^{13}C and ^{1}H n.m.r. studies of solid polyolefines

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The basis of ^{1}H and ^{13}C high-resolution n.m.r. investigations of solid polymers is outlined. The ^{13}C n.m.r. spectra of solid syndiotactic and isotactic polypropene (polypropylene) are discussed and their interpretation in terms of conformation and chain-packing effects are reviewed. The effects of decreasing temperature on the ^{13}C high-resolution spectrum of an annealed sample of isotactic polypropene is described and interpreted in terms of the crystal structure. The question of the proportion of the sample giving rise to ^{13}C signals is addressed and some results reported. The main cause for observing only part of the total sample is shown to be the ^{1}H rotating frame spin-lattice relaxation behaviour. The ^{1}H spin-lattice relaxation and spectral characteristics of a number of polyolefine samples are summarized and the role of spin-diffusion discussed. The heterogeneity revealed by the multicomponent $T_{1\rho}{}^{\theta}$ behaviour has been modelled numerically using a computer and the conclusions are outlined. The recovery behaviour of polybut-1-ene, following conversion to a *meta*-stable form by heating, is observed using both cross-polarization and single-pulse excitation techniques. In addition, an example of the investigation of a propene/ethylene copolymer by both ^{13}C and ^{1}H methods is described to illustrate the interdependence of the techniques.

(Keywords: polyolefins; ^{13}C and ^{1}H nuclear magnetic resonance; relaxation; solids; cross-polarization; morphology)

INTRODUCTION

N.m.r. studies of solid polymers have a long history and a considerable volume of literature. In the main, until about a decade ago, these investigations relied on the use of ^{1}H broad-line spectra and associated measurements of spectral moments and spin-lattice relaxation behaviour. More recently, other nuclei have become important, largely because of advances in technology and developments in n.m.r. techniques. In particular the use of ^{2}H and ^{13}C has become widespread. In this paper we describe some work carried out in our laboratory which involves investigations of solid polyolefines. It is presented as illustrative of some of the possibilities of both ^{13}C high-resolution n.m.r. spectroscopy and ^{1}H broad-line investigations. No attempt is made at a review of other work in the literature and the interested reader is referred to articles elsewhere for such reviews[1-4].

EXPERIMENTAL

Samples

Polyethylene. Two samples of high-density PE will be mentioned. PEI is a single-crystal mat obtained by slow crystallization of an 0.1% w/w solution in xylene at 70°C followed by washing with methanol and drying under vacuum at ambient temperature. The second sample, PEII, is a melt-crystallized sample, annealed at 403 K for 30 min.

Polypropene. The isotactic polypropene (often referred to as polypropylene) used was a commercially available grade, manufactured by ICI plc, having a melt flow index of 20 and an isotactic content in excess of 97% as determined by proton n.m.r. in solution via the racemic diad concentration[5]. PPI was fabricated as a thin film and was annealed at 433 K for 60 min.

PPII was also a thin film obtained by rapid quenching from the melt to 273 K followed by brief heating to 373 K to remove any of the smectic form.

Polybut-1-ene. This was a commercially produced sample with an X-ray determined crystallinity of ~30%. PBI was used as obtained whilst PBII was made by heating a sample of PBI to just above the melting temperature (~380 K) followed by rapid cooling to room temperature.

A propene/ethylene copolymer. A block copolymer comprising 85% propene as a main block and an end block made with a 50–50 mixture of ethylene and propene. The polymer was examined as made (PECI) but was also subjected to extraction with boiling heptane giving two further samples, the heptane soluble (PECII) and insoluble (PECIII) fractions.

N.m.r. measurements

^{1}H n.m.r. measurements were made at two operating frequencies of 60 MHz and 200 MHz using two separate spectrometers. The measurements at 60 MHz were made with a conventional high-power pulse spectrometer operating with a low-resolution magnet. Provision was available for adjustment of the r.f. field amplitude which, for spin-locking measurements, was generally 40 or

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60 kHz ($=\gamma_{1H}B_1/2\pi$). Data acquisition was by means of a digital signal averager. Samples were contained in 10 mm o.d. flat-bottomed glass tubes with the temperature controlled by a conventional gas-flow system, settable to $+5°C$.

The 200 MHz ^1H measurements were made on a computer-controlled double-resonance spectrometer, utilizing the high-frequency channel. The spectrometer is based around an Oxford Instruments wide-bore 4.7T high-resolution magnet and is operated by a Nicolet 1180 computer system and peripherals. The two frequency channels each allow for four pulses of separately adjustable r.f. phase at up to 1 kW output power, the latter being under computer control. Each channel has a broadband quadrature receiver followed by a dual-channel, 4-pole Bessel-function filter of variable bandwidth. The ^1H spectra were recorded using a digital fast transient recorder operating at up to 20 MHz with 8-bit resolution. Normally a sweep width of 312.5 kHz was used (3.2 μs dwell). Samples were contained in 5 mm tubes placed in the horizontal solenoid coil of a Bruker Z 32HP probe. Generally, 90° pulse lengths of the order of 1 μs were employed with lower r.f. fields being used for long spin-locking pulses (40–60 kHz).

