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Solid-State ^{13}C NMR Study of Polyethylene Reactor Powders

Introduction. Recently, a series of high molecular weight polyethylene reactor powders was synthesized under slurry and gas-phase reaction conditions by using Ziegler–Natta catalysis.[1] X-ray[1] and Raman LAM studies[2] indicate that these materials are highly ordered and crystalline. Questions remain concerning the type and degree of crystallinity present. Polyethylene has three known polymorphic forms. The most common is the thermodynamically stable orthorhombic, with the triclinic and monoclinic forms obtained under specific processing conditions as kinetically stable morphologies.[1] Transformation from the monoclinic to the orthorhombic crystal form has been reported to occur at 60 °C, as monitored via neutron and X-ray diffraction.[3] Preliminary X-ray work on the reactor powders of this study indicated the presence of both the orthorhombic and monoclinic forms, although quantitation was difficult.[1] Solid-state ^{13}C NMR spectroscopy has proven to be valuable in examining the structure and molecular motions of other types of polyethylenes.[4-10] We report here the results of a solid-state ^{13}C NMR investigation performed on the as-obtained reactor powders.

Experimental Section. The polyethylene samples were synthesized by the Union Carbide Corp. using Ziegler–Natta catalysis under either slurry or gas-phase conditions.[1] Temperatures used for the slurry process were 30, 60, and 85 °C and for the gas process 30 and 85 °C. The viscosity-average molecular weights ranged from 1.6×10^5 to 15×10^6 g/mol.

All NMR experiments were performed on a Bruker MSL-200 operating at 50.32 MHz for carbon. NMR spectra were acquired by using magic-angle spinning with cross polarization (CP/MAS) and without cross polarization (MAS). In both cases, high-power proton decoupling (HPD) was implemented during acquisition. Samples were typically spun at a rate of ∼3 kHz, which is sufficiently fast to remove spinning sidebands for aliphatic carbons at this field strength. The 90° pulse length for ^1H and ^{13}C was 3.6 μs. For CP/MAS experiments the cross-polarization time was 2 ms. All ^{13}C peaks were referenced to the upfield peak of adamantane (29.5 ppm). Peak deconvolution and quantitation was done by using LINESIM, a Bruker-supplied program that can fit a spectrum using either Lorentzian or Gaussian line shapes. ^{13}C T_1 data for the orthorhombic peak were acquired using the method described by Torchia.[11] T_1 values were determined from the peak intensities using SIMFIT, a Bruker-supplied program that can fit a variety of data using the standard simplex algorithm. For the variable temperature experiments, the temperature was increased at a rate of 1 °C every 2 min in order to prevent the VT-1000 temperature control unit from overshooting the target temperature by more than 1 °C.

Results and Discussion. Figure 1 shows the ^{13}C CP/MAS spectra for two of the as-obtained samples. The lower trace is of a sample synthesized under slurry conditions at 30 °C, and the upper trace is of a sample synthesized under gas-phase conditions at 85 °C. A peak at 34.2 ppm has been previously identified as belonging to polyethylene chains crystallized in the monoclinic form.[7] The larger peak at 32.8 ppm is characteristic of polyethylene crystallized in the orthorhombic form.[4,12,13] Solid-state ^{13}C CP/MAS NMR clearly shows that there is a considerable amount of monoclinic polyethylene present.

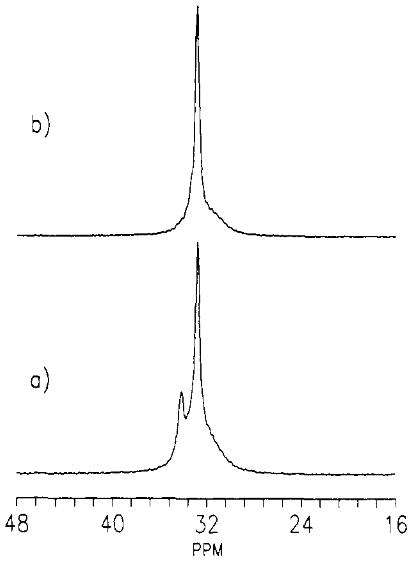

Figure 1. ^{13}C CP/MAS spectra of samples 1 (a) and 5 (b). The peak for the monoclinic crystal form of polyethylene appears at 34.2 ppm, while the peak for the orthorhombic form lies at 32.8 ppm. The number of scans was 128 for each, and the recycle delay was 3 s.

