

Spin-labeling Investigations of Polyamides and Polyesters

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Polyamides from sebacoyl chloride and hexamethylenediamine and polyesters from sebacoyl chloride and dihydroxybenzenes with 3-carboxy-2,2,5,5-tetramethylpyrrolidine-1-oxyl end groups were prepared. The ESR spectra of solid polymers indicated that the mobility of end group radicals is severely restricted. The ESR spectra of polyamides and polyesters were measured in *m*-cresol and chloroform solutions, respectively. The hard sphere radii of dissolved polymers were calculated by means of the Stokes-Einstein expression. A loosely arranged random-coil orientation of polymer chains in these solvents was indicated.

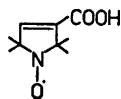
Spin-labeling technique has been used widely to study structural problems of soluble proteins in various solvents, orientation of molecules in membranes and structures of molecular aggregates in solvents.^{1,2} It is well known that the electron spin resonance (ESR) spectrum of free nitroxyl radicals in a polymer matrix consists of a triplet and is very similar to the spectrum of the same radicals in a high viscous liquid.³ On the other hand the ESR spectra of nitroxyl polymers consist of a single exchange-narrowed line.⁴ It can be concluded that spin-labeling of polymer end groups reflects the intermolecular relations in the polymer matrix.^{1,3}

We wish to report here the preparation and ESR spectra of condensation polymers of sebacoyl chloride with hexamethylenediamine, hydroquinone, catechol, and resorcinol with 3-carboxy-2,2,5,5-tetramethylpyrrolidine-1-oxyl end groups. The ESR spectra were analysed according to Edelstein *et al.*⁵

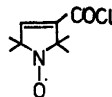
EXPERIMENTAL

Materials. 3-Carboxy-2,2,5,5-tetramethylpyrrolidine-1-oxyl (I) was prepared according to Rozantsev and Krinitskaya.⁶

3-Chloroformyl-2,2,5,5-tetramethylpyrrolidine-1-oxyl (II) was prepared according to Krinitskaya *et al.*⁷ from (I) just before each polymerization to get a reactive compound for end group labeling.

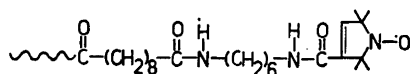


(I)



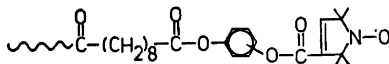
(II)

Spin-labeled polyamides from sebacyl chloride and hexamethylenediamine (IIIa–III d). Polyamide IIIa was prepared by modifying the interfacial polycondensation method of Beaman *et al.*⁸ To a solution of 0.007 mol of sebacyl chloride in 50 ml of *sym*-tetrachloroethane 0.0002 mol of II in 2 ml of benzene was added. The mixture was cooled to 0°C. To the vigorously stirred solution 0.021 mol hexamethylenediamine in 25 ml of water was added. The mixture was stirred 30 min at 0°C. The product was washed several times with water and ether and extracted with acetone until the ESR activity of the sample remained constant. The polymer was dried in vacuum overnight. The polyamides IIIb–III d were prepared in the same manner by using various amounts of radical II (to IIIb 0.0004 mol of II was added, to IIIc 0.0018 and to III d, 0 mol, respectively). Because radical II has only one covalently active group it causes the stopping of the condensation reaction. Thus also various amounts of radical in the reaction mixture give various molecular weights in the products. The yields were 60–70 %. The structural formula of the paramagnetic end of IIIa–III c is given below.



(IIIa–IIIc)

Spin-labeled polyesters from sebacyl chloride and dihydroxybenzenes (IVa–IVc). Polyester IVa was prepared by adding to 28.5 ml of benzene-pyridine mixture (15 : 1 v/v) 0.005 mol of sebacyl chloride, 0.0005 mol of radical II in 1.5 ml of benzene and 0.005 mol of hydroquinone. The reaction vessel was sealed and the solution was shaken at 24°C for 3 h and was left overnight. The precipitates were removed by centrifugation and the solution was poured into a large amount of chilled methanol-water mixture (19 : 1 v/v). The precipitated polymer was centrifugated, dried and dissolved in a small amount of benzene-pyridine mixture (15 : 1 v/v). The solution was precipitated with chilled methanol-water mixture. 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 other polyesters were prepared in the same way with the exception that instead of hydroquinone in IVb catechol and in IVc resorcinol were used. The yields were 10–15 %. The structural formula of paramagnetic end of IVa–IVc is given below.



