Electron Spin Resonance Study of Radical Formation in *cis*-Poly(phenylacetylene)/Ferric Acetylacetonate–Triethylaluminum (PPA/Fe–Al). 1. Procedure for Line-Shape and Saturation Analysis

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ABSTRACT: A line-shape and saturation treatment for inhomogeneously broadened electron spin resonance spectra is presented, which is an extension of the statistical approaches of Portis and Castner. The absorption and dispersion relations of this two-parameter model are presented analytically for direct application to first-derivative spectra. Evaluation of the model parameters $\alpha\rho$, a reduced field interval, and $\alpha\tau$, a reduced saturation and degree of inhomogeneity parameter, yields values of the spin–lattice and spin–spin relaxation times in addition to providing a relative measure of the degree of delocalization of π-radicals in conjugated polymers. A regression routine is developed that makes the line-shape and saturation treatment applicable to convoluted spectra.

Introduction

Since the landmark paper of Bloembergen et al.[1] there have been many treatments of the inhomogeneous broadening of magnetic resonance lines at all levels of complexity. Most of these studies have been concerned with specific aspects of the problem such as the rigorous treatment of unsaturated line shapes of powder spectra subject to g-factor anisotropy[2] or specific distributions of hyperfine fields.[3,4] Other approaches have dealt with the behavior of the intensity of the inhomogeneously broadened line undergoing power saturation under various passage conditions.[5] Often, however, insufficient experimental data are available to apply these approaches. Therefore, less rigorous, parametric-statistical treatments such as those of Portis[6] and Castner[7] must be utilized. A class of materials requiring the latter type of development is that of the now intensively studied electroactive conjugated polymers. For a recent review of the rapidly growing literature on the electron spin resonance investigations of these interesting materials refer to Bernier.[8]

Conjugated polymers usually possess low spin concentrations, 10^{15}–10^{18} spins/cm^3, characteristic of delocalized π-radicals whose signals saturate readily, $T_1T_2 = 10^{-13}$–10^{-11} s^2. This makes the resolution of unsaturated spectra, expecially in the wings, quite difficult and at times impossible. In addition to the noise in the wings of these spectra, integration of the first derivative mode is often hampered by the superposition of broad catalyst signals.[9,10] There have been several attempts at modeling the line shapes displayed by these polymers, particularly that of the much investigated polyacetylene, through the use of specific spin distributions of radicals of a given delocalization length. However, it has been pointed out[4] that the uniqueness of these distributions cannot be established. Generally, the recorded spectrum is a superposition of the resultant line shapes of a distribution of spin-density delocalization lengths. In view of the complexities involved it is not surprising that very few detailed saturation treatments have been reported for these materials.[11,12]

To handle the complexities peculiar to conjugated polymer spectra in general and to interpret the electron spin responance (ESR) spectra of *cis*-poly(phenylacetylene) (*cis*-PPA) in particular, we propose a new line-shape and saturation treatment. Since unique spin-density distributions cannot be established from ESR spectra we are led back to the statistical approaches of Portis and Castner as a starting point. In particular, we require a model that is not only applicable to the evaluation of relaxation times but also (1) provides for the rigorous extrapolation of partially saturated, first-derivative spectra to the unsaturated condition for accurate spin concentration determination, (2) enables the quick integration of spectra while avoiding the problems of signal noise and broad underlying signals in the wings, and (3) is of a simple analytical form so as to be readily employable in regression analyses for the deconvolution of partially resolved spectra such as have been reported for this polymer.[9,13]

In the following paper (part 2), we apply our line-shape and saturation treatment to the various ESR signals observed for *cis*-poly(phenylacetylene). Here we present the development of the model[14] and its extension to include repression analysis and discuss the type of information it provides.

