mal conditions (2 hr at 350°), but no isomer comparison is possible here, as 3 was not included in that work.

(19) (a) For comparison, all-aromatic (1,3- and 1,4-phenylene linked) polyamides, while exhibiting a higher temperature range of incipient breakdown (430–470°), gave relative residual weights of about 50–65% at 600° and 45–60% at 700° (15° min^{-1}; N_2).[19b,c] (b) J. Preston, *J. Polym. Sci., Part A-1*, 4, 529 (1966). (c) F. Dobinson and J. Preston, *ibid.*, 4, 2093 (1966).

A Study of Molecular Motion in Polymeric Solids by Electron–Electron Double Resonance

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ABSTRACT: Single-line ELDOR (electron–electron double resonance) has been used to study molecular motion in polymeric solids. Saturating one spin-packet in an inhomogeneous hyperfine envelope and observing another spin-packet within the same envelope provides a means to determine molecular reorientation as saturation transfer deenhances the ESR transition probability. The ELDOR reduction factor was found to increase with the decrease of temperature in a $1/T$ dependence for different nitroxides dissolved in polystyrene and polypropylene. There is no observable difference between the amorphous and semicrystalline polymers. The nitroxides are mainly in the amorphous phase and its motion is not affected by the presence of the crystalline phase. Polystyrenes spin-labeled on the terminal and side-chain phenyl groups were studied and were found to differ in ELDOR response. The motions of nitroxides in a given polymer are greater for the small-size di-*tert*-butyl nitroxide and smallest for the large maleimide nitroxide. There is also observed a matrix ELDOR signal at the free proton frequency of 13.5 MHz. It is observed only below T_g and in both amorphous and semicrystalline polymers. This may suggest a local order in a polymer solid. Matrix signals in monomer solids are only seen in the polycrystalline state but vanish in the glassy state.

The physico-mechanical properties of a solid polymer are dependent on the molecular motions. Several methods are useful in the study of these motions, such as dielectric relaxation, dynamic mechanical relaxation,[1] and wide-line NMR.[2] The purpose of this paper is to introduce a new technique electron–electron double resonance, ELDOR, which complements the others as well as offering some unique features.

Of course electron spin resonance, ESR, has been used quite extensively to probe molecular motion. The method has seen applications in biological systems[3] and in polymers.[4–11] All these studies[4–11] were made either on polymer solutions or on polymers in the vicinity and above their melting points. Such is the limitation of the EPR method because line width changes are measurable only for motions with $5 \times 10^{-9} \le \tau_c \le 10^{-7}$ sec which is the order of the magnetic anisotrophy. Beyond the short τ_c limit, where τ_c is the rotational correlation time, the line width is determined by unresolved hyperfine splittings. Above the long τ_c limit, powder ESR spectra were obtained.

ELDOR effects for free radicals in solution were first reported by Hyde, Chien, and Freed.[12] This and many subsequent studies explored the effect of saturating one ESR transition on another transition being observed with low microwave power. Since these transitions do not share any common energy level, the transfer of saturation depends upon relaxation processes. An intramolecular electron–nuclear dipolar (END) process and an intermolecular Heisenberg exchange process were found to be responsible for much of the ELDOR effect. Theories have been developed[12,13] to describe these.

Recently, the works of Dalton and coworkers[14] and in our laboratories[15] showed that the ELDOR spectra appear sensitive to τ_c as long as 10^{-3} sec. Therefore, ELDOR can be used to study molecular motions over seven orders of magnitude. In these studies emphasis was placed on single-line ELDOR where the pump and observing frequencies are both set within a single inhomogeneous ESR envelope.

The extension of ELDOR into the long τ_c region suggests the possibility of studying molecular motions in bulk polymers. The central purpose of this work is to apply ELDOR to the study of two types of motion in polymeric materials: those of the macromolecules and those of low molecular weight additives. Results on polystyrene with nitroxide labels either on the terminal groups or on the side chain phenyl rings are described. Also presented are the results of various nitroxide molecules added interstitially to polypropylene and polystyrene.

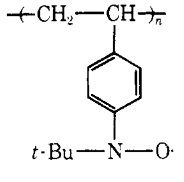
Experimental Section

Three nitroxides were used in the interstitial experiments. The 4-*N*-maleimido-2,2,6,6-tetramethylpiperidine-1-oxyl (maleimide) was synthesized according to the procedure of Griffith and McConnell.[16] 4-Hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TANOL) was obtained from Synvar and di-*tert*-butyl nitroxide (DTBN) from Eastman Organics.