^{13}C high-resolution spectra were measured using dipolar-decoupling (60 kHz decoupling fields) and magic-angle sample rotation (MAR)[6]. The ^{13}C signal was either obtained via cross-polarization from protons[7,8] or by normal spin-lattice polarization. Some of the ^{13}C spectra were measured on the double-resonance system described above, (i.e. $v_0^{13}C = 50$ MHz) using Andrew-Beams style of rotors fabricated from Macor and Delrin (polyoxymethylene). The latter formed the rotor base and, if sufficiently far removed from the coil, gives little or no signal. Sample volumes were approximately 0.3 cm^3. The probe is a Bruker CPMAR probe.

Other ^{13}C spectra were obtained on a spectrometer operating at 90 MHz/22.63 MHz based on an electromagnet. The probe system is a new design based on the spinning system described elsewhere[9,10]. This system employed cylindrical sample containers made of glass or Macor of 8 mm o.d. Only the sample plus coil is in the magnet and the probe is remotely tuned and matched for both frequencies. Once the magic-angle is set it remains constant even on changing samples, unlike the Andrew-Beams system used in our Bruker probe where it is necessary to include some solid KBr in the sample and observe the ^{79}Br resonance to allow adjustment of the angle on each sample[11].

The remotely-tuned probe on the 90/22.63 MHz spectrometer allows for variation of the sample temperature whilst performing CPMAR experiments and some results are given later using this facility.

GENERAL CONSIDERATIONS

Most solid polymers are structurally heterogeneous and the semi-crystalline polyolefins are no exception to this. This heterogeneity reveals itself in ^1H n.m.r. studies of these materials in a number of ways. Spectra may comprise a number of superimposed lines of differing width and shape[12-15] and spin-lattice relaxation may be more complex than a simple single exponential process. These ^1H n.m.r. properties are usually dominated by the magnetic dipolar couplings between the protons which

produce spectral lineshapes and relaxation behaviour characteristic of the spatial distributions of the protons and their relative movements due to thermal motions. Thus at a given temperature, crystalline and disordered regions of a polymer will tend to give rise to broader and narrower resonances respectively whilst spin lattice relaxation (T_1 and $T_{1\rho}$), which depends on motional frequencies of the order of the proton precession frequency in B_0 (typically of order 10^7–10^8 Hz) and B_1 (typically 10^4–10^5 Hz) respectively for T_1 and $T_{1\rho}$, can vary over a considerable range of values. Generally, the rotating frame relaxation is much more efficient than the T_1 process in solids. All the above is complicated by the fact that the proton dipolar coupling produces a spatial transport of nuclear magnetization, called spin-diffusion, which couples together the relaxation behaviour of different regions. Thus, as is shown below, a single uniform T_1 behaviour may be observed when $T_{1\rho}^{\theta}$ and spectra indicate heterogeneity.

Apart from the intrinsic value of these effects in the study of solid polymers, which we shall give examples of below, they are important in the use of ^{13}C high-resolution n.m.r. since, often the work done with this nucleus involves utilization of the process referred to as cross-polarization (CP)[6-8]. This is a method for enhancing the sensitivity of detection of magnetically dilute nuclei, such as ^{13}C, when they are in the presence of abundant and strongly magnetic nuclei such as protons, which is usually the case for solid organic polymers. The technique relies on the fact that the ratio of the equilibrium nuclear magnetizations for the two spin species in the same sample is given by

$$R = (M_0^{1H}/M_0^{13C}) = (N_{1H}\gamma_{1H}^2/N_{13C}\gamma_{13C}^2)$$

where N_{1H} and N_{13C} are the numbers of spins and the γ's are their magnetogyric ratios, which for a typical organic solid is of the order of 2000. Since n.m.r. signal strength is proportional to magnetization there is clearly an advantage in generating the ^{13}C signal via the ^1H magnetization. To carry out this transfer of magnetization it is necessary to irradiate simultaneously both ^1H and ^{13}C nuclei with resonant r.f. magnetic fields, B_1^{1H} and B_1^{13C} respectively, whose amplitudes are matched[8] such that

