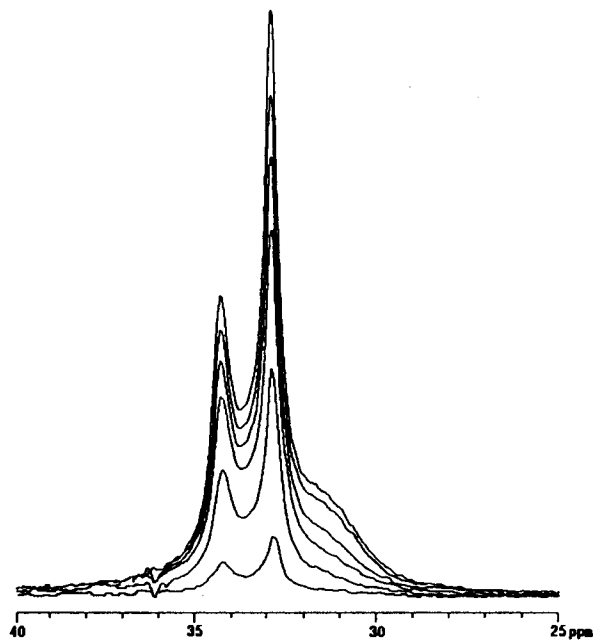
### Results and Discussion

Representative <sup>13</sup>C MAS and CPMAS spectra of powdered HEPE samples show three peaks, two relatively sharp peaks at 34.2±0.3 and 32.8±0.3 ppm and one broad upfield peak at 31.3±0.3 ppm, as shown in Figure 1. The contact time variation shows two upfield peaks grow much faster than the broad one at 31.3±0.3 ppm in Figure 2. The results of dipolar dephase experiments (Figure 3) indicate that the carbons of sharp peaks dephase faster than those of the broad peak. The pulse sequence repetition delay array experiment without CP clearly shows that the broad component

\*To whom the correspondence should be addressed.

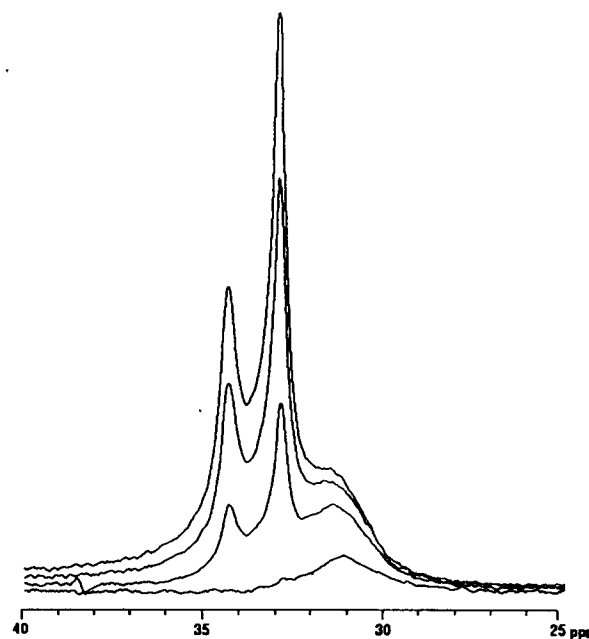


**Figure 1.** Carbon-13 (A) MAS and (B) CP/MAS spectra between 25 and 40 ppm of PE9-pwd. The top, middle, and bottom spectra in (A) and (B) are experimental spectra, simulated spectra, and individual components of the simulated spectra, respectively.

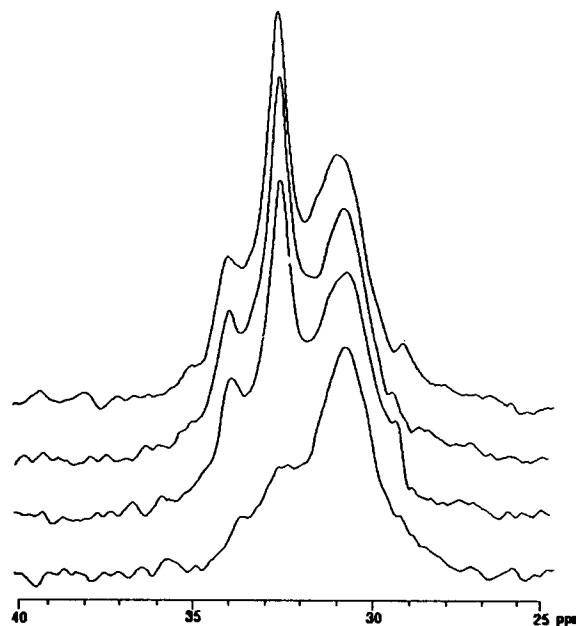


**Figure 2.** Contact time variation experiment of PE9-pwd. The contact time array values were 5, 15, 25, 40, 100, and 400  $\mu$ s from bottom to top.

