Characterization of the rigid phases in ethene–propene copolymers by solid state n.m.r. spectroscopy

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The application of solid state n.m.r. techniques to the characterization of ethene–propene copolymers is described. This study illustrates how the mechanical properties of a copolymer can be related to the polymer chemistry by the use of selective n.m.r. experiments. In particular, evidence for a rigid copolymer phase was sought to help identify the nature of the copolymer–polypropene matrix interface. No evidence for a rigid copolymer phase was in fact found, suggesting amorphous polypropene forms the interface. On the other hand there was clear evidence for crystallizable runs of ethene with a domain size in excess of 30 Å or so.

(Keywords: n.m.r. spectroscopy; copolymer; ethene)

INTRODUCTION

Polypropene is a tough, rigid polymer suitable in a wide range of applications. A major limitation, however, is that it cannot be used in areas requiring impact resistance at temperatures close to or below 0°C because of the transition of the amorphous fraction from a fluid state to a glassy one with the associated embrittlement. This has led to the extensive development of copolymers of ethene and propene in order to improve the low temperature toughness without unduly compromising the stiffness of the polymer[1]. Both random and block copolymers can be made. When block copolymers are prepared in a sequential manner, taking a polypropene particle as a seed for a subsequent polymerization involving ethene, little true copolymer is likely to be present and the polymer will be essentially a propene/ethene diblock more akin to a polypropene and polyethene. More true copolymer is formed if the second stage uses a mixture of ethene and propene. Under these circumstances a distinct rubbery copolymer phase will be produced, with mainly long ethene runs because of the differential activity of the catalyst to ethene and propene. At what stage it is sensible to talk about a polyethene rather than a long ethene run in a copolymer is unclear but within the context of the results presented later this distinction is purely semantic. For all intents and purposes we can use the two terms synonymously. In both of the above instances, one being a limiting case of the other, there will be a variety of phases present such as crystalline, amorphous and interfacial which may be pure polypropene, pure polyethene or copolymer.

In such a complex material the relationship between the chemistry of a particular phase and its contribution to the mechanical properties can be lost. Historically this information has been obtained by combining microscopy, both optical and electron, with the analysis of extracts or staining methods to highlight regions of a particular chemistry. From a knowledge of the polymer chemistry the mechanical properties can be inferred. A complementary approach is to make use of high resolution solid state n.m.r. to determine the chemical composition and nuclear spin relaxation times to examine the mechanical properties through the polymer dynamics. To an extent the work outlined here is exemplary because for the most part there is already a good empirical understanding of the manner in which the copolymer phase improves the low temperature toughness, while the detailed polymer microstructure can be found by solution state n.m.r. of the extracted copolymer.

One question which solid state n.m.r. is perhaps uniquely able to answer is whether any rigid copolymer phase is present. This is particularly relevant to the nature of the interface between the rubbery copolymer phase and the polypropene matrix. In essence we can identify two types of interface, one where the copolymer is linked directly to the rigid crystalline region and the other where there is intermediate amorphous polypropene domain. Only in the former case would we expect to see a rigid copolymer component. Previous work on ethene–propene copolymers using solid state n.m.r. has been limited[2,3]. In one case a comparison was made between the intact copolymer and two fractions consisting of the heptane solubles and insolubles while in the other case the complications associated with obtaining truly representative n.m.r. spectra were illustrated with a block and random copolymer. In neither case was a detailed interpretation given.

N.m.r. is an excellent tool for studying the chemistry of polymers both in solution and in solids[4–6]. In particular ^{13}C n.m.r. in solution is well able to distinguish

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between the homopolymers and copolymer on the basis of the ^{13}C chemical shifts[7], while high resolution ^{13}C n.m.r. spectra can be obtained from solid polymers by using magic angle spinning (m.a.s.) and high power proton decoupling. Often cross-polarization is used to enhance the sensitivity of the experiment[8]. Although some resolution is lost on going from solution to the solid state, because of the distribution of chemical shifts seen in the solid polymer, the same distinction between homopolymers is still possible in a solid and of especial importance a key copolymer resonance is readily observed. This resonance at 37.5 ppm corresponds to the ^{13}C nucleus in an ethene unit α to a propene when the run of ethenes is at least two long. If we observe this resonance we can clearly say that copolymer is present.

