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Nitroxide Spin Label Dimer Pairing: A Cautionary Note

ROBERT G. KOOSER

Knox College, Galesburg, Illinois 61401.

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The spin label technique has been widely used to study the dynamics of polymers in both the solution and the solid state and has been reviewed several times.[1-3] Although the technique has wide applicability, it appears that with certain types of spin labels a dimerization can take place which can obscure the interpretation of the results.

During an investigation of the polymer dynamics of nitroxide-labeled poly(hexene sulfone) (PHS) in dilute solutions, we encountered what appeared to be superposition electron spin resonance (ESR) spectra (see Figure 1), which are usually attributed to spin labels existing in two different motional domains. A careful examination of these spectra convinced us that the conventional interpretation in this case was incorrect and that the broader spectrum arises from dimer formation between two nearby nitroxide labels. An examination of the recent literature shows that dimer spectra may have occurred in other systems.

The self-association of free nitroxide radicals even in fairly dilute solutions has been known for some time, but evidently this phenomenon has not been widely appreciated. Marshall[4] reported the association of 2,2,5,5-tetramethyl-3-carboxypyrrolidine oxyl (carboxy–TEMPYO) and measured the exchange energy, equilibrium constants, and ΔH's. Later Veloso and Rassat[5] determined dipolar splittings and concentration dependences of dimer ESR spectra for two TEMPYO species, 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO), 2,2,7,7-tetramethylhexahydro-1,4-diazepin-5-one 1-oxyl, and 2,2,5,5-tetramethyloxazolidine 1-oxyl. The Veloso and Rassat article[5] clearly demonstrates that the association can occur at concentration levels usually thought to be dilute enough to avoid serious radical–radical interactions. They report that dimer spectral lines for carboxy-TEMPYO and its methyl ester appear at concentrations as low as 1.1×10^{-4} M. In the case of TEMPO and the oxazolidine 1-oxyl, both commonly used as labels, the minimum concentration was found to be 5×10^{-3} M, a concentration too high for most label studies. Clearly, in the case of the use of TEMPYO labels, one must be careful in data interpretation.

The confusion comes about because of a similarity in superposition spectra and dimer spectra under certain conditions. The theory of the ESR spectral appearance of radical dimers is the same as the well-known theory for biradicals.[6] When the exchange energy is less than the hyperfine coupling constant, the dimer spectrum has the typical nitroxide three lines separated by the coupling constant, a_N, but with sidebands from weakly allowed transitions.[5-7] Thus the spectrum takes on the appearance of the superposition of mobile and immobile labels.

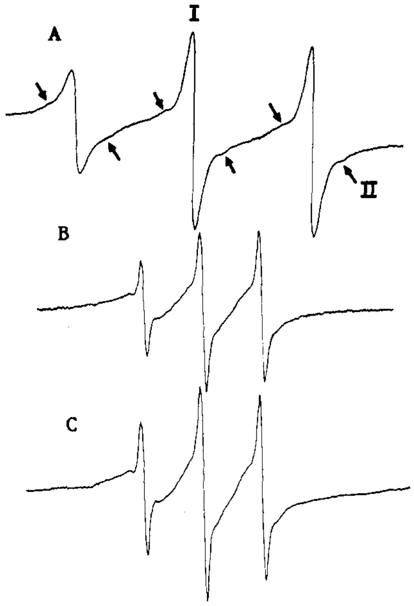

Figure 1. ESR spectra of TEMPYO-labeled poly(hexene sulfone) in toluene solution as a function of temperature (A, 22 °C; B, 12 °C; C, −28 °C) showing the "normal" three-line nitroxide spectrum (I) and the sidebands (II, marked by arrows) arising from radical pairing.

In our case, we synthesized a 1-hexene:1-hexen-6-ol (3–5 mol % alcohol) polysulfone by free radical initiated copolymerization of SO_2 and olefins at −10 °C in open tubes. The polymer was labeled by reaction of the copolymer with the acid chloride of carboxy-TEMPYO in dry benzene with excess dry pyridine. Spin label studies were done in dry, degassed toluene solution at 1.5 wt % polymer concentrations using a Varian V-4500 EPR spectrometer to record the EPR spectra. Spin concentration measurements using a dual sample cavity[8] indicated that the labeling was complete (3.0 mol % calculated; 3.5 ± 0.5 mol % measured). Figure 1 shows sample spectra as a function of temperature. The spectra resemble those obtained from the label in two different motional domains, a tantalizing interpretation considering the partial helical configuration[9,10] of this polymer. For convenience, let I designate the three sharp lines of the spectrum and II designate the broader, less intense sidebands.

Attributing the two portions to two different motional domains becomes unlikely in light of experimental evidence. Comparisons of ESR spectra of the labeled PHS in toluene, CH_2Cl_2, dioxane, and acetone-d_6 demonstrate no appreciable solvent dependence to the intensity ratios of I to II. This would be a surprising result if I and II resulted from motional differences as dielectric relaxation data show marked solvent dependence for PHS in benzene and dioxane.[11] The evidence points to an intramolecular process (association of labels in the same polymer molecule) where we note that the solutions are at the equivalent of 5×10^{-3} M, far above the minimum concentration for observable dimer effects for TEMPYO-type labels.[5] The ESR spectra of 0.15 wt % labeled PHS in toluene show no reduction in the intensity of II compared to I, further confirming the intramolecular origin.