fully reaches the equilibrium within 5 sec while the sharp components do not even after 1500 sec in Figure 4. Two peaks at  $34.2 \pm 0.3$  and  $32.8 \pm 0.3$  ppm have narrow full width at half height (FWHH) of 25-45 Hz while the peak at  $31.3 \pm 0.3$  ppm has much broader FWHH of 120-180 Hz and upfield shifted compared with the sharp peaks. All these experimental results agree with the previous report,<sup>2,11</sup> that the



**Figure 3.** Dipolar dephasing CPMAS experiment of PE9-pwd. The dipolar dephase duration array values were 0, 10, 20, and 60  $\mu$ s from bottom to top.



**Figure 4.** Pulse sequence repetition delay variation MAS (without CP) experiment of PEXL-pwd. The repetition delays were 5, 500, 1500, and 2800 s from bottom to top.

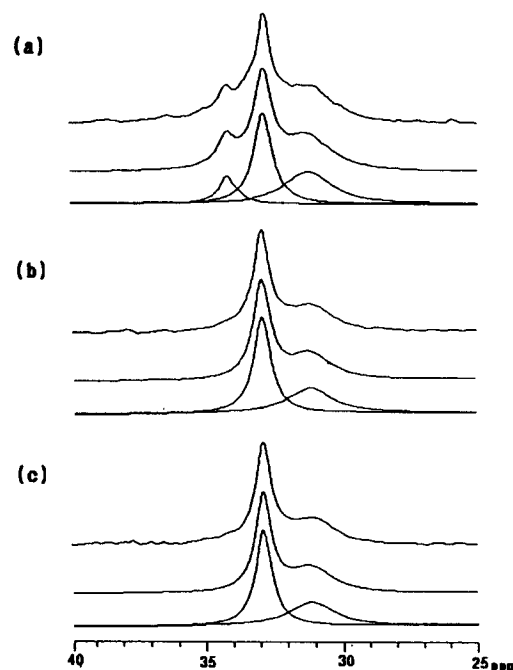
broad peak is from amorphous phase (AP) methylene carbon and the sharp peaks from the methylene carbon of the crystalline phase. AP has some *gauche* conformation of methylene chains as well as all other non-methylene components including branching points, which results in relatively loose and irregular packing. Thus, methylene carbons in amorphous phase would have more motion which reduces dipole coupling between carbon and proton. Also, presence of *gauche* conformation would shift the chemical shift of the methylene

carbons in amorphous phase upfield by  $\gamma$ -*gauche* effect.<sup>12</sup> On the other hand, the crystalline phases have more rigid molecular segments resulting from regular and compact packing of linear methylene chains in all *trans* conformation. This rigidity and compact packing would result in stronger dipole coupling. Thus, methylene peaks from crystalline phases with stronger dipole coupling would dephase faster in the dipolar dephase experiments and build up intensity faster in the contact time variation experiments. More motion in amorphous phase causes faster spin lattice relaxation of methylene carbons in amorphous phase resulting in faster amplitude grow in the pulse sequence repetition variation experiment in Figure 4. AP methylene component with strong dipole coupling due to restricted motion in nascent PE<sup>13</sup> and gel-spun ultra high molecular weight PE (UHMWPE) fibers<sup>14</sup> was reported. But AP methylene in our samples has too slow a dephasing rate to have the strong dipole coupling. Two methylene peaks from crystalline phases,  $34.2 \pm 0.3$  ppm peak and  $32.8 \pm 0.3$  ppm peak, were assigned as from monoclinic and orthorhombic crystalline phases (MCP and OCP), respectively, based on previous reports.<sup>5,13-15</sup> Intermediate phase<sup>14-16</sup> was also reported, however, its presence is not certain in our samples, if any.

It is well known that CP spectra are not easy to quantitate since the peak area in the spectra is not linearly proportional to the number of nuclei but a function of CP rates.<sup>1,2</sup> In turn, the CP rate is a function of carbon-proton dipole coupling strength and of dynamics.<sup>1,2</sup> This tendency appeared in our spectra in Figure 1 as smaller AP methylene peak intensity in the CPMAS spectrum than that of the MAS spectrum. Therefore, MAS spectra were used for quantitative study in this work although the repetition delay, 1500 sec, for the MAS spectra was much longer than the repetition time, 5 sec, for the CPMAS spectra. Taking the repetition delay longer than 1500 sec for MAS spectra would not increase the crystalline phase methylene peak intensities more than the experimental error range, 3%, according to our repetition delay variation experimental results.