Development of the Line-Shape Function

We now develop the line-shape function for inhomogeneously broadened resonance lines of magnetically dilute ($N_S < 10^{19}$ spins/cm^3) systems recorded under slow-passage conditions. An inhomogeneously broadened line results from a variation of local field values leading to a field distribution, $h(H' - H_0)$, of spin packets individually characterized by the line-shape function $g(H - H')$. Here H_0 and H' represent the mean of the field distribution and the resonance field of a spin packet, respectively. The latter must meet the resonance condition

$$\hbar\omega' = \gamma H' = (1/2)g\beta H' \tag{1}$$

where $\hbar$ is Planck's constant, ω' is the fixed frequency of the resonance cavity, and γ, g, and β are the electronic magnetogyric ratio, the g factor, and the Bohr magneton. The source of local field variation considered explicitly in this treatment is multiple hyperfine interactions; however, other sources such as g-factor anisotropy or dipolar interactions of spins with different resonance fields could be considered as well given the appropriate functionality of $h(H' - H_0)$.

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The field-dependent magnetic suspectibility for the inhomogeneously broadened resonance line is given by[6]

$$\chi(H) = \chi'(H) + i\chi''(H) \tag{2a}$$

with

$$\chi'(H) = \frac{\chi_0\gamma^2}{2h^2}\int_0^\infty \frac{H_0 h(H'-H_0)\,\mathrm{d}H'}{1+(1/4)\pi\gamma^2{H_1}^2T_1 g(H-H')} \times \int_0^\infty \frac{(1/2)H'' g(H''-H')\,\mathrm{d}H''}{(H''+H')(H''-H')} \tag{2b}$$

and

$$\chi''(H) = \frac{\chi_0\gamma^2}{2h^2}\int_0^\infty \frac{\pi H_0 g(H-H')h(H'-H_0)}{1+(1/4)\pi\gamma^2{H_1}^2T_1 g(H-H')}\,\mathrm{d}H' \tag{2c}$$

where χ' and χ'' are the dispersive and absorptive parts of the susceptibility, respectively. The static susceptibility is given by χ_0, H_1 is the maximum value of the magnetic component of the microwave field in the cavity, and T_1 is the spin–lattice relaxation time. Equations 2b,c are only valid under conditions where energy equilibration in the spin system is fast compared with variations in the field H. Therefore, experiments run at low to moderate power levels, or high power levels under slow-passage conditions, can be handled by our analysis. The criterion for slow passage is[5]

$$1/\gamma H_1 \ll (T_1T_2)^{1/2} \ll H_1/\omega_\mathrm{m}H_\mathrm{m} \tag{3}$$

where T_2 is the spin–spin relaxation time and ω_m and H_m are the frequency and amplitude of the H-field modulation employed in phase-lock signal detection.

The specification of the functionalities of $g(H - H')$ and $h(H' - H_0)$ is dependent on the nature of the spin systems being studied. We consider here a system of magnetically dilute spins undergoing multiple hyperfine interactions. Much of the treatment, however, is independent of this designation. We present here the development for a Gaussian distribution of Lorentzian spin packets, which are the most common experimentally observed line shapes under conditions of near inhomogeneous and near homogeneous broadening, respectively. Since this was also the specific case treated by Portis and Castner, comparison with and extension of their results is possible. Limitations imposed by the assumption of a Gaussian resonance frequency distribution relate to the physical model chosen and will be dealt with later. The assumption of a Lorentzian spin packet, however, restricts the analysis itself and will therefore be discussed here.

The Lorentzian function, as is well-known, is the first-order solution to the spin energy Schroedinger equation for a Hamiltonian dominated by dipolar and weak, isotropic spin exchange interactions.[15] The rigorous solution to this problem for magnetically dilute systems is shown by Grant and Strandberg[16] to add some Gaussian character to the outer wings of an otherwise Lorentzian line. The major consequence of ignoring this contribution is to cause divergence of the nonzero-order moments of the line shape. This is not considered to be a serious defect. Grant and Strandberg indicate that the higher moments cannot give a representation of the line shape for dilute spin systems. In addition to inducing divergent moments, the Lorentzian approximation is expected to lead to a poor reproduction of the outer wings of a resonance line. However, since reliable experimentally obtained spectra of the outer wings are rare for dilute samples subject to superimposed impurity spectra, this is also not a major shortcoming.

