NOTES

Additional Broadening of Electron-Spin-Resonance Spectra of Nitroxyl Radicals in Poly(Ethylene Oxide)

During the last few years, widespread attention has been devoted to the spin probe and labeling techniques where an unpaired electron is introduced into a polymer matrix by binding stable free nitroxyl radicals to polymers by secondary or covalent bonds. The electron-spin-resonance (ESR) spectra of radicals give information about the short range segmental relaxations of polymer chains in solutions, in melts and in the solid state.[1,2]

When the hyperfine interaction is solely with the nitrogen nuclear spin and the radicals are in a rapid motion ($10^{-9} \gtrsim \tau_c > 10^{-11}$ sec, where τ_c is the rotational correlation time), the ESR spectrum of nitroxyl radicals is known to consist of three Lorenzian lines. Their widths are given by

$$T_2^{-1}(m) = A + Bm + Cm^2 + X \tag{1}$$

where A, B, and C depend on the principal values of the $\mathbf{g}$ and $\mathbf{T}$ tensors and on τ_c; X takes into account other possible broadening mechanisms.[3] Stone et al.[4] have given a convenient solution to calculate τ_c by means of $T_2(m)$ data

$$T_2(0)/T_2(m_I) = 1 - 4/15^{\tau_c b \Delta \gamma B_0 T_2(0) m_I} + \tau_c b^2 T_2(0) m_I^2/8 \tag{2}$$

where

$$\Delta\gamma = -(|\mu_B|/\hbar)[g_z - \tfrac{1}{2}(g_x + g_y)],$$

$$b = (4\pi/3)[T_z - \tfrac{1}{2}(T_x + T_y)];$$

T_z, T_x, and T_y represent the z, x, and y components of the hyperfine tensor $\mathbf{T}$ in Hz; g_z, g_x, and g_y are the corresponding components of $\mathbf{g}$ tensor; μ_B is the Bohr magneton; $\hbar$ is Planck's constant per 2π; B_0 is the applied magnetic field; and $m_I = \pm 1$.

Defining the ratios $T_2(0)/T_2(+1)$, $T_2(0)/T_2(-1)$ as R_+ and R_-, it is readily shown that

$$R_+ + R_- - 2 = \tau_c b^2 T_2(0)/4 \tag{3}$$

Sensitive measures of R_+ and R_- are obtained from the ratios of peak-to-peak intensities Y of the relevant lines of the experimental ESR spectra. Thus

$$R_\pm = [Y(0)/Y(\pm 1)]^{1/2} \tag{4}$$

For organic nitroxyl radicals, which are the most important probes and labels of polymers, there are additional hyperfine interactions with protons. These interactions cause inhomogeneous broadening of spectral lines which must be corrected by computer simulations if accurate τ_c values to be obtained.[5] This is clearly indicated when the radical concentration is small ($c_{rad} \lesssim 10^{-3} M$) and when the line-broadening effect of oxygen is eliminated (degassing in high vacuum).

Recently, Kuznetsov et al. have proposed a so called "additional broadening" method that permits the measurement, with minimal error, of τ_c of organic nitroxyl radicals (together with the degree of anisotropic rotation of nonspheroidal radicals).[6] According to this method the effect of inhomogeneous broadening is minimized and the accuracy of measurements is improved with greater relaxation width $T_2^{-1}(m)$. This may be achieved by increasing either τ_c or the additional broadening linewidth X.

Kuznetsov et al. tested the applicability of eq. (2) in the presence of additional hyperfine interactions of t-butyl protons by simulating each nitrogen hyperfine line either by the sum of superhyperfine components (additional proton splitting) or by the convolution of a Lorenzian line over a Gaussian distribution. This analysis showed that the experimental correlation time (τ_{expt}) rapidly attains its true value (τ_c) with increasing X. Thus the correct measurement of τ_c for organic nitroxyl radicals can be carried out in the presence of additional relaxation broadening when the exchange broadened linewidth exceeds the envelope width due to unresolved proton splitting by a factor $\alpha \sim 1.3$. To achieve this one can use paramagnetic species, added to the system containing nitroxyl radicals under conditions of relatively slow exchange (the exchange line broadening must be much less than the frequency separation between the relevant spectral lines).

Kuznetsov et al. found that oxygen is a convenient paramagnetic broadening agent. Their study concerned the tumbling of nitroxyl radicals in decalin solution.

