complexes in Figure 4. All of these complexes are near maximum stoichiometry. The results show only a gradual decrease in conductivity with increasing BH_4^- doping levels (Figure 3); even at 51% BH_4^- the observed conductivity is intermediate between that of pure PEO·$NaBH_4$ and PEO·$NaBF_4$ complexes. Thus, ion transport in crystalline regions of PEO·NaX complexes is not limited to cation motion along helical channels. Ion transport between chains, and/or in amorphous regions, dominates the conductivity in these materials. Transport would then occur by either associative (quintuply or triply coordinated Na^+ in the transition state) motion of the cation between stable quasi-tetrahedral coordination geometries. The motion can occur either within or between helical regions: if a helix is blocked, it can be circumvented by transfer of the cation to an amorphous region or to a neighboring helix.

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Peroxy Spin Probe Studies of Motion in Poly(vinylidene fluoride)

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Abstract: Motional effects in poly(vinylidene fluoride) have been investigated using peroxy radicals as spin probes to contrast with previous studies of peroxy radical motion in polytetrafluoroethylene and in polyethylene. The predominant radical formed by radiolysis at 77 K is $-CF_2-CH_2$. In the presence of oxygen this radical readily converts to the peroxy radical $-CF_2-CH_2-O-O$. The electron spin resonance (ESR) spectrum of this peroxy radical was studied as a function of temperature from 77 to 360 K. The ESR spectrum measured at both 9 and 35 GHz revealed changes in the spectral line shapes due to averaging of the g anisotropy which is attributed to motion in this polymer. Various motional models including polymer chain-axis rotation, C–O bond rotation, and a cubic jump process were considered. The experimental variations in the spectra are best fit with a C–O bond rotation model with 180° jumps for a COO angle of 104° in a temperature range between 77 and 280 K. However, above 280 K extra lines between the $g_\parallel$ and $g_\perp$ regions of the spectra indicate that a cubic jump motional process dominates. This is presumably related to the greater freedom of motion at the higher temperature. The cubic jump motional process can be interpreted as a helical twisting motion of the end of a polymer chain.

Introduction

Peroxy radical formation is ubiquitous in irradiated polymers in the presence of oxygen and can easily be studied by electron spin resonance (ESR).[1] Peroxy radicals have been implicated in radiative and photooxydegradation processes of polymers. Not only must the chemistry of the peroxy radical be important in these polymer degradation processes, but also the types of internal motions of the peroxy radical site in the polymer framework must be of importance. Schlick and Kevan[2] have recently demonstrated that peroxy radicals are effective spin probes for elucidation of *specific* motional mechanisms in solids. It is possible to distinguish between rotation of the peroxy group around a C–O bond by a specific number of large angle jumps, cubic jump motion in which the g tensor of the peroxy radical is rotated around the body diagonal of a cube, and chain-axis rotation by large angle jumps in the case of polymeric systems. Two general classes of peroxy radicals may be formed in long-chain polymeric systems. One class consists of midchain peroxy radicals where the peroxy radical forms in the middle of the chain without breaking the carbon backbone. The other general class consists end-chain peroxy radicals in which a chain break occurs and the peroxy radical forms there. In a detailed study of peroxy radicals formed in γ-irradiated polytetrafluoroethylene it was found that both midchain and end-chain peroxy radicals could be studied independently. The temperature dependence of their ESR spectra indicated that the midchain peroxy radical principally undergoes cubic jump motion.[3] Peroxy radicals in polyethylene have been studied less completely, and the results indicate that either chain-axis rotation or C–O bond rotation motional mechanisms may be applicable,[4] although the most recent results suggest that chain-axis motion probably dominates for the midchain peroxy radicals in polyethylene.[5] On the other hand, when the polymer side groups can offer more steric hindrance to chain-axis motion such as in the methacrylates or in polypropylene, there is little evidence for chain-axis motion of the peroxy radicals formed in such polymers.[6]

Here we study the motion of peroxy radicals in poly(vinylidene fluoride) (PVF_2) and contrast the results to the cases of polyethylene and polytetrafluoroethylene. Although there appear to be few reports involving electron spin resonance studies of radicals produced in PVF_2,[7,8] there have been several recent reports on PVF_2 because of its net internal polarization.[9] This leads to a strong piezoelectricity,[10] pyroelectricity,[11] and interesting Brillouin scattering effects.[12] Thus the study of specific motional mechanisms as a function of temperature by the use of peroxy radical spin probes is not only of interest for comparison with other types of polymers but also because it may reveal information about the types of motion that are important in some of these effects due to the consequences of net polarization in the polymer.