(IVa–IVc)

Molecular weights. The polymeric nature of each polyamide prepared (IIIa–III d) was characterized in terms of its intrinsic viscosity in *m*-cresol at 30°C. The molecular weights of polyesters prepared (IVa–IVc) were measured using a vapour pressure osmometer (Perkin-Elmer Modell 115) in chloroform at 40°C.

ESR measurements. The ESR spectra were obtained from solid and dissolved polymers on a Varian E-4 spectrometer operating at a microwave frequency of 9.5 GHz. The magnetic field was modulated with an amplitude less than one-fourth of the linewidth. The measurements were made at 297°K and at 336°K using a thermostat. Its accuracy was $\pm 1^\circ$.

The isotropic ESR spectra of polyamides and polyesters were obtained at 336°K in diethylene glycol and in chloroform solutions, respectively. The concentration of nitroxyl radicals in solution was $\sim 10^{-5}$ M.

To get the parameters of the spin Hamiltonian, the glass spectra of the samples were measured at 100°K.

RESULTS AND DISCUSSION

The determined molecular weights are given in Table 1. The molecular weights of polyamides become smaller when the amount of nitroxide radicals in the beginning becomes greater. The relation between radical concentration and the $[\eta]$ of polyamides was linear in this concentration range.

Table 1.

Compound	Nitroxyl radicals added (mol)	$[\eta]$	Molecular weight
Polyamide IIIId	0.0000	0.85	9100
» IIIa	0.0002	0.50	5150
» IIIb	0.0004	0.45	4700
» IIIc	0.0018	0.38	4000
Polyester IVa	0.0005		2600
» IVb	0.0005		4200
» IVc	0.0005		4200

ESR Spectra of solid polymers. The glass spectrum at 100°K of polyamide IIIa is given in Fig. 1. The other glass spectra looked principally alike. An analysis based on the assumed axial symmetry of the spectra was carried out

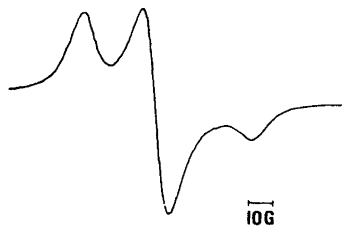


Fig. 1. The ESR spectrum of polyamide IIIa at 100°K.

according to Edelstein *et al.*⁵ It is known that the two outermost peaks of the glass spectrum of nitroxyl radicals are caused by the parallel transitions of the nuclear spin states $M_I = \pm 1$. This gives the possibility to determine $g_{||}$, and $A_{||}$. Thus the experimental isotropic quantities $\langle g \rangle$, and $\langle A \rangle$, obtained by the above mentioned method, together with the known relationships

$\langle g \rangle = \frac{1}{3}(g_{\parallel} + 2g_{\perp})$ and $\langle A \rangle = \frac{1}{3}(A_{\parallel} + 2A_{\perp})$ give the values for the parameters of the spin, which are collected in Table 2.

Table 2.

Compound	A_{\parallel} (G)	A_{\perp} (G)	g_{\parallel}	g_{\perp}
Polyamides IIIa – IIIc ^a	34.8	5.2	2.0050	2.0080
Polyesters IVa – IVc ^b	33.0	5.0	2.0048	2.0071

^a Isotropic $\langle A \rangle = 15.1$ G, $\langle g \rangle = 2.0070$

^b Isotropic values $\langle A \rangle = 14.9$ G, $\langle g \rangle = 2.0067$

The ESR spectra of polyamides and polyesters at 297°K and 336°K are given in Figs. 2 and 3. They are highly anisotropic, so the correlation times of nitroxyl radicals are in the region of slow rotations. The spectra of low molecular weight polymers (Fig. 2, IIIc and Fig. 3, IVa) indicate further strong spin-spin intermolecular interaction. In Table 3 are given the values of peak-to-peak separation of the outermost lines of the spectra.

