$P(\cdots\text{–A})$. These probabilities are given by simple expressions satisfying an elementary differential equation. For instance, for infinitely long chains and with $\tau = kt$:

$$\mathrm{d}\nu(\tau)/\mathrm{d}\tau = -e^{-\tau}\nu(\tau) - a(1 - e^{-\tau})\nu(\tau) \tag{3}$$

with the unique solution with $\nu(0) = 1$:

$$\nu(\tau) = \exp\{-a\tau - (1 - a)(1 - e^{-\tau})\} \tag{4a}$$

Similarly:

$$\tilde{\nu}(\tau) = \exp\{-\tilde{a}\tau - (1 - \tilde{a})(1 - e^{-\tau})\} \tag{4b}$$

While the kinetics of irreversible reactions with nearest-neighbor effects on *homopolymers* has been extensively studied by many authors since 1962, the more general and important problem of such reactions on *copolymers* is a more difficult mathematical problem, which, to our knowledge, was first solved by González and Hemmer.[11,12]

(II) The methods mentioned in statement I can be easily generalized to solve the kinetics of irreversible reactions with nearest-neighbor effects on copolymers.

Actually, González and Hemmer only applied their method to the general case of reactions of (second order Markovian) copolymers[11,12] and to the case of repeated reactions on homopolymers.[13] The case at issue, the first reaction of a homopolymer, is a special case of the two more general problems just mentioned.

A method which both explains and solves what other approaches do (first reaction on homopolymers) and also explains and solves problems where those other approaches fail is clearly superior. This is why we chose to word the introduction of our paper[4] as we did. The new references supplied by Dr. Platê and co-workers do not appear to change the situation in this respect.

Finally, we list the results announced in statement I. The reader can either derive them by straightforward application of eq 2 or he may specialize our results[11–13] to the case in question. For $l \geq 2$:

$$q_l(\tau) = (1 - e^{-\tau})^2\nu(\tau)\tilde{\nu}(\tau)\exp[-(l - 2)\tau] \tag{5}$$

For $l = 1$

$$q_1(\tau) = 1 - y(\tau) - (2 - e^{-\tau})\nu(\tau)\tilde{\nu}(\tau) \tag{6}$$

where the extent of reaction is given by

$$y(\tau) = 1 - e^{-c\tau}\left\{1 - (1 - a - \tilde{a} + c)\int_0^\tau \mathrm{d}s\, e^{(c-1)s}\nu(s)\tilde{\nu}(s) - (a + \tilde{a} - 2c)\int_0^\tau \mathrm{d}s\, e^{cs}\nu(s)\tilde{\nu}(s)\right\} \tag{7}$$

By consulting our solution of the differential equations for the densities of reacted sequences,[4] the reader may convince himself that the r_l's can all be expressed in terms of the q_l's and, hence, in terms of ν and $\tilde{\nu}$.

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Annealing-Induced Changes in Orientation and Mobility in the Noncrystalline Region of Drawn Linear Polyethylene: A ^{13}C NMR Study

Solid state ^{13}C NMR in organic systems[1,2] holds out the promise of simultaneously studying molecular mobility and orientation. Molecular mobility influences relaxation behavior[3] which, in turn, can be studied as a function of resonance position. The resonance frequency, ν_{res}, of a given carbon is related to molecular orientation through the equation

$$\nu_{\text{res}} = (2\pi)^{-1}\gamma_{\text{C}}B_0(1 - \lambda_{xx}{}^2\sigma_{xx} - \lambda_{yy}{}^2\sigma_{yy} - \lambda_{zz}{}^2\sigma_{zz}) \tag{1}$$

where γ_{C} is the gyromagnetic ratio, B_0 is the applied magnetic field, and the λ_{ii} are the direction cosines of the angle between B_0 and the direction corresponding to the ith principal value, σ_{ii}, of the chemical shift tensor of the carbon considered. Equation 1 is valid when the ^{13}C signal is obtained in the presence of high-power proton decoupling[1] and in the absence of magic angle sample spinning.[4]

Preliminary results on the changes in orientation and mobility in the *noncrystalline* component (NCC) of drawn linear polyethylene (LPE) are presented here as a function of annealing temperature for a single cold drawn sample having a nominal draw ratio of 15. The characterization of the noncrystalline region of drawn LPE is interesting from an engineering point of view because this region connects the strong, oriented crystalline domains, thereby playing a key role in determining the modulus.