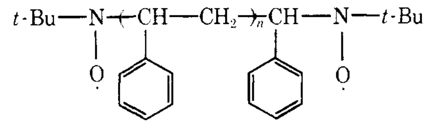
Amorphous polypropylene was Easbond from Tennessee Eastment Co.; semicrystalline polypropylene, Profax 6501, is the product of Hercules, Inc. Amorphous and semicrystalline polystyrene were from Monsanto and Dow Chemical Co., respectively.

To incorporate nitroxides into polystyrene and amorphous polypropylene, the polymer was dissolved in spectral grade benzene (Baker) and nitroxide was added. The solution was dropped onto Teflon sheets and the solvent was removed under vacuum to constant weight. In the case of semicrystalline polypropylene, it was swollen with a benzene solution of nitroxide for several days. The polymer was filtered and washed with benzene and vacuum dried to constant weight. The concentration of the additive was always less than 0.2% by weight which is $<10^{-3}$ *M*; it is found only in the amorphous phase.

Two different types of spin-labeled amorphous polystyrene were used in these experiments. One was labeled at the para position of the phenyl group (SL 1).



The other was terminal labeled (SL 2),



Both samples are the gift of Dr. P. M. Smith[5] of Aberdeen College, Scotland.

A Varian E-800 ELDOR unit was interfaced with a Varian E-9 spectrometer. The bimodal cavity supports two vertical TE_{102} modes which allow normal magnetic dipole transition for both modes. The observing power was 40 mW; the maximum klystron output of ca. 1 W was used for the pump mode. The modulation frequency was 270 Hz to avoid rapid-passage effects.[14,15] The modulation amplitude was such that it provides the maximum ESR signal intensity without causing any line broadening. The temperature of the sample was controlled by the flow rate of cold nitrogen through a thin wall quartz Dewar insert in the ELDOR cavity.

The detailed procedure for measuring single-line ELDOR has been previously discussed.[15b,c] Briefly, the ESR spectrum of the sample was first scanned. Then the observing frequency was positioned such as that indicated in Figure 1. The pump frequency was varied from $\Delta\nu$ = 60 to 5 MHz. Beyond 60 MHz there is no measurable ELDOR response. The ELDOR effect is expressed by a reduction factor $R(\Delta\nu)$ given by

$$R(\Delta\nu) = \frac{\text{ELDOR peak height}}{(\text{ESR signal height with pump off})} \quad (1)$$

Principles of Single-Line ELDOR. The principles of hyperfine ELDOR have been discussed previously.[12,13] However, the single-line ELDOR is a very recent development. A brief outline of the underlying principles and possible mechanisms would greatly facilitate the presentation of data and ensuing discussion.

Single-line ELDOR is concerned with saturation and observation at frequency differences corresponding to various sublevels of a given hyperfine state $|M_s, M_I>$. The energy of a sublevel, i.e., that of a spin-packet, is determined by its orientation, θ and ϕ, with respect to the external field. Saturation transfer is made possible by reorientation of the spin-packet. By the inclusion of a rotational diffusion operator,[14,17–19] the single-line ELDOR deenhancement can be obtained by solving the stochastic Liouville equation[14,19]

$$R(\theta, \phi, \mathrm{Sp}) = \frac{F(\theta, \phi, \mathrm{Sp})}{4\pi} \sum_l \frac{(2l + 1)P_l(\cos\theta)}{l(l + 1)D + {T_{1e}}^{-1}} \quad (2)$$

where $P_l(\cos\theta)$ are Legendre polynomials and F is the distribution function.

The effect of temperature and viscosity on R reflects those for D and T_{1e}. According to the Stokes–Einstein model,

$$D = kT/6\pi a\eta = 2a^2/(9\tau_c) \quad (3)$$

The temperature dependences of the spin-relaxation mechanisms follow from the equations for their associated transition probabilities. For g tensor and spin-rotational mechanisms, at low temperatures and X band so that $\omega_e\tau_c > 1$, this probability has the following functional dependence,[12]

$$W_e = AT/\eta \quad (4)$$

Where A is an essentially temperature-independent quantity. Combination of eq 2–4 showed that R has a η/T dependence. The diffusion probability, W_D, is of course in competition with the other saturation transfer paths such as W_N for electron–nuclear dipolar (END) relaxation, W_{ex} for exchange relaxation, and W_x for cross-relaxations.

