

Discriminatory Experiments in High-Resolution ^{13}C NMR of Solid Polymers

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SUMMARY

Cross-polarization spectra of solid polymers can be misleading when the material exhibits proton spin-lattice relaxation in the rotating frame which cannot be represented by a single exponential. Quantitative and qualitative demonstrations of the problem are given. The use of two experimental procedures for alleviating the difficulties is suggested, and examples for polyalkenes and for polyethylene terephthalate are illustrated.

High-resolution ^{13}C NMR spectra are now being obtained routinely for a variety of solids, including polymers, using cross polarization (CP) from the proton spins, together with high-power decoupling and magic-angle rotation. However, it needs to be emphasized that because polymers are usually heterogeneous a single CP experiment will give, at best, inadequate information and may be very misleading.

The problems arise because the efficiency of the CP experiment depends heavily on the behaviour of the proton reservoir with respect to spin-lattice relaxation in the rotating frame. For a simple (homogeneous) system, such as a pure crystalline organic compound of low molecular weight, the characteristic decay time $T_{1\rho}({}^1\text{H})$ is likely to be single-exponential, but for heterogeneous materials, such as polymers, this is frequently not the case. For instance, we have shown¹ that in a radiofrequency magnetic field B_1 of 1mT the spin-locked proton magnetizations of annealed and quenched isotactic polypropylene film in which the crystalline regions are in the α form exhibit a three-component decay, with values of $T_{1\rho}({}^1\text{H})$ as follows:-

annealed: 108ms (48%); 15ms (25%); 0.83ms (27%)

quenched: 31.7ms (44.5%); 6.4ms (23%); 0.67ms (32.5%)

It should be emphasised that these relative intensities are not simple measures of the concentrations of different domains in the sample because of the phenomenon of spin diffusion. The values of $T_{1\rho}({}^1\text{H})$ cover more than two orders of magnitude, and it is clear that cross-polarization with contact times of the order of 5ms will produce spectra largely characteristic of domains with the intermediate and long values of $T_{1\rho}({}^1\text{H})$ only.

In order to confirm the implications of the $T_{1\rho}(^1\text{H})$ data with regard to the accessibility of ^{13}C cross-polarization spectra, we have attempted quantification of the ^{13}C intensities for the two samples of polypropylene film. Hexamethylbenzene was chosen as the standard sample for comparison, and 41.8mg was packed into a standard 5mm o.d. rotor as described in reference 2. Spectra were obtained with 5ms contact time and 1s recycle time, and it is assumed that full cross-polarization is

