super-Lorentzian line shape. The profile of this line shape corresponds to the analysis of the overall spin–spin decay of magnetization using a wide-line pulse spectrometer. The magnitude of this effect appears to be a useful index of the extent to which nonbonded interactions stiffen the chain.

Gross inaccuracies may result if quantitative measurements of the relative proportions of order and disorder are attempted simply on the basis of the area of the "visible signal" in the high-resolution spectrum. The complex NMR signals for polysaccharides in solution are better interpreted by using a combination of wide-line pulse and high-resolution NMR techniques when it is possible to derive both the extent of conformational ordering and the relative magnitude of any constraints on chain flexibility in the disordered state. These methods, of course, presuppose a molecular weight that is sufficiently high for spin relaxation to be dominated by segmental motion rather than overall tumbling of the molecule.

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CIDEP and Spin–Lattice Relaxation Time Studies of Some Polymeric Phenoxy Radicals in Solution

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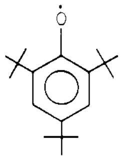
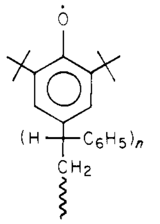
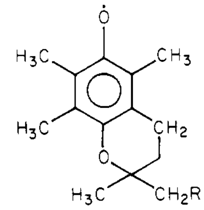
ABSTRACT: Photooxidation of polymeric phenols by duroquinone in solution produced both primary semiquinone and phenoxy radicals which exhibited the chemically induced dynamic electron polarization phenomenon. Measurements were obtained for the spin–lattice relaxation time T_1 and the line widths of the 2,4,6-tri-*tert*-butylphenoxy radical and polymeric derivatives of this radical: the polymer chain replaced the *tert*-butyl group at the 4-position. Also the vitamin E radical was investigated. The observed T_1's for the polymeric radicals were not significantly greater than for the monomeric phenoxy radical but the lines were broadened somewhat. The vitamin E radical, however, had a much larger T_1. A simple model in which the polymeric radicals were treated as rotating rods was used to explain these observations.

Introduction

The photochemical reactions between quinones and phenols in solution have been extensively used as model systems in our laboratory for chemically induced dynamic electron polarization (CIDEP) studies.[1] In addition to the mechanistic and kinetic information that can be obtained from CIDEP studies, another important physical parameter, the spin–lattice relaxation time, T_1, can be estimated from the polarization decay of a transient radical.[2] Freed and co-workers[3] have investigated the spin–lattice relaxation times of the benzoquinone series, while we have employed the time-resolved CIDEP technique to extend the semiquinone T_1 study to include the transient naphthosemiquinone and anthrasemiquinone series.[4,5] We found that T_1 is just as sensitive to the number of rings as it is to the size of the semiquinone radicals. In most of these systems the molecular size contribution toward the orientational correlation time τ_2 is a power of the effective molecular radius. An excellent recent analysis of T_1 of transient radicals in solution has been presented by Fessenden and co-workers.[2]

In this paper we examine a number of polymeric phenoxy radicals. These are derivatives of the 2,6-di-*tert*-butylphenoxy radical with a very long hydrocarbon chain attached to the 4-position of the ring. Also we looked at the radical formed from vitamin E. Although these are hardly spherical molecules, they nonetheless should have a large effective molecular radius. This in turn would imply large values for τ_2 and hence T_1; moreover, T_1 would be expected to be sensitive to chain length. Our experimental results are not in agreement with such expectations; they indicate that the length of the polymer chain has a

Table I
Experimental Values of T_1 for Some Polymeric Phenoxy Radicals in Toluene

radical	mol wt	*g* factor	*t*, °C	T_1, μs
	261	2.0047 ± 0.0004	−30 0 10	3.3 ± 0.5 2.8 1.8
	2 300[a] 10 000[a]	2.0043 2.0044	−30 −30	4.5 5.8
same as above but with deuterated styrene substituent	10 000[a]	2.0046	−30 0	5.2 4.5
 [b]	409	2.0046	−30 0	9.5 5.4

[a] Number-average molecular weights. [b] R = $(CH_2CH{=}C(CH_3)CH_2)_3H$.

modest effect on the magnitude of T_1. We have proposed a simple model, based upon randomly rotating rods, to explain our experimental results. Although the "rotating-rod" model is extremely naive it is hoped that the model, when further developed, can also be applied to account for some of the end-group NMR results of polymers in solution.