Additional evidence is indicated by the ESR spectrum of labeled, nonhelical[9] poly(cyclohexene sulfone) (PCHS) using 3 mol % 1-hexen-6-ol at a density of 17% of the

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Table I
Line-Width Data for Spin-Labeled PHC as a Function of Temperature

T, °C	A,[a] G	B, G	C, G
60	0.634	0.310	0.015
39	0.670	0.518	0.0
22	0.728	0.574	0.019
1	0.75	0.55	0.10
−26	0.71	0.45	0.16
−49	0.71	0.42	0.21
−74	0.95	1.0	0.16

[a] Fit to $\delta = A + B\mathbf{m} + C\mathbf{m}^2$, where **m** is the spectral index number of the line.

alcohol sites successfully labeled (determined by spin concentration measurements). ESR spectra of toluene solutions at 1.5 wt % polymer show a reduced intensity of II relative to I. The reduced label density in PCHS would cause less dimerization and hence the reduced intensity of II to the "normal" three-line nitroxide spectrum. If the spectra were due to different motional domains, one would expect the absence of II in PCHS since it does not have two configurational domains like PHS. Furthermore, the subsequent synthesis of PHS labeled with a compound with markedly less pairing tendency than TEMPYO (oxazolidine oxyl label from the copolymer of 1-hexene with 3–5 mol % 1-hexenyl-5-oxazolidine and then subsequent oxidation of the oxazolidine amine group) showed the complete absence of II, indicating that we are not seeing two different motional domains.

Careful measurements of the ESR line widths, δ, of I in the regions where overlap with II is not severe and subsequent fit to the usual quadratic dependence in the spectral index number, **m** ($\delta = A + B\mathbf{m} + C\mathbf{m}^2$), show that the dominant relaxation modes are not the usual rotational modulation of anisotropic g and hyperfine tensor components.[12] For instance, if rotational modulation is the dominant relaxation process, plots of C vs. B from spectra at different temperatures would increase monotonically with B.[13] The results of line-width measurements for PHS in toluene after correction for unresolved proton hyperfine splittings[14] by the method of Bales[15] are given in Table I. In our case, B did not change monotonically with either temperature or the coefficient C, indicating that there was more than one type of relaxation process at work. From previous results in the literature and the experimental evidence in this study, it seems clear that TEMPYO labels can undergo self-association even at dilute label concentrations.

Evidence of the same sideband spectra exists in several published reports of studies using TEMPYO labels.[16-19] In most cases the authors do not comment on the presence of the sidebands; however, in most reports, the radical concentration appears to be sufficiently low to remove any serious complications from radical associations. In one case[16] of spin-labeled poly(ethylene oxide) grafted on silica, the radical concentration is marginally high (about 1×10^{-4} M) and it is possible that the interpretation of the spectra as contributions from two motional domains is incorrect and instead should be viewed as arising from radical pairing. Also, Meurisse et al.[19] reported anomalous line-width behavior for TEMPYO spin probes in liquid crystal polyesters relative to other classes of probes. This too might be indicative of association.

This work has established that in the use of TEMPYO spin labels and probes extreme care must be exercised in eliminating any effects from biradical association.

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Registry No. Carboxy-TEMPYO, 2154-68-9; $(H_2C{=}CH(CH_2)_3CH_3)(H_2C{=}CH(CH_2)_4OH)(SO_2)$ (copolymer), 105502-59-8.

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^{13}C NMR Assignments of the Methylene Carbons in Polypropylene

H. N. CHENG*

Research Center, Hercules Incorporated, Wilmington, Delaware 19894

G. H. LEE

Sun Refining and Marketing Company, Marcus Hook, Pennsylvania 19061. *Received August 11, 1986*

Much work has been carried out to elucidate the ^{13}C NMR spectrum of atactic polypropylene.[1,2] The methyl pentads had been firmly assigned by 1975.[3] The methylene carbons were fully analyzed by Zambelli, Locatelli, Provasoli, and Ferro[4] (ZLPF) and by Schilling and Tonelli[5] (ST).

Although the assignments of ZLPF[4] and ST[5] agree for the most part, there are notable differences. Since the publication of the ZLPF and ST papers, there have been occasional efforts to verify the assignments. Suter and Neuenschwander[6] compared the ^{13}C NMR spectrum of epimerized polypropylene to both ZLPF and ST models. Unfortunately, the low magnetic field used (22.6 MHz) did not enable them to clearly distinguish between these models, and reasonably good agreement was found with both models. Cheng and Lee[7] used two-dimensional NMR and from the correlation of ^{1}H and ^{13}C methylene shifts found good agreement with the ST model. Fetters et al.[8] recently studied the ^{13}C NMR spectra of hydrogenated

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