After incorporating the appropriate functionalities for $h(H' - H_0)$ and $g(H - H')$, the dispersion and absorption curves for linear detection conditions are given by

$$D(H) = \frac{A\chi_0\gamma T_2 H_1 H_0}{(2\pi)^{1/2}\sigma_\mathrm{G}} \times \int_0^\infty \frac{\gamma T_2(H-H')\exp\{-(1/2)[((H'-H_0)/\sigma_\mathrm{G})^2]\}}{1+(1/4)\gamma^2{H_1}^2T_1T_2+\gamma^2{T_2}^2(H-H')^2}\,\mathrm{d}H' \tag{4a}$$

$$V(H) = \frac{A\chi_0\gamma T_2 H_1 H_0}{(2\pi)^{1/2}\sigma_\mathrm{G}} \times \int_0^\infty \frac{\exp\{-(1/2)[((H'-H_0)/\sigma_\mathrm{G})^2]\}}{1+(1/4)\gamma^2{H_1}^2T_1T_2+\gamma^2{T_2}^2(H-H')^2}\,\mathrm{d}H' \tag{4b}$$

where γT_2 is the reciprocal half-width of the Lorentzian spin packet, σ_G is the standard deviation of the Gaussian field distribution function, and A is a constant.

The dispersion integral is derived by equating the real solution of the complex Bloch equations[17] to the homogeneous dispersion relation for a single spin packet developed by Portis.

To simplify the integration of (4) we define

$$\eta = H' - H_0 \tag{5a}$$

$$\rho = H - H_0 \tag{5b}$$

$$1/\alpha = 2^{1/2}\sigma_\mathrm{G} \tag{5c}$$

$$S = (1/2)\gamma H_1(T_1T_2)^{1/2} \tag{5d}$$

$$\tau = (1 + S^2)^{1/2}/\gamma T_2 \tag{5e}$$

The combinations $\alpha\rho$ and $\alpha\tau$ are the principal dimensionless parameters of the line-shape model. The former is a reduced-field interval measured from the center of the inhomogeneously broadened line. The combination $\alpha\tau$ has a dual significance. For unsaturated spectra it represents the ratio of the individual spin packet width to the distribution envelope width, much like Castner's "a" parameter. For increasing H_1 values it gives a measure of the degree of saturation. The assumption of a single T_2 is implicit throughout this treatment.

Substituting eq 5 into eq 4 yields

$$D(\alpha\rho;\alpha\tau) = \frac{A\chi_0\alpha\tau_0 S\alpha H_0}{\alpha(\pi T_1T_2)^{1/2}}\int_{-\infty}^{\infty}\frac{(\alpha\rho-\alpha\eta)\exp[-(\alpha\eta)^2]}{(\alpha\tau)^2+(\alpha\rho-\alpha\eta)^2}\,\mathrm{d}(\alpha\eta) \tag{6a}$$

$$V(\alpha\rho;\alpha\tau) = \frac{A\chi_0\alpha\tau_0 S\alpha H_0}{(\pi T_1T_2)^{1/2}}\int_{-\infty}^{\infty}\frac{\exp[-(\alpha\eta)^2]}{(\alpha\tau)^2+(\alpha\rho-\alpha\eta)^2}\,\mathrm{d}(\alpha\eta) \tag{6b}$$

where $\alpha\tau_0$ gives the unsaturated values of $\alpha\tau$:

$$\alpha\tau = \alpha\tau_0(1 + S^2)^{1/2} \tag{7}$$

In deriving eq 6, the assumptions that peak-to-peak line widths are always less than 50 G and g factors are always close to 2.0 were made. Employing these assumptions enabled rigorous transformation of the limits on H' in (4) to the symmetric limits on $\alpha\eta$ in (6).

To eliminate the unknown instrumental constant A in eq 6 one can directly integrate eq 6b to obtain an expression for the total intensity of the inhomogeneously broadened line

$$\mathcal{A} = \int_{-\infty}^{\infty} V(\alpha\rho;\alpha\tau)\,\mathrm{d}\alpha\rho = \frac{A\chi_0\pi\alpha H_0}{(T_1T_2)^{1/2}}\frac{S}{(1+S^2)^{1/2}} \tag{8}$$

One can see that the absorption intensity follows the classic powder dependence of a purely inhomogeneously broadened line.