Experimental Section

Polystyrene derivatives of 2,6-di-*tert*-butylphenol were synthesized by the published procedure.[6] They were purified by successive reprecipitations from methanol until free of unreacted phenol and styrene as monitored by gel permeation chromatography with refractive index and UV (280 nm) detection, using a Waters chromatograph. Molecular weights of the phenols were estimated by vapor pressure osmometry.

The transient spin-polarized polymeric phenoxy radicals were generated by laser flash photolysis of a typical toluene solution 0.03 M in duroquinone and 0.5 M in the parent polymeric phenol. The CIDEP apparatus and the analysis of the experimental data to obtain T_1 were previously described in detail.[4] That analysis showed that the signal $h(t)$ at time t from a CIDEP spectrometer with an exponential response is

$$h(t) = b_1 + b_2 e^{-\lambda_1 t} + b_3 e^{-\lambda_2 t} + b_4 e^{-t/\tau}$$

The constants b_1, b_2, b_3, and b_4 are related to the initial polarization, the equilibrium polarization, the amplitude B_1 of the microwave magnetic field, the instrument response time τ, and the parameters λ_1 and λ_2. The parameters λ_1 and λ_2 respectively approach T_1^{-1} and T_2^{-1} as the microwave power approaches zero. In order to obtain a fit between the analysis and experimental decay curves, it was concluded[4] that τ lengthens and T_1 shortens as the microwave power is increased. In situations where T_1 is significantly longer than T_2 and τ, T_1 is obtained by extrapolating measured decay times for a sequence of low microwave powers to zero power.

Results and Discussion

The laser flash photolysis of a toluene solution containing benzoquinone and 2,4,6-tri-*tert*-butylphenol led to observations of both the semibenzoquinone radical and the phenoxy radical. Both of these primary radicals were highly polarized in the totally emissive mode[7] and their ESR resonances overlapped substantially. The CIDEP phenomenon of this system can be readily accounted for by the predominant phototriplet mechanism.[1] However, in order to determine the individual T_1 from the radicals' resonance lines, it is necessary to take measurements on lines that are not overlapped. Since the outer ESR lines of the phenoxy radical do not completely overlap with the narrower benzosemiquinone-d_4 resonance, we have prepared the deuterated benzoquinone and made T_1 measurements of the phenoxy radical on the outer lines of this system.

For each polymeric phenol only certain quinones are efficient for the polarization process. In many cases those quinones that are suitable for the polarization process produce semiquinones whose ESR spectra completely overlap the spectrum of the polymeric phenoxy radical. In those cases where the overlapping of the semiquinone–polymeric phenoxy ESR spectra is not complete, a further limitation is that the observed lines are the lower intensity outer ones. Monitoring the decay curve of a low-intensity line means that measurement of T_1 is difficult. Thus relatively few sytems can be investigated successfully.

The experimental values of T_1 for the 2,4,6-tri-*tert*-butylphenoxy radical and its 4-substituted polystyrene analogues are in Table I; also T_1 for the vitamin E radical is in Table I. It is apparent that increasing the chain length in the para position of the phenoxy radical increases the value of T_1 but the increase is not large even for a polymer with $\bar{M}_n \approx 10000$. The T_1 result for vitamin E is somewhat surprising; it is greater than the T_1's of the polymeric species. Finally, the lines are somewhat broadened; the observed line widths are ≈300 mG.

We can obtain a qualitative understanding of these results by treating the long-chain polymeric phenoxy radicals as a collection of rotating rods. The cross section of a rod is approximated as circular. There is free rotation about the rod axis and the motion is frozen about the transverse axes. The angular displacement and angular velocity variables for rotation about the rod axis are random variables. They contribute to T_1 through **G** tensor modulation and spin–rotation interaction. This simple model neglects many complex motions such as crankshaft motion of the polymeric chain and bending vibrations that allow the phenoxy moiety to oscillate with respect to the polymeric chain.

