Characterization of Stable Nitroxide Radicals on the Basis of Adduct Chromophore-Hindered Amine Utilizing EPR Spectroscopy in Solution and Polymer Matrix

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EPR spectra of 17 stable nitroxide radicals on the basis of 4-substituted 1-oxyl-2,2,6,6-tetramethylpiperidine in solution (benzene) and in polymer matrices (PVC, iPP) were studied. Four derivatives containing pyrene and five with naphthalene as chromophore were used. They differ from each other by the length and type of bridge, connecting covalently the piperidine radical to chromophore. Two biradicals containing phosphorus and sulfur and one triradical containing phosphorus were investigated.

In solution EPR spectra of probes containing one nitroxyl group provide triplet with line of equal intensity. The biradicals spectra were quintets and the triradical was septet. The purity of the prepared compounds was determined from the integrals of EPR spectra.

In polymer matrices at room temperature the EPR spectra of monoradicals derived from hindered amines provide anisotropic spectra, typical for nitroxyl radicals in solid phase.

Spin probes are widely used in polymer research. Frequently used probes are nitroxyl radicals. They are very stable in solid phase as well as in solutions. As class of stable organic radicals they were discovered for the first time in 1956 [1, 2]. Since that time significant attention has been paid to the study of their synthesis and their properties [3—5]. In the case of the most stable nitroxyl radicals, the NO˙ group is bonded to a tertiary carbon, for example di-*tert*-butylnitroxide, 2,2-dimethyloxazoline derivatives, pyrroline, and piperidine nitroxides. Under conditions that the probes can freely rotate the spectrum of nitroxide provides a triplet with lines of equal intensity. This is a result of interaction of free radical with the magnetic moment of nitrogen nucleus ($I = 1$).

For investigation of interaction of low-molecular organic nitroxides with polymer matrix the technique of spin probes is very often used. This method enables to study mobility of probe in microscopic environment utilizing the EPR technique. Some nitroxides easily diffuse into polymer [6]. It was found that these radicals are mainly localized in amorphous phase of polymer [7]. *Kusumoto et al.* [8] studied the motions of polymer chains on the surface of growing PE monocrystal in relation to the structure of surface. At low temperature the spectrum is anisotropic and consists of wide lines suggesting that the free rotation of the probe is hindered. With increasing temperature small splitting occurs because the probe starts freely rotate, which causes changes in the hyperfine structure of the spectrum. Above certain temperature a triplet occurs with equal-line intensities. The technique of spin probes is utilized for research of Overhausers effect, *e.g.* dipole—dipole interactions of free radicals with electrons and protons, *etc.*

In this paper we describe and compare the EPR spectra of 17 different nitroxyl radicals of 4-substituted 1-oxo-2,2,6,6-tetramethylpiperidines in solution and some of them in polymer matrix. The spectra of mono-, di-, and triradicals are compared in solution as well. Majority of the compounds *I—XV* are combined adducts of chromophore with the sterically hindered amine (4-substituted 1-oxo-2,2,6,6-tetramethylpiperidines) that have been utilized as fluorescence probes [9—14, 22]. They have been used as well as spin probes [19—21]. The main goal is to investigate the influence of environment on the shape of EPR spectra in fluid solutions and solid matrices as well as the influence of the size and the type of substituent and their linkage with paramagnetic centre in the ground state. Another aim of the paper is to quantify the presence of probes in order to judge the efficiency of oxidation of parent amines.

EXPERIMENTAL

A series of 17 different probes of nitroxide radicals was measured. Their structures are shown