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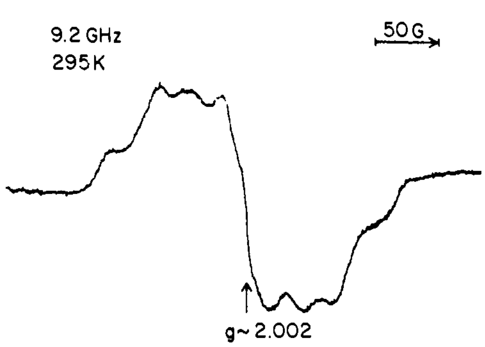

Figure 1. Room-temperature ESR spectrum of poly(vinylidene fluoride) γ-irradiated to 10 Mrad under vacuum.

Experimental Section

Powdered poly(vinylidene fluoride) was obtained from Aldrich Chemical Co. Samples were packed into 4-mm o.d. Suprasil quartz tubes, evacuated to about to 10^{-4} torr at 100 °C for 48 h, and γ-irradiated at 77 K by ^{60}Co γ-rays in a Gammacell-220 irradiator from Atomic Energy of Canada, Ltd. The typical dose was about 6 Mrad at a dose rate of 1.9 Mrad h^{-1}.

ESR spectra were obtained at X band (9.1 GHz) on a Varian E-4 ESR spectrometer and at Q band (35.0 GHz) on a Varian E-line ESR spectrometer. At X band temperature variation was carried out by circulating cold nitrogen gas, obtained by heating liquid nitrogen, through the ESR cavity using a flow system. At Q band experiments were done only at room temperature. Temperatures were measured to ±2 °C using a copper–constantan thermocouple with digital readout. The g values were estimated using diphenylpicrylhydrazyl (DPPH) with $g = 2.0036$ as a standard. Computer simulations were performed on a Tektronix-4052 minicomputer coupled with a digital plotter and interfaced to a Honeywell 60/66 large computer.

Results

γ-Irradiation of PVF_2 under vacuum at room temperature produces an alkyl-type radical with an ESR spectrum as given in Figure 1. Previous studies on PVF_2 radiolysis have been carried out at very high dose in which polyenyl radicals have been produced.[7,8] Apparently the alkyl-type radical produced at low dose has not been assigned. We note that the spectrum in Figure 1 is quite symmetrical with $g \sim 2.002$ and has at least seven partially resolved hyperfine components. The total spectral width is about 220 G and this will be the main criteria that we use to try to assign this spectrum. Alkyl radicals I–IV be expected to form in this

$$\underset{\text{I}}{-CF_2\dot{C}HCF_2-} \qquad \underset{\text{II}}{-CH_2\dot{C}FCH_2-} \qquad \underset{\text{III}}{-CH_2\dot{C}F_2} \qquad \underset{\text{IV}}{-CF_2\dot{C}H_2}$$

polymer. These radical types all involve α and β fluorine or proton hyperfine couplings. α-Fluorine couplings are typically 177 G for the parallel component and 25 G for the perpendicular component as exemplified by the CF_2CONH_2 radical.[13] β-Fluorine hyperfine constants vary from about 30 to 70 G in fluorinated polymers.[14] In polyethylene the α and β proton coupling constants are typically about 23 and 33 G, respectively.[15] The total spectral width for the various radical types considered, I to IV, can be roughly approximated as about 260 G for I, 300 G for II, 420 G for III, and 170 G for IV. The experimental width of about 220 G seems most compatible with either radical I or IV. A crude analysis assuming α proton splittings of 30 G and β fluorine splittings of 60 G predicts an even number of lines for I and an odd number of lines for IV. On this basis we suggest that the spectrum in Figure 1 is predominantly due to radical IV although there may be some mixture of radicals I and IV. We will find that the motional analysis of the temperature dependence of peroxy radical spectra seems compatible with an assignment of the spectrum in Figure 1 to predominantly radical IV.

