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MOLECULAR MOBILITY OF SPIN-LABELLED TEREPHTHALOYL CHLORIDE AND 1,10-DECANEDIOL COPOLYMER IN SOLUTION

F. SUNDHOLM*, A. M. WASSERMAN†, I. I. BARASHKOVA†,
V. P. TIMOFEEV‡ and A. L. BUCHACHENKO†

*Department of Chemistry, University of Helsinki, 00100 Helsinki 10, Finland, †Institute of Chemical Physics, U.S.S.R Academy of Sciences, Moscow 117334 and ‡Institute of Molecular Biology, U.S.S.R. Academy of Sciences, Moscow 117334, U.S.S.R.

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Abstract—Intramolecular mobility of spin-labelled terephthaloyl chloride and 1,10-decanediol copolymer in solution was investigated using a polymer in which the label was rigidly attached to the main chain methylene groups. Correlation times and effective segmental dimensions were measured, as were the frequency and amplitude of the high-frequency torsional vibrations of the main chain monomer units. The amplitude of high-frequency torsional vibrations was shown to increase with increasing temperature.

INTRODUCTION

ESR studies of spin-labelled macromolecules have yielded data on rotational correlation times and effective segmental dimensions [1, 2], as well as on local side-group mobility [3]. A side-group was labelled usually because of synthetic difficulties in introducing the spin label into the main chain; it could drastically interfere with the macromolecule structure.

Analyses of ESR spectra of spin-labelled macromolecules with a label in the main chain yield more accurate data on polymer chain local mobility. Until now, only a few ESR spectra of polymers with labels in the main chain have been analysed (e.g. polyethylene [4], polystyrene [5]). The present paper deals with the molecular mobility in solution of terephthaloyl chloride and 1,10-decanediol copolymers labelled in the main chain. A comparative analysis of the intramolecular mobility of the polymers is included.

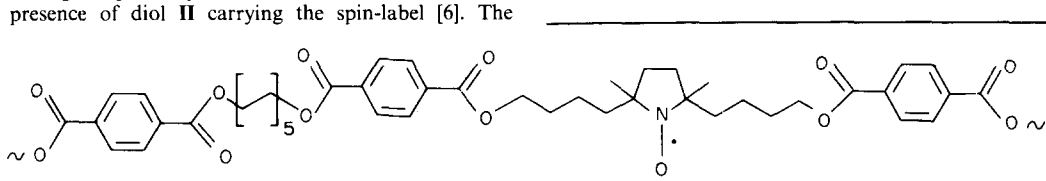
EXPERIMENTAL

The spin-labelled copolymer **I** was obtained by polycondensing terephthaloyl chloride and 1,10-decanediol in the presence of diol **II** carrying the spin-label [6]. The molecular model of a polymer segment is shown in Fig. 1. Copolymers with various contents of spin-label were synthesized: 1 per 10 diol molecules (copolymer FS-10, molecular mass $\bar{M}_w \cong 30{,}000$, melting point = 127–128°), 1 per 5 diol molecules (FS-20, $\bar{M}_w \cong 20{,}000$, melting point = 104–110°, 1 per 2 diol molecules (FS-50, $\bar{M}_w \cong 20{,}000$, melting point = 82–86°).

The ESR spectra were recorded on a Varian E-104A ESR spectrometer. Rotational correlation times of segments were determined as described previously [1, 7], by measuring the dependence of the value of $2A'_{\parallel}$ (the distance between the broad external extrema of the ESR spectrum) on solvent viscosity at a fixed temperature. The solvent was a mixture of chloroform and *m*-cresol; the viscosity was altered by varying the mixture composition. Spectra were measured over a temperature range of −30 to +120°.