I

II

III

IV

V

VI

VII

VIII

IX

X
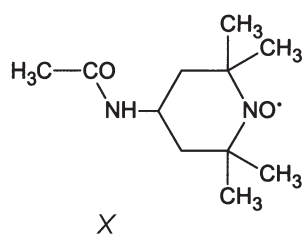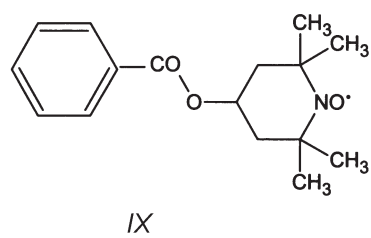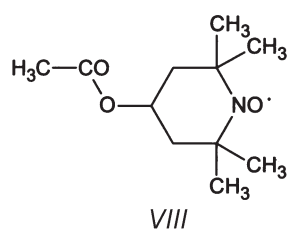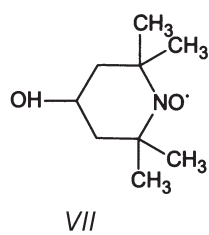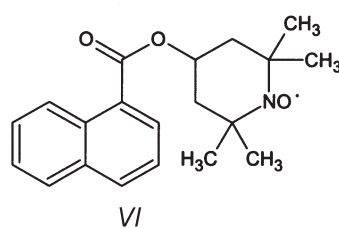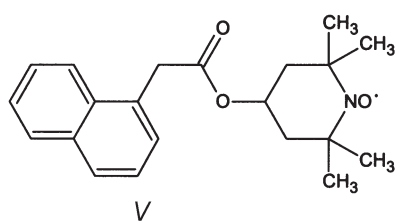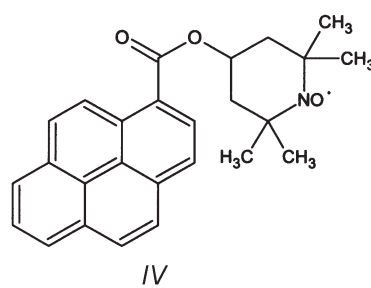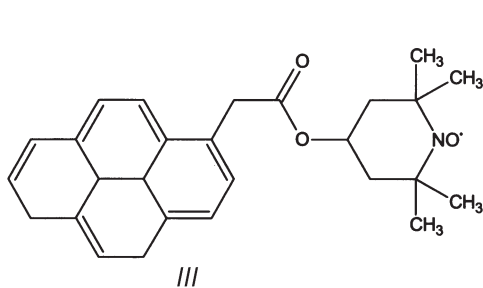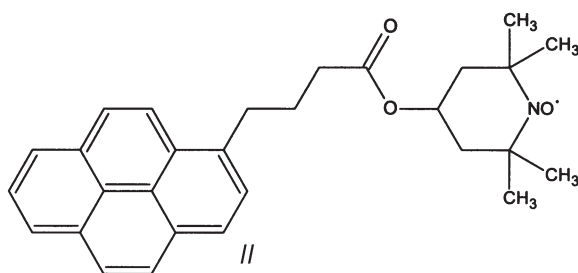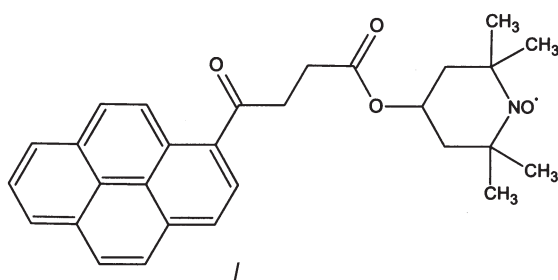
Formula 1