Now we have seen that copolymer can be uniquely identified we need to consider the characteristics of a rigid phase in order to see how these can be used to obtain a ^{13}C n.m.r. spectrum which is selective for this phase. Two general methods can be used to collect a selective n.m.r. spectrum[6,9]: using either differences in the nuclear spin relaxation times or the heteronuclear C–H dipolar coupling. As noted earlier, discriminatory effects have been seen in ethene–propene copolymers but the emphasis was on the possibility this gives for a misleading interpretation rather than the active use of a selective experiment. In fact the most common technique used to enhance the sensitivity of ^{13}C n.m.r. spectroscopy in solids, cross-polarization[10], in principle combines these two methods whilst also allowing the indirect use of ^{1}H n.m.r. relaxation times. Thus the rate of transfer of magnetization from the hydrogen to the carbon depends on the heteronuclear C–H dipolar coupling while the decay of the magnetization depends on the proton spin–lattice relaxation time in the rotating frame, $T^{\mathrm{H}}_{1\rho}$.

Both of these factors tend to favour the cross-polarization of a rigid phase. Thus in a rigid phase the heteronuclear C–H dipolar coupling will be maximized, giving a short rise time constant, T_{CH}, in the build up of cross-polarized intensity, and then as the phase becomes more mobile so the dipolar coupling will be reduced by molecular motion leading to a longer T_{CH}. Furthermore, for most polymers $T_{1\rho}$ is found to be long for rigid phases such as highly cross-linked matrices and the crystalline region in semi-crystalline polymers[11]. Consequently the ^{1}H magnetization will not decay significantly before appreciable spin transfer has occurred. This means that cross-polarization can be used to select rigid phases. Note though that the degree of selectivity is usually poor unless the two phases have marked differences in molecular mobility, an extreme example being in the limit of a highly mobile phase where cross-polarization may be totally ineffective.

The selectivity based on $T^{\mathrm{H}}_{1\rho}$ can be enhanced by use of a delayed contact cross-polarization experiment, in which a longer time is allowed for relaxation of the protons to occur in the spin-lock radio frequency field[12]. At the other extreme, to select the mobile phase where the dipolar coupling is greatly reduced, we can make use of the interrupted decoupling experiment in combination with single pulse excitation rather than cross-polarization[13]. Single pulse excitation is now essential to prevent the bias towards the rigid material in the cross-polarization technique.

The least ambiguous proton relaxation time for use in selective ^{13}C n.m.r. experiments is the spin–spin relaxation time, T_2, because it is unaffected by spin-diffusion and varies monotonically with the molecular mobility. However, differences in T_2 are not very useful for selecting a rigid phase; on the contrary they are most useful for identifying mobile phases. By combining a selection procedure based on differences in T_2 with cross-polarization it is possible to decide whether resonances in a cross-polarization spectrum are from a relatively mobile component. One such selective experiment is cross-polarization with a delayed spin-locking pulse[2]. During the delay between the initial ^{1}H $\pi/2$ pulse and the spin-locking pulse all the magnetization associated with the rigid phase is allowed to dephase, giving a cross-polarization spectrum which shows only the contribution from a mobile component with a long T_2.

One of the most important characteristics of a rigid phase are the long carbon spin-lattice relaxation times, T^{C}_1. For example in polyethene T^{C}_1 ranges from less than 1 s for the amorphous phase to over 900 s in the crystalline region, with an intermediate value of around 25 s in an interfacial region[4]. The combination of cross-polarization and a long delay in the ^{13}C T_1 selection[13] will enhance the degree of selectivity in favour of a rigid domain.

The four selective n.m.r. experiments described above were used in an attempt to identify a rigid copolymer phase. The reason for introducing four selective n.m.r. experiments rather than just the one is a simple one, namely the presence of complications which can blunt the effectiveness of any one experiment. Two major complications are possible, one being that the selection procedure may be site-specific rather than phase-specific. This is particularly true for quaternary carbons, which will tend to have long carbon T_1 and weak heteronuclear C–H dipolar coupling regardless of the phase they are in. For this reason it is best not to rely on quaternary carbons in a selective ^{13}C n.m.r. experiment. The second complication is that spin-diffusion may lead to averaging of the nuclear spin relaxation times, particularly those of ^{1}H.