The rotating-rod model is developed quantitatively by obtaining the equations of motion for the spin magnetization of all rods with a given orientation θ with respect to the static magnetic field $\vec{B}_0$. The solutions of the equations of motion are averaged over all orientations. This results in longitudinal and transverse decay modes that are essentially exponential but there is a spread in the Larmor frequencies. Nyberg[8] used elegant arguments to describe the evolution of the spin polarization for an assembly of freely rotating molecular radicals. His development was aided by the properties of irreducible spherical components of tensors in the averaging procedures. The rotating-rod model is treated by analogous arguments but the details are more tedious because there is not free rotation about all axes. Nonetheless spherical coordinates are convenient for our development.

The spin Hamiltonian $\hbar\Omega$ is

$$\Omega = \omega_B\left(S^0 + \frac{g^{0\alpha}}{g}S_\alpha\right) + ((g - g_e)\omega^\alpha + g^{\beta\alpha}\omega_\beta)S_\alpha$$

with $\omega_B = g\mu_B B_0/\hbar$. In this expression the **E** tensor has been related to the **G** tensor by the approximation $E^{\beta\alpha} = G^{\beta\alpha} - g_e d^{\beta\alpha}$; $d^{\beta\alpha}$ is the metric, $g^{\beta\alpha}$ are the second rank parts of the **G** tensor, and $g = {}^1/_3 G^\alpha\alpha$ is the scalar part. The covariant spherical basis vectors $\vec{e}_\alpha$ are related to the Cartesian unit vectors $\vec{i}_j$ by $\vec{e}_\pm = 2^{-1/2}(\mp\vec{i}_1 + i\vec{i}_2)$ and $\vec{e}_0 = \vec{i}_3$. The spherical basis vectors $\vec{e}_\mu{}'$ in the rotating rod frame of reference are related to the laboratory frame basis vectors $\vec{e}_\alpha$ by

$$\vec{e}_\mu{}' = L^\alpha{}_\mu\vec{e}_\alpha$$

the transformation coefficients $L^\alpha{}_\mu$ are functions of the Euler angles ϕ, θ, χ.

In the perturbation calculation the Hamiltonian is split into an unperturbed part, $\Omega^{(0)}$, that does not contain random variables and a perturbed part, $\Omega^{(1)}$, that contains random variables. These take the forms

$$\Omega^{(0)} = q^\alpha S_\alpha$$

$$\Omega^{(1)} = Q^\beta = Q^\beta S_\beta$$

with

$$q^0 = \omega_B\left(1 + \frac{g_{ZZ}{}'}{g}L^0{}_0L^0{}_0 - \frac{g_{XX}{}' + g_{YY}{}'}{g}L^0 + L^0{}_-\right)$$

$$q^\pm = \omega_B\left(\frac{g_{ZZ}{}'}{g}L_0L^\pm{}_0 - \frac{g_{XX}{}' + g_{YY}{}'}{2g}(L^0{}_+L^\pm{}_- + L^0{}_-L^\pm{}_+)\right)$$

$$Q^\beta = \omega_B\left(\frac{g_{XX}{}' - g_{YY}{}'}{2g}\right)(L^0{}_+L^\beta{}_- + L^0{}_-L^\beta{}_+) + (g - g_e)\omega^\beta + g^{\beta\alpha}\omega_\alpha$$

$g_{XX}{}'$, $g_{YY}{}'$, and $g_{ZZ}{}'$ are the principal axis components of the second rank part of the **G** tensor; these are in the molecular frame of reference. A collection of rods with polar angles ϕ, θ are treated as an "ensemble of ensembles". In each ensemble the random variables χ and $\omega_0{}'$ have particular values and the results for the ensemble of ensembles follow by taking averages over χ and $\omega_0{}'$. As is well-known,[8,9] a master equation can be developed for the dynamics of the spin-density operator ρ, and the spin polarization $\bar{S}_\gamma$ is given by $\mathrm{tr}\{S_\gamma\rho(t)\}$. In our case the equations of motion become

$$\dot{\bar{S}}_\gamma = \epsilon_{\gamma\alpha\beta}q^\alpha\bar{S}^\beta - (d_{\alpha\beta}\bar{S}_\gamma - d_{\gamma\beta}\bar{S}_\alpha)\int_0^\infty \mathrm{d}t'\, e^{-i\beta\omega_B t'}\langle Q^\alpha(t)Q^\beta(t - t')\rangle$$

This result is valid up to second order in accuracy.