Equation 6 can be more easily integrated by treating it as Fourier convolution integrals

$$\frac{1}{2\pi}\int_{-\infty}^{\infty} F(\beta)G(\beta)\,\exp(i\beta x)\,\mathrm{d}x = \int_{-\infty}^{\infty} f(u)g(x-u)\,\mathrm{d}u \tag{9}$$

where $F(\beta)$ and $G(\beta)$ are the Fourier transforms of $f(u)$ and $g(u)$, respectively. This yields

$$D(\alpha\rho;\alpha\tau) = \frac{\mathscr{A}}{4\pi\alpha}(2\alpha\rho J_0 + iJ_1) \tag{10a}$$

$$V(\alpha\rho;\alpha\tau) = \frac{\mathscr{A}}{2\pi}J_0 \tag{10b}$$

with

$$J_K = \int_{-\infty}^{\infty}\beta^K \exp(-(1/4)\beta^2 - \alpha\tau|\beta|)\exp(i\alpha\rho\beta)\,\mathrm{d}\beta \tag{10c}$$

The integrals J_K, $K = 0, 1$, are solved by defining the complex quantity $z = re^{i\theta}$, with

$$r = [(\alpha\rho)^2 + (\alpha\tau)^2]^{1/2}; \qquad \theta = \arctan(\alpha\rho/\alpha\tau) \tag{11}$$

to give for the dispersion, D, and absorption, V

$$D(\alpha\rho;\alpha\tau) = \frac{-2\mathscr{A}\alpha\tau}{\pi\alpha}\mathrm{Ers}, \qquad V(\alpha\rho;\alpha\tau) = \frac{2\mathscr{A}}{\pi}\mathrm{Erc} \tag{12}$$

where the functions Erc and Ers follow the matrix relation

$$\begin{bmatrix}\mathrm{Erc}\\ \mathrm{Ers}\end{bmatrix} = \frac{\pi}{2}\exp[(\alpha\tau)^2 - (\alpha\rho)^2] \times \begin{bmatrix}\cos(2\alpha\rho\alpha\tau) & \sin(2\alpha\rho\alpha\tau)\\ \sin(2\alpha\rho\alpha\tau) & -\cos(2\alpha\rho\alpha\tau)\end{bmatrix}\begin{bmatrix}\mathrm{Re}\,[\mathrm{erfc}\,(z)]\\ \mathrm{Im}\,[\mathrm{erf}\,(z)]\end{bmatrix} \tag{13}$$

The quantities in the last bracket are the real and imaginary components of the complimentary error function, erfc, and the error function, erf, of the complex argument z.[18]

The functions Erc and Ers are respectively symmetric and antisymmetric about $\alpha\rho = 0$. Erc, which gives the shape of the absorption curve, displays a very complex dependence on $\alpha\tau$. However, in the limit as $\alpha\tau$ approaches 0 or ∞, Erc becomes Gaussian and Lorentzian, respectively.

The $\alpha\rho$ derivatives of the dispersion and absorption curves, the mode observed in phase-lock signal detection, may be obtained quite readily by making use of the following identities

$$\partial\mathrm{Erc}/\partial(\alpha\rho) = -2\alpha\rho\mathrm{Erc} - 2\alpha\tau\mathrm{Ers} \tag{14a}$$

$$\partial\mathrm{Ers}/\partial(\alpha\rho) = 2\alpha\tau\mathrm{Erc} - 2\alpha\rho\mathrm{Ers} - 1 \tag{14b}$$

yielding

$$\frac{\partial D}{\partial(\alpha\rho)} \equiv D' = \frac{2}{\pi\alpha^2}[-2(\alpha\tau)^2\mathrm{Erc} + 2\alpha\rho\alpha\tau\mathrm{Ers} + \alpha\tau] \tag{15a}$$

$$\frac{\partial V}{\partial(\alpha\rho)} \equiv V' = \frac{2}{\pi\alpha}(-2\alpha\rho\mathrm{Erc} - 2\alpha\tau\mathrm{Ers}) \tag{15b}$$

Higher derivatives may be easily obtained through repeated application of eq 14.