A necessary preliminary before a selective ^{13}C n.m.r. spectrum can be acquired is the measurement of various nuclear spin relaxation times in order to find one which will give a high degree of selectivity. For the purposes of the current study the proton relaxation times T_1, $T_{1\rho}$, T_2 and T_{1xz} were measured as well as a qualitative estimate of the ^{13}C T_1.

EXPERIMENTAL

N.m.r. measurements were carried out on a Bruker MSL-200 NMR spectrometer operating at 200.13 MHz for ^{1}H and 50.32 MHz for ^{13}C. Prior to the ^{1}H n.m.r. experiments the spectrometer was set up using the multiple pulse tune up procedure to ensure that the rf pulses were of equal amplitude and orthogonal as well as to minimize phase transients[15]. The ^{1}H $\pi/2$ pulse was set to be 2 μs. T^{H}_1 were determined by the saturation recovery method[16] and $T^{\mathrm{H}}_{1\rho}$[17] using a spin-locking field of 40 kHz. The multiple pulse relaxation time T_{1xz} was found by spin-locking in the xz plane whilst applying an MREV-8 pulse sequence[18]. Experimental errors were determined from the appropriate regions of the relaxation time curves. All the ^{1}H relaxation curves were analysed by non-linear least squares fitting[19] with the convergence criteria of either a χ^2 of less than or equal to the number of data points (NP) collected or χ^2 less than $1.1 * NP$ and successive iterations differing by less than a tolerance of 0.01. Fitting commenced with one exponential and the number of exponentials increased until convergence was achieved.

High resolution ^{13}C m.a.s. n.m.r. experiments were carried out using a Bruker double bearing probe with a zirconia rotor. Spinning speeds of 3 kHz were typically used and when difficulties were experienced with spinning the coarse particles, laponite was used to balance the rotor. A single contact of between 2 and 5 ms, spin-lock pulse sequence was used to cross-polarize when required[10].

The copolymer studied was prepared by sequential polymerization and had a nominal rubber content of 44%.

RESULTS

A qualitative and thus semi-selective ^{13}C single pulse excitation (s.p.e.) m.a.s. n.m.r. spectrum of the ethene–propene copolymer is shown in *Figure 1a* together with a partial assignment of the resonances. Quantitative information would only be obtained if the recycle delay between transients was long enough to ensure that the magnetization of the phase with the longest T_1^C relaxation time, normally the crystalline one, had returned to thermal equilibrium. In effect the spectrum will be biased towards the more mobile species in the sample and is thus to some degree selective. This is not unusual, indeed it is the norm for the solid state n.m.r. spectra of heterogeneous materials to show some degree of selectivity because of the differences in the nuclear spin properties. To achieve a greater degree of selectivity we can combine the s.p.e. experiment with a presaturating train of pulses and hence acquire only the faster relaxing components. Although the resolution in the ^{13}C n.m.r. spectrum is poorer for the solid polymer than in solution, a few types of ethene unit in the copolymer can be identified, namely the $\alpha\gamma^+$ at 37.0 ppm, the $\beta\beta$ at 24.9 ppm and the $\beta\gamma$ at 28.0 ppm, where the Greek symbol denotes the locations of the nearest branch carbons and the superscript + a chain equal to or longer than the branch indicated.

A propene insertion in an ethene run, EPE, is indicated by the methine resonance at 34.0 ppm, though in this spectrum overlap occurs with a resonance from a crystalline ethene run. Indeed, unique information is provided in the solid state n.m.r. spectrum by the two resonances which are seen for the long ethene runs, $\delta^+\delta^+$ at 33.1 ppm and 30.0 ppm, which can be assigned to crystalline and amorphous phases in the sample based on the chemical shifts seen in polyethene. The presence of a ^{13}C resonance which can be assigned to a crystalline polyethene provides direct evidence for crystallizable runs of ethene in the copolymer, as has also been seen earlier[2]. This illustrates the intriguing possibility of monitoring particular phases of a given polymer through the n.m.r. spectrum rather than by relaxation time properties. Such effects are, however, unusual, at least in terms of our ability to resolve the different chemical shifts.