Under some conditions[15c] there is observed superimposed on the single-line ELDOR envelope one or two peaks at $\Delta\nu = \nu_p - \nu_0$ of 13.5 and 27 MHz. These frequencies correspond to the free proton precession frequency (ν_H) and $2\nu_H$ at the magnetic fields of the X band, ca. 3300 G. Analogous signals were observed in ENDOR and have been attributed to interaction with nonbonded matrix protons.[20,21] The interaction is most likely to be dipolar in nature and the process may be represented by

$$|M_s, M_I(\theta, \phi)> + H|\alpha> \rightleftharpoons |M_s, M_I(\theta', \phi')> + H|\beta> \quad (5)$$

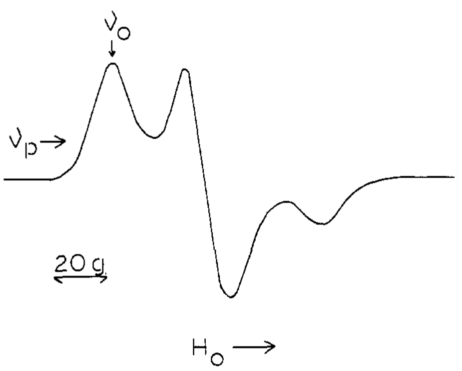


Figure 1. ESR spectrum for nitroxide radical in a solution at −150°C. In this solvent the radical was completely immobilized. In the ELDOR experiments reported herin, ν_0 was positioned as shown; ν_p swept into or away from ν_0 on the low field side.

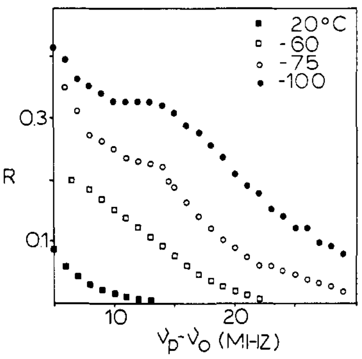


Figure 2. Single-line ELDOR response for maleimide in paraffin oil solution. Samples at 20 and −60°C are glasses and the others polycrystalline. M_I = +1 turning point is the location of ν_0 of the parallel component.

with a probability of W_H equal to[11]

$$W_H(\mathrm{END}) = (1/10){\gamma_e}^2{\gamma_H}^2\hbar^2 \sum_m ({D_n}^{(m)}{D_n}^{(-m)})\tau_c \quad (6)$$

In eq 6 $|M_s, M_I(\theta,\phi) >$ is the hyperfine state having nuclear spin orientation θ,ϕ, and $H|\alpha>$ and $H|\beta>$ are the state functions for the matrix protons. In eq 6 the γ's are the gyromagnetic ratios, and the ${D_n}^{(m)}$ are the anisotropic dipolar terms discussed by Freed and Fraenkel.[22]

Results

Paraffin Oil. The motion of maleimide nitroxide in paraffin oil has been studied as a model for polymer melt. The single-line ELDOR data for maleimide from +60 to −60° were reported previously (Figure 4 of ref 15b). The +20 and −60° results are reproduced in Figure 2 here. Down to −60°, the sample remains glassy. There is no matrix signal in all spectra above this temperature. Paraffin oil becomes polycrystalline below it. The spectra obtained at −75 and −100° in Figure 2 show clearly the matrix peak at 13.5 MHz; there is a hint of a feature at 27 MHz in the −100° spectrum.