$$\gamma_{1H}B_1^{1H} = \gamma_{13C}B_1^{13C}$$

This so-called Hartmann–Hahn matching condition ensures that the two spin systems may exchange magnetization efficiently via their mutual magnetic dipolar couplings. Typically, cross-relaxation times are of the order of a few hundred microseconds. To initiate the magnetization transfer the ^1H spin system is prepared in a suitable state, the most common being the so-called spin-locking of M_0^{1H} along B_1^{1H}. This involves rotating M_0^{1H} into the plane perpendicular to B_0 and then aligning B_1^{1H} with M_0^{1H}. This spin-locked state can be maintained for a time determined by the ^1H spin-lattice relaxation in the rotating frame characterized by one or more time constants, $T_{1\rho}$. The CP process is carried out by irradiating the ^{13}C spins with the properly matched amplitude of B_1^{13C} during the persistence of spin-locked ^1H magnetization. The maximum gain in signal of ^{13}C in this process is given by $(\gamma^{1H}/\gamma_{13C})$ which is close to four. Generally, a single CP contact of this type is carried out and then the ^{13}C transverse magnetization is
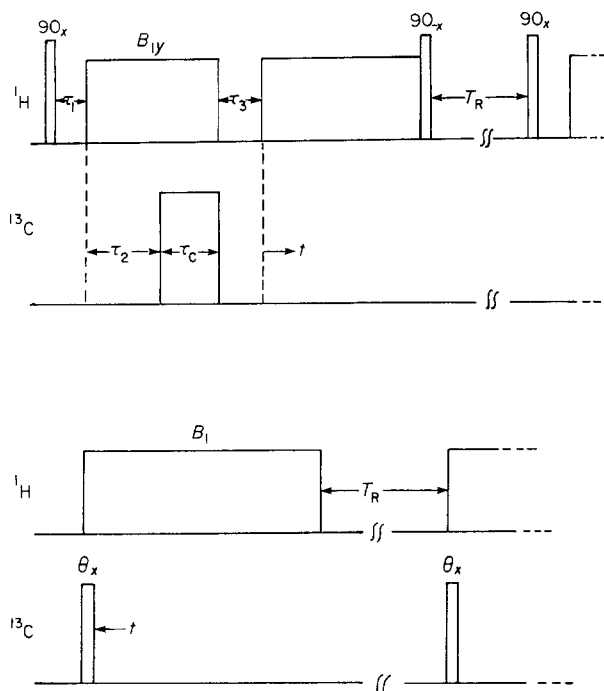
Figure 1 Typical pulse sequences used in obtaining ^{13}C n.m.r. spectra of solids. (a) A general double-resonance, cross-polarization sequence; (b) the single-pulse excitation sequence. The details of each sequence are discussed in the text

detected under conditions of high-power dipolar decoupling (i.e. strong irradiation of the ^{1}H spins at their resonance frequency to decouple them from the ^{13}C spins) and fast magic-angle rotation of the sample[6]. The combined techniques are usually referred to as CPMAR or CPMAS n.m.r. The use of CP to generate the ^{13}C signal is advantageous in terms of sensitivity both because of the factor of four gain in signal strength mentioned above and the fact that repetition of the process is now limited by the ^{1}H spin-lattice relaxation which is generally faster than that for the ^{13}C spins. In addition, for heterogenous materials such as polymers, in which there may be regions of differing mobility, the CP process tends to emphasize those ^{13}C spins in the more rigid regions.

An alternative approach is to rely on the natural ^{13}C magnetization to obtain the ^{13}C spectrum. This approach, which we have called single-pulse excitation (SPE) is the same as normal ^{1}H decoupled pulsed n.m.r. of ^{13}C in liquids with the difference that the decoupling field has to be much larger in order to remove the stronger dipolar couplings. The SPE experiment provides signals from those ^{13}C spins which have spin-lattice relaxation times comparable to or less than the recycle time of the pulse sequence. Thus, if the recycle time is made long enough, all the ^{13}C spins will be observed by this approach. In general ^{13}C, T_1's in rigid crystalline solids are very long and this method would be used to observe signals from more mobile regions, e.g. amorphous or non-crystalline regions in polymers. Two typical double-resonance pulse sequences used for ^{13}C high-resolution n.m.r. in solids are shown in *Figure 1*. The cross-polarization sequence (*Figure 1a*) has the following features. A 90°_x pulse is applied on the ^{1}H channel and the magnetization is spin-locked with a field B_{1y}. The delay τ_1 is usually zero but is indicated here to suggest the possibility of using T_2 as a means of selectively retaining only part of the proton magnetization for subsequent use.

A further delay, τ_2, allows discrimination or selection by means of differing ^{1}H T_{1_ρ} values before a contact pulse on the ^{13}C channel produces a ^{13}C signal by polarization transfer from the protons. It is clear that ^{13}C signal can only be derived from the proton magnetization remaining after both the T_2 and T_{1_ρ} effects in times τ_1 and τ_2 have acted. A further delay, τ_3, allows for discrimination based on ^{13}C–^{1}H dipolar coupling strengths[16]. Following CP the ^{13}C signal is recorded in the presence of the strong dipolar decoupling field. Following this, when $\tau_3 = 0$, a 90_{-x} pulse flips any remaining ^{1}H magnetization back along B_0.[17] The time T_R is a period during which the ^{1}H system undergoes spin-lattice relaxation following which the procedure is repeated, the ^{13}C signals being accumulated in the spectrometer computer. *Figure 1b* illustrates the alternative SPE experiment in which the ^{13}C signal is generated via its own spin-lattice processes. In this case the time T_R is crucial in determining which ^{13}C spins give signals. Only those for which $T_1(^{13}C) \lesssim T_R$ will be detected. As already indicated, these sequences are usually combined with magic angle sample rotation to yield 'liquid-like' spectra[6].

With these general comments in mind we now discuss a number of investigations of polyolefines using these techniques.

^{13}C SPECTRA OF POLYPROPENES

Effects of conformation

The ^{13}C spectrum of solid syndiotactic polypropene has been described elsewhere[18]. The interesting feature of this spectrum is a 1:1 splitting of the methylene carbon resonance of 8.7 ppm. This was interpreted in terms of the conformation of this molecule in the solid, which X-ray diffraction had suggested to be a 4*2/1 helix in which there are two distinct and equally probable sites for methylene groups: one on the helix axis, the other on either side of this axis. Consideration of shielding effects of γ-substituents suggest a shift difference of ~ 8 ppm between the two sites which is close to the observed value. In addition the higher frequency peak, assigned to the site on the outside of the chain, shows additional broadening/splitting consistent with interchain effects (see below).