A complication in the ^{13}C n.m.r. spectrum, which limits the direct inferences we can make about the mobility of the copolymer phase, is the lack of resolution, which prevents ethene homopolymer resonances being distinguished from those of a copolymer ethene run, $\gamma^+\gamma^+$. Thus we cannot deduce from the presence of the crystalline type long ethene run resonance that the copolymer has a rigid component.

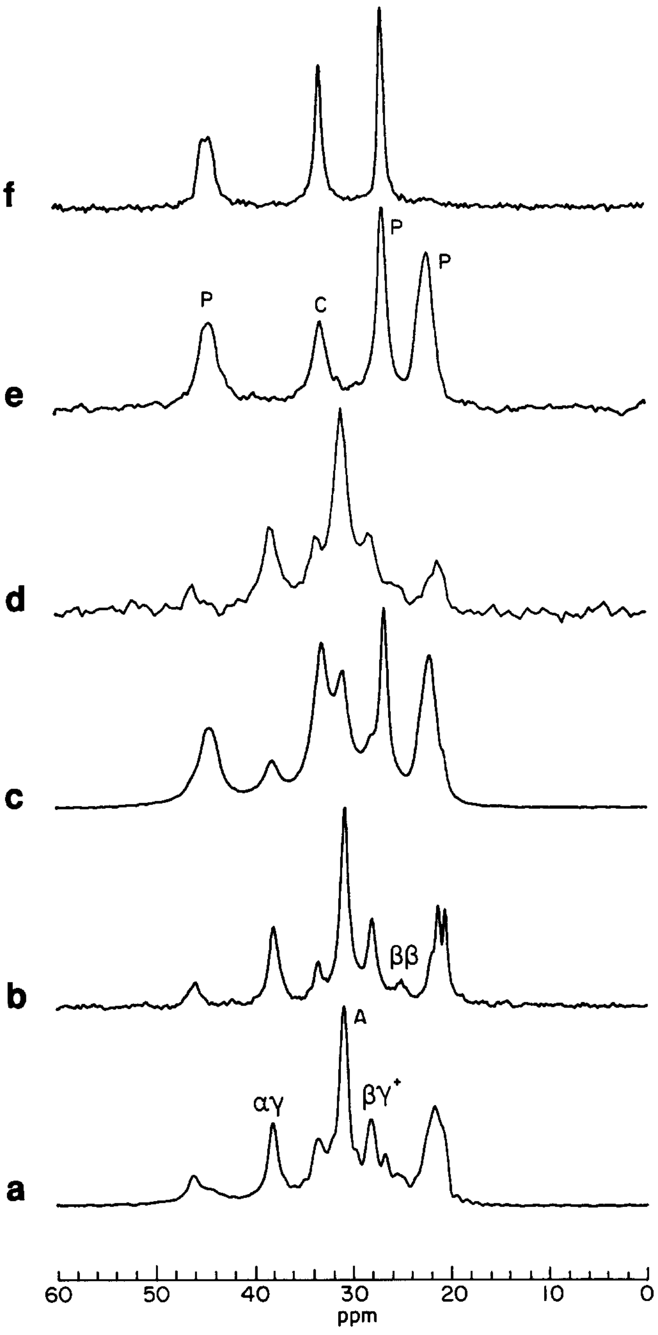

Figure 1 ^{13}C m.a.s. n.m.r. spectra of the ethene–propene copolymer acquired at 50.32 MHz using m.a.s. speeds of 3–4 kHz. Copolymer resonances are denoted by Greek letters which indicate the nearest branch point. A is amorphous polyethene and C crystalline polyethene. P indicates resonances from the propene units. (a) S.p.e. using a recycle delay of 10 s; (b) s.p.e. with a 100 μs interruption in the high power proton decoupling using a 10 s recycle delay; (c) c.p. with a contact time of 2 ms; (d) c.p. with a delay of 100 μs before spin-locking and a 2 ms contact time; (e) c.p. with a 20 ms delayed contact pulse of 2 ms; (f) c.p. with a ^{13}C T_1 delay of 2 s and a 2 ms contact time