In the presence of air at room temperature the alkyl radical spectrum in Figure 1 rapidly transforms to a peroxy radical spectrum as shown in Figure 2. The peroxy radical is clearly identified by its characteristic g values of $g_{\parallel} = 2.0037$ and $g_{\perp} = 2.005$ at 77 K as shown in Figure 2. Based on our assignment of the alkyl radical spectrum we assume that this peroxy radical is $-CF_2-CH_2-O-O$.

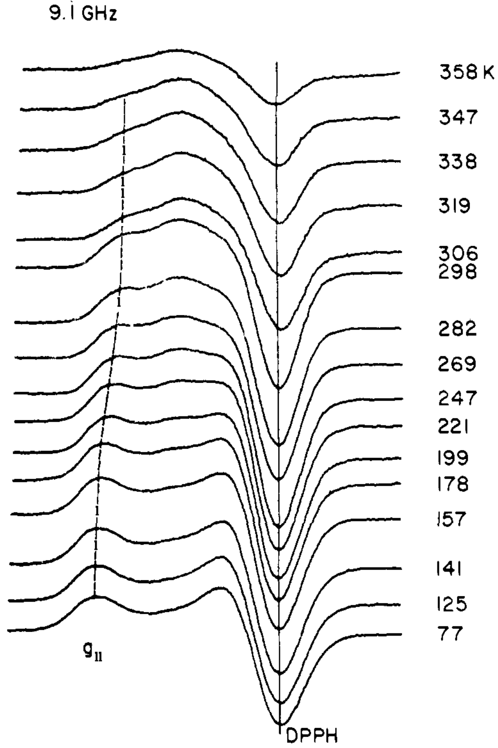

Figure 2. Temperature dependence of the ESR spectra of peroxy radical in poly(vinylidene fluoride). The dashed line indicates the shift of the $g_{\parallel}$ feature.

The alkyl and peroxy radicals in PVF_2 increase linearly with γ-dose to about 3 Mrad and reach a plateau at about 7 Mrad.

In Figure 2 the temperature variation of the ESR spectra of the peroxy radical measured at 9.2 GHz is given. There is little change in the spectra between 77 and 140 K, but at higher temperatures two prominent features are observed. First, the $g_{\parallel}$, component shifts from 2.037 at the lower temperature to 2.030 at higher temperatures in a roughly linear fashion. Second, a broad "extra" feature is observed between the $g_{\parallel}$ and $g_{\perp}$ regions above ca. 250 K. The intensity of this "extra" feature increases monotonically with temperature above 250 K. These observed ESR spectral changes are completely reversible with temperature.

To obtain a better resolved spectrum of the "extra" feature, an ESR spectrum was recorded at Q band (35 GHz) at 298 K and is shown in Figure 3. This "extra" feature clearly has a doublet structure which is only resolved at 35 GHz. Such temperature-dependent "extra" features in the ESR spectra of peroxy radicals were originally observed for the triphenylmethylperoxy radical and interpreted in terms of specific motional mechanisms.[2] Such features have also led us to delineate specific motional mechanisms of peroxy radicals in polytetrafluoroethylene[3] and will be of use in determining the motional mechanism in PVF_2 here.

Simulated ESR Spectra

As mentioned in the Introduction the temperature-dependent ESR spectra due to motional averaging of the g-anisotropy of peroxy radicals can often be successfully simulated by using the method of modified Bloch equations for a chain-axis rotation model with 90 or 120° jumps, a CO bond rotation model with 120 or 180° jumps, and a cubic jump model.[2–4,6,16] The theoretical expressions for the simulations as well as simulated spectra for the various motional models have been given in our previously