The temperature dependence of the single-line ELDOR was shown in Figure 3 as a plot of R values at $\Delta\nu$ = 6 MHz vs. T^{-1}; the data include those given in ref 15b. In the glassy region R increases linearly with T^{-1}; the slope is the same as a similar plot for maleimide in ethylbenzene.[15b] At −73°, where paraffin oil turned paracrystalline in our experiments, there is a discontinuous increase in R, after which R seems to increase slower with further lowering of temperature. Entirely analogous behavior was observed with the ethylbenzene system; the single-line ELDOR line shape changes and a matrix signal emerges when the sam-

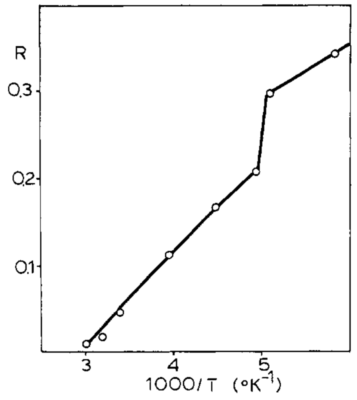


Figure 3. Plot of the ELDOR magnitude at 6 MHz $\Delta\nu$ for the maleimide–paraffin oil solution. Data include those of Figure 2 and ref 15b.

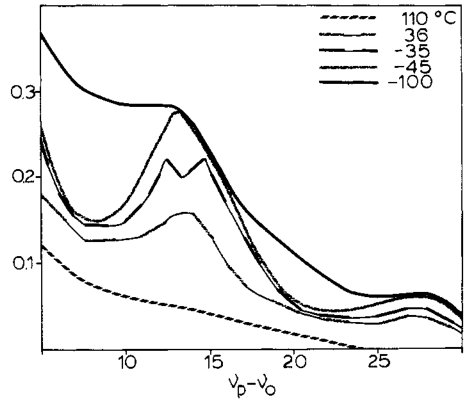


Figure 4. ΔM_I = O ELDOR for maleimide in amorphous polystyrene. ν_o is at the low field turning point. Lines represent averages of a number of scans ($\nu_p > \nu_o$).

ples change from glassy to polycrystalline. Hyde and coworkers[20] observed the matrix ENDOR signal only in polycrystalline samples but not in glassy samples.

Maleimide in Polystyrene. The ELDOR results on maleimide in amorphous polystyrene are given in Figure 4; Figure 5 showed the spectra in semicrystalline polystyrene. In these figures, averages for the line shape at each temperature are plotted for clarity. The spectra were assumed to be made up of the monotically decreasing $R(\nu_p - \nu_o)$ function of the single-line ELDOR and the matrix ELDOR as the additional contribution. The latter is shown in Figure 6 to reach a maximum at about −44°. At the high-temperature region, the R values for matrix ELDOR extrapolate to zero at 101 ± 5°. This corresponds to the T_g of polystyrene. We will use the subscript M, i.e., R_M, to indicate the matrix signal, where R without the subscript refers to the single-line ELDOR deenhancement. The latter increases monotonically with $1/T$.

There is also a second matrix signal at 27 MHz. Because it is weaker than the 13.5 MHx matrix signal, the error involved in estimating its intensity is correspondingly greater. The signal is more prominent at −45° with $R_M \sim 0.065$ which is about 40% of the R_M at 13.5 MHz.

The data for amorphous and semicrystalline polystyrene are the same within experimental error. At the highest temperatures the values of R in one semicrystalline sample seem to rise. This behavior is sometimes observed also in other amorphous polystyrene samples. This point will be discussed further below.

TANOL and DTBN in Amorphous Polystyrene. Two other nitroxides, TANOL and DTBN, both smaller in size

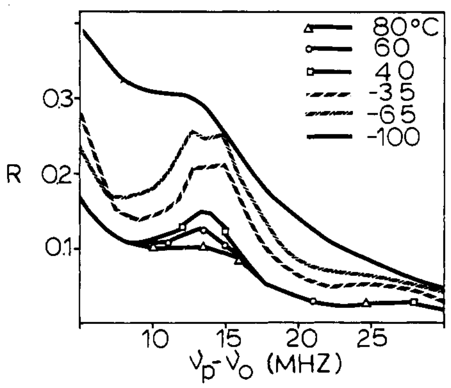


Figure 5. ΔM_I = O ELDOR for maleimide in semicrystalline polystyrene. ν_o is at the low field turning point. Lines represent averages of a number of scans ($\nu_p > \nu_o$).

