we made drawings. This is rather easy up to $n = 10$. Indeed, the configurations divide into symmetrical groups and present geometrical properties which much simplify the work. For $10 < n \leq 15$, we made an exact enumeration with a computer. The numerical values so obtained show that $\langle r_n^2 \rangle_0^{y=n-2} < \langle r_n^2 \rangle_0$ and that $\langle r_n^2 \rangle_0^{y=n-2}$ rapidly tends toward $\langle r_n^2 \rangle_0$.

For $n = 15$, as an example, we obtain

$$C_{15} = 7\,489\,728$$

$$\langle r_{15}^2 \rangle = 36.55$$

Let us note that in the case of a poor solvent we account for increased interactions between two nearby second-neighbor segments (segments p and $p + 2$) but ignore equally increased interactions of type $(p, p + 4)$, $(p, p + 6)$, ... etc. Nevertheless, we have separately measured the end-to-end distance of the drawn configurations presenting second contacts between segments distant on the chain. The mean-square end-to-end distance of this group is inferior but rapidly approaches the value of this coefficient for all the configurations having $y = n - 2$ (the difference is about 10% for $n = 15$). The probability of the minimum end-to-end value $\langle r_n^2 \rangle = 2$ (corresponding to the maximum number of second contacts between distant segments) also rapidly decreases when n increases.

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Communications to the Editor

Electron Paramagnetic Resonance Method for the Determination of Orientation in the Amorphous Regions of Polymers

In order to completely characterize the orientation induced in partially crystalline polymers, one must obtain the amorphous orientation function $f_{\mathrm{am}} = \langle (3 \cos^2 \alpha - 1)/2 \rangle$, where α is the angle between the stretching direction and the polymer chain axis. This parameter has generally been determined by combining birefringence or sonic modulus measurements with a knowledge of the sample crystallinity and the corresponding orientation function for the crystalline region.[1,2] A shortcoming of this indirect procedure is that the value of f_{am} so obtained may be subject to cumulative errors, and consequently there is a need for more direct methods of measuring this important parameter. In this communication we report an EPR method which exploits the angular dependence of the spectrum obtained from a spin probe incorporated into the partially ordered amorphous regions of low-density polyethylene.

The present study was initiated as a result of recent work in our laboratory showing very dramatic effects of sample orientation on the EPR spectra of trapped radicals in partially aligned matrices.[3,4] In particular, the relative intensity of the parallel and perpendicular features in the EPR spectrum of $C_2F_4^-$ in the methylcyclohexane-d_{14} matrix showed a pronounced angular dependence,[4] suggesting that this sensitive anisotropic property could be used to determine low degrees of orientation. This technique has now been applied to oriented polymers, the basic requirements being (i) the incorporation of C_2F_4 into a well-defined morphological region and (ii) that the EPR spectrum of $C_2F_4^-$ generated by γ irradiation should not be masked by signals from other radiation-produced radicals. As will be evident from the results, both of these requirements are met by polyethylene.

A low-density polyethylene (Aldrich) supplied in the form of pellets was heated to 175 °C and pressed to form a film which was subsequently stretched at 70 °C to obtain stretch ratios between 2 and 5. This elongated film (ca. 1-mm thick) was then cut into narrow strips which were stacked together and placed in a Suprasil or Spectrosil sample tube. As shown in Figure 1, samples were prepared with the stretching direction in the film stack being either parallel (A) or perpendicular (B) to the axis of the sample tube. Tetrafluoroethylene (PCR, Inc.), which had been degassed on a vacuum line, was condensed into the sample tube at −196 °C from a storage bulb held at −78 °C. The amount of C_2F_4 transferred into the tube was about 10 mol % of the C_2H_4 repeating units in the polyethylene sample, and this was sufficient to generate a pressure of ca. 5 atm in the sealed tube at room temperature. The sample tubes were stored for 1 week at ambient temperature and then irradiated at −196 °C with ^{60}Co γ rays for a total dose of ca. 1 Mrd. EPR measurements were made on the γ-irradiated samples at 80 K and higher temperatures as previously described.[5]

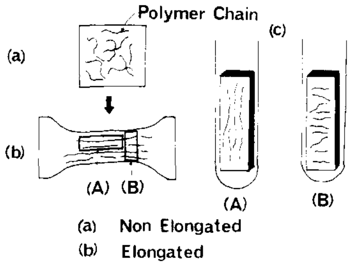

Figure 1. Schematic representation of polymer chains before (a) and after (b) elongation showing the development of orientation along the stretching direction. The two configurations A and B of the elongated polymer film in the EPR tube are shown in c.