For LPE the methylene chemical shift tensor components and their assignments have been determined.[5–7] With respect to external tetramethylsilane (Me_4Si) as a reference, σ_{xx} is 51.4 ± 1.3 ppm and is assigned to the direction parallel to the intramethylene H–H vector, σ_{yy} is 38.9 ± 1.3 ppm with a direction parallel to the H–C–H angle bisector, and σ_{zz} is 12.9 ± 1.3 ppm and is parallel to the chain axis. Figure 1 shows two ^{13}C spectra obtained by spin-lock cross-polarization (SLCP).[1] These spectra contain contributions from both the NCC and the crystalline component (CC). The top spectrum is that of polycrystalline LPE, while the lower spectrum is the drawn LPE with B_0 parallel to the drawing direction. The polycrystalline line shape agrees qualitatively with the shape expected from theory[8] for a purely crystalline substance. The spectrum of the drawn LPE is centered at 12.9 ppm, indicating that most of the chain segments are aligned in the drawing direction; however, an amplification (×8) of this spectrum shows that some of the chain segments have not been well oriented by drawing and that the time averaged segment orientation seen locally at these

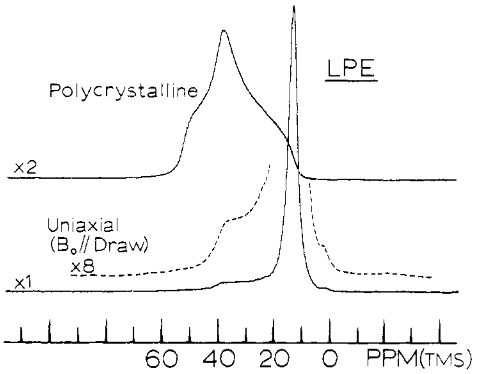

Figure 1. Spin-lock cross-polarization spectra of linear polyethylene. The upper spectrum is characteristic of an unoriented melt-crystallized specimen; the lower spectrum arises from the drawn (×15) material. The dashed line is the latter spectrum amplified eight times; the unoriented spectrum is amplified two times relative to the lower spectrum. The small shoulder near 2 ppm in the lower spectrum is a dipolar satellite (cf. D. L. VanderHart, *J. Magn. Reson.*, **24**, 467 (1976)), arising from pairs of ^{13}C nuclei three bonds apart.

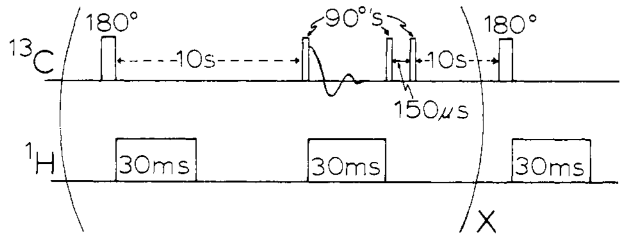

Figure 2. The (180°–10 s–90°–10 s)$_x$ experiment used to isolate the noncrystalline component ^{13}C signal. The two 90° pulses separated by 150 μs ensure ^{13}C saturation. The 30 ms proton pulse following the 180° carbon pulse helps to minimize transient Overhauser effects.

carbon sites lies well away from the draw direction (cf. eq 1).