MODEL OF SPIN-LABEL MOTION

The model of spin-label motion and the methods of determining rotational correlation times of the segmental motion of synthetic polymers, according to the dependence of the value $2A'_{\parallel}$ on solvent viscosity, have been described in detail [1, 2, 7]. It seems probable that the label may engage in two kinds of motion that lead to averaging of the anisotropic dipolar



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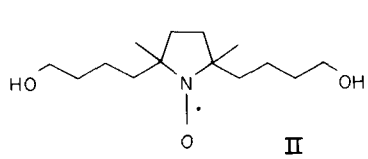

II

interaction and of the Zeeman interaction, i.e. slow diffusional rotation of segments having correlation times $\tau_{seg} \geqslant 5 \times 10^{-9}$ sec and fast anisotopic motion of the label itself relative to the segment with correlation times $\tau_l \leqslant 1 \times 10^{-9}$ sec. The label assumes a pattern of amplitude restricted motion in a cone having the opening equal to 2α [8]. The fast motion

Address correspondence to: Dr Franciska Sundholm, Department of Chemistry, University of Helsinki, E. Hesperiankatu 4, SF-00100 Helsinki 10, Finland.

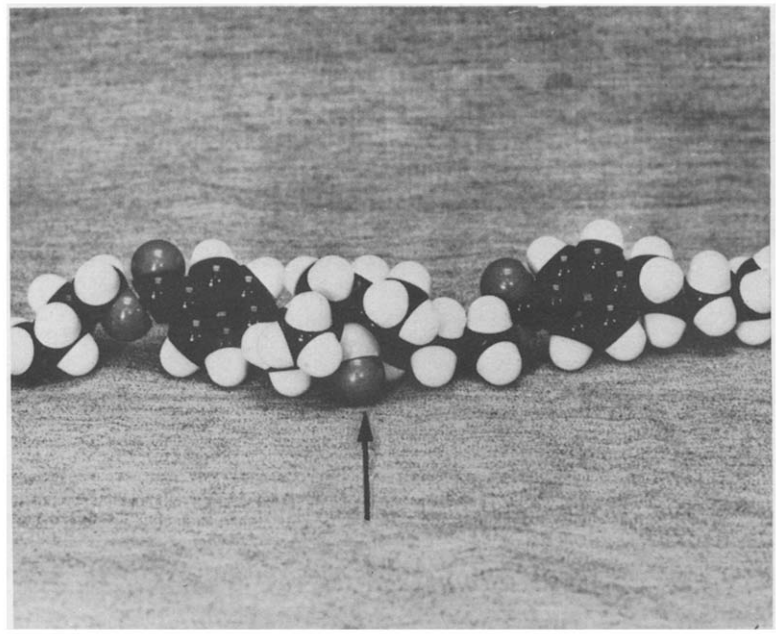

Fig. 1. Stuart–Brygleb molecular model of the spin-labelled polymer. The oxygen atom of the nitroxide radical is indicated by an arrow.

of the label itself leads to a partial averaging of the anisotropic hyperfine interaction that may be quantitatively characterized by a parameter S [9, 10]

$$S = \frac{\Delta\bar{A}}{\Delta A} = \frac{\bar{A}_{\parallel} - a}{A_{zz} - a} \tag{1}$$

where

$$\Delta A = A_{zz} - \frac{A_{xx} + A_{yy}}{2};$$

$\Delta\bar{A} = \bar{A}_{\parallel} - \bar{A}_{\perp}$, A_{xx}, A_{yy} and A_{zz} are the principal values of the hyperfine tensor, $\bar{A}_{\parallel}$ and $\bar{A}_{\perp}$ are the partially averaged axisymmetric principal values, and a is the isotropic hyperfine coupling constant of the ^{14}N nucleus. Should the label rotate together with the segment (or engage in single-axis rotation by itself about an axis parallel to the π-orbital of the unpaired electron of the nitroxyl fragment), the previously disclosed model stipulates the S-value as 1. An increase in the amplitude of the label rotation leads to smaller S-values; with $S = 0$, label motion is almost independent of segment motion. Semi-amplitude of the motion of the label itself is connected with the parameter S thus:

$$S = 1/2\,(\cos^2\alpha + \cos\alpha) \tag{2}$$

EXPERIMENTAL RESULTS

Examples of experimental ESR spectra of FS-10 copolymer 0.5% by weight solution are shown in Figs 2 and 3; the measurement of the experimental parameter $2A'_{\parallel}$ is also demonstrated. For FS-20 and FS-50 copolymer solutions, similar spectra were obtained. The isotropic hyperfine coupling constant a was measured in solution and is 15.25 ± 0.1 G for all the copolymers. The parallel component A_{zz} of the A tensor is 36.5 G, measured by Dr Lebedev and Dr Poluektov. It has been shown previously [10] that