Effects of crystal packing

The ^{13}C spectra of samples PPI and PPII have been presented elsewhere[19]. The essential features of the spectra of these isotactic polypropene samples are that PPI, the highly annealed material, shows splittings of the methyl and methylene resonances in approximately a 2:1 ratio, the more intense peak being to high-frequency in each case. Close examination of the methine resonance shows a shoulder in the same sense. The quenched sample does not show these splittings, of order of 0.5–1.0 ppm, and the spectra indicate a shift of resonance intensity in the PPII methylene and methyl regions to the frequencies characteristic of the lower intensity signals in these regions in PPI. The interpretation given to these observations was that the unit cell of α isotactic polypropene contains paired left and right-handed 3:1 helices and that this generates distinguishable sites for methyl, methine and methylene carbons in a 2:1 ratio by virtue of inter-chain interactions. The effect of quenching, on this basis, would seem to be an increase in resonance intensity at frequencies characteristic of the more open environment
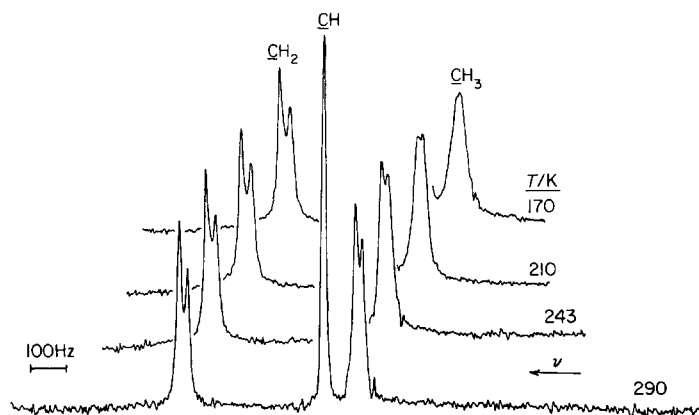
Figure 2 Variation with temperature of the ^{13}C high-resolution n.m.r. spectrum of annealed isotactic polypropene (PPI). Each spectrum is the result of 2000 FID's acquired with a 60 kHz decou0ling field, 5 ms contact time and 2 s recycle time. The spectrometer frequencies were 90 MHz for ^{1}H and 22.633 MHz for ^{13}C. For clarity the methane peak has been omitted except for the spectrum at 290 K

associated with interactions between chains in different pairs and hence the suggestion that quenching traps a significant fraction of the chains in a non-paired arrangement. X-ray diffraction still indicates the same basic structure so these effects are on a very local scale.

Effects of decreasing temperature

Lyerla *et al.* have reported that on decreasing the temperature of solid isotactic polypropene the ^{13}C n.m.r. signal from the methyl group broadens due to interference of the modulation of the ^{13}C–^{1}H dipolar coupling due to the thermal motion of the methyl group with that due to the strong proton decoupling[20]. *Figure 2* shows the temperature variation of the ^{13}C spectrum of the annealed sample, PPI, obtained using the VT probe system mentioned in the experimental section. The spectra show similar behaviour to that reported by Lyerla *et al.* but, owing to the resolution of different peaks in this sample, various other features are apparent. Firstly, the methylene signal shows little change over the range of temperatures covered, showing the maintenance of resolution with temperature variations. Indeed, the Hartmann–Hahn matching and the general electronic properties of the probe also remained unchanged. Secondly, it is clear that, as the temperature is lowered from 300 K, the larger of the two methyl resonances is the first to broaden. This can be taken as supporting the assignment of this splitting, given elsewhere[19] and mentioned above, to the existence of paired helices of opposite handedness. The methyls within the close-meshed pair of helices would be likely to experience more hindrance to their motion than those on the outside, this leading to the observed behaviour with temperature.

Quantitative considerations

Observations of the ^{13}C spectra of polybut-1-ene led us to determine the proportion of the total carbon in the polypropene samples that was being detected by the usual cross-polarization experiment. The probe system 90° pulse length was calibrated using adamantane and the efficiency of the cross-polarization process checked using hexamethylbenzene. The proportion of carbon was then determined by comparing known masses of PPI and II

with calibration samples of hexamethylbenzene. The results obtained indicated that for PPI and PPII approximately 80% and 70% respectively was being observed[21]. The reason for this is apparent when the ^{1}H relaxation properties are considered. For the CP process the ^{13}C signal produced depends on both the ^{1}H T_{1_ρ} behaviour and the ^{13}C–^{1}H cross-relaxation time[22]. If the former is short then it may not be possible to obtain thermal equilibrium between the two spin systems before the proton bath is significantly heated by the spin-lattice process (T_{1_ρ}). In the case of many polymer samples ^{1}H T_{1_ρ} behaviour is multiexponential in character and, for PPI and PPII has a short-time component which is of the order of 600–800 μs which, in turn, is associated with a narrow (long T_2) component in the ^{1}H spectrum. These two factors make it extremely unlikely that any significant cross-polarization arises from that part of the proton magnetization. This largely accounts for the deficit in the CP experiments mentioned above.