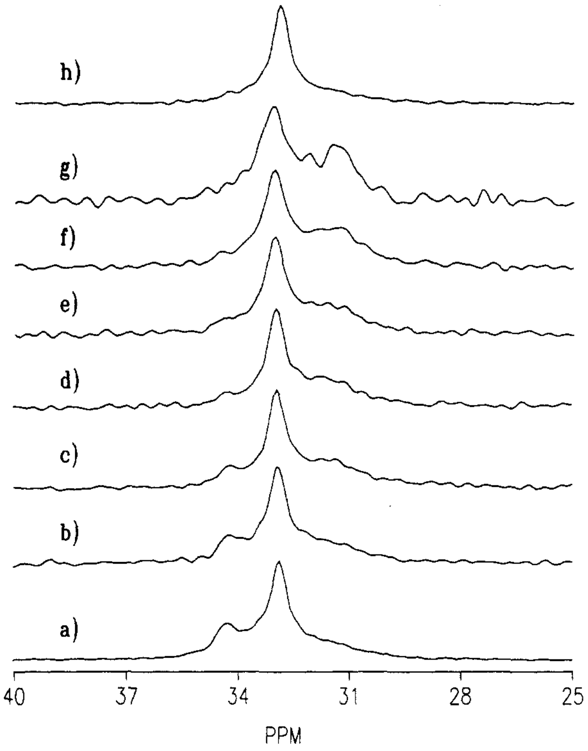

Figure 2. ^{13}C CP/MAS spectra of sample 1 acquired at (a) 27 °C, (b) 50 °C, (c) 56 °C, (d) 62 °C, (e) 68 °C, (f) 74 °C, (g) 80 °C, and (h) 27 °C after being heating and cooled. Note the decrease in the monoclinic peak as the temperature is raised. The number of scans was 32, and the recycle delay was 4 s.

Table I summarizes the results of polymer synthesis conditions and qualitative ^{13}C CP/MAS analyses performed on seven polyethylene reactor powders. The presence of the monoclinic form in the samples depends strongly on the synthesis temperature. This is consistent with the fact that conversion from the monoclinic to the orthorhombic form occurs at ∼60 °C. Indeed, it is surprising to find evidence of the monoclinic form even in samples synthesized *at* 60 °C. Possible explanations for its occurrence include crystallization induced by strain generated during synthesis or the presence of preferential nucleation sites on the catalytic surface.[1]

Figure 2 summarizes the results of a variable-temperature CP/MAS NMR study performed on sample

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Table I
Synthesis Conditions and Characterization Data of Polyethylene Reactor Powders

sample no.	monoclinic present	orthorhombic present	reaction conditions	mol wt[a]
1	yes	yes	slurry, 30 °C	5.95
2	yes	yes	slurry, 30 °C	14.92
3	yes	yes	slurry, 60 °C	1.57
4	no	yes	slurry, 85 °C	0.36
5	no	yes	slurry, 85 °C	4.80
6	yes	yes	gas, 30 °C	1.93
7	no	yes	gas, 30 °C	0.16

[a] Viscosuty-average molecular weight in 10^6 g/mol.

Table II
Summary of ^{13}C T_1 Values for Polyethylene Reactor Powders[a]

exptl	predtd[b]	exptl	predtd[b]
750 s (2300 s)	~1500 s	730 s (2600 s)	~1000 s

[a] T_1 value for the crystalline component of the orthorhombic peak only, based on a three-component fit. Values in parentheses are for the materials crystallized from the melt. [b] Based on the Raman LAM determined crystallite thickness and the relationship in ref 5.

Table III
Summary of Line-Fitting Analysis for Polyethylene Reactor Powders[a]

sample 1		sample 6		sample 7	
ppm	% area	ppm	% area	ppm	% area
34.3	12	34.2	9		
33.6	24	33.6	30	33.0	58
32.9	45	32.8	36	32.8	17
31.4	19	31.6	25	31.6	25

[a] Analyses were performed by using LINESIM, a line-fitting program supplied by Bruker for the Aspect-3000 computer.

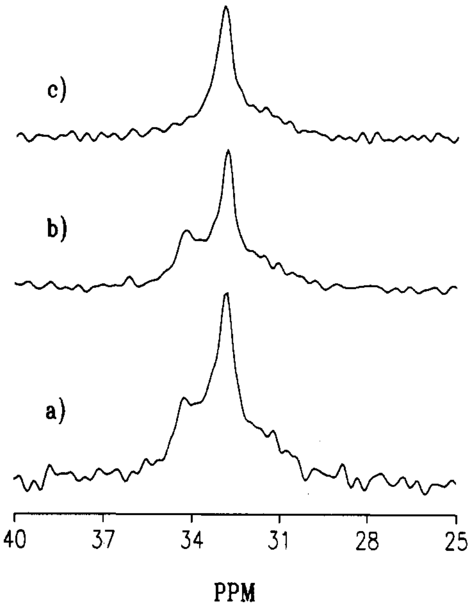

Figure 3. ^{13}C HPD/MAS spectra of samples 1 (a), 6 (b), and 7 (c).