Clearer evidence about the nature of the copolymer is provided by the interrupted decoupling s.p.e. experiment, for when the decoupling is interrupted dephasing of the ^{13}C magnetization occurs at a rate dependent upon the $^{13}C-^{1}H$ dipolar coupling. Now, in a mobile, or rubbery, phase where molecular motion will tend to reduce the dipolar coupling from the rigid lattice values, much smaller dephasing and hence loss of intensity will occur in the spectrum. Consequently the interrupted decoupling spectrum will tend to select for the more mobile species as is evident from the ^{13}C n.m.r. spectrum shown in *Figure 1b* by the reduction in intensity of the polypropene resonance at 26.5 ppm. Essentially the spectrum corresponds to the rubbery copolymer phase together with a small amount of atactic polypropene as expected. Since rigid components in the polymer will not contribute to the n.m.r. spectrum we can be clear in our assignment of the resonance at 34.0 ppm to the propene methine from an EPE triad while the splittings of the methyl resonances are consistent with different E/P triads. Unfortunately, the poorer resolution in the ^{13}C n.m.r. spectrum of the solid precludes a more detailed interpretation. In particular we cannot resolve an $\alpha\beta$ type ethene unit indicative of a single ethene insertion in a mainly polypropene chain.

Note that the interrupted decoupling experiment in principle is not purely phase selective, though to a large degree it is so in this case. This is because the dipolar coupling may be reduced by a limited local motion such as a methyl group rotation or may be small because the carbon does not have a directly bonded hydrogen as with quaternary carbons. If we take this into consideration together with a less marked differential in dipolar coupling it is evident that selection methods based only on the effect of motion on a heteronuclear dipolar coupling may not be clear cut. Similar comments apply to selective experiments based on the carbon T_1 because one of the most important mechanisms for the relaxation process is modulation of the $^{13}C-^{1}H$ dipolar vectors.

As we have seen above, selection procedures based directly on the ^{13}C spin suffer from poor selectivity because of the site specific character of the heteronuclear dipolar coupling and ^{13}C relaxation times. From this standpoint the indirect use of ^{1}H relaxation times seems to be attractive since they tend to be phase rather than site specific. Matters are not straightforward though, because in order to use the ^{1}H relaxation times the effect must be carried through into the ^{13}C n.m.r. spectrum by using cross-polarization, which we have seen earlier is itself selective to a certain degree.

An illustration of this is provided by the ^{13}C m.a.s. n.m.r. spectrum in *Figure 1c*, where cross-polarization has been used. This spectrum is clearly different from the s.p.e. one in *Figure 1a*, with the intensity of the resonances associated with the copolymer phase much reduced, in keeping with the expectation that cross-polarization will favour the more rigid components. An alternative interpretation of this spectrum is that we are in fact seeing a smaller fraction of a more rigid copolymer, perhaps in an interfacial region and not a poorly cross-polarized bulk copolymer. We can resolve this question to some extent by measuring the rise time constant T_{CH} in the cross-polarization process by varying the contact time. A short T_{CH} will be indicative of a rigid phase and hence favour the interpretation in terms of an interfacial region. Qualitatively the evidence supports the idea of a poorly cross-polarized phase because increasing the contact time to 5 ms leads to an increase in the intensity of the copolymer resonances, but we cannot rule out a contribution from a more rigid fraction. To obtain a cleaner phase selection we need to turn to the ^{1}H relaxation times and generate a combined ^{1}H and ^{13}C selective n.m.r. experiment.