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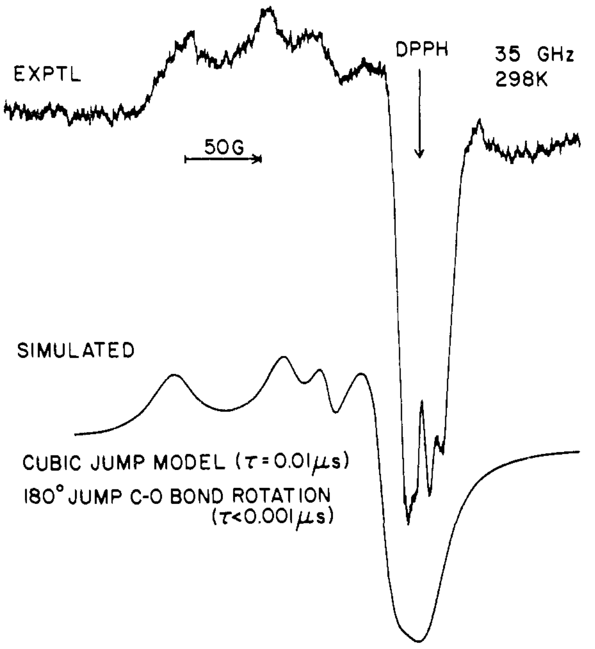

Figure 3. Upper: 35-GHz ESR spectrum of the peroxy radical in poly(vinylidene fluoride). Lower: Simulated ESR spectrum of the peroxy radical for a motional model involving (1) C–O bond rotation with 180° jumps for a COO bond angle of 104° and a correlation time $\tau < 0.001$ μs, and (2) cubic jump motion with a correlation time $\tau = 0.01$ μs. The low-temperature rigid limit g tensor for a "static" configuration used in the C–O bond rotation model is $g_1 = 2.037$, $g_2 = 2.0078$, and $g_3 = 2.0020$. These g values are averaged to $g_1^r = 2.030$, $g_2^r = 2.008$, and $g_3^r = 2.003$ by fast C–O bond rotation. These g^r values are used as the "static" values in the cubic jump model calculation. The line-width parameter in the simulated spectrum is 18 MHz.

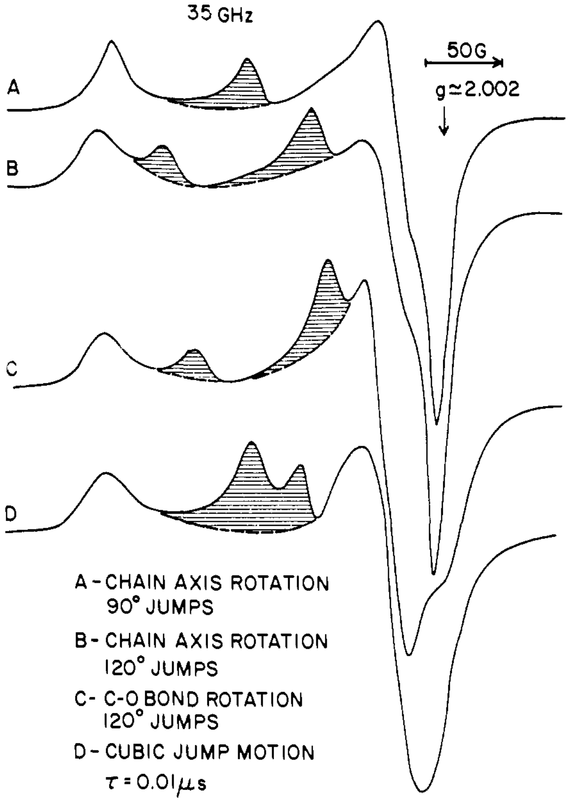

Figure 4. Simulated ESR spectra for peroxy radicals for the following motional mechanisms at an intermediate correlation time of $\tau = 0.01$ μs: (A) chain-axis rotation by 90° jumps, (B) chain-axis rotation by 120° jumps, (C) C–O bond rotation by 120° jumps with a COO angle of 104°, (D) cubic jump motion. In these simulations the rigid limit g tensor and a line width of 20 MHz were used.