Regression Analysis

We have developed a nonlinear regression routine, employing the line-shape function of the previous section to obtain values of α and $\alpha\tau$ from experimental spectra as well as enabling us to deconvolute more complex spectra as was observed for the *cis*-poly(phenylacetylene) specimens described in the subsequent paper. In developing the regression routine we have extended the method of Marquart et al.[19] to include variable line shapes and saturation effects as well as provide for a statistical procedure to establish confidence limits for the regressed parameters. The solution scheme is based on a nonlinear least-squares analysis employing a Newton–Raphson algorithm with analytical derivatives to solve the inherent system of nonlinear equations given by

$$\mathscr{J}\Delta\vec{b} = -\vec{G}, \qquad G_p = \partial\mathrm{SSE}/\partial b_p \tag{16}$$

$$\vec{b}^{i+1} = \vec{b}^{i} + 0.75\Delta\vec{b}$$

where SSE is the error sum of squares and the p,qth element of the Jacobian, $\mathscr{J}$, is given by $\partial G_p/\partial b_q$. The update of the parameter estimators, $\vec{b}$, is damped slightly to avoid divergence of the iteration scheme.

The significance of fit of the line-shape model can be established by defining a $100(1-\alpha)\%$ confidence limit contour about the global minimum[20]

$$\mathrm{SS}_\alpha = \mathrm{SSE}[1 + m/(n-m)F_{m,n-m,1-\alpha}] \tag{17}$$

for m parameters, n data points, and F distribution value at $(m,n-m)$ degrees of freedom. To obtain approximate confidence intervals for the parameter estimators, we make the assumption that the contours closely approximate an m-dimensional ellipsoid. The component axis of this ellipsoid can be considered as representational of the confidence limits of the individual parameters. By expanding SS_α in a Taylor series about the global minimum, denoted by SSE, we obtain approximate confidence limits as

$$\Omega_p = b_p(\alpha) - \beta_p = \pm\{[\mathrm{SS}_\alpha - \mathrm{SSE}]/(\partial^2\mathrm{SSE}/\partial\beta_p^{\,2})\}^{1/2} \tag{18}$$

where β_p is the value of the estimator b_p at the global minimum. This form has the advantage that at convergence all quantities are known, $\partial^2\mathrm{SSE}/\partial\beta_p^{\,2}$ simply being the pth diagonal element of the Jacobian. The ellipsoid confidence contour was tested along all the component axes and was found to reproduce the true contour, SS_α, to better than 1% accuracy. It, however, failed badly in describing SS_α along the axis of the scaling factor of a minor signal during the deconvolution of superimposed spectra. Application of regression analysis to saturation curves was, however, very sensitive to the proportion of the minor signal and was generally used for this purpose.

The convergence criterion for the optimization of m parameters b_p, $p = 1, ..., m$, was set at

$$\frac{1}{m}\sum_{i=1}^{m}\left|\frac{\Delta b_i}{\Omega_i}\right| < 0.05 \tag{19}$$

The convergence characteristics of the iteration scheme are dominated by two factors, the goodness of the initial parameter values and the number of parameters being regressed. Initial parameters once established for a particular sample could be employed for all spectra of that sample with good convergence behavior. It is our experience that convergence becomes quite slow when more than eight parameters are being regressed; therefore, when treating superimposed spectra, the functionality of the line giving the minor contribution is held fixed during optimization. Attempts at accelerating covergence via a Wegstein (independent parameter) update formula[21] proved ineffective, probably due to the large variation in