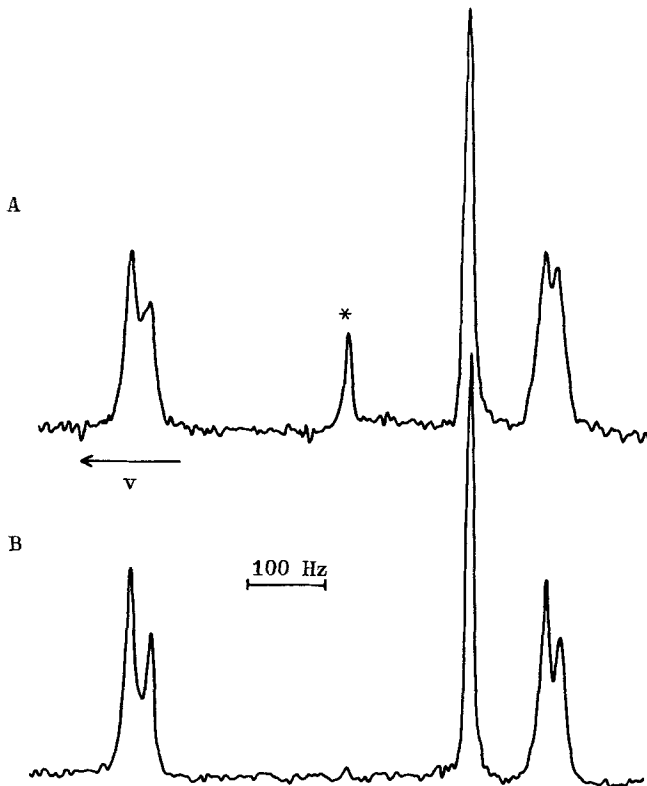


Fig. 1 Carbon-13 CP spectra of two propylene/ethylene copolymers containing ca. 10% of end-block material. A. End-block consisting almost entirely of ethylene units. B. End-block containing ca. 40% of ethylene units. Conditions: Recycle time 1.5s; contact time 1ms (A) and 5ms (B); number of transients 4000 (A) and 1000 (B); decoupler power 60 kHz; spectrometer frequency 22.63 MHz. The peak marked with an asterisk may be assigned to "crystalline" polyethylene chains

obtained (the proton relaxation parameters are $T_1 \approx 85\text{ms}$ $T_{1\rho} \approx 63\text{ms}$). The experiment was repeated with the samples of annealed and quenched polypropylene film, using a contact of 5ms and a recycle time of 3s. For the polypropylene samples the proton T_1 is single-exponential and of the order of 700ms (annealed 658ms; quenched 703ms). The observed intensities were corrected for loss from the components with intermediate and long $T_{1\rho}$ (^1H) and compared to the result for the standard hexamethylbenzene. The results of these carbon-spin counting experiments show that 81% of the carbon in the annealed sample is being detected and 71% for the quenched sample, compared to the values 73% and 68%, respectively, to be expected on the basis of the proton $T_{1\rho}$ values. We believe these data to be sufficiently in agreement, considering the uncertainties in both sets of data and in multi-exponential analysis.

The difficulties of interpretation presented by cross-polarization spectra are illustrated in Fig. 1, which shows spectra for samples of propylene/ethylene copolymers. A naive deduction from the spectra would be that the sample giving Fig. 1A contains a detectable amount of ethylene whereas that of Fig. 1B does not. In fact the proportions of ethylene are ca. 10% and ca. 4% respectively. In both cases there are long sequences of isotactic polypropylene, and the ethylene is present in ca. 10% of end-block material. In the sample of Fig. 1A the majority of the end-block is ethylene, allowing long runs of crystallisable polymer, whereas for the sample of Fig. 1B the ethylene, together with very short polypropylene sequences, forms an end-block which is in a rubbery state. The apparent absence of ethylene signal for Fig. 1B is therefore due to (i) relatively inefficient cross-polarization for the mobile end-block material, (ii) relatively short $T_{1\rho}$ (^1H) for the end-block and (iii) the increased contact time (5ms) for Fig. 1B as compared to that (1ms) for Fig. 1A.

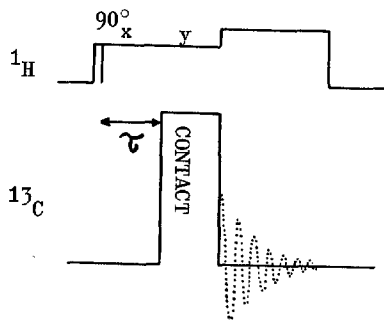


Fig. 2 The delayed contact pulse sequence

Such results demonstrate the desirability of using techniques other than the straightforward cross-polarization procedure. We present here examples of results from two such procedures. The first is the use of delayed contact, for which the appropriate pulse sequence is shown in Fig. 2. During the pre-contact delay, γ , spin-locking is maintained in the ^1H channel so that domains of low $T_{1\rho}$ (^1H) lose ^1H magnetization preferentially, and are thus discriminated against. A similar result would be obtained by a long contact procedure i.e. incorporating the delay γ into the contact time. When the delayed contact experiment was attempted (with ,

$\tau = 25$ ms) for the α -crystalline form of annealed polypropylene no qualitative change was observed in the appearance of the ^{13}C spectrum. This strongly suggests that the spectra corresponding to the intermediate and long $T_{1\rho}$ (^1H) components are indistinguishable, and implies that they arise from environments that are similar in character.

