

Spin Labeling of Poly(ethylene Glycols)

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It has been shown that certain chemical, structural and kinetic information can be obtained from the paramagnetic resonance of synthetic organic free radicals ("spin labels") that are attached to biopolymers.¹ In order to widen the application of spin labeling technique especially to the chemistry of synthetic polymers, we have attached 3-chloroformyl-2,2,5,5-tetramethylpyrroline-1-oxyl(I) radicals covalently to poly(ethylene glycol) (PEG) samples of various molecular weights.

Results. The measured ESR spectra are shown in Fig. 1. Fig. 1A is the spectrum of free radical (I) in chloroform solution. It is a typical spectrum of rapidly tumbling free nitroxyl radical in solution. Figs. 1B–1E are the ESR-spectra of spin labeled PEG samples. The asymmetrical broadening of the spectra is to be ascribed to the anisotropy of the *g*-factor. In Table 1 are given both the values of peak-to-peak separation of the outermost lines of the spectra and the values of correlation time (τ) calculated by standard methods.^{2,4}

The last value of correlation time is approximative because of slow tumbling rate.

These results show that the covalently bonded nitroxide radicals act in PEG-matrix very much like in the viscous fluid. This is in accordance with earlier studies

of free nitroxide radicals diffused into polymer matrix.^{5,6} From Fig. 1 and Table 1 it can also be seen that when the molecular weight of PEG grows the tumbling rate of linked radicals becomes slower and the spectrum resembles more and more the spectrum of nitroxide radicals in rigid glass.⁷ It is of interest to note that τ is roughly linearly dependent on the logarithm of molecular weight. So the activation energy of tumbling must grow when the molecular weight of PEG grows. Nitroxyl radicals occluded, but not covalently bonded to the polymer do not seem to behave in this manner.⁸ It seems evident that spin label methods can be used for the estimations of molecular weights of polymers.

Experimental. The PEG samples (molecular weights 600 ± 30 , 1550 ± 100 , 4000 ± 500 and $20\,000 \pm 3000$) investigated were of commercial origin (Fluka AG and E. Merck AG). The spin label (I) was prepared by the method of Krinitskaya *et al.*² To a solution of 1×10^{-4} mol of 3-carboxy-2,2,5,5-tetramethylpyrroline-1-oxyl in a mixture of 2 ml dry benzene and 0.13 ml of dry pyridine were added 1.2×10^{-4} mol of thionyl chloride and, after 15 min, 0.5×10^{-4} mol of PEG. In the experiment with PEG Mw 20 000 18 ml of dry benzene was added. The solution was shaken at room temperature for 2 h and left overnight. Then it was poured into a large excess of ether. The light-yellow product was centrifuged, dried and dissolved in chloroform. The chloroform solution was precipitated with ether. This dissolving-precipitating procedure was repeated so many times that the ESR activity of the sample remained constant. The product was dried in vacuum overnight.

The ESR spectra were measured with a Varian E-4 spectrometer at 9500 Mc at 23°C.

Table 1.

Spectrum	Mw of PEG	Peak-to-peak separation	τ
1A	—	32.2 G	4.4×10^{-11} sec
1B	600 ± 30	33.6	1.9×10^{-9}
1C	$1\,550 \pm 100$	38.5	4.1×10^{-9}
1D	$4\,000 \pm 500$	44.3	18.4×10^{-9}
1E	$20\,000 \pm 3000$	60.5	34.8×10^{-9}

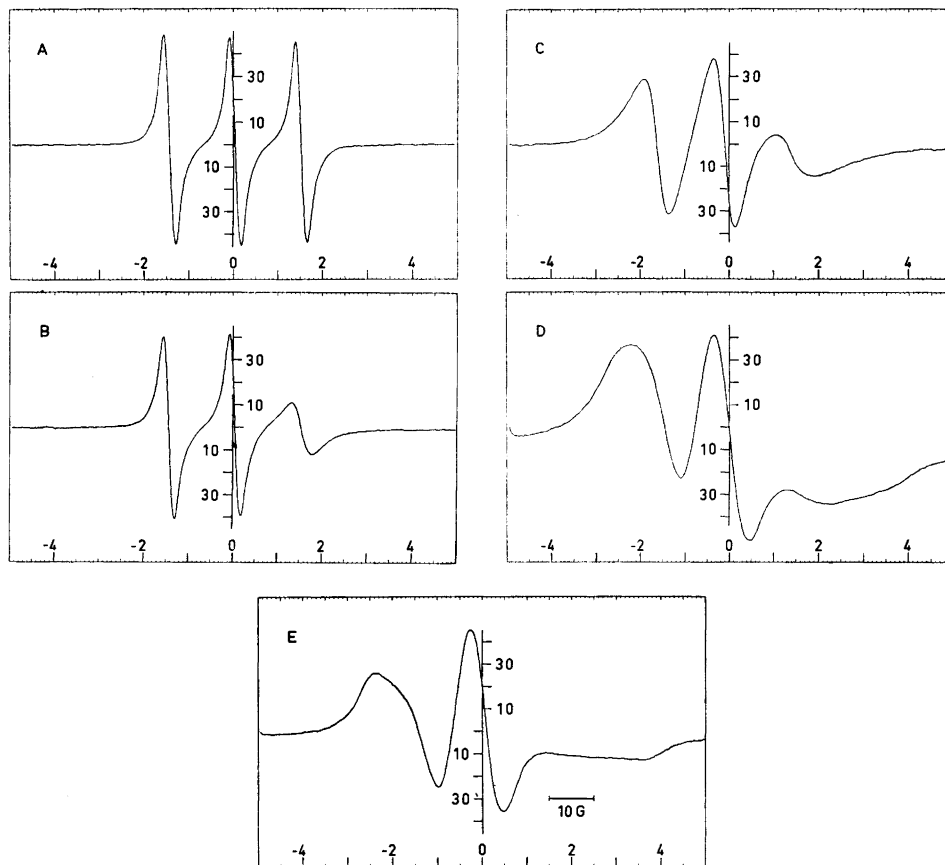


Fig. 1. 1A. The ESR spectrum of free spin label (I) in chloroform; 1B–1E. The ESR spectra of spin label (I) attached to PEG samples of various molecular weights. The scale at the lower right is equivalent to 10 Gauss.

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