The solid line in Figure 2a shows the EPR spectrum of a nonelongated polyethylene film which had been treated with C_2F_4 and irradiated in the same way as the elongated samples. The prominent outer features marked by the stick diagrams correspond closely to those obtained for the spectrum of $C_2F_4^-$ in a methyltetrahydrofuran (MTHF) glass. As discussed elsewhere,[4,6] this powder spectrum consists of parallel and perpendicular features resulting from hyperfine interaction with four equivalent fluorines. Assuming the values of $g_\parallel$ (2.0022) and $g_\perp$ (2.0033) reported previously,[4] the anisotropic hyperfine couplings $^{19}A_\parallel$ (4) and $^{19}A_\perp$ (4) were found by spectral simulation to be 133.2 and 74.8 G, respectively, in good agreement with the values obtained for $C_2F_4^-$ in the MTHF glass.[6] In accordance with previous interpretations,[4,6] the axial and parallel hyperfine

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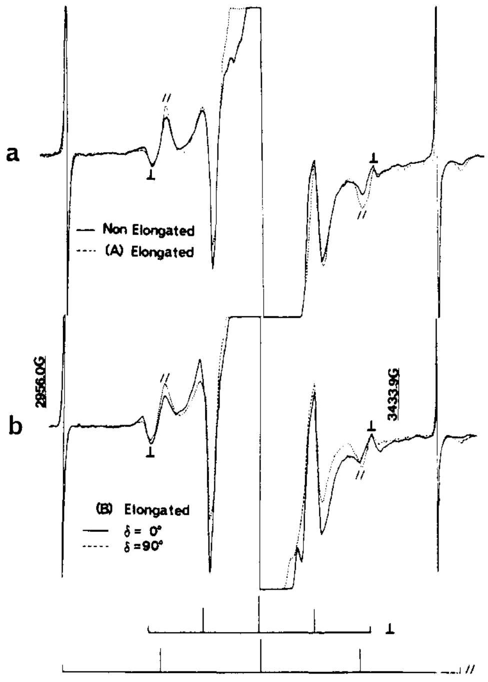

Figure 2. EPR spectra of γ-irradiated polyethylene samples containing tetrafluoroethylene recorded at 86 K. The upper spectra (a) are of a nonelongated and an elongated sample (stretch ratio = 4) in configuration A (see Figure 1 and text). The lower spectra (b) were obtained with the elongated sample in sample configuration B at rotation angles (δ) of 0 and 90° between the direction of elongation and that of the magnetic field. The sharp doublet ($A \approx 506$ G) in all the spectra is from hydrogen atoms produced on the walls of the tube.

tensors for the four equivalent fluorines are thought to result from the free rotation of a planar $C_2F_4^-$ σ radical about the C–C bond so that this becomes the molecular symmetry axis.

Also shown in Figure 2a is the EPR spectrum of an elongated sample (A). Since the magnetic field is always perpendicular to the stretching direction for this configuration, the EPR spectrum showed no dependence on the rotation angle of the tube. Comparison with the spectrum of the randomly oriented (nonelongated) sample shows, however, that the intensities of the parallel features are enhanced while those of the perpendicular features are reduced. This result implies that the preferred orientation of the C–C symmetry axis of $C_2F_4^-$ is perpendicular to the stretching direction in the polymer and, therefore, perpendicular to the polymer main chain.

When the sample in configuration B was examined, the EPR spectrum showed a very marked angular dependence, as illustrated in Figure 2b. For the external magnetic field along the stretching direction ($\delta = 0°$), the intensities of the parallel features are reduced and those of the perpendicular feature are enhanced in comparison with the spectrum obtained for the field perpendicular to the stretching direction ($\delta = 90°$). These results are consistent with the previous conclusion that the C–C axis in $C_2F_4^-$ is perpendicularly disposed to the stretching direction in the polymer.

The anisotropy shown in Figure 2 can be considered to reflect the degree of order in the amorphous regions (vide infra). In order to estimate the orientation parameter f_{am}, we developed a computer simulation program to calculate the EPR spectrum of $C_2F_4^-$ as a function of f_{am} and the rotation angle δ. Details of this program will be given in a forthcoming paper. Essentially, the program resembles existing procedures of this type[7,8] except that the expressions for direction cosines are greatly simplified by the representation of the director (stretching direction) and the external magnetic field in a principal axis system, leading to a considerable saving of computer time.