Based on measurements of ^{13}C longitudinal relaxation times, T_{1c}, which are related to spectral densities of molecular motions in the megahertz region,[9] an experimental definition of the NCC of LPE has been adopted.[10] The pulse sequence for the experiment used to isolate what will be referred to hereafter as the NCC signal is given in Figure 2; it is called a (180°–10 s–90°–10 s)$_x$ experiment. No cross-polarization is involved; magnetization builds up via T_{1c} processes. Equal proton decoupling pulses are applied at both the 180° and the 90° pulses in order to minimize transient Overhauser intensity distortions[11] from carbons with $T_{1c} > 10$ s. Two additional 90° pulses separated by 150 μs follow the observation decoupling pulse to ensure ^{13}C saturation. Equal 10 s intervals are chosen to reduce the intensity contributions from carbons with $T_{1c} > 10$ s. In fact, if transient Overhauser effects are ignored, a carbon contributing unit intensity at equilibrium will have an intensity $[1 - \exp(-10\ \mathrm{s}/T_{1c})]^2$ in this experiment. Therefore, those carbons with $T_{1c} < 2$ s will be seen at full intensity while those carbons with $T_{1c} > 100$ s will have less than 1% of their full intensity. In drawn LPE at ambient temperature (28 °C), T_{1c} for carbons in a purely crystalline environment is of the order of 700 s. On the other hand, a substantial number of carbons have $T_{1c} < 2$ s; these latter carbons will certainly be classified as noncrystalline. For reference, a methylene carbon isotropically reorienting with a $T_{1c} = 2$ s has a correlation time[9] of 3.2×10^{-6} s or 1.2×10^{-11} s because T_{1c} is a double valued function of the correlation time. Both of the correlation times cited are sufficiently short to produce motional narrowing of proton broadline resonances; therefore this separation based on relaxation may single out a group of chain segments quite similar to those designated noncrystalline by proton broadline line shape analysis.[12] There are typically 15–25% of the carbons, however, which have T_{1c} values intermediate between 2 and 700 s. This fact makes the choice of 10 s and the definition of the NCC in the proposed experiment somewhat arbitrary. This arbitrariness, while not negligible, is not overwhelming. The consistent application of this definition of the NCC allows one to follow changes in mobility as a function of orientation during a process such as annealing. As an aside, it is gratifying that LPE carbons do not have a strictly bimodal distribution of T_{1c}, for why should a tie chain, for example, exhibit the same motion as a free chain end? Also, proton broadline NMR of undrawn[12,13] as well as drawn[14-17] LPE has been recognized to consist of more than two components. Finally, transient Overhauser intensity distortions are minimal in these ^{13}C experiments since the proton T_1's are of the order of 1 s.

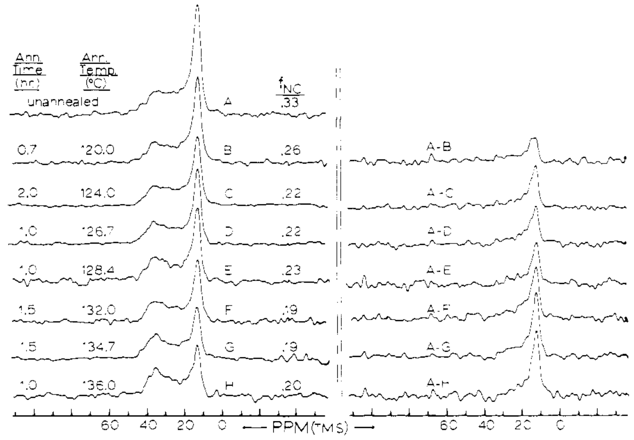

Figure 3. Room temperature ^{13}C spectra of the noncrystalline component of drawn (×15) linear polyethylene as a function of consecutive annealing times and temperatures. The pulse sequence of Figure 2 is used to isolate this noncrystalline resonance. The noncrystalline fraction, f_{NC}, is also indicated and is based on a total intensity measure obtained in a (90°–5000 s)$_x$ experiment. Difference spectra relative to the unannealed spectrum are displayed on the right and show that the principal effect of annealing is to stiffen the originally oriented, mobile chains.