After the time correlation function $\langle Q^\alpha(t)Q^\beta(t - t')\rangle$ is treated by well-known methods, with χ and $\omega_0{}'$ as random variables, we obtain the following results for the spin polarization $\bar{S}_\alpha(t)$ when the initial value is $\bar{S}_\alpha(0)$:

$$\bar{S}_\pm(t) = \left\{\left(1 - \left(\frac{3}{2}\frac{g_{ZZ}{}'}{g}\right)^2\frac{u^2(1 - u^2)}{2}e^{\pm i\omega_B{}'t}\right)e^{-t/T_2} + \left(\frac{3}{2}\frac{g_{ZZ}{}'}{g}\right)^2\frac{u^2(1 - u^2)}{2}e^{-t/T_1}\right\}\bar{S}_\pm(0) \quad (1)$$

$$\bar{S}_0(t) = \left\{\left(1 - \left(\frac{3}{2}\frac{g_{ZZ}{}'}{g}\right)^2 u^2(1 - u^2)\right)e^{-t/T_1} + \left(\frac{3}{2}\frac{g_{ZZ}{}'}{g}\right)^2 u^2(1 - u^2)\cos(\omega_B{}'t)e^{-t/T_2}\right\}\bar{S}_0(0) \quad (2)$$

where $u = \cos\theta$ and the Larmor frequency $\omega_B{}'$ is

$$\omega_B{}' = \omega_B\left(1 + \frac{g_{ZZ}{}'}{g}\frac{3u^2 - 1}{2} + F\frac{1 + u^2}{1 + (\omega_B\tau_2)^2} + \frac{\tau_\omega}{2\tau_2}G\frac{1 - u^2}{1 + (\omega_B\tau_\omega)^2} + \left(\frac{3}{2}\frac{g_{ZZ}{}'}{g}\right)^2\frac{u^2(1 - u^2)}{4}\right) \quad (3)$$

with

$$F = \left(\frac{g_{XX}{}' - g_{YY}{}'}{2g}\right)^2(\omega_B\tau_2)^2\frac{1 - u^2}{2}$$

$$G = \left(\frac{g - g_e + g_{ZZ}{}'}{2}\right)^2$$

The relaxation times are

$$\frac{1}{T_1} = \frac{1}{\tau_2}\left(F\frac{1 + u^2}{1 + (\omega_B\tau_2)^2} + G\frac{1 - u^2}{1 + (\omega_B\tau_\omega)^2}\right)$$

$$\frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{\tau_2}(F(1 - u^2) + Gu^2) \quad (4)$$

Aside from second-order corrections, T_1 and T_2 respectively are the longitudinal and transverse relation times. From Nyberg's work the corresponding expression for T_1 of freely rotating monomers is

$$\frac{1}{T_1} = \frac{1}{\tau_2}\left\{\frac{1}{5}\left(\frac{g_{XX}{}'^2 + g_{YY}{}'^2 + g_{ZZ}{}'^2}{g^2}\right)\frac{(\omega_B\tau_2)^2}{1 + (\omega_B\tau_2)^2} + \left(\frac{1}{3}(g - g_e)^2 + \frac{1}{9}(g_{XX}{}'^2 + g_{YY}{}'^2 + g_{ZZ}{}'^2)\right)\frac{1}{1 + (\omega_B\tau_\omega)^2}\right\}$$

The Larmor frequency of a rotating rod, eq 3, is dependent upon is orientation. A collection of rods with random orientations has a spread in Larmor frequencies

Table II
Calculated Results for T_1(monomer) and $T_{1\,\mathrm{eff}}$(polymer) for Some Values of g'_{XX} and g'_{YY}[a]

g'_{XX}	g'_{YY}	T_1-(monomer), μs	$T_{1\,\mathrm{eff}}$-(polymer), μs
0.0000	0.0005	5.97	24
0.0000	−0.0005	5.97	9.3
0.0000	0.0010	5.37	48
0.0000	−0.0010	5.37	6.7
0.0005	0.0010	4.89	>100
0.0005	−0.0010	5.56	9.2
−0.0005	0.0010	5.56	23
−0.0005	−0.0010	4.89	5.1
0.0010	0.0010	4.25	>100
0.0010	−0.0010	5.37	13
−0.0010	−0.0010	4.25	4.0