Initial evidence for the presence of two major phases is provided by the ^{1}H free induction decay (f.i.d.) which can be fitted to an exponential and Gaussian function in the ratio of 0.77:0.23. It must be noted that the fit is rather poor and in simple statistical terms unacceptable, but this is none too surprising for it assumes that all the homopolymer phases have the same Gaussian form and time constants while the copolymer and atactic polypropene have the same exponential decay, to say nothing of the functional form of a hypothetical rigid copolymer phase. In part then the poor fit is a consequence of the complexity of the system but also in part it is because of the excellent signal-to-noise which can be obtained for an f.i.d. With an experimental error standard deviation of 0.0001 we must fit components down to the 0.1% level or so depending on the exact functional form and time constants these phases have. The differences expressed in the f.i.d. are those of T_2, the spin–spin relaxation time and clearly, judging from the time constants in *Table 1*, the differential is marked, suggesting excellent discrimination could be achieved through the use of this relaxation time. A further advantage of using differences in T_2, as noted earlier, lies in the absence of spin-diffusion effects. Spin-diffusion is the transfer of spin magnetization between domains of different intrinsic relaxation times leading to the observation of partially or completely averaged relaxation times. Clearly if such a process is present it will make phase selection at best difficult and at worst impossible.

A selective ^{13}C n.m.r. experiment based on differences in the proton T_2 makes use of a delayed spin-lock in the cross-polarization pulse sequence. During the delay before spin-locking all the ^{1}H magnetization associated with the short T_2 phase decays leaving only the magnetization from the mobile phase. In this manner we can remove the contribution of rigid phases to the cross-polarization spectrum, and thus in this case we will be able to see directly whether the copolymer resonances seen in the earlier cross-polarization n.m.r. spectrum are present because of poor cross-polarization from a highly mobile copolymer phase. As shown in *Figure 1d* we can obtain a ^{13}C n.m.r. spectrum corresponding to cross-polarization from the mobile phase and as expected it is of copolymer and in all probability atactic

Table 1

	Fraction and time constant					
Relaxation time	I^1	T^1	I^2	T^2	χ^2	Q
T_1	0.73	0.32 s	0.26	0.1 s	168.3	1.0[a]
T_2	0.77	0.3 ms	0.23	11.9 μs	8550.0	0.0[b]
$T_{1\rho}$	0.74	4.4 ms	0.26	15.3 ms	78.0	1.0[c]
T_{1xz}	0.69	2.7 ms	0.31	8.0 ms	6330.0	0.0[d]

[a] 1 exponential $\{\chi^2 = 621.6, Q = 0.0\}$ $NP = 256$, $T_1 = 0.24$ s

[b] Two-phase model inadequate given the experimental signal-to-noise (exponential–Gaussian)

[c] 1 exponential $\{\chi^2 = 2392.0, Q = 0.0\}$ $NP = 256$, $T_{1\rho} = 7.5$ ms

[d] High χ^2 because of the chemical shift oscillations of the first 15 points. 3 exponential fit converges to the same fit as the 2 exponential model

polypropene as well. Although at first sight this may seem surprising, given the narrow ^{1}H linewidth of the mobile phase, it rather highlights the poor degree of selectivity possible in the cross-polarization process and hence the need for additional selection methods.

One possibility worth considering is that cross-polarization is occurring by a scalar coupling mechanism, rather than the normally dominant dipolar one; however, in practice this is not likely to be the case. The reason for this is not any intrinsic inefficiency in the scalar coupling mediated polarization transfer, but rather the extreme sensitivity of the process to the radiofrequency field match[20,21]. Polarization transfer is only possible if the difference in the two r.f. fields is less than the scalar coupling; since this will be only of the order of 100 Hz such a condition will almost certainly not be met using standard set-up procedures. Now, since we can cross-polarize the mobile phase it is apparent that the presence of copolymer resonances in the standard cross-polarization pulse sequence does not imply there is a rigid copolymer phase but neither does it discount this possibility.

Only small differences are seen in the T_1^{H} as shown in *Table 1* but perhaps more importantly it is not at all obvious from the actual relaxation times which relaxation time corresponds to the rigid phase. We could base an argument on the similarity of the proportions of the two phases found in this fit to that found in the f.i.d. decomposition, but it is by no means clear that these are the same two phases. In this particular case the evidence is sufficient to justify such an assumption, but in general this will not be so. Given the difficulty of assigning the T_1 relaxation times to a specific phase simply on the basis of their magnitude no attempt was made to use these as a selection method. However, should we wish to use T_1^{H} selective experiments we could incorporate an initial T_2 dephasing into a saturation recovery pulse sequence and thereby correlate the T_1^{H} values with the long T_2 component.

