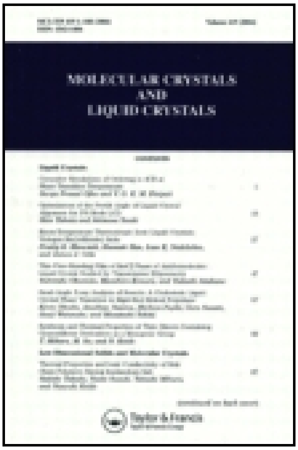

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Spin Labelling at Oxidation Sites in Polymers

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SPIN LABELLING AT OXIDATION SITES IN POLYMERS

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Abstract The selective spin labelling of polypropylene films for monitoring the molecular dynamics at the oxidation sites has been obtained by reacting 3-chloroformyl-2,2,5,5-tetramethylpyrroline-1-oxyl with the OH groups formed in the photooxidation. The line shape changes of the ESR spectrum of the spin label, detected as a function of the temperature, have been interpreted in terms of a very anisotropic motion with fast rotation about a molecular axis oriented approximately along the N-O bond; also evidence of the presence of two different populations of nitroxides with different mobilities has been obtained. The use of sulphonyl radicals as novel probes for molecular motion in polymers has also been tested.

Keywords: Spin Label, Polypropylene films, Electron Spin Resonance, Motional Anisotropy, Oxidation sites, Radiation, Molecular Dynamics

INTRODUCTION

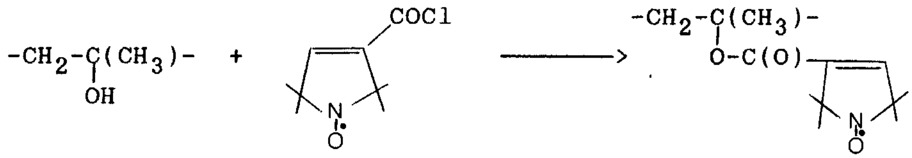
The justification of this work comes from the idea that the products arising from the oxidative degradation of polymers can be used to insert spin labels. The spin labels are therefore located at the reaction site and can yield information on the reaction site, its morphology and the nature and frequency of the motion at that site. These techniques are different than the usual ones. Normally the label is first added to the molecule and the molecular assembly is then formed. The label may thus cause a perturbation of its environment in its vicinity. In the technique reported here, the molecular assembly, be it polymer as in this communication, or crystals, is first formed and the spin label is then added in situ. This may cause less perturbation than normal. In addition, the very fact that the label can be added tell us something about the nature of the unperturbed matrix. In previous work, examples of the use of peroxyradicals for monitoring the molecular motion in connection with the progress of oxidation processes in crystalline organic compounds and polypropylene have been reported (1,2,3,4,5). In this work a demonstration is given of the possibility of spin labelling isotactic polypropylene using nitroxide radicals and sulfonyl radicals as probes of motion.

Spin Labelling of Photooxidized Polypropylene with Nitroxide Radicals

Isotactic polypropylene films (97.5% isotacticity, bioriented films 38 μ thick) were submitted to photooxidation in a Uvicon apparatus at about 40-60°C up to an absorbance of 0.004/micron at the carbonyl band (1713 cm-1). The photooxidation process is known to yield a variety of compounds, among which are terminal and intrachain ketones and alcohols as major products which arise mainly from the radical attack on the tertiary C-H bonds:

$$-CH_2CH(CH_3)CH_2- \longrightarrow CH_3C(=O)CH_2- \;,\; -CH_2C(=O)CH_2-$$
$$\longrightarrow -CH_2C(OH)CH_2- \;,\; \text{etc.}$$

The insertion of nitroxyl labels has been achieved by reacting the OH groups with 3-chloroformyl-2,2,5,5,-tetramethylpyrroline-1-oxyl according to the reaction (6):



The films of polypropylene were refluxed in benzene solutions for 5 hr, and then washed with boiling benzene until there was no trace of nitroxide in the washing benzene, and then dried under vacuum at 60°C. The concentration of the nitroxide thus attained was large enough (c.a. 10^{-5} mol/l) to yield ESR signals suitable for molecular dynamics studies of the polymer (Fig.1).