$$2\bar{A}'_{\parallel} = 2\bar{A}_{\parallel} + C'(T/\eta)^{\beta_{\parallel}} \tag{3}$$

where C' is a constant depending on the effective dimensions of the segment containing the spin-label and $\beta_{\parallel}$ ranges between 0.74 and 0.83 as S decreases from 1.0 to 0.5. The value 0.74 was chosen for the exponent since the experimental values for S are close to 1 and vary only little with solvent composition and temperature in the system under consideration. Figure 4 shows the dependence of $2A'_{\parallel}$ on $(T/\eta)^{0.74}$ for copolymer FS-10. Two features of the figure deserve closer scrutiny. Firstly, with lower viscosity, $[(T/\eta)^{0.74} \geqslant 3(\text{K cp}^{-1})^{0.74})]$ the linear dependence of $2A'_{\parallel}$ on $(T/\eta)^{0.74}$ is obvious; this result means that all conditions of the label motion model are satisfied: $\tau_{seg} \geqslant 5 \times 10^{-9}$ sec, $\tau_l < 1 \times 10^{-9}$ sec (i.e. rotation of the label itself serves in a permanent way, regardless of viscosity of the solvent, to average the anisotropic hyperfine interaction) and the dependence of the rotational correlation times of the segments on solvent viscosity follows the Stokes–Einstein equation. The deviation from linearity at high viscosities results from violation of the spin-label fast rotation conditions, and the rotation of the label itself contributes to the averaging of the anisotropic hyperfine interaction depending on the viscosity. By extrapolating the value of $2A'_{\parallel}$ to $(T/\eta)^{0.74} = 0$, we find the averaged values of $2\bar{A}_{\parallel}$ and calculate S using equation (1). Calculated values of S are collected in Table 1.

Secondly, isotherms for different temperatures fail to coincide and parameter S does not equal 1 (which would have been reasonable to expect from a label rigidly attached to the macromolecule segment); moreover, parameter S is slightly temperature-dependent. This result means that high-frequency spin-label motion within the main polymer chain occurs, with a correlation time t_l not exceeding

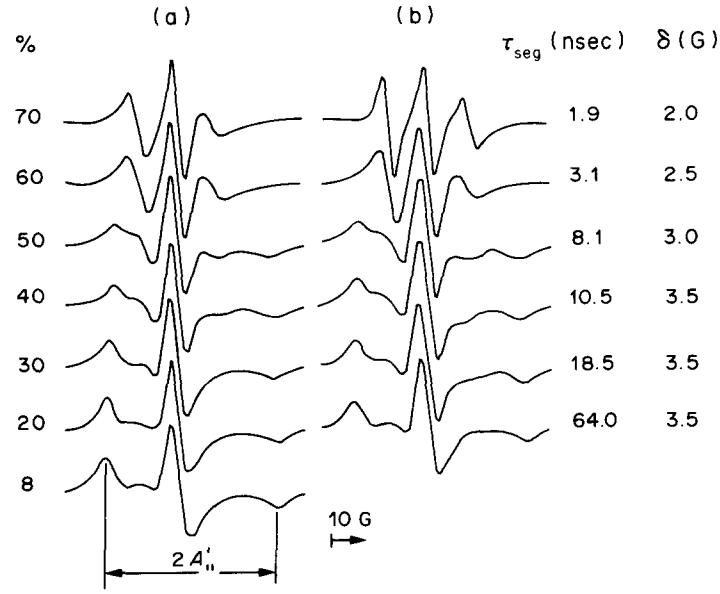

Fig. 2. (a) Experimental ESR spectra of FS-10 copolymer 0.5% w/v in solution at −20°. Solvent: mixture of *m*-cresol and chloroform, percentage of chloroform indicated in spectra. (b) Theoretical spectra calculated at $S = 0.93$; τ_{seg} and δ (peak-to-peak residual derivative line width) values indicated on spectra.