^{1}H RELAXATION AND SPECTRA

In this section we present a summary of results which have been described in detail elsewhere[23]. The proton spin-lattice relaxation in each of PPI, PEII, PPI, PPII and PBI at room temperature is described by a single characteristic relaxation time. The on-resonance rotating-frame spin-lattice relaxation ($T_{1_\rho}{}^{90}$), on the other hand, requires a minimum of three exponential processes for its description in each case. Of particular note is the fact that the long time behaviour of the $T_{1_\rho}{}^{90}$ process is strongly dependent on the physical history of the samples. Thus for PEI and PEII the long-time component relaxation times are 60 and 190 ms respectively, whilst for PPI and PPII they are 109 and 30 ms respectively.

Further measurements of the spin-lattice relaxation behaviour in the off-resonance rotating frame, with the magnetization spin-locked at the 'magic angle' of 54.7° with respect to the B_0 (Z) axis, showed that the relaxation became a lot slower, whilst remaining three-component.

A number of possible explanations are possible for this overall relaxation behaviour but the most likely is that the three relaxation components relate to three physically distinct regions in the polymers in which the protons have different n.m.r. properties. This heterogeneity of structure in semi-crystalline polymers is well-known[2,3] and the number of spectral components used to fit experimental data has varied. For example, Bergmann[13] and Smith *et al.*[15] have used three components to fit spectral lineshapes but Bergmann has more recently chosen to describe the data in terms of a crystalline component plus an amorphous component describable by a lineshape involving a distribution of correlation times[24]. Analysis of spectra in this way to yield information on crystallinities etc. is quite successful but subject to a degree of arbitrariness in choice of lineshape functions.

Spin-lattice relaxation, on the other hand, is subject to the complication of spin-diffusion[23]. This, as stated above, is a spatial transport of magnetization via homonuclear dipolar couplings and leads to a coupling of the spin-lattice relaxation of spatially separated regions. This can be invoked to explain why single T_1's are observed and multiple $T_{1_\rho}{}^{90}$s. In the first place, T_1, being dependent on fluctuations at ω_0 and $2\omega_0$ ($\omega_0 = \gamma B_0$) is often considerably longer than $T_{1_\rho}{}^{90}$, which depends on low-
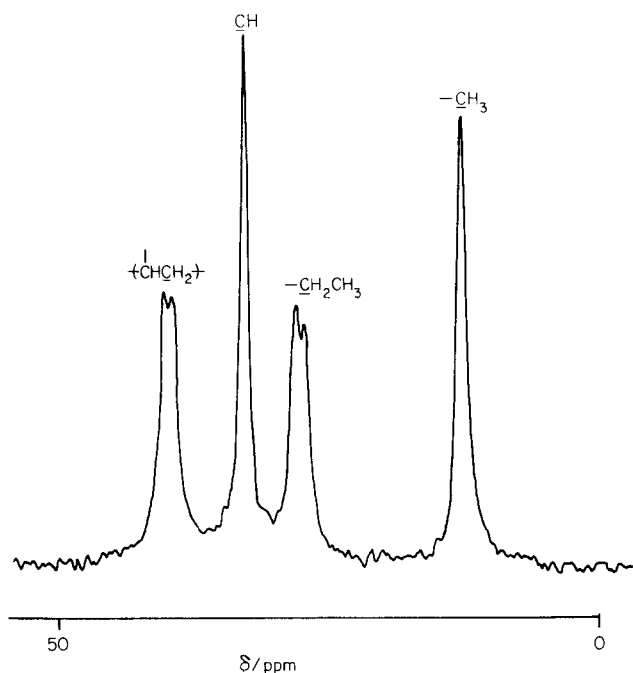
Figure 3 ¹³C high-resolution n.m.r. spectrum of solid polybut-1-ene (PBI) at 300 K. 2000 FID's were added and were obtained with a 60 kHz decoupling field strength, 1 ms contact and 1 s recycle time. The spectrometer frequencieswere as for *Figure 2*. The peak assignments are: δ=12.0 ppm, CH_3; δ=268 (doublet), CH_2 (sidechain); δ=31.3, CH; δ=38.3 (doublet), CH_2 (backbone)

frequency fluctuations, of order ω_1 ($=\gamma B_1$). In addition the spin-diffusion coefficient, D_s, is proportional to the secular dipolar interaction strength which, under on-resonance spin-locking is scaled by 0.5. Thus T_1 gives a longer timescale for a faster diffusion process to take effect.

The observations that $T_1{}_\rho{}^{54.7°}$ was on a considerably longer timescale than $T_1{}_\rho{}^{90}$ indicated that even for $T_1{}_\rho{}^{90}$, spin-diffusion is causing a partial mixing of the intrinsic relaxation properties. To illustrate this, as reported elsewhere[23], we have simulated the relaxation behaviour for a three region system allowing for spin-diffusion in one dimension. The equation governing this behaviour is

$$\dot{M}_\alpha(x) = D_s^q\{\partial^2 M_\alpha(x)/\partial x^2\} + R_j^q\{M_\alpha^{eq} - M_\alpha(x)\}$$

where α labels the magnetization component (e.g. z for T_1, etc.), q the region ($q=1$, 2 and 3) and j the relaxation process (l,l_ρ, etc.). $M_z^{eq} = M_0$ otherwise $M^{eq} = 0$. The spin-diffusion coefficients and relaxation rates are different in each region (hence the label q) but constant within each region (not a function of x). Numerical solutions of this equation using values for the sizes of crystalline lamellae etc. taken from other sources demonstrated that the observed behaviour of $T_1{}_\rho{}^{90}$ could be explained on the basis of the model. In particular, it demonstrated that the long-time $T_1{}_\rho{}^{90}$ components largely reflect the time for magnetization to diffuse out of the crystalline regions into the less ordered regions which, for these materials at the temperature used, act as relaxation sinks.