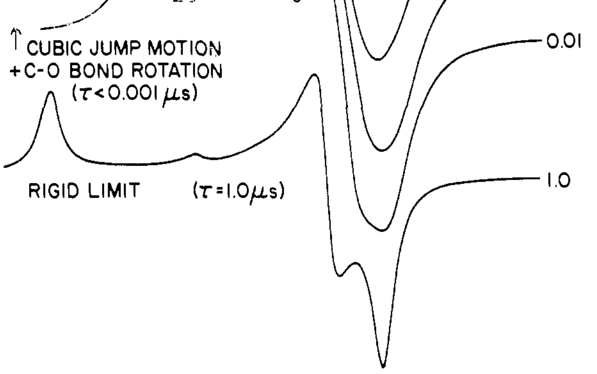

Figure 5. Simulated ESR spectra of peroxy radical motion for cubic jump motion at various correlation times, τ, in the presence of fast C–O bond rotation by 180° jumps. The lower spectrum is the rigid limit simulation for $\tau = 1.0$ μs and the experimental g tensor. The other spectra are simulated with the averaged values of the g tensor derived from fast C–O bond rotation by 180° jumps. The line-width parameter is 18 MHz in all the simulated spectra.

cited papers and we will not repeat the formalism here.

In the present PVF_2 system the major averaging feature in the spectra in Figure 2 at lower temperature is a small shift in the $g_\parallel$ component. This type of spectral change was also seen for the methacrylate polymers and for polypropylene.[6] This spectral change is characteristic of a CO bond rotation model with 180° jumps for a COO bond angle of 104°. The other motional models mentioned will not account for the observed spectral change at low temperature in Figure 2 so this specific one is identified.

However, at higher temperature above about 280 K we see an additional spectral feature in Figure 2 which becomes more prominent at higher temperatures, namely, the existence of "extra" features between the $g_\parallel$ and $g_\perp$ regions. Such "extra" features are a physical consequence of motional averaging of the g-anisotropy and may be regarded as a type of line-shape change. These features indicate that after nearly complete averaging of CO bond rotation *via* 180° jumps there is an additional motional mechanism that becomes important at temperatures above 280 K. To identify this additional motional mechanism we have simulated 35-GHz ESR spectra for several different motional models for an intermediate jump time of $\tau = 0.01$ μs in Figure 3. One sees that the chain-axis rotation model with 90° jumps gives only a single extra feature, whereas the experimental spectrum shows two closely spaced extra features. Also the chain-axis rotation model for 120° jumps gives two extra features, but they are much more widely spaced than in the experimental spectrum. The CO bond rotation model with 120° jumps and a COO angle of 104° give two extra features more widely spaced than those observed experimentally. No simulation is shown for CO bond rotation with 180° jumps, but in this case there are no extra features observed at all. However, the cubic jump model shown in Figure 4 shows two closely spaced extra features which are in quite good agreement with those observed experimentally. Thus we deduce that the additional motional mechanism that becomes important at high temperatures is a cubic jump motion.

Figure 5 shows simulations involving both the CO bond rotation model with 180° jumps at low temperature and the cubic jump model at higher temperature which exhibit the features found in the experimental spectra shown in Figure 2. The simulations in Figure 5 are made for 35-GHz ESR spectra because the resolution of the various spectral features is more clear than at 9 GHz. For the static spectrum at low temperature with $\tau = 1$ μs the g tensor of the experimental spectrum is used as given in the figure caption so the experimental spectrum is reproduced. For the CO bond rotation model with 180° jumps the only spectral change as τ is decreased is a shift in the $g_\parallel$ component from 2.0037 to 2.0030 for rapid motion with $\tau = 0.0001$ μs. Experimentally it is found that the g does shift by this extent. Thus the spectrum at 280 K is completely averaged with respect to this CO bond rotation model with 180° jumps. To then apply the cubic jump model one uses the g tensor for this averaged situation rather than the static g tensor for the low-temperature spectrum. This g tensor averaged by CO bond rotation is $g_1^r = 2.030$, $g_2^r = 2.008$, and $g_3^r = 2.003$. For a correlation time for the cubic jump model of $\tau = 0.01$ μs, the overall simulated spectrum is in quite good agreement with the experimental spectrum observed at room temperature in Figure 3. Figure 5 then shows what happens to this spectrum at shorter τ values corresponding to higher temperatures. The position of the $g_\parallel$ component does not change as the cubic jump motion increases in frequency, but it broadens and ultimately disapears exactly as seen in the experimental X-band spectra in Figure 2. In Figure 5 the prominent doublet extra feature for $\tau = 0.01$ μs broadens into a singlet which broadens further as τ is decreased. This behavior is exactly what is observed with less resolution in the X-band spectra in Figure 2. Thus this set of combined specific motional mechanisms that we have deduced fit the experimental spectra quite well.