The original LPE in this experiment was Marlex 6001 ($M_n = 15\,300$, $M_w = 193\,000$), which was cold drawn using dumbbells cut from 1 mm thick, unoriented sheet. Cold drawing took place at 72 °C at a strain rate of 0.11 cm/s. The material included in the sample covered draw ratios from 14–18 with a nominal average of 15. Lengths of LPE, 7 mm long, were cut carefully, stacked parallel to one another, and loaded into a cylindrical poly(tetrafluoroethylene) sample holder. The drawing direction of the LPE was normal to this cylinder axis. Annealing took place under argon. The LPE was free to contract but because of lateral constraints placed on the sample holder during annealing, the increase in cross-sectional area was limited to about 10%.

The NMR measurements were performed at 15.08 MHz for ^{13}C and a 68 kHz radiofrequency field strength was used for decoupling protons. The sample was bathed in a nitrogen atmosphere during these experiments in order to minimize relaxation effects due to paramagnetic oxygen.

Figure 3 shows spectra resulting from (180°–10 s–90°–10 s)$_x$ experiments performed at 28 °C on the sample of drawn LPE. The top spectrum is the original material. Strictly speaking, however, the unannealed sample had previously been held at 65 °C for 24 h in an unrelated experiment; it will be assumed that this thermal treatment caused negligible molecular rearrangement, particularly since drawing took place at a higher temperature. Spectra obtained after successive annealings follow. Spectra are normalized to a total intensity proportional to f_{NC}, the noncrystalline fraction. Difference spectra referenced to the unannealed sample are also displayed. The f_{NC} values are based on a total intensity determined in a (90°–5000 s)$_x$ experiment in which all carbons contribute full equilibrium intensity. Since signal to noise is compromised by the long waiting period in this latter experiment, f_{NC} values are probably no better than ±0.05 in an absolute sense, but changes in f_{NC} values are probably good to ±0.01. A final annealing at 138.1 °C for 1 h melted the sample; this spectrum is not shown.

The first and most obvious feature of the spectra in Figure 3 is that there is a substantial fraction of the NCC which is oriented within 15° of the drawing direction and, therefore, resonates in the 12–15 ppm range. Upon being annealed, this oriented, mobile material decreases in intensity; the most dramatic changes occur during the 120 and 124 °C annealing steps. After 124 °C, the next discernible decrease in this region occurs at 132 °C, followed by a slight additional reduction at 134.7 °C. In contrast, the poorly oriented chain segments with resonances greater than 25 ppm show virtually no change in peak intensity from the starting material through the 132.0 °C annealing. A measurable increase is observed, however, following the 134.7 and 136 °C annealings. In the region near 22 ppm, a decrease of intensity is also visible as one increases the annealing temperature.

A very tempting conclusion from these spectra is that annealing stiffens only those chains which have been oriented originally by the drawing process since little change is observed in the region of poor orientation. In principle, however, the alternative explanation that some oriented chains relax during annealing while an equivalent number of poorly oriented chains stiffen or crystallize cannot be dismissed on the basis of the data alone. Nevertheless, if one adopts the former explanation, then a reduction of intensity in the oriented region could correspond to annealing out of crystalline imperfections and/or a decrease in the number or mean length of tie molecules. To choose among these possibilities, one must also consider other evidence such as the fact that annealing is usually accompanied by a decrease in modulus[18-21] even after the modulus has partially recovered following annealing with fixed ends.[20] Also, the crystalline orientation, as monitored by a separate NMR measurement, did not change appreciably during annealing. Of the possibilities presented here, a reduction in the number of tie chains would appear to be the explanation most consistent with the NMR data and the modulus reduction. It has been suggested[18] that annealing decreases the modulus by increasing the enthalpy content of the noncrystalline chains, particularly the tie chains which relax to more liquid-like conformations. This conclusion was partially based on the observation that density changes, and therefore crystallinity changes, were minor. These NMR results suggest a large change in crystallinity and a negligible transfer of intensity from the oriented region to the region in the vicinity of 31–32 ppm which would be characteristic of the mean resonance position for chain segments with liquid-like conformation. Resolution of these differing points of view requires further experimentation since there are notable differences between this experiment and that of ref 18 in the following areas: drawing temperature, annealing time, molecular weight distribution, and crystallinity measurement method.