It seems that the additional broadening method can be a valuable tool also in spin probe and labeling studies of polymer systems. So, e.g., Wasserman et al. got, by using oxygen as a broadening agent and using eq. (2), τ_c values which are in good agreement with τ_c values calculated by other methods.[7]

It can be concluded that nitroxyl radicals as such can be used as broadening agents. In this paper the use of stable free nitroxyl radical 3-carbamoyl-2,2,5,5-tetramethylpyrroline-1-oxyl (I) as a paramagnetic probe and as a broadening agent in poly(ethylene oxide) (PEO) is discussed.

The studied material was a commercial high molecular-weight PEO sample with $M_w \sim 600,000$ (BDH Chemical Ltd.). Radical (I) was prepared by the method of Rozantsev et al.[8] PEO samples with different amounts of radical (I) (100 ppm $\rightarrow$ 3600 ppm) were prepared by dissolving suitable amounts of PEO into chloroform solutions of radical (I) and evaporating the solvent.[9] The samples were homogenized by melting and slow cooling to room temperature. The samples for ESR measurements were degassed in a vacuum line (2.5×10^{-3} Torr) and sealed into ESR tubes under dynamic vacuum.[10]

The ESR spectra were measured in the temperature range 275–365 K using a Varian E-4 X-band spectrometer equipped with a Varian E-257 variable temperature accessory. The temperature calibration was made by an iron constantan thermocouple. The modulation amplitude used was 0.25 G and the microwave power was 1 mV. The melting points were measured by a Perkin-Elmer differential scanning calorimeter (1 B).

In Figure 1 are given the linewidths of the middle peaks of ESR spectra as a function of the inverse value of temperature ($1/T$). The lower limit of radical concentration (100 ppm) represents the concentration below which the additional relaxation broadening in PEO is absent.[10]

The experimental rotational correlation times (τ_{expt}) were calculated according to eq. (2) from the ESR spectral data.[9,10] The results are collected in Figure 2.

It can be seen that, although linewidths increase considerably when the radical concentration is increased, τ_{expt} is independent of radical concentration within the experimental error. The mean activation energy (E_a) calculated from the data of Figure 2 is 40 kJ/mol.

It is interesting to note that the ($1/T$, $\ln\tau$) line is continuous over the melting region of PEO (T_m = 333 K is given by an arrow). In low and medium M_w PEO (M_w = 1000–22,000) a discontinuous melting transition with a high apparent activation energy was earlier reported.[9,10] It was suggested that this transition during melting is caused by the dissipation of strain forces in the amorphous phase. Esterification studies indicated that these strain forces are generated by —OH end groups. The results of this report are in accordance with our earlier suggestions because in high M_w PEO the end group effect is negligible. Therefore the rotations of probe radicals are not affected by the melting of the crystalline phase in high M_w PEO.

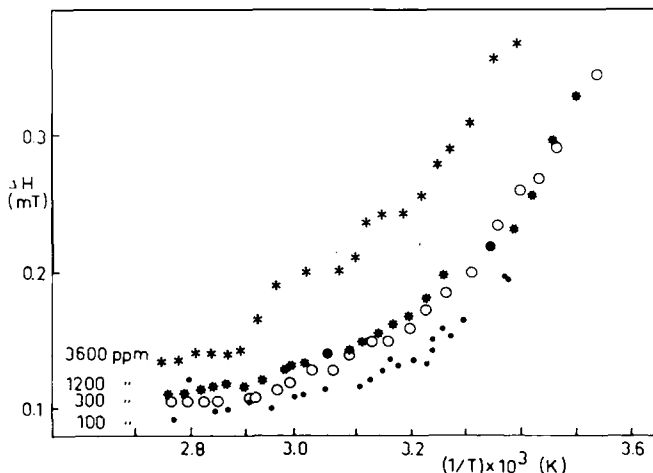Several earlier studies have indicated that segmental relaxations of polymer chains contribute