[a] $\tau_2 = 10$ ps, $\tau_\omega = 10$ fs, $\omega_B = 5.83 \times 10^{10}$ s^{-1}, and $g = 2.0045$.

that depends upon g_{ZZ}'/g. A value of 0.001 for g_{ZZ}' would give a line width of 3 G, which is 10 times the experimental value of 300 mG. This overestimation of the line width is a consequence of our model, which does not allow motion about the axes transverse to the rod axis. A more realistic model of very hindered rotation about the transverse axes should attenuate the $(3 \cos^2 \theta - 1)/2 = P_3^0(\cos \theta)$ term in the first-order term of the Larmor frequency ω_B'.

The decay curves for the components of spin polarization perpendicular to an parallel to the static magnetic field $\vec{B}_0$ are obtained by averaging eq 1 and eq 2 over all orientations θ for each of a sequence of times. Our experimental results are for the longitudinal relaxation time T_1 for the decay of the spin polarization component S_0 parallel to B_0. An effective relaxation time, $T_{1\,\mathrm{eff}}$ is obtained by fitting the averaged results of eq 2 to an exponential decay curve $\bar{S}_0(t) = \bar{S}_0(0)e^{-t/T_{1\,\mathrm{eff}}}$. Since the instrument response time is about 0.230 μs, the second-order oscillating term in eq 2 will not be observed experimentally; the period of oscillation is $2\pi/\omega_B' \cong 1.1 \times 10^{-10}$ s. We thus neglected this term in our averaging procedure. The averages were performed with the following values for the parameters in eq 2 and 3: $\tau_2 = 10$ ps, $\tau_\omega = 10$ fs, $g_e = 2.0023$, and $\omega_B = 5.83 \times 10^{10}$ s^{-1}. The experimental result for g is 2.0045. These calculations were done for several sets of values for g_{XX}' and g_{YY}', which, along with the results for $T_{1\,\mathrm{eff}}$, are shown in Table II. Also the value of T_1 for a freely rotating monomer with the same parameters is given. A casual glance at the results in this table indicates that they are sensitive to g_{XX}' and g_{YY}'. The ratio $T_{1\,\mathrm{eff}}$(polymer):T_1(monomer) varies from about 1:1 to over 25:1.

In earlier work[3] we argued that the main contribution to the **G** tensor components are from the π system. For the 2,4,6-*tert*-butylphenoxy radical and the 4-substituted polymeric radicals, the systems are of comparable size and the **G** tensor components should be roughly the same. If, in addition, they have the appropriate values, then the results in Table II indicate that a modest difference between $T_{1\,\mathrm{eff}}$(polymer) and T_1(monomer) is possible. Also the apparently long-time T_1 of the vitamin E radical has a possible explanation. Reference to Table II shows that small changes in g_{XX}' and g_{YY}' can have pronounced effects upon T_1.

Very clearly, our first model greatly oversimplifies the problem. In so doing, we are aware of the excellent work on the dynamics of polystyrene in solution, particularly Ullman's recent "quasi-blob" model[10] for flexible polymers and Monnerie and co-workers' ESR line shape analysis of polystyrene nitroxide radical based on a three-state model with due consideration to the "local motions".[11] The line shape analysis probes the dynamic properties reflected in the transversal relaxation time T_2, whereas our experimental method deals only with a direct measurement of T_1. We believe that in a polymeric radical in solution T_1 may be less sensitive to the local motion in the part of the molecule remote from the unpaired spin site. Nonetheless, this is not to say that motions such as the crankshaft rotation in the chain are not important in a realistic model. Rather, we approach this complex problem using initially an oversimplified "rotating-rod" model to gain some qualitative insights into the experimental results. In particular, the values of individual second rank **g** tensor components are very critical in situations where there is hindered rotation. With further systematic experimental investigations, it is hoped that a more sophisticated model including some of the local motions will be developed to account for the dynamics and the spin–lattice relaxation of polymeric phenoxy radicals in solution.

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