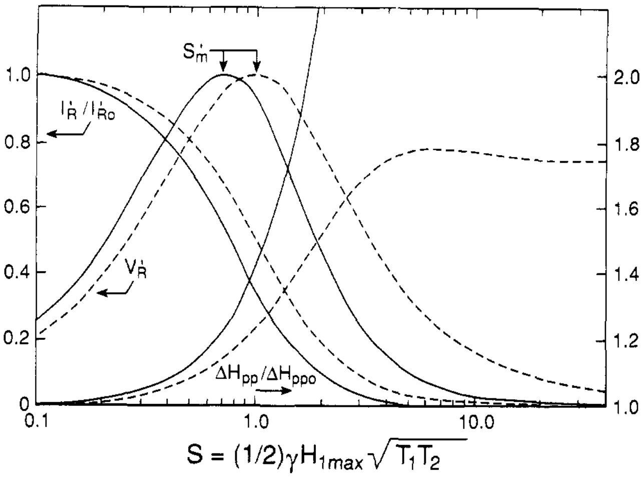

Figure 1. Saturation curves for a pointlike sample (—) and a bulk sample (- - -). $H_{1\max}$ is the maximum microwave field in the resonance cavity.

the influence of the various parameters on the solution scheme.

Discussion of Model

Previously the dependence of the line shape, and its variation with incident microwave power (i.e., S), on the two variables $\alpha\rho$ and $\alpha\tau$ was established. The physical parameters of interest for a given spin system are the spin–spin and spin–lattice relaxation times, T'_2 and T_1, and the field distribution width σ_G. These can be obtained from $\alpha\rho$ and $\alpha\tau$ through relations 5. Consequently, the task at hand is to determine $\alpha\rho$, or more specifically α, and $\alpha\tau$ from line-shape and saturation data. This can be accomplished by way of a regression analysis as discussed in the previous section. Here we discuss some of the limitations of the model in its present form, particularly with regard to interpreting the results for T_1, T_2, and σ_G, and suggest modifications and approximations that will aid in the development of the regression analysis.

The first, and certainly a major, limitation of the model described in the second section is that the microwave-field and H-field modulation amplitude variations experienced by a typical sample tube are not accounted for. We call this the "bulk sample" case, as contrasted with the "pointlike" sample case presented earlier. As might be expected, the largest differences between the two cases are observed in their power-saturation behavior. Saturation curves of a pointlike and bulk sample for $\alpha\tau_0 = 1$ are given in Figure 1. Results for the bulk sample are for a TE_{102} cavity for which analytical expressions are available. In general, however, numerical integration over the field and modulation amplitude distributions must be employed.[22] Plotted as a function of the saturation parameter, S, are the reduced first derivative height, V'_{Rm}, the quantity $I'_R = V'_Rm/P^{1/2}$, where P is the incident microwave power, and the reduced peak-to-peak line width, $\Delta H_{pp}/\Delta H_{ppo}$. It should be noticed that the pointlike analysis predicts a continuous broadening of the resonance line with increasing S, unlike the bulk sample behavior. The shift toward larger S in the V'_{Rm} and I'_R curves of the "bulk" case occurs because the average value of S over the sample, $\langle S\rangle_S$, is less than the maximum S, the latter being given in Figure 1. For spectra recorded at powers at or below that of maximum signal height (i.e., $S \leq S'_m$), the line shapes vary little between the bulk and "pointlike" sample cases. This enables the determination of T_1, T_2, and σ_G from a single line-shape regression at S'_m, provided the regressed value of $\alpha\tau$ is interpreted as $\alpha\tau = \alpha\tau_0(1 + \langle S^2\rangle_S)^{1/2}$.

We next deal with the sensitivity of the saturation curves and the line-shape function to the degree of inhomogeneous broadening. For spectra dominated by the resonance field distribution (i.e., $\alpha\tau_0 < 0.1$) the line shape is given by this distribution, which in our case is Gaussian. Consequently, line-shape regression analysis cannot help us distinguish among lines with different $\alpha\tau_0$ values in this regime. Fortunately, the characteristics of the V'_{Rm} versus S curves are very sensitive to $\alpha\tau_0$ in this regime and therefore can be used to evaluate it. This regime has been thoroughly treated by Castner and therefore will not be discussed further. For $\alpha\tau_0 > 0.1$ the effect of the Lorentzian spin packet becomes felt and the behavior of the saturation curves approaches that of a homogeneously broadened line. Consequently, the line shape becomes sensitive to $\alpha\tau_0$ and the saturation curves of V'_{Rm} and I'_R become $\alpha\tau_0$ independent. Most of the spectra of the conjugated polymers fall into this regime.[22] However, line-shape regression analysis must still be accompanied by a saturation study since only T_2 and σ_G can be established from the line shape. For many conjugated polymers there is the additional problem that unsaturated spectra are unobtainable. A regression analysis at the maximum of the V'_{Rm} versus S curve alleviates this difficulty. As a practical guide, the line shape becomes indistinguishable from a Lorentzian function for $\alpha\tau_0 > 5$ although the analytical limit is $\alpha\tau_0 = \infty$.