1×10^{-9} sec, leading to a partial averaging of the anisotropic hyperfine interaction; the amplitude of fast reorientation increases with increasing temperature. Such reorientation probably takes the form of torsional vibrations of methylene groups of the macromolecule main chain.

Correlation times of segment rotation were calculated thus. For each experimental $2A'_{\parallel}$ value, the value of $\Delta_{\parallel} - 2\bar{A}_{\parallel}$ was estimated, and τ_{seg} was pinpointed using the theoretical dependence of $\Delta_{\parallel}$ on τ_{seg} [7, 11]. Table 1 also contains semi-amplitudes for high frequency torsional vibrations of main chain methylene groups calculated via equation (2).

It can be concluded that the correlational times of segment rotation of FS-10, FS-20 and FS-50 copolymers do not differ substantially. The dependence of τ_{seg} on solvent viscosity is dictated by the Stokes–Einstein equation, while the method of changing viscosity is irrelevant, be it via varying the solvent composition or the temperature (Fig. 5). The effective hydrodynamic segment diameter ($2r$), determined on the basis of these data, is 18 Å.

It should be mentioned that the introduction of the label into the main chain not only yields data on the macromolecule segment mobility, but also allows one to determine the frequency and amplitude of the

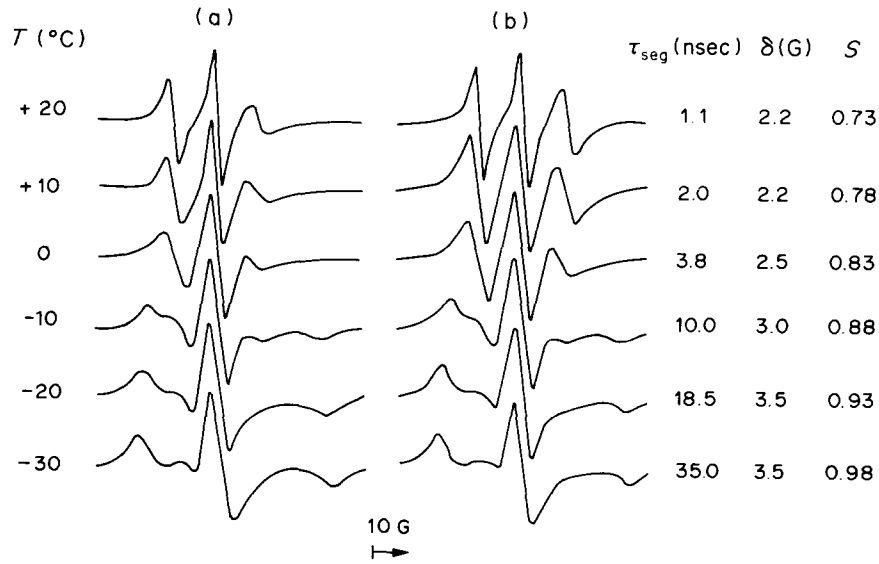

Fig. 3. (a) Experimental ESR spectra of FS-10 copolymer 0.5% w/v in solution in chloroform–*m*-cresol 30/70 at various temperatures. (b) Theoretical spectra calculated using τ_{seg}, S, δ values indicated on spectra.

Table 1. Correlation times of segment rotation of terephthaloyl chloride and 1,10-decanediol copolymer, S and α parameters

Polymer	T °C	τ_{seg} (nsec) 30% vol $CHCl_3$ + 70% vol cresol	$CHCl_3^*$	$S \pm 0.02$	$\alpha°$
FS-10	−30	35.0	1.0	0.98	8
	−20	18.5	0.8	0.93	18
	−10	10.0	0.7	0.88	23
	0	3.7*	0.6	0.83	28
FS-20	−27	26.0	0.9	0.98	8
	−20	16.0	0.8	0.92	19
FS-50	−24	21.0	0.9	0.94	16
	−18	13.5	0.8	0.92	19
	−11	7.5	0.7	0.90	21

*Determined by extrapolating according to the Stokes–Einstein equation.

torsional vibrations of the main chain methylene units. The amplitude of fast reorientation increases with rise in temperature: at −30°, $\alpha = 8°$, at 0° $\alpha = 28°$. The value of the amplitude of fast torsional vibrations of the macromolecule main chain units, for polystyrene and poly(methyl methacrylate) at 25° in solution, as determined by polarized luminescence, is 13° [12].