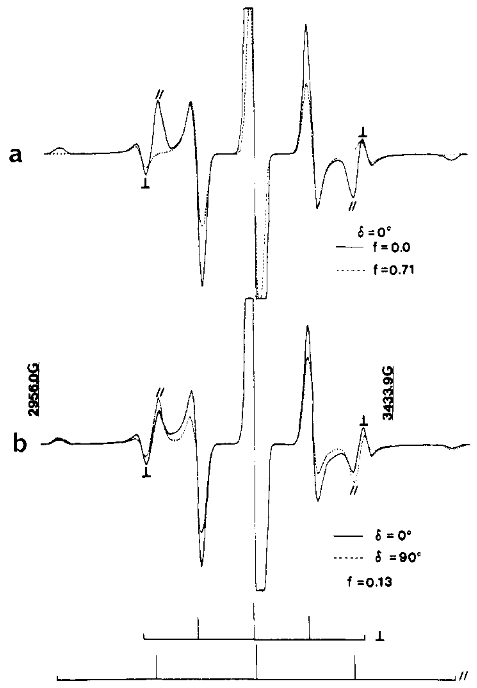

Figure 3. Simulated EPR spectra of $C_2F_4^-$ for various degrees of orientation. The upper spectra (a) show a comparison between the nonoriented ($f = 0.00$) case and a highly oriented ($f = 0.71$, $\delta = 0°$) case. No significance should be attached to the relative intensity of these two spectra. The lower spectra (b) show the angular dependence ($\delta = 0$ and $\delta = 90°$) for a low degree of orientation ($f = 0.13$).

Figure 3 shows examples of the computer-simulated spectra which were generated for different orientation parameters and rotation angles. As expected, Figure 3a shows a very strong dependence of the EPR spectrum on the degree of order, the spectrum for $f = 0.71$ at $\delta = 0°$ giving the perpendicular features almost exclusively when contrasted to the powder pattern for a random orientation ($f = 0$). For $\delta = 0°$, the intensities of the parallel components were found to be very sensitive to the value of f. Since our experimental results in Figure 2b reveal a strong dependence of the intensity ratio $I_{\parallel}/I_{\perp}$ on the rotation angle, the corresponding spectra ($\delta = 0°$ and 90°) were simulated for steadily increasing values of f. The profiles of the experimental spectra in Figure 2b for polyethylene with a stretch ratio of 4 show good agreement with the spectra calculated in Figure 3b for $f = 0.13$. Similar experiments with isotactic polypropylene films resulted in a value of $f = 0.22$ for a stretch ratio of 4.

Although an exact correspondence would not be expected, the f values obtained in this study are comparable to those obtained by other techniques[1,2] for the amorphous regions of polyethylene and polypropylene subjected to the same degree of elongation. It should also be noted that the orientation parameters derived for the crystalline regions of these polymers are much higher for the same stretching conditions.[1,2,9,10] These observations confirm our premise that tetrafluoroethylene is incorporated only into the amorphous regions of polyethylene and polypropylene, the C_2F_4 molecule being too large to be accommodated between the polymer chains in the crystalline phases.

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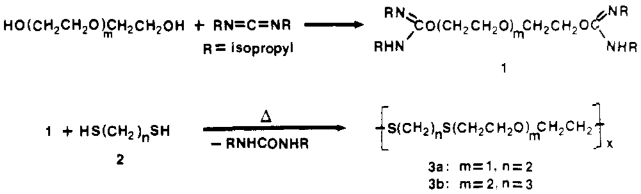
Sequential Copolymers of Oxyethylene Oligomers and α,ω-Poly(methylenedithiols)

Poly(oxyethylene) $(CH_2CH_2O)_n$, poly(thioethylene) $(CH_2CH_2S)_n$, and their homologues and copolymers are currently under widespread investigation. One main area of interest involves theoretical and experimental conformational analysis. Dielectric measurements[1] and viscosity[2] determinations are two techniques applicable to such studies. A few examples of the polymers recently examined include poly(1,3-dioxolane), $[CH_2OCH_2CH_2O]_n$,[2] poly(thiodiethylene glycol), $[CH_2CH_2OCH_2CH_2S]_n$,[3] and poly(1,3-dioxa-6-thiocane), $[CH_2CH_2OCH_2OCH_2CH_2S]_n$.[1]