It can be seen from the peak-to-peak separations that the mobility of labeled polyamide molecules at constant temperature becomes greater when the molecular weight of the sample becomes smaller. These spectra, compared with earlier results for polymers with more weak intermolecular interactions,⁹

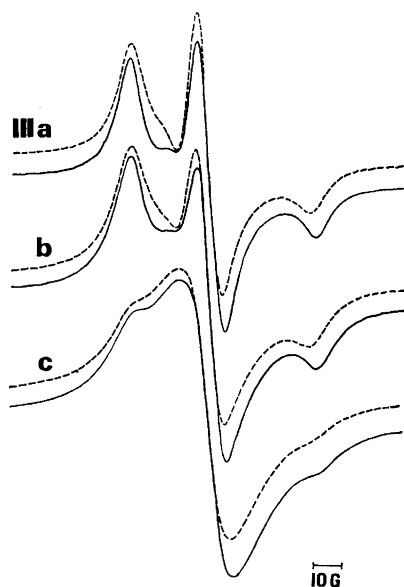


Fig. 2. The ESR spectra of spin-labeled polyamides (— 297°K, - - - 336°K).

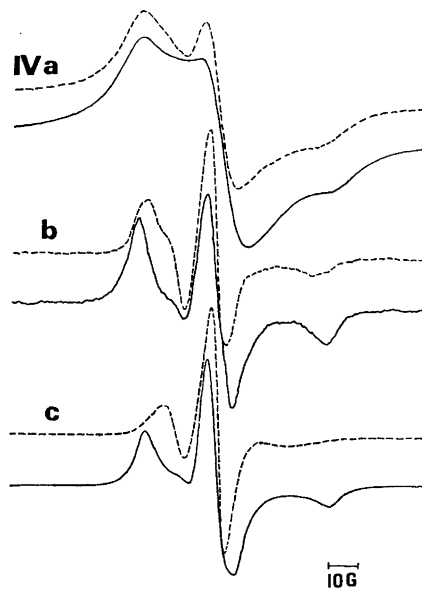


Fig. 3. The ESR spectra of spin-labeled polyesters (— 297°K, - - - 336°K).

Table 3.

Compound	Molecular weight	Peak-to-peak separation (G)		
		100°K	297°K	336°K
Polyamide IIIa	5150	69.6	66.6	64.4
» IIIb	4700	69.6	66.2	63.0
» IIIc	4000	69.6	66.0	60.0
Polyester IVa	2600	66.0	62.0	42.0
» IVb	4200	66.0	63.0	52.0
» IVc	4200	66.0	61.0	59.0

seem to indicate that strong intermolecular bonds restrict markedly the motions of covalently bonded radicals. Further it is evident that the velocity of the increase of motional freedom as a function of temperature is dependent on the steric conditions of polymers (*cf.* polymers IVa – IVc of Table 3).

Spin-labeled polymers in solution. The spin-labeled polyamides and polyesters were dissolved in *m*-cresol and chloroform, respectively, to study the effective Stokes radii of molecules. The solutions were diluted so much that the dissolved polymers did not more affect the microviscosity of solutions. The Stokes-Einstein expression for τ_c ,

$$\tau_c = \frac{4\pi\eta a^3}{3kT} \quad (1)$$

predicts that at constant temperature, τ_c is a linear function of η . By measuring τ_c and η it is possible to estimate the equivalent hard-sphere radius of the tumbling molecule. In Fig. 4 are given the ESR spectra of polyamide IIIa



Fig. 4. A. Polyamide IIIa in *m*-cresol. B. Polyester IVa in chloroform ($T = 297^\circ\text{K}$).

and polyester IVa in *m*-cresol and chloroform, respectively, at 297°K. The other solution ESR-spectra looked principally alike. The correlation times were calculated according to Barratt *et al.*¹⁰ by means of the expression

$$\tau_c = \frac{\delta\nu(M = -1) + \delta\nu(M = +1)}{\delta\nu(M = 0)} \left\{ \frac{15\pi\sqrt{3}\delta\nu(M = 0)}{8b\Delta\gamma H} \right\} \quad (2)$$

where $\delta\nu(M = 0, \pm 1)$ are the measured spectral line widths,

$\Delta\gamma = \beta/\hbar(g_{11} - g_{\perp})$ and $b = \frac{4\pi}{3}(A_{11} - A_{\perp})$. In Table 4 are given the values of τ_c and the corresponding hard sphere radii (a) of polymer molecules calculated

Table 4.