The poorly oriented chain segments do not seem to participate in the annealing process in spite of the fact that the lamellae are thickening. Therefore, annealing does not seem to promote orientation and potential load bearing for these chain segments, although because of their orientation, it was doubtful whether these segments contributed significantly to the modulus in the unannealed sample. This same material has also been characterized as having a high degree of molecular motion since these carbons exhibit a T_{1c} of about 300 ms and show motional narrowing at 28 °C when compared to low temperature (−100 °C) line shapes. For a model of isotropic motion, a T_{1c} of 300 ms corresponds to a correlation time of either 4.8×10^{-7} or 8×10^{-11} s. The fact that the maximum intensity occurs at about 35 ppm in this region instead of 32 ppm, which is the mean chemical shift of the NCC carbons in LPE, only indicates that molecular motion is not isotropic on a time scale of about 1 ms. Whether one can deduce from the maximum of this wing that there is preferred orientation in this mobile, short-T_{1c} component of the NCC line shape depends on the specific model for the anisotropic motion; this is a topic not taken up here.

In conclusion, for drawn LPE, the (180°–10 s–90°–10 s)$_x$ experiment performed at ambient temperature provides a convenient way of monitoring changes in orientation and mobility of NCC chain segments. The definition of the NCC signal is admittedly somewhat arbitrary, but changes which appear are real and can be analyzed quantitatively. The more comprehensive discussion of this experiment[10] will also include studies of the changes in line shape with draw ratio and drawing technique, presentation of the relaxation data upon which this measurement is based, and a discussion of the technique for monitoring crystalline orientation. The strength of this ^{13}C technique for studying the NCC is that this method is quantitative for comparative purposes, it provides much more detailed information than is contained in, say, the average value of $\cos^2 \theta$ obtained by other techniques,[22,23] and in contrast to broadline NMR techniques, it offers insight into correlation time changes which are not necessarily reflected in NMR line shape or line width changes. The generalizability of this technique for examining the NCC of other semicrystalline polymers is not straightforward. First, the monomer unit should contain no efficiently relaxing carbon such as a methyl carbon in order to keep the crystalline T_{1c} long. Second, the chemical shift anisotropy overlap in a polymer with several kinds of carbons will complicate this analysis although ^{13}C enrichment of specific sites at modest levels could moderate this problem.

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EPR Investigations of Irradiation Effects on Polymers Containing Nitroxide Spin Probes Exhibiting a Bimodal Distribution of Motional Correlation Times

The electron paramagnetic resonance (EPR) method employing stable nitroxide radicals as spin probes is becoming increasingly important in the study of molecular motions and morphology in polymeric substances.[1] This communication is concerned with a new experimental approach involving γ irradiation and thermal heat treatment techniques for polymers containing nitroxide spin probes that exhibit a bimodal distribution[1,2] of motional correlation times. The implications of these results on the molecular motions of the spin probes and the associated polymer main-chain segmental motions will be discussed.

The polymer system studied was the alternating block copolymer consisting of equal amounts (wt%) of bisphenol A-polycarbonate (BPAC) and poly(dimethylsiloxane) (DMS), containing nominally 0.08 wt % of the spin probe 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TANOL).[3] Before irradiation, the copolymer samples show essentially three different types of EPR spectra, depending on the temperature at which the measurement is made.[4] These spectra are displayed in Figure 1.

At low temperatures between about 77 and 220 K, the EPR spectra consist of broad hyperfine lines whose overall line shape is that expected from a single type of TANOL spin probe undergoing slow tumbling motions[5] (see Figure 1a). Above approximately 360 K, the observed spectra exhibit three motionally narrowed hyperfine lines (Figure 1c). At intermediate temperatures, approximately from 220 to 360 K, the observed spectra appear to be the superposition of the broad line (Figure 1a) and narrow line (Figure 1c) spectra (see Figure 1b).[6] (In Figure 1, the peaks that belong to the broad line spectrum are denoted by S and those of the narrow line spectrum by F.) We have also found that the ratio of the integrated EPR intensity of the narrow line spectrum to the broad line spectrum, denoted by α, increases with increasing temperature.