Analysis of the ESR spectra of nitroxide spin labels.

Tests for detecting the degree of alignment of the nitroxide radicals were performed by recording the ESR spectra as a function of the angle between the main stretch direction of the films and the magnetic field. The lack of observation of any appreciable angular dependence led to the conclusion that the nitroxide radicals are randomly oriented and therefore confined to the amorphous phase. This result may appear partially at variance with the observations stemming from the spin labelling experiments with peroxyradicals which have shown a significant degree of alignment at the oxidation sites (4,5); the difference may be explained by considering that, because of the steric hindrance due to the molecular size, only the amorphous regions are accessible to the reactant acyl chloride. Therefore, as a method for spin labelling at the oxidation sites, the use of nitroxides seems to be less efficient than the use of molecular oxygen.

The line shape changes recorded as a function of the temperature have been analyzed using the model of the "very anisotropic rotational reorientation" by adopting the procedure based on the rigorous theory of J .H. Freed and coworkers (7). In the present case the nitroxide was assumed to undergo a rapid rotation about a molecular axis approximately along the direction of the bond connecting the polymer chain to pyrroline moiety, whilst the motion perpendicular to this axis was much slower. This model implies that the N-O bonds must undergo some precession motion about the x direction (Fig.1) with a relatively small angle of precession which has been neglected in the computer simulation.