In contrast to the MAS spectra of the powdered HDPE sample, the HDPE in sheet or pellet form do not have OCP methylene peak (Figure 5). This difference was observed for all HDPE samples in this work including electron beam irradiated samples (Table 1). Methylene peak intensities from AP didn't change much before and after the powdering procedure (Table 1). Thus, phase transformation mainly from OCP to MCP has occurred during powdering at 77 K which would apply strain to the sample. Our observation is consistent with the solid-solid phase transition from OCP to MCP in the oriented PE under compression studied by XRD.<sup>17</sup> According to previous report,<sup>5,18</sup> the energy difference between MCP and OCP in *n*-alkane is very small and the phase with lower energy is determined mainly by the carbon number of the alkyl chain and methyl group arrangement.

Another observation is that AP methylene peak intensity of PEO-plt seems bigger than that of PEO-sht (Figure 5 and Table 1). However, the intensity difference is within experimental error range. Some AP was reported to convert to crystalline phase under high pressure.<sup>7</sup> Since PEO-sht was made from PEO-plt by applying high pressure at high temperature, the phase transition from AP to OCP is expected. The discrepancy indicates that the cooling rate and the pres-



**Figure 5.** Carbon-13 MAS spectra between 25 and 40 ppm of (A) PEO-powder, (B) PEO-sheet, and (C) PEO-pellet. The top, middle, and bottom spectra in (A), (B), and (C) are experimental spectra, simulated spectra, and individual components of the simulated spectra, respectively.

**Table 1.** Relative Methylene Peak Area of <sup>13</sup>C MAS Spectra and Gel Content Measured by the ASTM D 2765-90

Sample	MCP*	OCP*	AP*	Gel Content(%)
PEO-plt	0	58	42	0
PEO-sht	0	62	38	0
PEO-pwd	17	47	36	0
PE9-sht	0	61	39	46
PE9-pwd	19	38	43	NM**
PEXL-sht	0	50	50	>75***
PEXL-pwd	18	35	47	NM**

\*MCP, OCP, and AP represent monoclinic crystalline phase, orthorhombic crystalline phase, and amorphous phase, respectively. All peak areas are described in % and the error range of peak area measurement is within 3% unless stated otherwise. \*\*not measured. \*\*\*This was not measured in our laboratory, however, it should be >75% to be approved as an ondol pipe.

sure in cooling period probably played major roles in forming phases of PEO-sht rather than the high pressures and temperature applied in molding.

Orientation of individual crystalline phases domains in the sample was determined to be random from the observation that different orientations of PE9-sht in the magnetic field did not change the spectra.

In summary, solid state <sup>13</sup>C MAS NMR can clearly detect morphological change of HDPE due to mechanical/thermal treatment. Only OCP and AP were observed from the HDPE in sheet or pellet form and powdering at 77 K induced the phase transformation from part of OCP to MCP. This phase

conversion by powdering was observed for all HDPE samples in this work including electron beam irradiated ones. This result implies that the powdering process routinely done in analytical laboratories can alter physical properties of the original samples via phase transformation so that the process should be taken with consideration. Increase of crystallinity due to high temperature and pressure was negligible, probably because the pressure during cooling period was low.