1. The sample was allowed to equilibrate ~20 min at each temperature before data acquisition was initiated. The sample was not maintained at any one particular temperature for more than 35–45 min (including total acquisition time). The monoclinic to orthorhombic transformation has begun by 50 °C (as monitored by the decrease in the monoclinic peak height) with complete transformation occurring by 80 °C. The decrease in the 34.2 ppm peak was also observed in MAS/HPD spectra, confirming conversion of the monoclinic crystal form to the orthorhombic form. There is a no definite transition temperature for this conversion for sample 1, but rather a continuous transformation takes place. This may involve a gradual increase in orthorhombic crystal sizes or a quasi-equilibrium between monoclinic and/or amorphous domains and the orthorhombic crystal surfaces. Alternatively, the rate of solidification during synthesis may be so high that strain-induced crystallization in the intercrystalline regions causes formation of monoclinic domains, which relax and recrystallize on annealing. It is important to note that the transition range for conversion of monoclinic to orthorhombic is similar to that of the α-transition reported for various polyethylene samples.[5]

The crystallite thicknesses for these polyethylene reactor powders range from 200 to 330 Å according to DSC and Raman LAM studies.[2] However, ^{13}C T_1 values determined for samples 1 and 7 were substantially smaller than what are normally observed for thermodynamically stable polyethylene crystallites of similar thicknesses.[5] Table II compares the results of the ^{13}C T_1 evaluations along with the predicted values. The differences in the predicted and experimental T_1 values may be due to the nature of the interfacial region of these as-obtained powders. That is, they do not have a traditional interphase region, where methylene chain segments become highly entangled while looping into and out of the crystallite surface. Instead, the chain loops have few (if any) entanglements, making these polyethylene powders a close analogue to single-crystal materials containing some surface disorder and localized amorphous regions. This physical model is supported by the extreme ductility of these materials (unreported results). The reduced number of entanglements may also permit enhanced mobility of the crystallite surface chain segments, thereby producing smaller T_1 values for adjacent crystalline domains. In order to determine whether the morphology of the polyethylenes was the contributing factor for the T_1 values, samples 1 and 7 were heated to 178 °C overnight and slowly cooled to give melt-crystallized materials. The crystalline T_1 values for these samples are typical for the orthorhombic crystalline peak of high-density polyethylenes (Table II, values in parentheses). The smaller T_1 values for the nascent powders are indeed a result of their unusual morphology.

Figure 3 gives the spectra of samples 1, 6, and 7 acquired by using the MAS/HPD technique. For these spectra, the recycle time was 2000 s, which is ~2.7 times the longest ^{13}C T_1 value measured for these materials. Thirty-two scans were acquired for each spectrum, which was then fitted with Lorentzian peaks in order to quantitate the various crystalline types plus noncrystalline component present. The results of the line-fit quantitations are given in Table III. Interestingly, the best fit is obtained by using four Lorentzians rather than the expected three. These peaks correspond to the monoclinic, orthorhombic, interphase amorphous, and some additional crystalline component at ~33.0–33.6 ppm. Recently, Kaji and coworkers have assigned a similar peak in UHMWPE fibers as a yet to be identified crystalline component.[10] While the low signal-to-noise and extended acquisition times make more sophisticated analyis unreasonable, we believe the values determined are accurate to within 5–10%.

Conclusion. The morphology of polyethylene reactor powders is strongly dependent on the synthesis temperature and conditions. ^{13}C CP/MAS NMR spectroscopy offers a sensitive qualitative and quantitative method for the characterization of such materials in their as-obtained, sometimes thermodynamically unstable states.

Both monoclinic and orthorhombic forms of polyethylene were observed, even for reactor powders whose synthesis temperatures were near the monoclinic-to-orthorhombic transition temperature. Variable-temperature CP/MAS NMR results show that gradual conversion from the monoclinic to the orthorhombic crystalline form occurs, with complete conversion observed at 80 °C. A great deal of the crystal–crystal transformation already takes place by 50 °C. ^{13}C T_1 data on two of the materials indicate substantial differences in the interfacial regions compared to samples recrystallized from solution or the melt. In addition, the relative amounts of crystalline and noncrystalline material present are readily determined from quantitative HPD/MAS NMR spectroscopy.

Overall, these results substantiate the value solid-state NMR spectroscopy has for analyzing such materials. The method is nondestructive, involves well-defined and well-resolved peaks, and is more quantitative than X-ray diffraction, which is very dependent on the size and perfection of the crystals or crystallites and cannot easily see domains smaller than ca. 50 Å. NMR spectroscopy gives a measure of composition and morphology involving molecular level conformations and packing, even for ordered domains that contain only a few chain segments and that may be only ca. 30 Å wide. Finally, the effects of interface morphology are reflected in the crystalline T_1 values.

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