Compound	τ_c (s)	a (Å)
Polyamide IIIa	5.3×10^{-9}	6.9
» IIIb	5.1×10^{-9}	6.6
» IIIc	5.0×10^{-9}	6.5
Polyester IVa	1.2×10^{-10}	6.0
» IVc	1.4×10^{-10}	7.0
» IVc	1.3×10^{-10}	6.5

by the expression (1). The effective Stokes radii of Table 4 are considerably greater than the corresponding ones, measured by the same method, for free radicals (I) in *m*-cresol ($a=1.9$ Å) and chloroform ($a=2.9$ Å). These values are smaller than the real radii of the molecules as was stated earlier.⁵ The effective Stokes radii of polymers are much smaller than expected from the molecular weights of polymers. This indicates that the end group radicals still possess a great amount of motional freedom relative to the polymer backbone and that a loosely arranged random coil orientation of polymer chains is present.

According to the theory of Kivelson¹¹ the line width of hyperfine multiplets of an ESR spectrum is influenced by the hyperfine anisotropy, the *g*-factor anisotropy and the correlation time. Assuming a Lorentzian line shape, the expression is

$$\Delta H_{mI} = (a_1 + a_2 m_I + a_3 m_I^2) \quad (3)$$

where ΔH_{mI} is the peak-to-peak line width of the absorption derivative, and

$$a_1 = \tau_c \left[\frac{4}{45} \left(\beta \hbar^{-1} \Delta g B_0 \right)^2 + \frac{3b^2}{20} \right] + \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} \left[\frac{1}{15} \left(\beta \hbar^{-1} \Delta g B_0 \right)^2 + \frac{7b^2}{20} \right] + K \quad (4)$$

$$a_2 = -\tau_c [b \beta \hbar^{-1} \Delta g B_0] \left[\frac{4}{45} + \frac{1}{5(1 + \omega_0^2 \tau_c^2)} \right] \quad (5)$$

$$a_3 = \tau_c \frac{b^2}{8} - \left[\frac{\tau_c}{1 + \omega_0^2 \tau_c^2} \right] \left[\frac{b^2}{40} \right] \quad (6)$$

Here $\Delta g = (g_{||} - g_{\perp})$, B_0 is the applied field in Gauss, K represents the contribution of relaxation processes to the linewidth which are independent of τ_c and $b = 2/3 \times (A_{||} - A_{\perp})$. By insertion of τ_c in eqns. 4–6 and by using the experimental value [(derivative height) \times (derivative width)² = constant] for ΔH_{mI} it is possible to calculate K . Thus for polyamides a value of $K = 0.30 \times 10^7 \text{ s}^{-1}$ is obtained. For polyesters it is $\sim 0.60 \times 10^7 \text{ s}^{-1}$ at 297°K. These data are of the same order of magnitude as earlier results for free nitroxyl radicals in solutions.¹²

REFERENCES

1. Ingham, J. D. *Rev. Macromol. Chem.* **3** (1968) 279.
2. Griffith, O. H. and Waggoner, A. S. *Acc. Chem. Res.* **2** (1969) 17.
3. Rozantsev, E. G. *Free Nitroxyl Radicals*, Plenum Press, New York 1970, p. 172.
4. Griffith, O. H., Keana, J. F. W., Rottschaefer, S. and Warlick, T. A. *J. Am. Chem. Soc.* **89** (1967) 5072.
5. Edelstein, N., Kwok, A. and Maki, A. H. *J. Chem. Phys.* **41** (1969) 179.
6. Rozantsev, E. G. and Krinitskaya, C. A. *Tetrahedron* **21** (1965) 491.
7. Krinitskaya, L. A., Buchachenko, A. C. and Rozantsev, E. G. *Zh. Organ. Khim.* **2** (1966) 1301.
8. Beaman, R. G., Morgan, D. W., Koller, C. R., Wittbecker, L. and Magat, E. E. *J. Polymer Sci.* **40** (1959) 289.
9. Törmälä, P., Martinmaa, J., Silvennoinen, K. and Vaahtera, K. *Acta Chem. Scand.* **24** (1970) 3066.
10. Barratt, M. D., Green, D. K. and Chapman, D. *Biochim. Biophys. Acta* **152** (1968) 20.
11. Kivelson, D. *J. Chem. Phys.* **33** (1960) 1107.
12. Lenk, R., Theobald, J. G. and Uebersfeld, J. *Compt. Rend.* **261** (1965) 4071.
13. Bullock, A. T., Butterworth, J. H. and Cameron, G. G. *European Polymer J.* **7** (1971) 445.

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