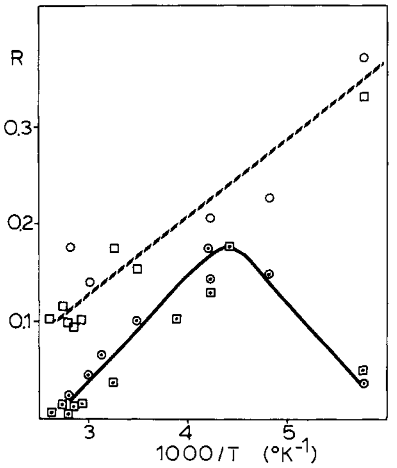


Figure 6. ELDOR magnitude for matrix and single-line contributions to the line shape for maleimide in polystyrene: (□) R at 6 MHz for amorphous polymer; (○) R at 6 MHz for semicrystalline polymer; (⊡) R_M for amorphous polymer; (⊙) R_M for semicrystalline polymer.

than maleimide, were incorporated into amorphous polystyrene. The results are shown in Figures 7 and 8. The matrix ELDOR signals in these samples are generally much weaker than those for maleimide. R_M values reach a maximum at about −64° (Figure 9a) which is about 20° below the temperature for maximum R_M in maleimide. Aside from the anamolous increase of R value at the highest temperatures which has already been commented on above, the single-line ELDOR has R values which increase linearly with $1/T$. The slopes for this variation are the same for the three nitroxides (Figures 6 and 9b), but the lines were shifted horizontally with respect to one another. The value of R = 0.25 was reached at −63.6, −80.7, and −125° for maleimide, TANOL, and DTBN, respectively. This order parallels with the decreasing molecular size and deviation from a spherical shape.

Maleimide in Polypropylene. The ELDOR spectra of maleimide in amorphous and semicrystalline polypropylene are shown in Figures 10 and 11, respectively. The matrix signal begins to emerge at 0° and is very intense at −50°. These are some noted dissimilarities in the ELDOR spectra of polypropylene and polystyrene. In polypropylene the matrix signal almost seems to be borrowing intensity from the normal ELDOR. That is, in the spectra at −10° in both Figures 10 and 11, the single-line ELDOR intensities are much lower than expected based on observations on polystyrene and paraffin oil. This "borrowing effect"

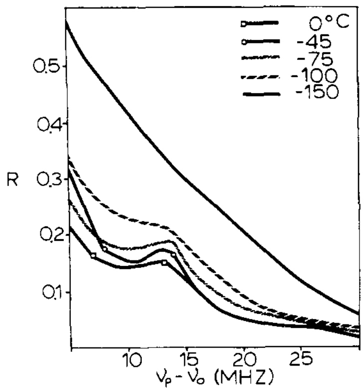


Figure 7. ΔM_I = O ELDOR for TANOL in amorphous polystyrene. ν_o is at the low field turning point. Lines are averages of a number of scans.

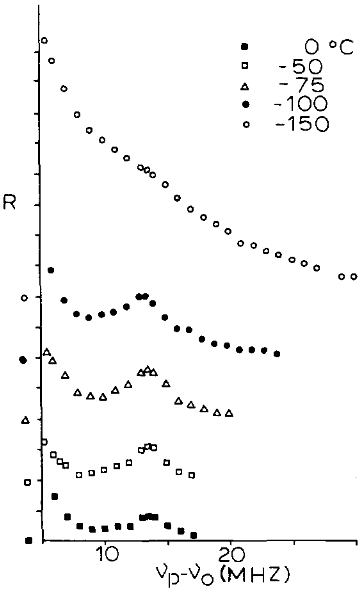


Figure 8. ΔM_I = O ELDOR for DTBN in amorphous polystyrene. Divisions on the R scale are 0.05 units each. The zero has been shifted for each curve for clarity; zero point has been marked on the axis with the appropriate symbol. ν_o is at the low field turning point ($\nu_p > \nu_o$).

may in fact account for the increased R values at high T at 6 MHz for the maleimide–polystyrene system above. The "borrowing" in the latter case is of much smaller magnitude than for polypropylene.

In general, the results for amorphous and semicrystalline polypropylenes are the same. The intensities of the matrix signals and ν_M are nearly the same. The spectra at elevated temperatures are actually superimposable.

Spin-Labeled Polystyrene. The ELDOR spectra of the two spin-labeled polystyrenes (Figures 12 and 13) showed significant differences between themselves and with other systems discussed above. The SL 1 sample differs most markedly from all the others. The matrix signal in SL 1 is well-resolved; R_M is nearly constant between 0.06 and 0.10 from −100 to +100°C. The single-line ELDOR intensity also has small temperature dependence. The plot of R (6 MHz) vs. $1/T$ in Figure 14 is only about one-third of that for maleimide in polystyrene (Figure 6) and for SL 2.