A second area being explored involves the crystallinity and thermal behavior of these polymers. While poly(oxyethylene) (POE) melts around 66 °C, poly(thioethylene) (PTE) has a melting point of 210 °C.[4] We are interested in the effect on the thermal behavior of PTE of nonrandom replacement of thioethylene units with oxyethylene moieties. From a different perspective, the nonrandom substitution of oxyethylene units in POE with dithio(polymethylene) groups poly(1,3-dioxa-6-thiocane), also attractive. Related work with low molecular weight alkoxy-end-capped POE indicated significant changes in crystallinity and fusion properties with increases in the length of the alkyl groups.[5] The crystallinity of a series of sequential copolymers with increasing polymethylene chain length between thioether groups would, thus, be of fundamental interest.

A more recent development in the chemistry of POE and its derivatives lies in their similarity to the macrocyclic crown ethers. The cation binding ability of the crown ethers has led to widespread application as phase-transfer catalysts (PTC).[6] We recently reviewed the use of crown ethers and PTC in polymer chemistry.[7] One important discovery is the ability of POE to act as an efficient PTC in a manner similar to crown ethers. This suggests a potential of oxy–thio copolymers, for example, to function as PTC and cation-complexing agents. Thio-containing polymers should interact especially well with certain transition-metal ions. We are currently developing a program involving synthesis of such sequential copolymers for examination of their physical and catalytic behavior.

Scheme I



The poly(thiodiethylene glycol) and poly(1,3-dioxa-6-thiocane) mentioned above were obtained by condensation methods which gave only low molecular weight polymer. In a recent review of the chemistry of isoureas,[8] we had suggested the use of bisisoureas derived from oligo(oxyethylenes) for polymer synthesis by condensation with appropriate difunctional nucleophiles. We find that this method appears to be generally applicable to the synthesis of oxy–thio copolymers. The synthesis (Scheme I) involves initial formation of the bisisourea 1 (as previously described[8]) from the simple, high-yield addition of the oligo(oxyethylene) to excess *N*,*N*′-diisopropylcarbodiimide. Purification of 1[8] is followed by thermal condensation with an α,ω-dithioalkane **2** to give the copolymer **3**.

A typical procedure involves the bisisourea of diethylene glycol (1, $m = 1$) prepared and purified as previously described[8] and ethanedithiol (2, $n = 2$; freshly distilled at 0.2 mmHg and 30 °C). The reagents 1 (3.58 g, 0.01 mol) and **2** (0.94 g, 0.01 mol) were mixed together with anhydrous KF (0.93 g, 0.016 mol) in a polymerization tube which was then sealed under nitrogen. The tube was placed in an oil bath and the temperature gradually brought to 140 °C, where it was held for 3 days. The cooled mixture was then separated into several fractions by sequential extraction with benzene, tetrahydrofuran, methanol, water, and finally chloroform. The polymer was recovered in fair-to-good yield from the chloroform extract by rotary evaporation. Reprecipitation from chloroform into methanol gave pure polymer **3a** with a melting point of 87–91 °C and an intrinsic viscosity of 0.22 dL/g in chloroform at 30.0 °C. Anal. Calcd for $C_6H_{12}S_2O$: C, 43.87; H, 7.36. Found: C, 44.60; H, 7.72.

Essentially the same procedure was used for condensation of triethylene glycol bisisourea (1, $m = 2$) and 1,3-propanedithiol (2, $n = 3$) to give polymer **3b** with an intrinsic viscosity of 0.96 dL/g. No melting point was obtainable for this tacky, soft material.

The ^1H and ^{13}C NMR spectra of polymers **3a** and **3b** are given in Figure 1. The ^1H integration ratios and chemical shifts are entirely consistent with the expected product structures. The ^{13}C NMR shifts, intensities, and T_1 relaxation parameters are similar to those of POE and a new class of polyureas recently synthesized in this laboratory containing a structurally related macrocycle in the polymer backbone.[9]

The generality of this procedure is being further explored for a series of oligo(oxyethylene) bisisoureas with several additional alkane and aromatic dithiols. The full paper will contain additional synthetic details and complete physical and spectroscopic characterization of these now readily available sequential copolymers.

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