Other experiments involving partially relaxed proton spectra have been carried out, and, in particular, experiments using $T_1{}_\rho$ behaviour to spatially label the sample have been reported[23]. These involve, *inter alia*, a prepara-

tion period in which the system is allowed to relax ($T_1{}_\rho{}^{90}$) until only the long-time component remains. This magnetization is then placed along $B_0(z)$ to allow maximum spin-diffusion and the progress of this mixing is examined via the spectrum obtained with a 90° pulse. These experiments again confirm the overall behaviour and heterogeneity discussed above.
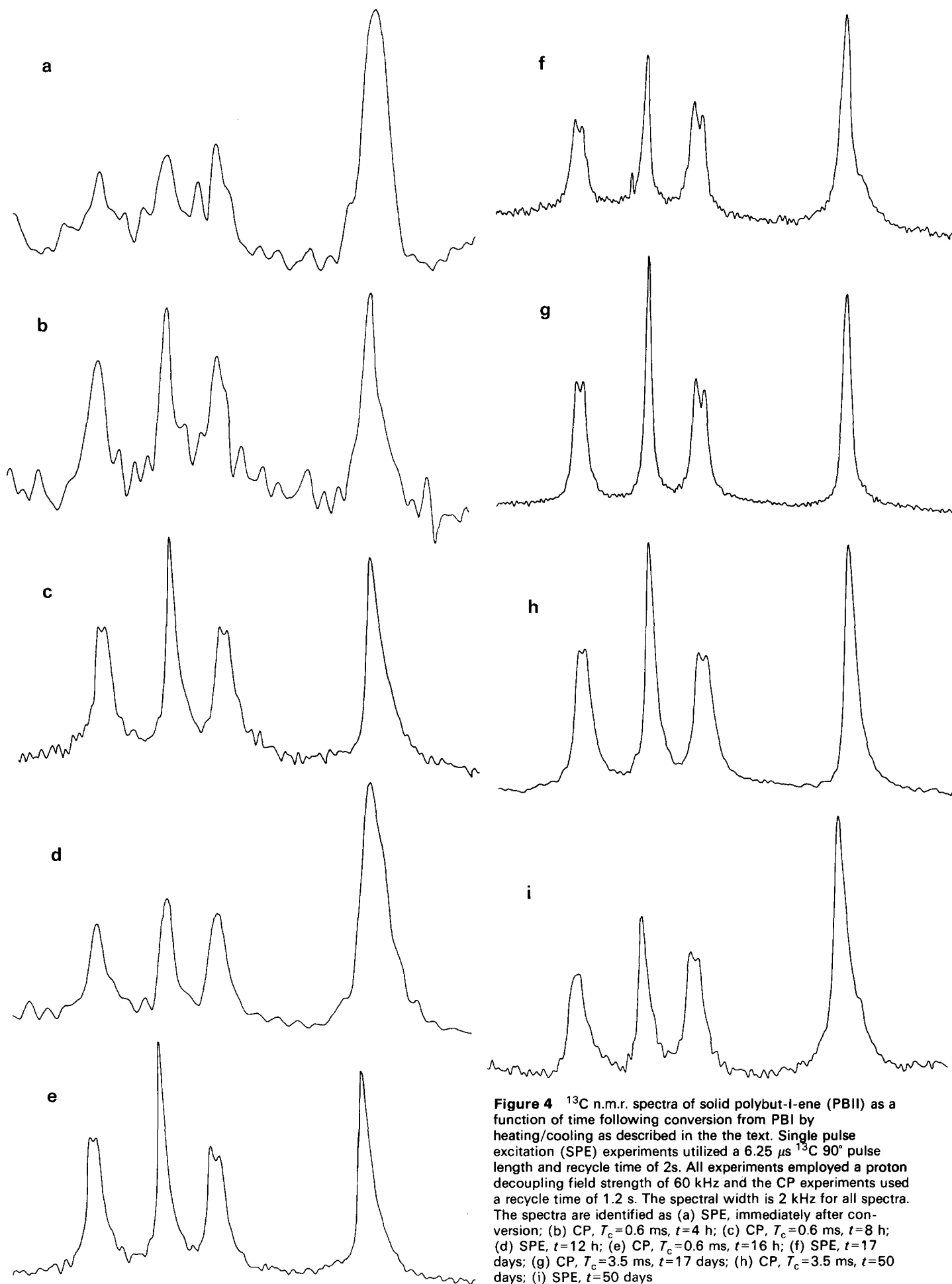
ISOTACTIC POLYBUT-1-ENE

