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Crystallization Conditions

Influence of Crystallization Conditions on the Location of Side-Chain Branches in Ethylene Copolymers as Studied by High-Resolution Solid-State ^{13}C N.M.R.

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ABSTRACT

High-resolution solid-state ^{13}C N.M.R. experiments have been carried out on a series of Ziegler-Natta ethylene copolymers containing a small amount of side chain branches. Selective observations of the amorphous and crystalline phases of these compounds have shown that a small quantity of methyl branches can be accomodated in the crystalline zones, in a way which is independent of the thermal history of the sample. On the contrary, branches longer than methyl appear to be mainly located in the amorphous and interfacial areas and the composition of each phase depends on the thermal treatment undergone by the sample.

In polyethylenes and ethylene copolymers, the accomodation of some side groups in the crystalline phase of the material has been investigated by several techniques. From the analysis of the melting temperature/composition relations in ethylene-type copolymers from diazoalkenes containing varying amounts of either methyl or n-propyl side groups arranged in random sequence distribution, it has been concluded (RICHARDSON et al., 1963) that while small quantities of the methyl side groups are incorporated into the crystalline phase at equilibrium, the larger side groups are excluded. These conclusions appear to be disputed by wide-angle X-ray diffraction studies of ethylene copolymers. The unit cell dimensions are known to expand and distort as the concentrations of either methyl, ethyl, n-propyl or n-butyl side groups are increased (WALTER and REDING 1956, EICHORN 1958, COLE and HOLMES 1960, SWANN 1962, BAKER and MANDELKERN 1966). However these unit cell variations do not necessarily demonstrate the incorporation of the branches into the lattice, as the unit cell dimensions may be affected by the crystallite size (RICHARDSON et al., 1963). They can also be affected by the details of folds, fold surface and the interior defect in crystals (DAVIS et al., 1968). Moreover the results appear generally dependent on the crystallization conditons. A detailed study (BAKER and MANDELKERN, 1966) has shown that in the methyl copolymers, a proportion of the side groups enters the lattice as an equilibrium condition, while, in the n-propyl copolymer containing small concentrations of side groups, the lattice spacings are close to those of the homopolymer. These conclusions can be compared with the interpretation of crystalline lattice dimension data reported by SHIRAYAMA et al. (1972): Branches smaller than C3 would be accomodated in the lattice, whereas branches larger than C4 would be excluded from the lattice, enter the amorphous domain and produce smaller

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crystals. Using a different approach combining nitric acid degradation and ^{13}C N.M.R. in solution, it has later been found (CUTLER et al., 1977) that the ethyl and butyl groups are mainly excluded from the crystalline zones.

A new insight to this problem can be provided by the recent developments of high-resolution solid-state ^{13}C N.M.R. Polyethylene has already been the subject of a number of N.M.R. studies and it was shown that several of its N.M.R. parameters such as ^{13}C chemical shifts (EARL and VANDERHART 1979, FYFE et al. 1979, VANDERHART 1979, DECHTER et al. 1981, SCHROTER and POSERN 1981, KITAMARU et al. 1982), ^{13}C spin-lattice relaxation times T1 (^{13}C) (VANDERHART 1979, HEMPEL and SCHNEIDER 1981, AXELSON 1982, AXELSON et al. 1983) and proton spin-lattice relaxation times in the rotating frame $T_{1\rho}$ (^{1}H) (MCBRIERTY,1979) depend on the nature of the environment. Therefore this technique appears well suited to investigate the problem of the accomodation of the branches in a series of ethylene copolymers with side groups of increasing lengths, as a function of both the nature of the comonomer and the thermal history of the sample.

Experimental Section

^{13}C N.M.R. experiments were performed at 75.47 MHz on a Bruker CXP 300 spectrometer, using high power proton decoupling (H_1=51kHz) and rapid magic angle rotation (3.5 KHz-4.0 KHz spinning speeds) in boron nitrure rotors.

Two basic pulse programs were employed to investigate the molecular packing of the semi-crystalline polyethylene copolymers. The delayed contact pulse sequence is a variation of the normal cross-polarization pulse sequence, in which the contact between the proton spin-locked state and the carbon reservoir under the Hartmann-Hahn condition is established after a pre-contact delay (AUJLA et al. 1982). Cross-polarization durations were 1 ms. During the pre-contact delay, spin-locking is maintained in the proton channel, so that domains of low $T_{1\rho}$ (^{1}H) loose ^{1}H magnetization preferentially and are thus discriminated against. In these experiments, spin-temperature inversion techniques were used to minimise base line noise and roll (STEJSKAL and SCHAEFER, 1975). Flip-back (TEGENFELDT et al., 1979) was also systematically employed to shorten the delay time between two successive pulse sequences.