The matrix signal is also small for SL 2. However, it does show the kind of temperature dependence shown earlier reaching a maximum value of R_M of about 0.07 and disappears completely at −150°. The slope of R vs. $1/T$ plot for this material is slightly smaller than those seen with interstitial nitroxides.

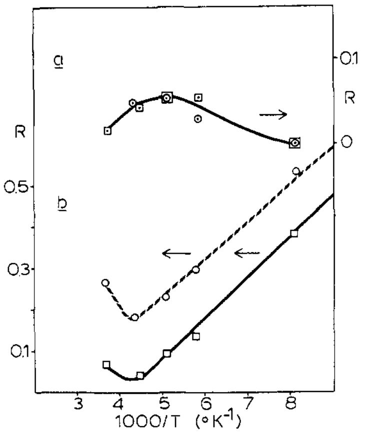


Figure 9. ELDOR magnitudes for separated contributions to line shape: (□) R at 6 MHz for amorphous polymer with DTBN; (○) R at 6 MHz for TANOL; (⊡) matrix signal for DTBN; (⊙) matrix signal for TANOL.

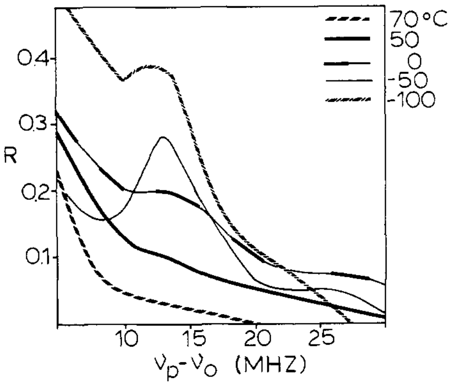


Figure 10. ΔM_I = O ELDOR for maleimide in semicrystalline polypropylene. ν_o is at the low field turning point. Lines are averages of a number of scans.

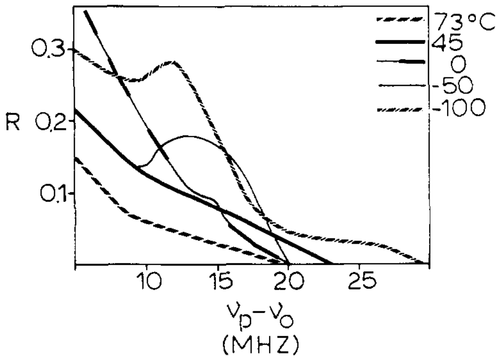


Figure 11. ΔM_I = O ELDOR for maleimide in semicrystalline polypropylene. ν_o is at the low-field turning point. Lines are averages of a number of scans.

Discussion of Results

Temperature Dependence of Single-Line ELDOR. The single-line ELDOR deenhancement is expected to have an η/T dependence according to eq 2–4. However, the actual results in many of the above figures show a simple $1/T$ dependence. This is because polymer viscosity cannot be satisfactorily represented by an equation of the Arrhenius type[23] but is sensitive to free volume.[24] Above T_g, η is inversely proportional to the excess free volume due to

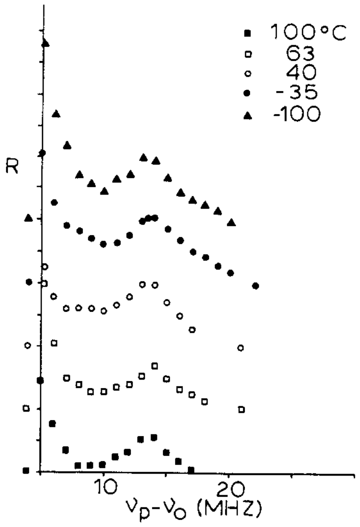


Figure 12. Single-line ELDOR for polystyrene labeled at the para position of the phenyl side chains (SL 1). ν_0 is at the low field turning point. The R scale has zero shifted for each curve; zero is indicated by the approximate symbol. Units of the R scale are 0.05/division.