The ¹³C spectrum of PBI obtained using CPMAR is shown in *Figure 3*. This spectrum shows splittings of the methylene resonances, probably arising from the details of the crystal structure as with the isotactic polypropene. The ¹H $T_1{}_\rho$ behaviour of this material[23] is again three component with the longest component being of the order of 243 ms and the short-time component ($T_1{}_\rho \sim 500 \mu s$) being a much larger proportion of the total signal than for the PE or PP samples. After heating to the melt and cooling, the sample was examined by both the CP and SPE experiments to record ¹³C spectra at various times after the transformation to the 11:3 helix structure which this treatment brings about. *Figure 4* illustrates the results. It should also be noted that the ¹H $T_1{}_\rho$ immediately after the transformation is close to being a single exponential with $T_1{}_\rho \sim 400 \mu s$. This fact clearly explains why the CP experiment fails to give a good spectrum immediately following the transformation (*Figure 4b*). On the other hand, the SPE experiment also fails to give a well-resolved spectrum (*Figure 4a*) and, since the ¹H, T_1 is ~ 250 ms the ¹³C T_1's are unlikely to be very long so this is perhaps unexpected. The likely explanation is that the chains are executing substantial motions which give rise to large linewidth contributions which probably arise from the interference of the decoupler frequency and the thermal motion in their effects on the ¹³C–¹H dipolar coupling described earlier.

As the recovery of the material towards the 3:1 helix forms proceeds (*Figure 4c→4i*) the CP and SPE experiments increasingly give improved quality spectra both in terms of signal-to-noise and resolution implying an increased rigidity and crystallinity. It is interesting to note that the best spectra are obtained after some two weeks of annealing but that the final spectra, taken after two months, seem to have lost resolution. This could be because the material which crystallizes first gives better quality crystals and that the eventual apparent decrease in resolution arises from the slower conversion and crystallization of less perfect chains which would contribute resonance intensity over a range of frequencies.

PROPENE–ETHYLENE CO-POLYMERS

We have undertaken studies of a number of propene–ethylene copolymers and the results of one such investigation are given here. The samples were as described in the experimental section. *Figure 5* shows the ¹H spectra (normal and partially $T_1{}_\rho{}^{90}$ relaxed) for PECII and III, the heptane soluble and insoluble fractions respectively. These show that PECIII behaves rather similarly to PPI and II as described elsewhere[23]. PECII, however, shows the presence of a very sharp spectrum with a small underlying broad component which is revealed in the partially relaxed spectrum. *Figure 6* illustrates the ¹³C spectra for all three samples under different conditions.
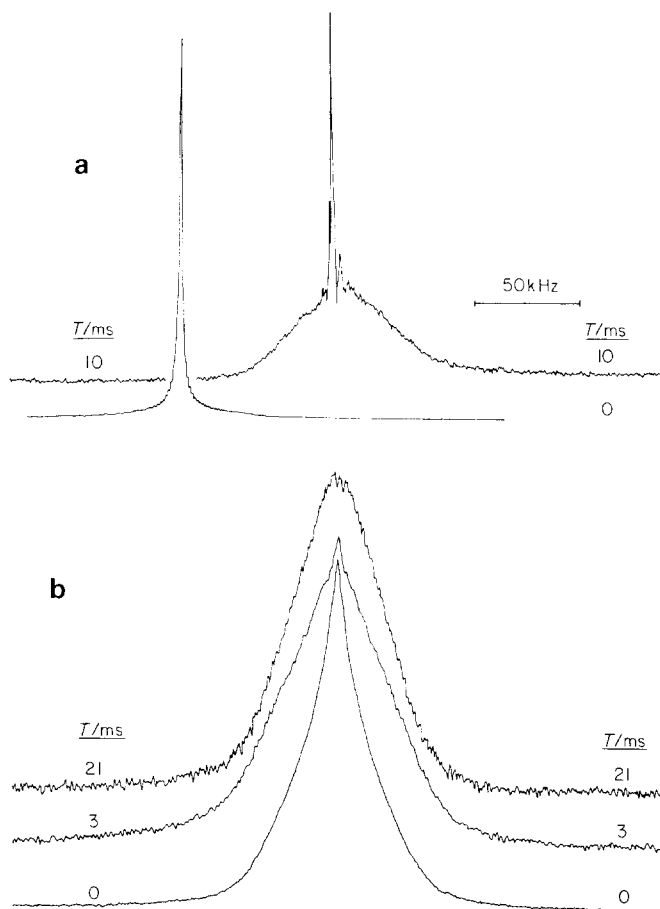
a

b

c

d

e

f

g

h

i

Figure 4 ^{13}C n.m.r. spectra of solid polybut-l-ene (PBII) as a function of time following conversion from PBI by heating/cooling as described in the the text. Single pulse excitation (SPE) experiments utilized a 6.25 μs ^{13}C 90° pulse length and recycle time of 2s. All experiments employed a proton decoupling field strength of 60 kHz and the CP experiments used a recycle time of 1.2 s. The spectral width is 2 kHz for all spectra. The spectra are identified as (a) SPE, immediately after conversion; (b) CP, T_c=0.6 ms, t=4 h; (c) CP, T_c=0.6 ms, t=8 h; (d) SPE, t=12 h; (e) CP, T_c=0.6 ms, t=16 h; (f) SPE, t=17 days; (g) CP, T_c=3.5 ms, t=17 days; (h) CP, T_c=3.5 ms, t=50 days; (i) SPE, t=50 days