Discussion

This work has again shown that peroxy radicals are very effective probes for identifying specific motional mechanisms in polymers. It is of interest to compare the results on PVF$_2$ with our previous study on the motion of peroxy radicals in polytetrafluoroethylene. In polytetrafluoroethylene[2] it was possible to identify and separately study two different structural types of peroxy radicals, midchain peroxy radicals and end-chain peroxy radicals. The midchain peroxy radicals were found to undergo a polymer chain-axis rotational motion whereas the end-chain peroxy radicals underwent a cubic jump motion and became completely averaged to give an isotropic ESR spectrum at room temperature. The fact that we deduce the predominant high-temperature motional mechanisms to be of the cubic jump type in PVF$_2$ is consistent with our identification of the peroxy radical in this system as an end-chain peroxy radical.

However, because of the two motional mechanisms that we have deduced in different temperature regions for the end-chain peroxy radical in PVF$_2$, we have reexamined the results on the end-chain peroxy radical in polytetrafluoroethylene[3] and find that there is also evidence there for two motional mechanisms which we did not recognize originally. If one examines Figure 2 in ref 3 it is seen that between 133 and 178 K the $g_\parallel$ component of the end-chain peroxy radical in polytetrafluoroethylene shows a small shift which we now recognize as characteristic of CO bond rotation with 180° jumps. Above 178 K the $g_\parallel$ component broadens and becomes undetectable but does not continue to shift. At the same time the prominent extra feature similar to what is also observed in PVF$_2$ is seen to increase, broaden, and ultimately become the position of the average isotropic spectrum at high temperature. In the case of the end-chain radical in polytetrafluoroethylene this averaging is complete by room temperature.

A very interesting difference between the motion of the end-chain peroxy radicals in polytetrafluoroethylene and poly(vinylidene fluoride) is that the temperature range in which the motional changes occur is much higher in poly(vinylidene fluoride). This implies much more hindered motion in this polymer than in the completely fluorinated one. Substitution of fluorine for hydrogen in a polymer like polyethylene introduces a larger dipole moment and a larger van der Waals radius for that atomic substitution.[17] However, these factors cannot account for the more hindered motion in poly(vinylidene fluoride) with respect to polytetrafluoroethylene. We suggest that the difference is primarily due to differences in the configurations of the main polymer chain in these two types of polymers. In poly(vinylidene fluoride) the planar zig-zag conformation is not favored; instead a trans-gauche-trans-minus–gauche conformation is suggested both in recent crystal structure work[18] as well as in a comprehensive reevaluation of the dielectric properties of fluorinated polymers.[17] In contrast, in polytetrafluoroethylene (PTFE) a planar zig–zag conformation is favored.[17]

The very interesting point is that the difference in the temperature ranges over which the motion of the end-chain peroxy radical becomes rapid in PVF$_2$ and PTFE seems to correlate with the different morphology of the polymer chain backbone. The type of motion that each end-chain peroxy radical undergoes seems to be identical on a molecular scale. This may not be too surprising for the case of an end-chain radical, but it would be interesting to try to followup this point for midchain polymer radical motion.

We cannot make a similar comparison of the temperature range or the type of motion of end-chain peroxy radicals in polyethylene because only midchain peroxy radicals are predominantly formed in polyethylene.[5]

Since the cubic jump motional model has become of some general importance for the motion of end-chain peroxy radicals, it is of interest to try to develop a more detailed molecular picture of this motion. The cubic jump occurs when the three principal g values of the g tensor exchange about the body diagonal of a cube in a three-jump process. From a molecular view this implies that the polymer molecule or the end of the polymer molecule tumbles in three-dimensional space in a helical twisting motion. Such a molecular motion seems more probable for the end of the polymer chain than for the middle of one. It also is clear from the analysis presented in this paper on PVF$_2$ and PTFE that the activation energy for this helical twist motion is greater than that for CO bond rotation of a peroxy radical at the end of a polymer chain.

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