We must note in passing that acceptable fits were obtained to a two-phase model when it is perhaps obvious that there must be more than two, for example crystalline polyethene and polypropene as well as copolymer. The reason for this lies in the signal-to-noise ratio of the saturation recovery curve. If we wish to fit to more exponentials, especially when the time constants of these phases differ by a small factor, we need a better signal-to-noise ratio. Since the purpose of the present study was not to characterize thoroughly the phases present by ^{1}H n.m.r. the two-domain analysis is sufficient; indeed any deficiencies with this model relevant to the question in hand will be apparent in the selective experiments. We can use the fact that we see two different T_1^{H} values to estimate that the domain size of the phases corresponding to these relaxation times must be at least 200 Å or so, otherwise a single averaged value would be seen.

One of the most useful differences in ^{1}H relaxation times is found for $T_{1\rho}$ in crystalline and amorphous phases. For most polymers $T_{1\rho}$ is significantly longer in a crystalline phase than in an amorphous one. Since the values of $T_{1\rho}$ found for a rubbery phase are similar to those for an amorphous one, if not shorter, we can in principle distinguish between a rigid and mobile phase. If we wish to select only the long $T_{1\rho}$ component this can be readily done by simply delaying the contact pulse on the ^{13}C spins until all the spin-locked ^{1}H magnetization associated with the shorter component has decayed away, giving the so called delayed contact experiment. Confirmation of the empirical rule about the longer $T_{1\rho}$ belonging to the crystalline phase is provided by the delayed contact ^{13}C c.p.m.a.s. n.m.r. spectrum shown in *Figure 1e*, where the only long run ethene resonance seen corresponds to the crystalline chemical shift. An important aspect of this observation is that it shows this phase must possess a long $T_{1\rho}$ largely unaveraged by spin diffusion. Thus we can conclude that the domain size of the crystallizable run of ethenes is in excess of 30 Å or so. Further examination of this spectrum reveals that the $\alpha\gamma^+$ and $\beta\gamma$ copolymer resonances are not present, demonstrating clearly that there is not a rigid copolymer phase.

Generally speaking we must consider the complications which spin-diffusion can cause when using ^{1}H magnetization in a selective n.m.r. experiment because of the averaging out of the differences between the constituent phases. However, in this specific instance no further precautions are in fact necessary because the spectrum shows no evidence for a copolymer and hence we do not need to be concerned whether it arose from the effects of spin-diffusion. For the general case though, taking the present ^{1}H relaxation times as an example, although spin diffusion is reduced by a factor of two in spin-locking experiments we cannot be sure that the $T_{1\rho}$ decay is not influenced by its effects. Strong evidence that spin-diffusion is not a complicating factor is provided by the T_{1xz} results where there is no evidence for a component with a significantly longer decay, characteristic of an isolated crystalline region. In simple terms we can assume that T_{1xz} and $T_{1\rho}$ reflect a similar frequency range of motions but with the notable difference that spin-diffusion is effectively quenched by the multiple pulse sequence used in the measurement of T_{1xz}. In the light of the T_{1xz} results, namely the absence of a much longer component and the good fit to two components, we can be confident that the long $T_{1\rho}$ component does represent the crystalline phase and not some averaged value of a crystalline and interfacial region. Hence the delayed contact ^{13}C c.p.m.a.s. n.m.r. spectrum only shows the crystalline regions.

A further experiment which can be used to explore the possibility of a more rigid copolymer phase is to use ^{13}C T_1 selection. Previous work on linear polyethene has established that three different regions can be identified from the ^{13}C T_1, corresponding to amorphous, interfacial and crystalline domains. Qualitatively it was observed that the ethene–propene copolymer showed three ^{13}C T_1 regimes, a short T_1^{C} of less than 2 s, an intermediate T_1^{C} of 20–30 s and a long T_1^{C} in excess of 100 s. The intermediate T_1^{C} could be taken as evidence for an interfacial region which may correspond to the copolymer phase. Despite the site specific character of T_1^{C} we can be confident that if a rigid copolymer phase is present, say as an interfacial region, it will have a T_1^{C} of at least 2 s. Hence a ^{13}C T_1 selective experiment based on a relaxation delay of 2 s will show whether there is a rigid copolymer phase.