The broad line spectrum represents a slow motional phase (S) of TANOL radicals with long correlation times, while the narrow line spectrum represents a fast motional phase (F) with short correlation times. In terms of the proposed model for the microstructure of the BPAC/DMS block copolymers,[7] the fast phase consists of TANOL radicals located in rubbery DMS regions which are undergoing fast main-chain segmental motions, whereas the slow phase is composed of TANOL radicals undergoing slow tumbling in rigid BPAC domains and/or in rigid DMS regions whose segmental motions are restricted by their proximity to the BPAC domains. Thus, the assumption that the spectrum of Figure 1b consists of both the broad line and narrow line spectra indicates that both rigid and rubbery regions are present in the copolymer system.

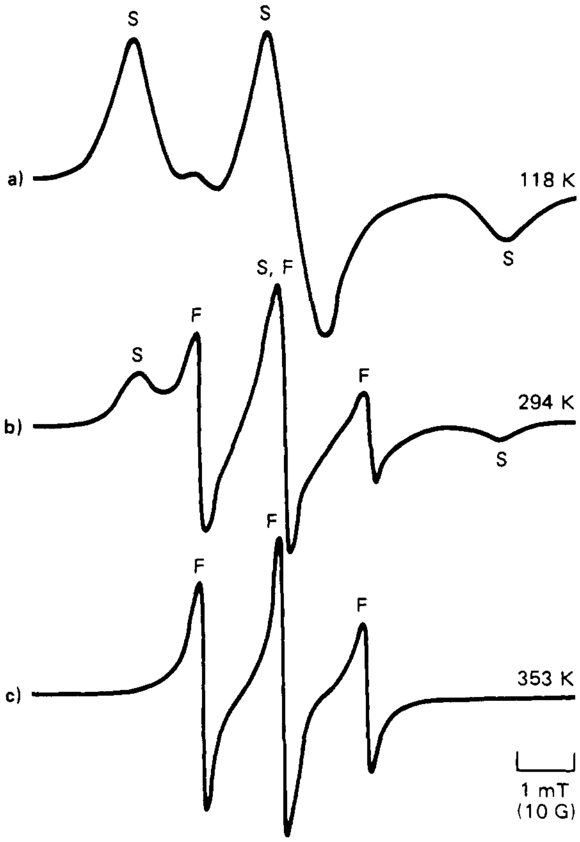

Figure 1. First-derivative EPR spectra observed at different temperatures from TANOL spin probes in 50-50 wt % BPAC-/DMS block copolymer.

One should also consider the possibility that the EPR spectrum of Figure 1b arises from a single radical phase that undergoes anisotropic motion[5] resulting in an incomplete averaging of the hyperfine and g-anisotropy. Another important consideration is concerned with the interphase regions between the mobile and rigid regions where the segmental motions and the radical motions should be intermediate between the fast and slow rates. If the TANOL radical translational diffusion rates across the interphase regions are fast but still slow enough that the spectra are not dynamically averaged, the rapid radical penetration between the fast and slow phases will determine a temperature-dependent equilibrium of interconverting fast and slow spin probe species characterized by α. Alternatively, if the translational diffusion rates are slow compared to the time of the experiment, the fast and slow phases are noninterconverting species, and the temperature dependence of α is a measure of how the relative amount of mobile regions changes with temperature. As described below, the irradiation and thermal treatment experiments provide some definitive information about these questions.

The copolymer samples were irradiated with a γ-ray flux of 1.2×10^6 rad/h at room temperature for periods ranging from 3 days to 1 week, by using an existing ^{60}Co source. As a result of the γ irradiation, the EPR intensities of both