Figure 3 shows the results of a delayed contact experiment on a sample of ICI 'Melinex' polyethylene terephthalate film. This film is estimated by X-ray diffraction to be ca. 35% crystalline. The proton $T_{1\rho}$ behaviour of this sample was found to be a superposition of two exponential processes with the time constants and proportions:

$$T_{1\rho}^A = 23\text{ms}, p^A = 35\%; T_{1\rho}^B = 4.5\text{ms}, p^B = 65\%.$$

Proton spin-lattice relaxation is single-exponential, with $T_1 = 1.68\text{s}$.

The ^{13}C spectrum resulting from a normal CP sequence (Fig. 3A) shows evidence of high-frequency shoulders on both the carbonyl and the methylene peaks, which disappear when there is a delay of 12ms before contact (Fig. 3B). Moreover Fig. 3B shows better resolution between the peaks due to the quaternary and protonated aromatic carbons. The changes are undoubtedly due to loss of the spectrum of the domains with the shorter $T_{1\rho}$ (^1H) and, to our knowledge, constitute the first reported useful application of the delayed contact procedure. It is likely that these domains correspond to amorphous regions of the sample. A CP spectrum of a fully amorphous sample is shown in Fig. 3C. This amorphous sample was prepared by melt casting a film on to a cold (ca. 15°C) surface to produce a rapid quench into the solid state. The proton relaxation parameters are: $T_1 = 1.08\text{s}$; $T_{1\rho} = 4.4\text{ms}$ (76%) and $880\mu\text{s}$ (24%). The longer value of $T_{1\rho}$ is very similar to the shorter of the two values for the partially crystalline material. The resonance lines of Fig. 3C are all broader than those of Fig. 3B, and the maxima for the peaks from the carbonyl and methylene fall at the positions of the shoulders shown in Fig. 3A, thus confirming the source of the difference between Fig. 3A and Fig. 3B.

The second discriminating technique we wish to discuss here is one which we refer to as single pulse excitation (SPE). In this procedure the carbon signal is excited by a short pulse (flip-angle $\leq 90^\circ$) and is observed in the presence of the usual strong, dipolar proton-decoupling. The experiment relies on direct polarisation of the ^{13}C spins in the B_0 field via their spin-lattice relaxation processes and detects only those ^{13}C spins for which $T_1^{13}\text{C} \leq T_p$ where T_p is the period of time between repetitions of the exciting pulse. If T_p is long enough then all ^{13}C spins will be observed. The procedure is analogous to that normally used for high-resolution ^{13}C NMR of solutions except for the requirement of higher-power proton decoupling. The utility of the SPE experiment has been illustrated by Fyfe et al.³ and by Earl and VanderHart⁴, Fig. 4 reproduces a spectrum resulting from our own work^{5,6} and described in a review lecture, subsequently published⁵. It shows a SPE spectrum for a commercially available rubbery copolymer of ethylene and propylene ('Nordel' 1500, du Pont) which yields very little in the way of a CP spectrum. Proton spin-lattice relaxation in the rotating frame is double-exponential, with $T_{1\rho}^A = 5.2\text{ms}$, $p^A = 70\%$; $T_{1\rho}^B = 1.4\text{ms}$, $p^B = 30\%$, whereas in the laboratory frame relaxation is single-exponential, with $T_1 = 108\text{ms}$. The principal ^{13}C peak shown by 'Nordel' 1500 (Fig. 4) is due to methylene carbons in relatively long chains - the ratio of ethylene to propylene monomer units in the sample is 7:1. The assignments of the other peaks⁷ are shown on Fig. 4. The