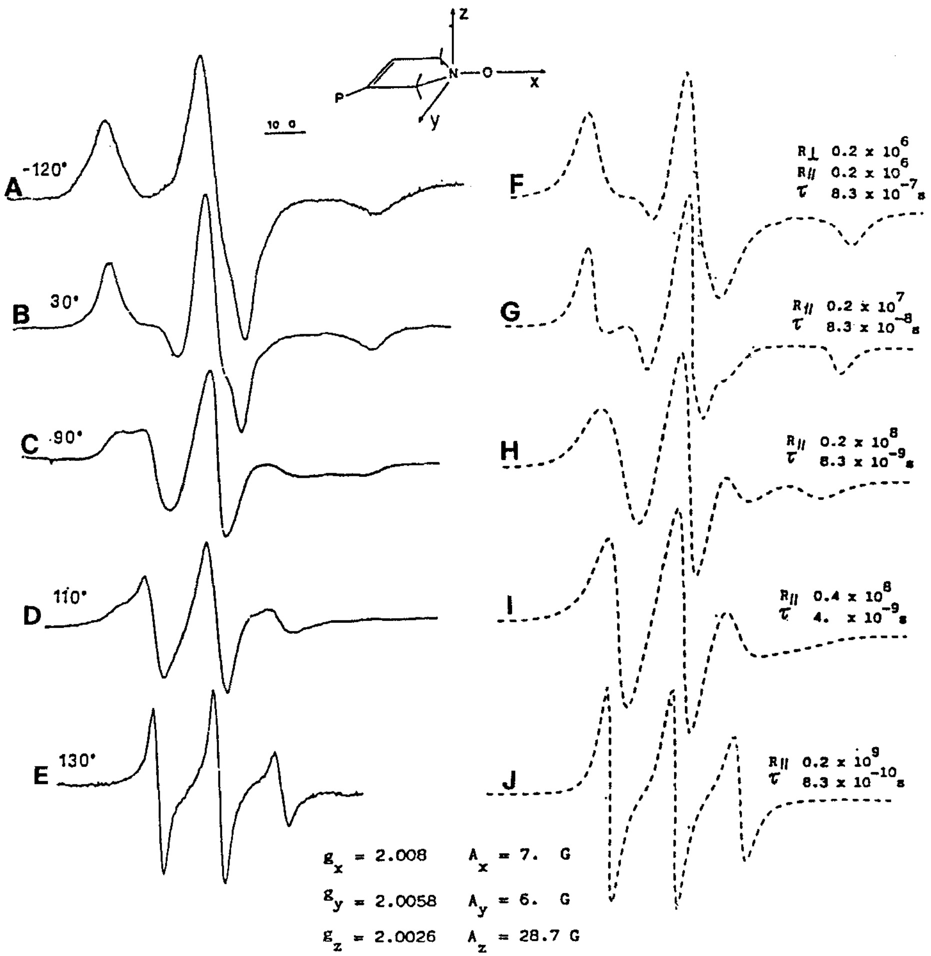


FIGURE 1 Experimental and calculated ESR spectra of the nitroxide spin labels. The calculations have been performed under the approximation of a very anisotropic rotation with $R_{//} >> R_{\perp} = 0.2\text{x}10^6$ (rad/s). The correlation times refer to $R_{//}$. (The axis of rotation defined by the polymer-C-N direction, the N-O bond precession angle being assumed negligible).

In the simulations shown in Fig. 1, the parallel value of the rotational tensor $R_{//}$, which is related to the fast component of the motion, was varied through the range 10^6 to 10^9 rad./sec whilst the perpendicular value $R_{\perp}$ was kept constant at a rigid limit value of about 10^6 rad./s. The spectrum recorded at 130 °C could also be simulated by applying the simplified theory of Hubbell and McConnell (8) which uses a time independent Hamiltonian with effective axial A' and g' tensors obtained from the principal values and the direction cosines α_i through the equations:

$$A' = \Sigma\alpha_i^2 A_i \quad ; \quad A' = \Sigma(1-\alpha_i^2)$$

$$g' = \Sigma\alpha_i^2 A_i \quad ; \quad g' = \Sigma(1-\alpha_i^2)$$

This method could not be used for the lower temperature spectra where time dependent effects induced by $R_{//}$ were significant. The comparison of the experimental and computed patterns show some discrepancies which could not be interpreted by changing the motion parameters (direction of the fast rotation axis, the ratio $R_{//}$ / $R_{\perp}$ and the frequency). In particular it was not possible to reproduce the partially resolved doublet structures in the low field peaks C, D of the spectra (Fig.1). It is seen by inspection that these features can be accounted for by admixing increasing fractions of the spectrum L to the spectra H or I. This is equivalent to assuming the presence of two different populations of nitroxides undergoing motion with different rates, the fraction of more mobile nitroxides increasing with increasing temperature.

Spin Labelling With Sulfonyl Radicals

Sulfonyl radicals RS(O)O· are intrinsically stable species with most of the unpaired spin density localized on the sulphur and oxygen atoms (9). As a consequence, their ESR spectra show no h.f. structure but a significant g anisotropy, which can be used to probe motional states in solids.

The spin labelling of polypropylene with sulfonyl radicals has been achieved by adopting a method originally developed by G.Adler and coworkers for crystalline amides (1 and references therein). Powder samples of isotactic polypropylene were submitted to gamma irradiation under vacuum to generate the tertiary macroalkyl radicals $-CH_2\dot{C}(CH_3)CH_2-$ and then allowed to react with SO_2 according to the equations:

$$CH_2CH(CH_3)CH_2- \longrightarrow -CH_2\dot{C}(CH_3)CH_2-$$

$$-CH_2\dot{C}(CH_3)CH_2- + SO_2 \longrightarrow -CH_2C(SOO^{\bullet})(CH_3)CH_2-$$

The irradiations were performed at 77 K with total doses of about 1.5 Mrad. After the irradiation the samples were warmed up to room temperature and then exposed to SO_2. A nearly complete conversion of the initial radicals was achieved in about 24 hours at room temperature.

The sulfonyl radicals thus obtained gave strong ESR signals which could be monitored for molecular dynamics studies over a wide temperature range from -196 to 70-80 °C (Fig. 2).