In non-viscous solvents, e.g. chloroform, the condition $\tau_{seg} > 5 \times 10^{-9}$ is not valid and ESR spectra fail to produce broad external extrema; in this case segment mobility was estimated by extrapolating according to the Stokes–Einstein equation the values of correlation times determined at high solvent viscosity (Table 1).

Experimental ESR spectra were compared to theoretical ones simulated as described previously [10, 13] assuming the rotation of the segment to be isotropic Brownian diffusion and using the g- and A-tensor values of FS-10 spin-labelled copolymer, determined in a mixture of chloroform (30% vol) and m-cresol via 2-mm ESR spectroscopy:

$$g_{xx} = 2.0080,\ g_{yy} = 2.0053,\ g_{zz} = 2.0022,$$
$$A_{xx} = A_{yy} \simeq 6\ \text{G},\ A_{zz} = 36.5\ \text{G}$$

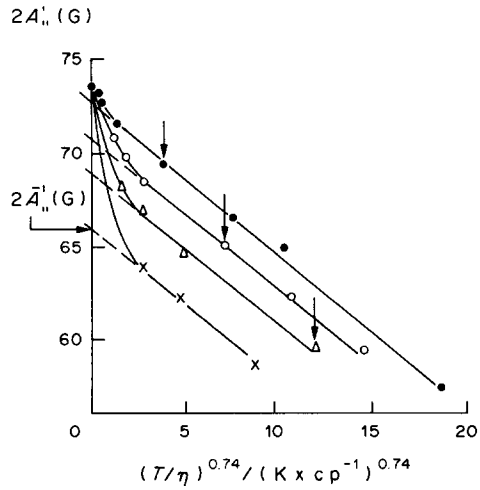

Fig. 4. The dependence of $2A_{\parallel}'$ in ESR spectra of FS-10 copolymer 0.5% w/v in solution on $(T/\eta)^{0.74}$. Solvent: mixture of chloroform and m-cresol; the arrow indicates values corresponding to 30% chloroform in mixture. (×) 0°; (△) −10°; (○) −20° and (●) −30°.

Experimental τ_{seg} and S values were used for spectra simulation. Table 2 illustrates $2A_{\parallel}'$ values determined experimentally and theoretically.

Two groups of spectra were subject to analysis.

1. Spectra recorded at constant temperature (−20°) and different solvent viscosities (Fig. 2). Theoretical spectra in Fig. 2b have been calculated with a fixed S value and varying τ_{seg} values.

2. Spectra recorded in a single solvent (a mixture of chloroform and m-cresol, 30% chloroform) at varying temperatures (Fig. 3a).

τ_{seg} and S values used to simulate experimental spectra at 10 and 20° were determined by extrapolating the values taken at −30, −20, −10 and 0°.

Results described in Figs 2 and 3, as well as in Table 2, show that experimental spectra exhibiting broad external extrema $\tau_{seg} > 5 \times 10^{-9}$ can be satisfactorily interpreted by simulation. For spectra at $\tau_{seg} < 5 \times 10^{-9}$ sec, simulation is not a good method, probably because these spectra do not admit of segregated averaging of the effective Spin–Hamiltonian, brought on by the motion of the label itself and the motion of the label and the macromolecule segment together. The latter case obviously demands calculations that are more accurate such as those described by Polnascek [13] and Freed [14].

Rotational correlation times and effective segmental dimensions of the copolymer under study are

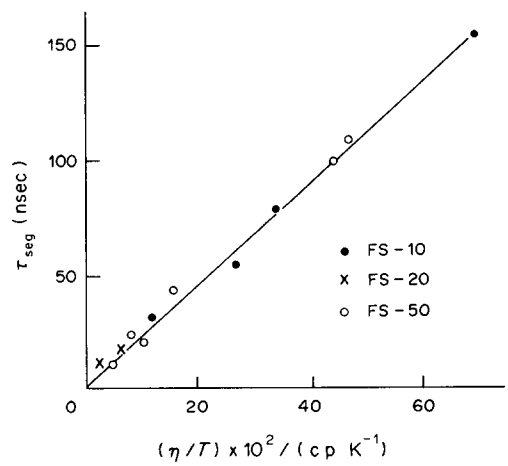

Fig. 5. the dependence of τ_{seg} on solvent viscosity in Stokes–Einstein equation.