### References

1. *High Resolution NMR Spectroscopy of Synthetic Polymers in Bulk*; Komoroski, R. A., Ed.; VCH Publisher Inc.: Deerfield Beach, Florida, 1986.
2. *Solid State NMR of Polymers*; Mathias, L. J., Ed.; Plenum Press: New York and London, 1991.
3. Shimizu, Y.; Harashina, Y.; Sugiura, Y.; Matsuo, M. *Macromolecules* **1995**, *28*, 6889.
4. Gomez, M. A.; Cozine, M. H.; Schilling, F. C.; Tonelli, A. E.; Bello, A.; Fatou, J. G. *Macromolecules* **1987**, *20*, 1761.
5. VanderHart, D. L.; Khoury, F. *Polymer* **1984**, *25*, 1587.
6. Randall, J. C. *Characterization of Long-Chain Branching in Polyethylenes using High Field Carbon-13 NMR*; In *Polymer Characterization by ESR and NMR*; ACS Symposium Series 142, Woodward, A. E.; Bovey, F. A. Eds.; American Chemical Society; 1980.
7. Earl, W. L.; VanderHart, D. L. *Macromolecules* **1979**, *12*, 762.
8. Refer to Samsung product catalog.
9. (a) Whitaker, R. B.; Craven, S. M.; Etter, D. E.; Jendrek, E. F.; Nease, A. B. *Ind. Eng. Chem. Proc. Res. Dev.* **1983**, *22*, 657. (b) *Annual Book of ASTM Standards*.
10. *Sysrem Operation Manual VNMR 4.3 Pub. No. 87-1951 00-00 Rev. G0993*; Varian NMR Instruments: Palo Alto, 1993; p 340.
11. Schroter, B.; Posern, A. *Makromol. Chem.* **1981**, *182*, 675.
12. Tonelli, A. E. *NMR Spectroscopy and Polymer Microstructure: The Conformational Connection*; VCH Publisher: New York, 1989.
13. Morin, F. G.; Delmas, G.; Gilson, D. F. R. *Macromolecules* **1995**, *28*, 3248.
14. Tzou, D. L.; Schmidt-Rohr, K.; Spiess, H. W. *Polymer* **1994**, *35*, 4728.
15. Kitamaru, R.; Horii, F.; Zhu, Q.; Bassett, D. C.; Olley, R. H. *Polymer* **1994**, *35*, 1171.
16. Cheng, J.; Fone, M.; Reddy, V. N.; Schwartz, K. B.; Fisher, H. P.; Wunderlich, B. *J. of Polym. Sci., Polym. Phys.* **1994**, *32*, 2683.
17. Seto, T.; Hara, T.; Tanaka, K. *Japanese J. Appl. Phys.* **1968**, *7*, 31.
18. VanderHart, D. L. *J. Magn. Reson.* **1981**, *44*, 117.

## The Generation of Stable Carbon Radicals by Pyrolysis of Poly(2,4-hexadiyne-1,6-diol)

Sang Won Park and Jeong Soo Kim\*

Dept. of Polymer Sci. and Eng.,  
Chungnam National Univ., Yuseong-Gu,  
Taejeon 305-764, Korea

Received June 29, 1996

Recently, organic ferromagnets have become issues in pure and applied sciences.<sup>1</sup> Many theoretical models and possible organic structures were proposed as possible candidates for them.<sup>2</sup> Most of them are based on the ferromagnetic interaction among unpaired electrons of charge-transfer-complex or alternating hydrocarbons.<sup>3</sup> Application of topologically symmetrical  $\pi$ -electron orbitals in alternating hydrocarbons is an interesting approach for polymer chemists toward organic ferromagnets, in which the degeneracy of  $\pi$ -nonbonding orbital is unlimited. Based on this model, several polymeric structures with polyradicals have been prepared, and some of them have showed the ferromagnetic behavior in laboratorial sense in spite of very poor reproducibilities and structural unclearness.<sup>4</sup>

Ovchinnikov and coworkers have reported the possibility of polymeric carbons, which have the ferromagnetic coupling of concentrated unpaired  $\pi$ -electrons.<sup>5</sup> They have obtained the carbon materials which shows a comparable magnetization with  $\alpha$ -Fe by controlled pyrolysis of polyacrylonitrile and following magnetic separation, although detailed synthetic or pyrolytic process was not elucidated. The ferromagnetism of above polymeric carbon was assumed to be caused by the intermediate graphite-diamond structure, in which  $sp^2$  and  $sp^3$  hybrid orbitals are perfectly alternating.

The ferromagnetic carbon obtained from pyrolyzed PAN indicates that the highly ordered polymeric crystal can be a more useful precursor than the amorphous polymer if they can be pyrolyzed with high carbon yield. The diacetylene compound can be one of the best candidates for the purpose. We selected here 2,4-hexadiyne-1,6-diol as a diacetylene compound that has hydroxymethyl side chain, which is assumed to be pyrolyzed with high carbonyield as cellulose or PVC.

### Experimental

**Materials.** Propargyl alcohol, acrylonitrile, and methacrylic acid were reagent grade from Aldrich Chemical Co. and used without further purification.

**Suspension polymerization of polyacrylonitrile (PAN).** PAN was obtained by general method of suspension polymerization. 0.1 g of poly(vinyl alcohol) was dissolved with 300 g of distilled water in 1 L four-neck-flask, and the mixture of 96 g of acrylonitrile and 4 g of methacrylic acid was added. The bath temperature was maintained at 60 °C and 0.25 g of potassium sulfate and 0.1 g of potassium metabisulfite were then added. PAN powder was obtained through filtering and drying. The molecular weight of PAN was about 320,000 g/mol, which was calculated from the measured intrinsic