A ^{13}C m.a.s. n.m.r. spectrum acquired using the combination of cross-polarization selection and T_1^{C} selection is shown in *Figure 1f*. Clearly there is no evidence for the key copolymer αk resonance at 38 ppm indicating that the vast majority of copolymer present has a T_1^C of less than a second. This result suggests somewhat intriguingly that little true copolymer is to be found at the interface of the rubbery copolymer and the homopolymer blocks; or rather that copolymer which is present at the interface must be at the more mobile end and the bulk of the interface is then a homopolymer block. More detailed ^{13}C T_1 relaxation time measurements and selective n.m.r. experiments are required if we wish to elaborate on this structure. No methyl carbon resonance is seen in the ^{13}C T_1 selective experiment because of their short T_1^C, illustrating the site-specific character of this procedure.

The fundamental premise when trying to interpret n.m.r. relaxation times in terms of the mechanical properties is that the loss processes involved in n.m.r. relaxation are related to those in the dissipation of mechanical energy. If not actually describing the same response of the sample to a mechanical stress the molecular dynamics associated with the n.m.r. relaxation time must at the very least report on the true response. In many respects the situation is analogous to dynamic mechanical experiments[22,23] with the advantage that molecular group specific data are obtained but with the disadvantage that the sample is not placed under any mechanical force. Most success appears to be in the use of $T_{1\rho}^C$ to understand the impact resistance of a polymer[24]. In short, brittle polymers generally are found to possess long $T_{1\rho}$, indicating the absence of spectral density in the 10–100 kHz frequency range, whereas tough polymers have short $T_{1\rho}$.

Complications arise when using proton $T_{1\rho}$ because of spin diffusion and the effect of specific groups, such as methyl groups, as relaxation sinks. In the present example, if we do use $T_{1\rho}^H$ then the rubbery copolymer phase which has a short $T_{1\rho}^H$ would be identified as being a tough component, while the crystalline components are brittle since they have a long $T_{1\rho}^H$. This of course agrees nicely with what we know about ethene–propene copolymers. The more general application of such ideas is possible but greater care would need to be taken in establishing the mechanism giving rise to a particular relaxation time.

CONCLUSION

^1H n.m.r. relaxation time measurements indicate the presence of two distinct phases in the ethene–propene copolymer studied. On the basis of the two-component T_1^H decay we can deduce that the domain size is in excess of 200 Å, otherwise spin-diffusion would lead to a single averaged value. Selective ^{13}C m.a.s. n.m.r. experiments, based on the ^1H n.m.r. relaxation times and ^{13}C–^1H dipolar coupling, allow us to characterize the composition of the two phases. The fraction of the sample with the long $T_{1\rho}^H$ corresponds to rigid, crystalline homopolymer phases of ethene and propene while the fraction with a short $T_{1\rho}^H$ is amorphous homopolymer, atactic polypropene and true copolymer. While there is strong evidence for crystallizable ethene runs in the copolymer there is no evidence for a rigid copolymer fraction, implying that copolymer cannot be present throughout the interface between the homopolymer phases and rubbery portion: it can only be present at the more mobile rubber end.

The delayed contact ^{13}C c.p.m.a.s. n.m.r. experiment shows that the $T_{1\rho}$ of the crystallizable runs of ethene is effectively unaveraged by spin-diffusion, allowing a lower limit of 30 Å to be placed on the size of this domain. Somewhat surprisingly the ^1H relaxation times for the sets of crystalline and amorphous phases are the same. This does not indicate intra crystalline or intra amorphous region spin-diffusion is occurring; rather it is a reflection of the fact that the signal-to-noise ratio in the ^1H n.m.r. relaxation decays is not sufficient to allow two time constants differing by only a small factor to be distinguished. Support for this interpretation is provided by non-linear least squares analysis of computer simulated relaxation decays[25]. As this example amply illustrates, the combination of ^1H n.m.r. relaxation time analysis and ^{13}C m.a.s. n.m.r. spectroscopy is a powerful method for observing selected phases in a heterogeneous material.

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