Table 2. $2A_{\|}$ values from experimental and theoretical spectra

T (°C)	Solvent (chloroform volume in mixture, %)	τ_{seg} (nsec)	$S \pm 0.02$	$2A'_{\|}$ (G) exper.	$2A'_{\|}$ (G) theor.
−20	20	64.0	0.93	68.5	68.5
	30	18.5	0.93	65.2	65.4
	50	10.5	0.93	62.4	63.0
	60	8.1	0.93	60.5	61.3
−10	30	10.0	0.88	60.5	60.8
−20	30	18.5	0.93	65.2	65.4
−30	30	35.0	0.98	69.3	69.4

Table 3. Rotational correlation times (at 25° and solvent viscosity of 0.89 cp.) and effective segmental dimensions of spin-labelled macromolecules

No.	Polymer	Solvent	τ_{seg} (nsec)	$2r$ (Å)
1.	FS copolymer	Chloroform	0.7	18
2.	Poly(4-vinylpyridine) [2]	Ethanol	2.6	28
3.	Poly(vinylpyrrolidone) [2]	Ethanol	3.5	31
4.	Poly(vinylcaprolactam) [2]	Ethanol	6.5	36
5.	Chytosan [14]	0.33 M CH_3COOH	14.5	52

compared with the corresponding parameters of other polymers in Table 3.

The FS copolymer exhibits greater segmental mobility; segmental mobility of this polymer determined by the spin-label technique, depends on the mobility of the methylene units connecting the label to the aromatic rings. Rotational correlation times of segments of carbon chain polymers, as illustrated in Table 3, are greater than those of the FS copolymer; they increase with increasing volume of the substituent in a side-group. For cytosan, a polymer with a rigid structural chain, segmental mobility is slight, while segmental dimensions are greater than for other polymers.

CONCLUSIONS

Line broadening and its temperature dependence have been studied for labelled polymers in solution [15]. It was shown that for a labelled polymer, poly(vinyl pyridine), in a polar solvent, ethanol, only dipole and exchange interactions of the labels inside the macromolecule determine the linewidth of the ESR spectra at concentrations less than 1 wt% of macromolecule. It is believed that the same argument is valid in this case. On the other hand, since linewidths of the ESR spectra of polymers FS-10, FS-20, and FS-50 do not differ significantly, the intermolecular dipole contribution to the linewidth is similar for the three polymers in solution.

All spectroscopic parameters (a, A and g) were determined for each solvent composition and each temperature used from ESR spectra measured under similar conditions. This feature means that effects of solvent polarity and possible hydrogen bonding are included in the calculations, and that the results give a true picture of the polymer behaviour in this solvent system.

Previous investigations [1, 2, 10] have proved that analyses of temperature–viscosity correlations of ESR spectra of spin-labelled polymers with a label in a side-group yield correlation times and effective segmental dimensions of macromolecules. The introduction of the label into the main chain allows not only for assessment of rotational correlation times and effective segmental dimensions, but also for the determination of the high frequency motion frequency and amplitude of the macromolecule main chain monomer units. Such motion is in all probability intramolecular torsional vibration growing in amplitude with increasing temperature.

In spin-labelled terephthaloyl chloride and 1,10-decanediol copolymer, the label is rigidly attached to the methylene units of the main chain, and hence it reflects accurately the mobility of the segments in this part of the backbone: it is greater than for carbon chain polymers with side-chains. It should be noted, however, that the intramolecular mobility measured in this manner does not reflect the mobility of polymer chain sections that include terephthaloyl groups which must be less than intramolecular mobility of parts of the polymer chain that include only methylene units.