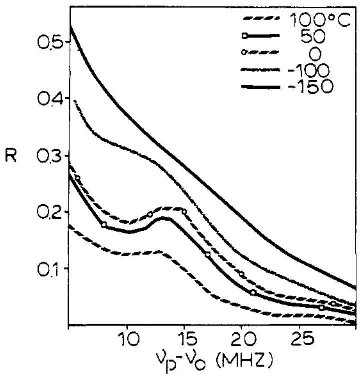


Figure 13. Single-line ELDOR response for terminally labeled polystyrene (SL 2). Lines are averages of a number of scans. ν_0 is at the low-field turning point.

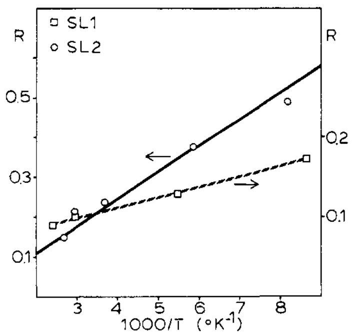


Figure 14. R at 6 MHz for (○) SL 1 and (□) SL 2 vs. T^{-1}. Data are from Figures 12 and 13.

thermal expansion and kinetic agitation. At temperatures below T_g, any changes in free volume with temperature will be much smaller than above it as determined by the polymers thermal expansion coefficients.[25,26] In our measurements below T_g, the observed $1/T$ dependence of R is reasonable.

Matrix ELDOR. The matrix ELDOR effect described above can be definitely attributed to relaxation processes involving nonbonded protons. For instance, R_M for maleimide in perdeuterated polystyrene is only about 65% as large as R_M in normal polystyrene.[15c] Work is underway in our laboratory to see whether the matrix signal can be completely eliminated for perdeuterated maleimide in perdeuterated polystyrene.

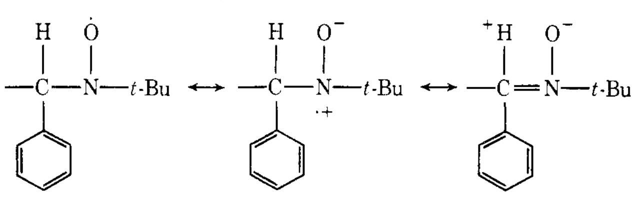
The interaction between the electron spin and the proton spin is probably dipolar in nature. This is supported by the observation that R_M at $2\nu_H$ is about 40% of the value at $1\nu_H$. Similar dependence of M_I was observed in hyperfine ELDOR where the electron–nuclear process is the main relaxation mechanism.[12]

In Figure 6, R_M is seen to have a maximum value at −44°. Similar behaviors are observed in Figure 9a. The explanation may be the following. The probability of W_H(END) is proportional to $\tau_c/(1 + \omega_H{}^2\tau_c{}^2)$. At high temperatures $\omega_H{}^2\tau_c{}^2 \ll 1$ and $W_H(\text{END}) \propto \tau_c$; at low temperatures $\omega_H{}^2\tau_c{}^2 \gg 1$ and $W_H(\text{END}) \propto \tau_c{}^{-1}$. The turning point should occur at $\omega_H{}^2\tau_c{}^2 = 1$. For the free proton precession frequency, this corresponds to $\tau_c = 10^{-8}$ sec.

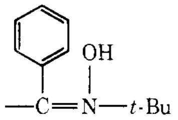
Even though matrix ELDOR is not seen in glassy nonpolymeric systems, it is prominent in amorphous polymers. Hyde and coworkers[20,21] have concluded that only protons less than 6 Å away can interact with the electron to give END relaxation. If the process is reversible as proposed in eq 5, then it will be facilitated if several protons having nearly the same orientation are present in the vicinity of the electron spin. The proton spin flipped by the END interaction can in turn flip another one and so on. In this manner W_H(END) may be facilitated. According to this argument, the results suggest some short-range order in the polymeric systems.

Spin-Labeled Polystyrenes. The results in Figure 12 showed that the slide-chain spin-labels in SL 1 have short correlation time with only a slight temperature dependence. In fact, τ_c does not become long enough even at −150° to cause a decrease in the matrix ELDOR intensity. The nitroxide group is single bonded to a *t*-Bu group and a phenyl group. It is probably capable of undergoing low activation energy motion such as torsional oscillation. This is not true for either maleimide or TANOL where the nitrogen is in the heterocyclic ring. Even in the case of DTBN, the nearly spherical molecule probably moves as a whole unit.