Finally, we must deal with the problem of assigning a physical interpretation to the calculated values of T_1, T_2, and σ_G. We first consider the relaxation times. If a spatially uniform spin temperature is maintained throughout the resonance experiment, spin–spin relaxation processes are far more effective than spin–lattice relaxation processes, then the calculated value of T_2 is dependent only on the density of spin centers in the sample, and the calculated value of T_1 will be an average over the most rapid spin-relaxation processes in the sample.[23] The uniqueness of the spin–spin relaxation time, T'_2, and its identification with the reciprocal line width, T_2, can only be established, however, if all spins precess at the same Larmor frequency. For resonance lines subject to hyperfine splittings this condition cannot be met; therefore, the width of each line of the hyperfine spectrum is subject to both lifetime and pure dipolar broadening. Within the framework of our model, the latter effect will be manifested in the estimated value of the distribution width, σ_G. The calculated value of T_2 is that of a homogeneously broadened spin packet and is therefore related to the true spin–spin relaxation time, which is constant for all lines of the hyperfine spectrum. Investigations on the relaxation processes in conjugated polymers indicate that spin–lattice relaxation is more than 2 orders of magnitude slower than spin-temperature equilibration.[11,12] Consequently, the uniformity of the spin–spin relaxation rate, as assumed in the model, should be observed.

There are two situations where the assumptions of the simple model may break down. For samples with heterogeneous doping by electron acceptors or donors, multiple, separated spin systems may be observed with different T_1's and T_2's. Saturation studies of samples with catalyst residues, even if present at only 1 mol %, must be carefully interpreted. These paramagnetic species can control both spin–spin and spin–lattice relaxation via dipolar and cross-relaxation processes.[23,24] The effect is important when the spin–lattice relaxation time of the catalyst species is longer than the spin–spin relaxation time of the π-radical of the polymer. The influence of the catalyst increases with decreasing temperature due to the strong temperature dependence of its T_1.

The greatest difficulty in providing a physical interpretation for a model parameter lies with the Gaussian distribution width, σ_G, and in fact the assumption of a Gaussian envelope itself. For a delocalized spin subject to many, n, identical hyperfine splittings of equal magnitude, a Gaussian distribution of resonance fields would result with a width inversely proportional to $n^{1/2}$. This simplistic picture is rarely applicable to real polymers. These systems are subject to considerable structural complexity. The extent of delocalization of a radical is distributed over many lengths rather than possessing a unique value. In addition, the distribution of spin densities within a given delocalization length is rarely uniform and is subject to variable degrees of chain twists. The distribution width, σ_G, in addition to being affected by nonresonant dipolar broadening also contains a contribution from anisotropic hyperfine interactions. In view of the complexities, the Gaussian approximation appears to be justified; however, σ_G can only be used as a relative measure of the delocalization length distribution for a particular polymer system.

Conclusions

Using the methods described, it is possible to obtain, separately, relaxation times and resonance field distribution widths over the entire range of saturation behavior from pure homogeneous to pure inhomogeneous broadening from first derivative spectra. For near inhomogeneously broadened spectra, where the spin packet width is less than 10% of the field distribution width, a saturation treatment is the appropriate mode of analysis. For spectra subject to a lesser degree of inhomogeneity, all the parameters can be obtained from a single line-shape analysis on a spectrum recorded at the power level of maximum signal height. The determination of spin concentrations from partially saturated spectra is possible by means of a simple, yet rigorous, extrapolation procedure. Complex spectra subject to superimposed signals with multiple relaxation times can be treated since the model is readily amenable to regression analysis.

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