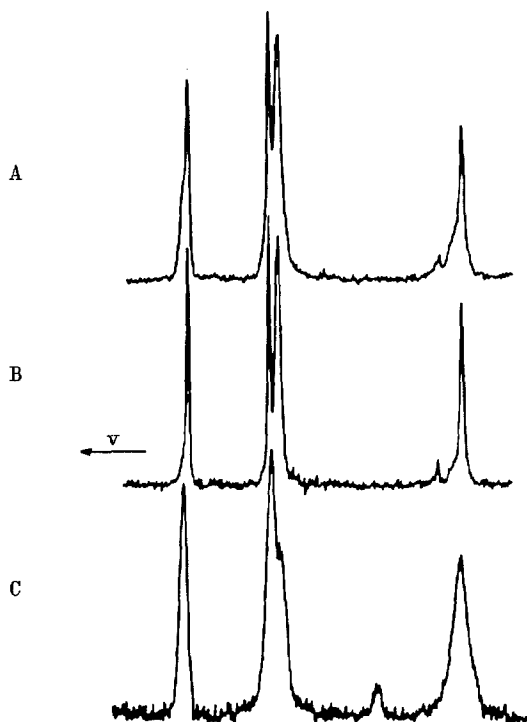


Fig. 3 Carbon-13 spectra (at 22.63 MHz) of polyethylene terephthalate film:-

- A. Sample of ca. 35% crystallinity with normal CP conditions (5000 transients).
- B. Sample as in A, using CP with a pre-contact delay of 12ms. (18000 transients).
- C. Normal CP spectrum of an entirely amorphous sample (4000 transients).

All three spectra were obtained using a contact time of 1ms and a recycle time of 2s

superimposed single peak is from a sample of highly crystalline polyethylene and shows a shift from the peak due to methylene units in the copolymer of 2.4ppm to high frequency, in agreement with observations of Fyfe et al³ and Earl and VanderHart⁴ on crystalline and amorphous regions of pure polyethylene. It should be emphasized that control of T_p for a SPE experiment is crucial in discriminatory experiments. A low value for T_p will discriminate against regions of the sample with long $T_1(^{13}\text{C})$ which are usually the more rigid (crystalline) domains. This provides a markedly different type of discrimination from that mediated by $T_{1\rho}(^1\text{H})$ in a CP experiment.

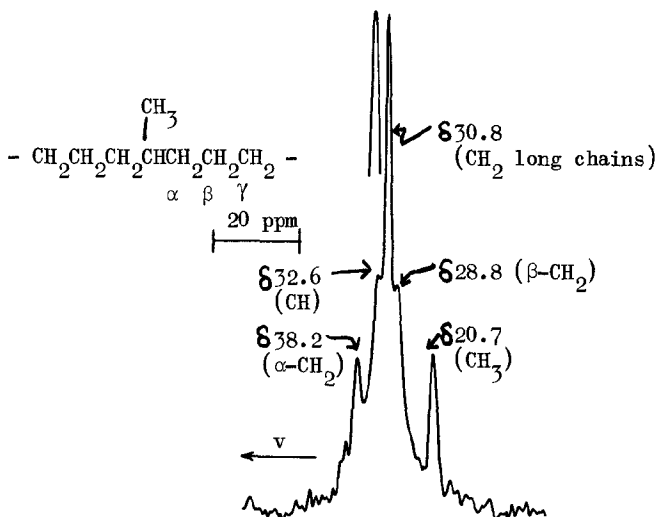


Fig. 4 Carbon-13 SPE spectrum (at 22.63 MHz) of a rubbery ethylene-propylene copolymer obtained with 15000 transients (90° pulses; recycle time 300ms). The superimposed peak is from the crystalline region of polyethylene, obtained by CP (2000 transients; contact time 1ms; recycle time 1s)

The experimental arrangements for the work reported here are described in earlier papers,^{1,2,3,6} as is the provenance of the polypropylene samples. All spectra were obtained using high-power (60 kHz) decoupling and magic-angle rotation.

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