On the other hand, the terminal spin-labels in SL 2 behave more normally than SL 1 both in the magnitude of R values and its temperature dependence. The >NO· group is singly bonded to a *tert*-butyl and a benzyl group. The nitroxide in SL 2 apparently has a long τ_c and has greater barrier for motion than SL 1. The restriction may be the result of hyperconjugation



or the contribution of



to the structure.

Motion of Interstitial Molecules. It has already been noted above that at a given temperature the values of R for various nitroxides are different. This is a manifestation of the τ_c for the molecule being considered. If this is true, then the R values for all the nitroxides should be comparable for a given τ_c. Using the method devised by McConnell and coworkers,[27] τ_c can be estimated from the ESR spectra. This has been done and the results of single-line ELDOR at $\Delta\nu = 6$ MHz were compared at identical τ_c for the three nitroxides. The data do not fall on a single curve as might have been expected from our previous work.[15b] This may reflect the size differential for these nitroxides; the molecular volumes of DTBN, TANOL, and maleimide are in the approximate ratio of 1:1.2:1.6 from molecular models. From the τ_c estimated from the EPR, we find R values of 0.13, 0.19, and 0.32 at $\tau_c = 2 \times 10^{-8}$ sec for maleimide, TANOL, and DTBN, respectively. The ratios of R for the three are 1:1.5:2.5 and in not particularly good agreement with the molecular volume ratios. The trend is correct but the ratios are functions of τ_c. At $\tau_c = 9 \times 10^{-9}$ sec, for instance, the R values are 0.06, 0.12, and 0.18 for ratios of 1:2:3.

It is not surprising that the ELDOR spectra of maleimide in amorphous and semicrystalline polymers are about the same. In the latter cases, the additive is actually found only in the amorphous region of the polymer.

The interstitial additive has lower mobility in polystyrene than in polypropylene at comparable temperatures. For instance, at −100°, τ_c for maleimide in polystyrene is 5×10^{-7} sec and it is an order of magnitude shorter for maleimide in polypropylene.

It is appropriate to compare this new technique ELDOR with other more established techniques such as mechanical and dielectric measurements for transition temperatures of polymer motion and the NMR technique for the determination of correlation frequencies.

Early studies of polystyrene with torsion pendulum[28] revealed the α peak at 116° for 0.9 c/s, which is dependent on molecular weight. The α peak is clearly due to the glass transition since T_g occurs at 100° in atatic polymer.[29–32] T_g for polypropylene, the β relaxation, is found to be at 0° (∼1 c/s).[33,34] There does not seem to be any correlation between single-line ELDOR intensity and T_g. The intensities are too weak above 100° for interstitial nitroxides in amorphous and semicrystalline polypropylene and polystyrene and spin-labeled polystyrenes; they become measurable below 100°. On the other hand, the matrix ELDOR signal is only resolved at 0° for polypropylene but is always observed for polystyrene. Thus there may be a correlation between matrix ELDOR and T_g. This is reasonable since the matrix ELDOR mechanism depends upon the rigidity of environment. It is likely that only below T_g are the protons of the spin-label and those of the neighboring polymer molecules sufficiently immobil for the propagation of spin polarization.

In addition to the T_g's, there are α and γ transitions at 50 and −90°, respectively for polypropylene. Polystyrene has a β and a γ transition at 30 and −120°, respectively. In ELDOR there is no significant change in either the matrix or the single-line signal in the vicinity of any of these temperatures. Therefore, local modes of polymer chain motion are not transmitted to the spin-label either interstitial or attached to the polymer.

NMR has long been used to study molecular motions in polymers.[35,36] Both NMR and ELDOR are inferior to dynamic mechanical measurements for the determination of transition temperatures because changes of NMR line width or of ELDOR intensity are usually much more gradual than that of dynamic mechanical properties with temperature. Both magnetic resonance techniques are more sensitive to local environment. NMR is sensitive to the crystallinity of the polymer; the second moment of the line width of atactic polymer is always less than that of isotactic polymer.[35] On the other hand, the spin-labels on the polymer chain or added interstitial are present in the amorphous phase only so ELDOR is not sensitive to the presence of a crystalline phase. However, because of that it can be used to advantage because in NMR the contribution of the crystalline phase has to be subtracted from the total line width. Both methods can yield valuable information regarding correlation time of motion in polymers and should be valuable when used in conjunction with the other tools of polymer physicists.

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