The latter sequence is the single pulse excitation sequence (EARL and VANDERHART 1979, FYFE et al. 1979, AUJLA et al. 1982). The carbon magnetization is excited by a 90° pulse and is observed in the presence of a strong dipolar proton decoupling. This experiment detects only the ^{13}C spins for which T_1 (^{13}C) is much shorter than the period of time t_{rep} between two successive exciting pulses. Therefore a low value for t_{rep} discriminates against regions of the samples with long T_1 (^{13}C) which correspond to the crystalline domains in the samples under study (HEMPEL and SCHNEIDER 1981, AXELSON et al. 1983). Here t_{rep} was taken as 3s.

No digital broadening was applied prior to Fourier transformation of the free induction decay.

Four random Ziegler-Natta ethylene copolymers: ethylene-propene, ethylene-butene, ethylene-hexene and ethylene-octene copolymers, containing only a small amount of the ethylene comonomer were chosen for this study (Table I). Each sample was subjected to two different thermal histories, one being quench cooled in a solid carbon dioxide methanol mixture, and the other slowly cooled at 5K/hour from the melt to room temperature.

comonomer	side group* (/1000C)	crystallinity** (%) quenched	slowly cooled
propene	52	30	34
butene	19	34	41
hexene	10	40	48
octene	12	37	42

* as determined by I.R. spectroscopy .
** as determined by X-Ray Diffraction.

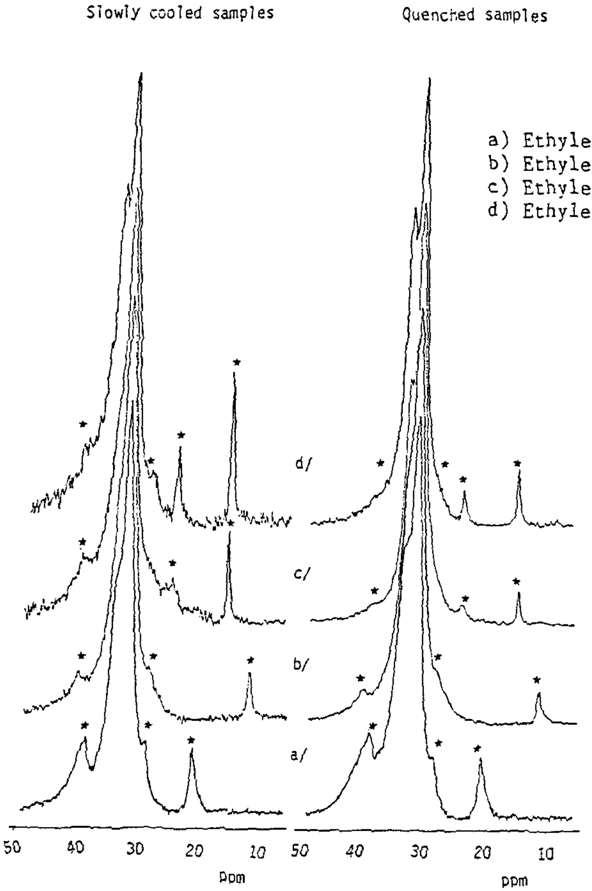
TABLE I. Side group content and crystallinity of the ethylene copolymers.

Results and discussion

The ^{13}C MAS N.M.R. spectra of the quenched and slowly cooled ethylene copolymers samples taken at 30°C with the single pulse excitation sequence and the delayed contact pulse sequence are displayed in Fig. 1 and 2 respectively. For all the samples under study, each spectrum obtained with the single pulse excitation sequence and a repetition time t_{rep} of 3s (Fig.1) contains a main line, corresponding to the main chain polyethylene carbons, centered at about 31 ppm, and a downfield shoulder or even a second peak at about 33 ppm. However, in the spectra obtained with the delayed contact pulse sequence and a pre-contact delay time of 10ms (Fig.2), the ^{13}C N.M.R. resonance line of the main chain polyethylene carbons appears as a sharp peak at about 33 ppm. According to the work of EARL and VANDERHART (1979), the upfield peak is assigned to the noncrystalline component in polyethylene. Its ^{13}C spin-lattice relaxation time is very short as compared to the ^{13}C spin-lattice relaxation time of the polyethylene carbons located in the crystalline parts of the material. Therefore the amorphous phase of the copolymer is observed in the single pulse excitation sequence with a short repetition time, while the crystalline areas are mostly discriminated against. In the delayed contact pulse sequence, the non-crystalline carbons which have a short proton spin-lattice relaxation time in the rotating frame are discriminated against while the crystalline ones are observed leading to a downfield peak at 33ppm, in agreement with reported data (EARL and VANDERHART, 1979).