Fig. 1. Effect of radical concentrations to linewidths (ΔH) of middle components of ESR spectra as a function of the inverse value of temperature; radical concentrations ($\bullet$) 100 ppm, ($\bigcirc$) 300 ppm, ($\star$) 1200 ppm, and ($\ast$) 3600 ppm.
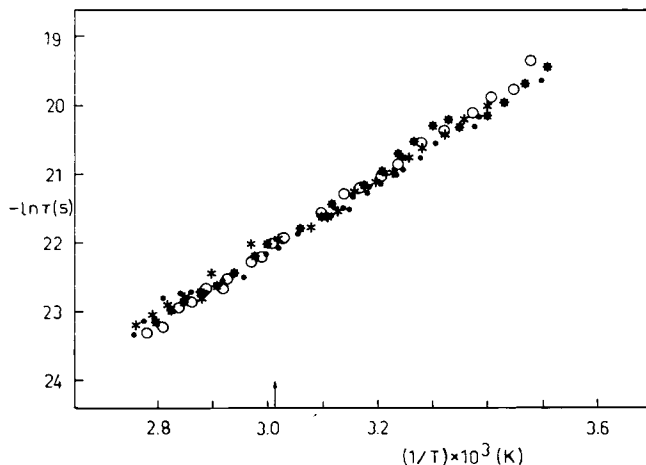
Fig. 2. Rotational correlation time $\tau_{expt}(-\ln\tau)$ as a function of the inverse value of temperature for PEO samples of different radical concentrations; symbols are the same as in Figure 1. The melting point (333 K) is given by an arrow.

strongly to the correlation times of probe radicals.[1,2,7,9–12] In Figure 3, τ_{expt} values are compared with relaxation times of dielectric γ relaxation (τ_r) of PEO reported by Ishida et al.[13]

It can be seen that τ_{expt} fairly well represents the γ relaxation time of PEO in the high-temperature region. Also the E_a values are in good agreement with each other (40 kJ/mol for ESR method, ~35 kJ/mol for dielectric method).

These results, with earlier observations, indicate that spin probe and labeling studies can be used as rapid and convenient methods to study the short range, high-frequency motions of polymers. Because the additional broadening practically does not affect τ_c values it is evident that probe and labeling methods can be used to study quantitatively local microdynamics of heterogeneous polymer systems (e.g. filled and reinforced polymers and polymer blends) where unequal radical distribution
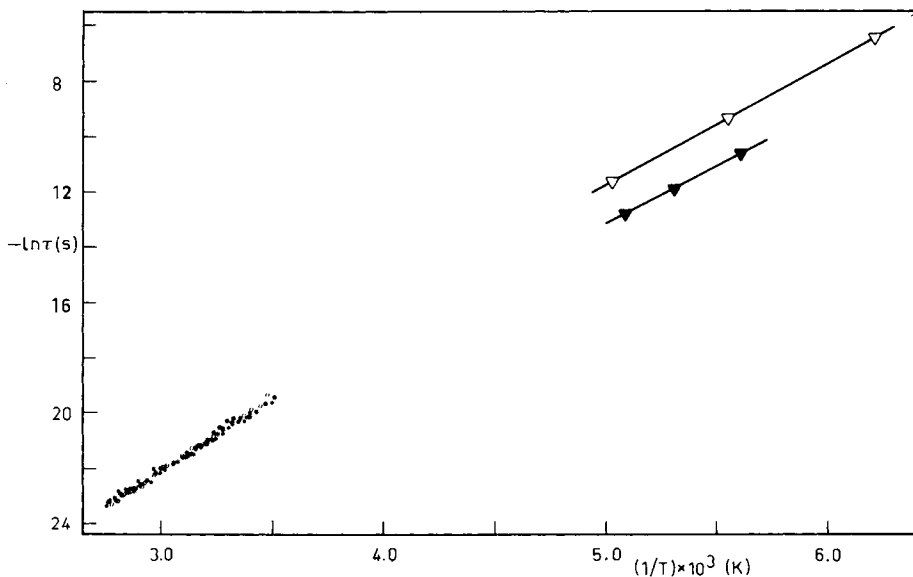

Fig. 3. Comparison of dielectric (ref. 13) and spin probe relaxations in PEO. Dielectric relaxation: ($\triangledown$) melt crystallized, ($\blacktriangledown$) solution crystallized PEO. Spin probe relaxation: melt crystallized PEO; the symbols are the same as in Figures 1 and 2.

may cause spin-spin exchange broadening.   The first qualitative spin probe study of filled polymers have already been published.[14]

Reliable τ_c data are also obtained during additional broadening conditions from systems, such as fibers, where the rapid and accurate determination of probe radical concentration is not possible.

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