Figure 5 [1]H n.m.r. spectra of (a) PECII and (b) PECIII, the heptane soluble and insoluble fractions of the propene/ethylene copolymer PECI. The spectra were recorded at $v_0{}^{1H} = 200$ MHz following spin-locking $\{(\omega_1/2\pi) = 40 \text{ kHz}\}$ for a time T as indicated. Typically, 400 FID's were accumulated with a recycle time of 3 s and a solid echo was used to measure the signal after the end of the spin-lock
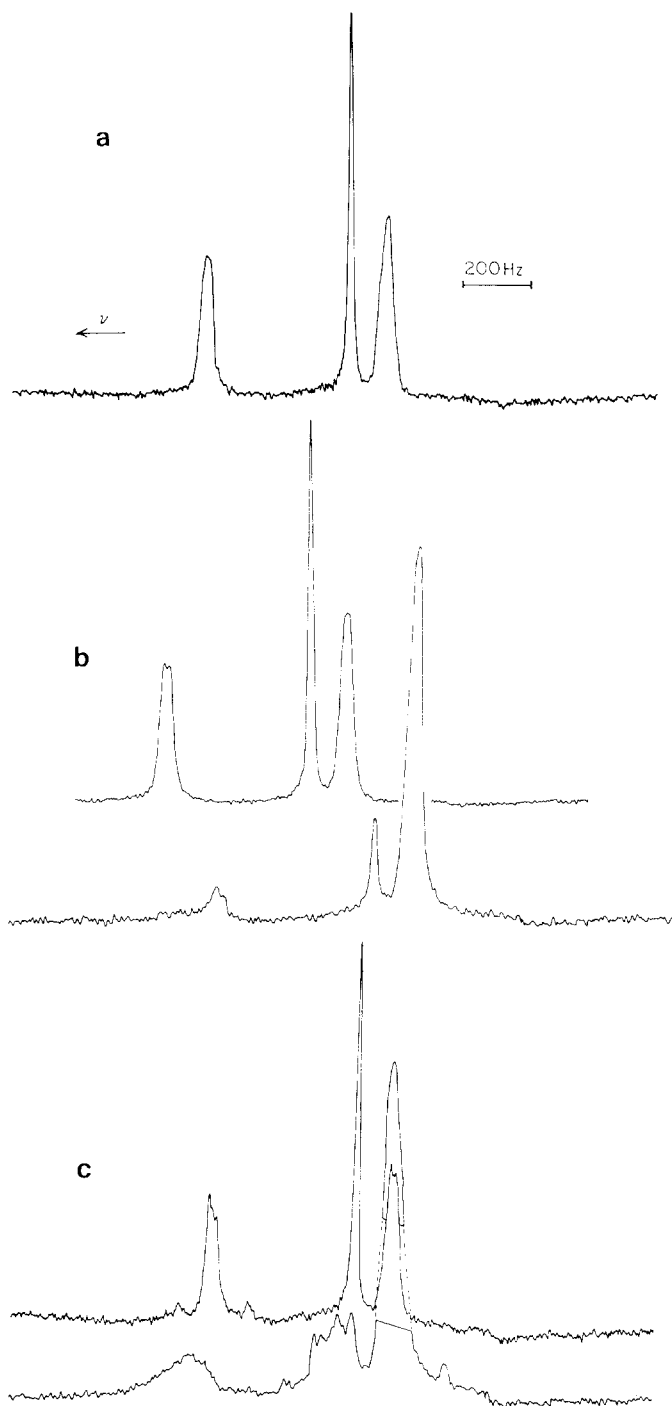
Figure 6a shows the standard CPMAR experiment for PECI. It is essentially the spectrum of isotactic polypropene[19] although the methylene and methyl peaks seem more symmetric. Use of the delayed contact experiment produces changes in this spectrum which are not presented here but which indicate a composite nature of the spectrum. *Figure 6(b)* shows the spectra obtained by means of the CPMAR and SPE experiments on PECIII, the heptane insolubles. These exhibit some distinctive features. The methylene resonance in the CP spectrum shows some signs of resolved splitting although the methyl still does not. The SPE experiment, with a recycle time of 1 s, gives a dominant, unsplit methyl resonance and smaller methine and methylenes. This arises because the methyl groups in the crystalline portions of the main polypropene block have sufficient motions to give [13]C T_1 values short enough to contribute significantly to the SPE experiment with this recycle time. The smaller methine and methylene signals are probably associated with more mobile fractions of the main polypropene block.

Figure 6c shows the CPMAR and SPE spectra for PECII, the heptane solubles. The CPMAR spectrum is essentially that of isotactic polypropene although there are no obvious resolved splittings and there may be additional resonances in the methylene region. The SPE spectrum with a recycle time of 1 s however shows quite a different pattern of lines. The relative intensities of the

Figure 6 (a) CPMAR ^{13}C high-resolution n.m.r. spectrum of PECI. 4000 FID's were accumulated using a contact time of 1 ms, a recycle time of 1 s and a 60 kHz decoupling field strength. (b) ^{13}C spectra of PECIII obtained using SPE (lower trace) and CP (upper trace). The recycle time for both experiments was 1 s with other conditions as for (a). (c) As for (b) except the sample is PECII, the heptane soluble fraction of PECI

lines are varied by changing the recycle period. For example the peak at the frequency corresponding to the methine resonance in isotactic polypropene is lost when the recycle time is reduced to 0.3 s. The detailed interpretation of these observations will be dealt with elsewhere.

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