Analysis of the ESR Spectra of the Sulfonyl Spin Labels

The ESR spectra of $RS(=O)O^{\cdot}$ spin labels show the characteristic features expected from an axially symmetric g tensor with $g_{//} = 2.016$, $g_{\perp} = 2.003$ (Fig.2). Under the effect of the motional modulation a characteristic decrease of the $g_{//}$ to $g_{\perp}$ separation was observed with increasing the temperature which was interpreted by the modified Bloch equations formalism (10) to be due to the fast rotation about the C--S bond. In order to account for the observed shrinkage of g and in agreement with the predictions of MsXα calculations (11) a bent structure close to tethraedral had to be assumed for the sulfonyl group. The onset of time dependent effects was observed at a temperature as low as -100°C. This probe seems therefore to be more suited than the nitroxides for investigating slow motions at low temperatures.

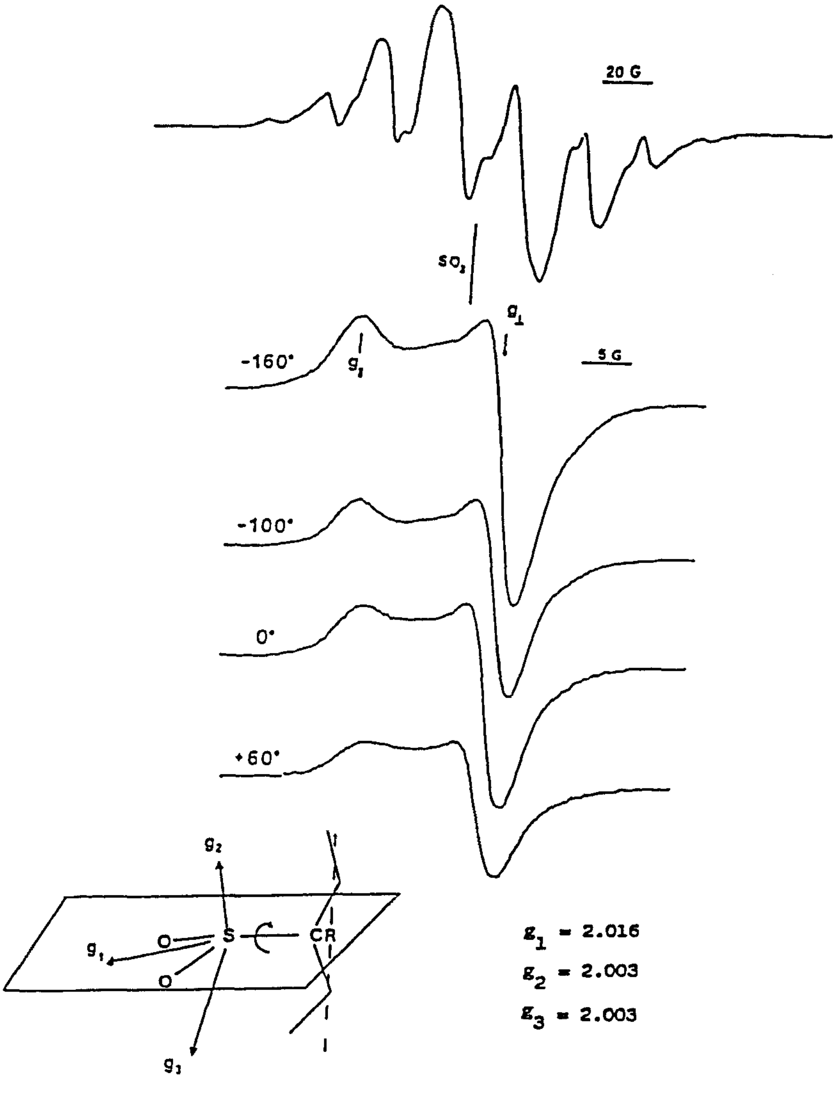


FIGURE 2 ESR spectra of the sulphonyl radical spin label recorded as a function of the temperature, showing the decrease of the $g_{//}$ to $g_{\perp}$ separation due to the slowing down of the rotation about the C-S bond. The top spectrum is that of the polypropylene tertiary macroalkyl radical before the admission of SO_2.

ACKNOWLEDGMENTS

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