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REFERENCES

1. A. M. Wasserman, V. P. Timofeev, T. A. Alksandrova, T. M. Karaputadze, A. B. Shapiro and Yu. E. Kirsch, *Eur. Polym. J.* **19,** 333 (1983).
2. A. L. Buchachenko and A. M. Wasserman, *Pure appl. Chem.* **54,** 507 (1982).
3. A. T. Bullock and G. G. Cameron, *Structural Studies of Macromolecules by Spectroscopic Methods*, (Edited by K. J. Ivin), p. 273. Wiley, London (1976).
4. A. T. Bullock, G. G. Cameron and P. M. Smith, *Eur. Polym. J.* **11,** 617 (1975).
5. C. Friedrich, F. Lauprêtre, C. Noel and L. Monnerie, *Macromolecules* **14,** 1119 (1981).

6. F. Sundholm and M. Johansson, *Euchem Conference on Stable Nitroxide Radicals, Syntheses and Applications* (Abstracts) Finland (1981).
7. I. V. Dudich, V. P. Timofeev, M. V. Volkenstein and A. Yu. Misharin, *Molek. Biol. U.S.S.R.* **11,** 685 (1977).
8. O. H. Griffith and P. C. Jost, *Spin Labeling, Theory and Applications*, (Edited by L. J. Berliner), p. 454. Academic Press, New York (1976).
9. W. L. Hubbell and H. M. McConnell, *J. Am. chem. Soc.* **93,** 319 (1971).
10. A. M. Wasserman, T. A. Aleksandrova, I. V. Dudich and V. P. Timofeev, *Eur. Polym. J.* **17,** 342 (1981).
11. V. P. Timofeev, I. V. Dudich and M. B. Volkenstein, *Bioph. Struct. Mech.* **7,** 41 (1980).
12. E. A. Anufrieva, Y. Y. Gotlieb, M. G. Krakovyak and V. D. Pautov, *Vysokomolek, Soedin.* **18A,** 2740 (1976).
13. V. F. Polnaszek, Ph.D. Thesis, Cornell University (1975).
14. J. Freed, *Spin Labeling, Theory and Applications*, (Edited by L. J. Berliner), p. 53. Academic Press, New York (1976).
15. T. A. Aleksandrova, A. M. Wasserman, A. I. Gamzazade, S. V. Rogozhin, I. A. Cimenel and V. P. Timofeev, *Vysokomolek. Soedin.* **25B,** 219 (1983).
16. A. L. Buchachenko, A. M. Wasserman, T. A. Aleksandrova and A. L. Kovarskii, *Molecular Motion in Polymers by ESR*, (Edited by R. F. Boyer and S. E. Keinath), pp. 33–53. Hardwood, New York (1980).

APPENDIX

Equation (1) is derived thus.

$$S = \frac{\overline{\Delta A}}{\Delta A} \tag{1}$$

where

$$\Delta A = A_{zz} - 1/2\,(A_{xx} + A_{yy}),\ \overline{\Delta A} = \bar{A}_{\parallel} - \bar{A}_{\perp},$$

A_{xx}, A_{yy}, A_{zz} are the principal values of the hyperfine tensor. $\bar{A}$ and $\bar{A}$ are the partially averaged components of dipolar interaction in the system studied depending on the precession angle of the nitroxide label with respect to the macromolecule segment thus (cf. ref. 2)

$$\bar{A}_{\parallel} = \mathrm{a} + \frac{\Delta A}{3}(\cos^2\alpha + \cos\alpha), \tag{2}$$

$$\bar{A}_{\perp} = \mathrm{a} - \frac{\Delta A}{6}(\cos^2\alpha + \cos\alpha) \tag{3}$$

where a is the isotropic hyperfine coupling constant equal to $1/3(A_{xx} + A_{yy} + A_{zz})$. Assuming axial symmetry for the nitroxide fragment, we write $A_{zz} = \mathrm{A}_{\parallel}$ and $A_{\perp} = 1/2\,(A_{xx} + A_{yy})$, hence $\Delta A = 3/2(A_{\parallel} - a)$ and $\overline{\Delta A} = 3/2(\bar{A}_{\parallel} - a)$. Thus

$$S = \frac{\bar{A}_{\parallel} - a}{A_{\parallel} - a} \tag{1'}$$

for the axially symmetric nitroxide fragment.