1. Ethylene-propene copolymer.

The lines due to the presence of the propene comonomer (noted as *) are weak but clearly visible in the single pulse excitation spectra. Moreover the intensities of these peaks relative to that of the main chain CH_2 peak are almost identical in both the quenched and slowly cooled samples. Therefore the slow cooling process does not modify the



a) Ethylene-propene copolymer
b) Ethylene-butene copolymer
c) Ethylene-hexene copolymer
d) Ethylene-octene copolymer

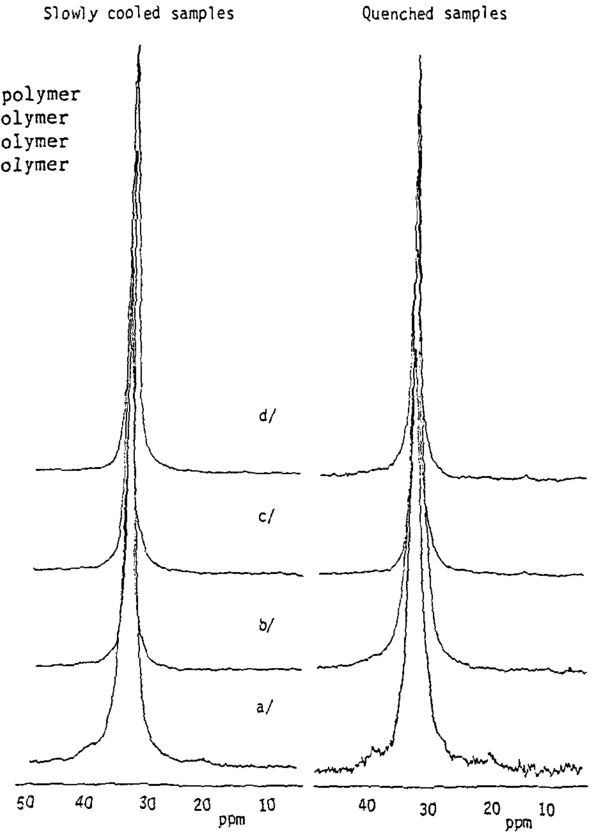


Figure 1 ^{13}C MAS N.M.R. spectra of quenched and slowly *cooled samples of ethylene copolymers taken at 30°C with the single* pulse excitation sequence (Repetition time:3s).

Figure 2 ^{13}C MAS N.M.R. spectra of quenched and slowly cooled samples of ethylene copolymers taken at 30°C with the delayed contact pulse sequence (Pre-contact delay time:10ms).

relative side group composition of the fast relaxing ($T1(^{13}C)$) amorphous regions, although it increases the crystallinity of the sample (Table 1). In the same way, the comonomer ^{13}C lines can be observed in the spectra taken with the delayed contact pulse sequence (Fig.2) and their relative intensities with respect to the polyethylene main peak do not depend on the thermal treatment (quenching or slow cooling) undergone by the sample. These last results lead to the conclusion that a small number of methyl branches can be accomodated in the crystalline zones of the material independently of the thermal history of the copolymer, even if the treatment increases the crystallinity.

2. Ethylene copolymers with longer branches.

In the ethylene-butene, ethylene-hexene and ethylene-octene copolymers, the relative intensities of the resonance lines due to the presence of the comonomer are larger in the slowly cooled samples than in the quenched ones in the spectra taken with the single pulse excitation sequence (Fig.1). For these copolymers, the slow cooling process not only increases the crystallinity content of the material, but also modifies the composition of each phase. The branches can hardly be incorporated in the organized regions and are preferentially located in the amorphous phase. This result is corroborated by the fact that the lines due to the presence of the comonomer can hardly be observed within the limits of instrumental sensitivity using the delayed contact pulse sequence (Fig.2), which points out that the amount of branches accomodated in the crystalline regions of these copolymers is very low. Moerover, in the single pulse sequence spectra (Fig.1), the longer the branch, the larger the intensity differences between the spectra of the quenched and slowly cooled samples. As the branches have been shown not to enter significantly the crystalline areas, this last result indicates that the slow cooling process also affects the relative proportion of branches contained in the intermediate regions which are not observed by using the two pulse programs. $T_1(^{13}C)$ and $T_{1\rho}(^1H)$ determinations are now in progress in our laboratory to refine this set of conclusions which are in fairly good agreement with observations drawn by RICHARDSON et al. (1963), BAKER and MANDELKERN (1966) and CUTLER et al(1977). Indeed the study of ^{13}C N.M.R. spectra has pointed out the existence of small quantities of methyl groups incorporated into the crystalline phase and has shown that the relative branch level contained in both amorphous and crystalline phases is independent of the crystallization conditions. In the same way the lattice spacings in a given methyl copolymer were found independent of the crystallization conditions (BAKER and MANDELKERN, 1966). On the contrary in the ethylene copolymers containing a small amount of branches longer than methyl branches, the branches in the crystalline phase can hardly be detected within the limits of experimental sensitivity. Branches can be located in the amorphous and interfacial regions, and the composition of each phase depends on the thermal treatment undergone by the sample.

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