in Formula 1. The preparation of 1-oxyl-2,2,6,6-tetramethylpiperid-4-yl ester of 4-oxo-4-(pyren-1-yl)-butanoic acid (*I*), m.p. = 95—99 °C, 1-oxyl-2,2,6,6-tetramethylpiperid-4-yl ester of (pyren-1-yl)acetic acid (*III*), product in oil form, 1-oxyl-2,2,6,6-tetramethyl-piperid-4-yl ester of pyren-1carboxylic acid (*IV*), m.p. = 174—176 °C was described in paper [9]. Preparation of 1-oxyl-2,2,6,6-tetramethylpiperid-4-yl ester of 4-(pyren-1-yl)butanoic acid (*II*) (m.p. = 110—112 °C) was described in paper [10]. Preparation of 1-oxyl-2,2,6,6-tetramethylpiperid-4-yl ester of (naphth-1-yl)acetic acid (*V*), m.p. = 41—42 °C and 1-oxyl-2,2,6,6-tetramethylpiperid-4-yl ester of 1-naphthoic acid (*VI*), m.p. = 98—101 °C was described in [11]. Synthesis of 1-oxyl-2,2,6,6-tetramethylpiperidin-4-ol (*VII*), m.p. = 71—72 °C, 1-oxyl-2,2,6,6-tetramethyl-piperid-4-yl acetate (*VIII*), m.p. = 47—51 °C, *N*-(1-oxyl-2,2,6,6-tetramethylpiperid-4-yl)acetamide (*X*), m.p. = 147—149 °C was described in [12]. Preparation of 1-oxyl-2,2,6,6-tetramethylpiperid-4-yl benzoate (*IX*), m.p. = 91—92 °C and 1-oxyl-2,2,6,6-tetramethylpiperid-4-yl stearate (*XI*), m.p. = 37—39 °C was described in [13], of *N*-(1-oxyl-2,2,6,6-tetramethylpiperid-4-yl)-1,8-naphthylimide (*XII*), m.p. = 227—229 °C in [14]. Probes *XIII* (1-oxyl-(2,2,6,6-tetramethylpiperid-4-yl)-1-naphthylamide, m.p. = 193—196 °C) and *XIV* (1-oxyl-(2,2,6,6-tetra-methylpiperid-4-yl)-2-(1-naphthyl)acetamide, m.p. = 144—147 °C) were prepared according to [11]. Probes *XV* 2,6-di(*tert*-butyl)-4-methylphenyl di-(1-oxyl-2,2,6,6-tetramethylpiperid-4-yl) phosphite, m.p. = 120—122 °C, *XVI* di(1-oxyl-2,2,6,6-tetramethylpiperid-4-yl) sulfoxide, m.p. = 98—101 °C, and *XVII* tri(1-oxyl-2,2,6,6-tetramethylpiperid-4-yl) phosphite, m.p. = 95—118 °C were prepared at the Institute of Organic Chemistry, Technical University, Dresden in laboratory of Dr. W. Habicher. Biradical *XVI* and triradical *XVII* have been already characterized in [11, 21]. 1-Oxyl-2,2,6,6-tetramethylpiperidin-4-ol (probe *VII*) was used as internal standard as the best-defined radical on the basis of available data from literature.

For EPR measurements in solution we used benzene (Lachema, Brno, Czech Republic, UV spectroscopy grade) as solvent. There were two reasons for the choice of this solvent. First one is a good solubility of all probes in it and the second one is that its dipole moment equal to zero makes it very suitable for EPR measurement.

Polymer films doped with probes were prepared by casting (when polymer is soluble) from THF solution or by hot pressing of impregnated polymer powder. Films of PVC (Neralit 628, Spolana, Neratovice, a.s., Czech Republic, $M_m = 1.11 \times 10^5$) were prepared by casting 0.02—2 mg of probe in 1 cm³ tetrahydrofuran solution of polymer (5 g/100 cm³) on a glass plate (28 mm × 35 mm). Isotactic polypropylene (iPP) films were prepared by hot pressing of impregnated powder (200 °C for 1 min) in two molalities of probe 0.002 mol

kg⁻¹ and 0.02 mol kg⁻¹. Probe was dissolved in 10 cm³ of chloroform and added to 1 g of nonstabilized powder (Daplen, PCD Polymere, Schwechat, Austria). After 24 h of impregnation solvent was removed, powder was dried and hot-pressed.

EPR spectra were measured with X-band spectrometer E-4 Varian (USA) interfaced on PC with program Symphonia Bruker.

RESULTS AND DISCUSSION

Quantitative measurements were made in benzene solutions, $c \approx 1 \times 10^{-3}$ mol dm⁻³ (exact concentrations are listed in Table 1). Integrals of EPR spectra for the studied materials, concentrations of used solutions, integrals recalculated to unique concentration and relative concentration according to the internal standard (probe *VII*) are summarized in Table 1. Theoretical values of relative concentrations of probes *I—XIV* are 100, for probes *XV* and *XVI* 200, and for *XVII* 300. The values of integrals are proportional to the number of radicals, so the relative concentration – c_r provides information about the amount of radicals in the probes. We assume that the relative concentration of radicals in standard is 100 %. Assuming that preparation of probe solutions was done with certain error (probe weighting, dilution), a value of relative concentrations around 90 % proves the high purity of the given probe. On the other hand, lower value (74 % for probe *V*) suggests that probably the probe was not well purified by column chromatography and contains some impurity (possibly the starting parent amine).

EPR spectra of probes *I—XIV* are triplets with equal-line intensities. Typical spectrum of monoradical is shown in Fig. 1. The hyperfine splitting is the result of interaction of the unpaired electron with the nucleus ¹⁴N ($I = 1$) and the number of lines is determined according to the formula $2nI + 1$ (where n is the number of nitrogen atoms). The measured line width was 0.4—0.45 mT and the hyperfine splitting constants were for the most cases 1.53 mT. This value slightly depends on the structure of radicals and on
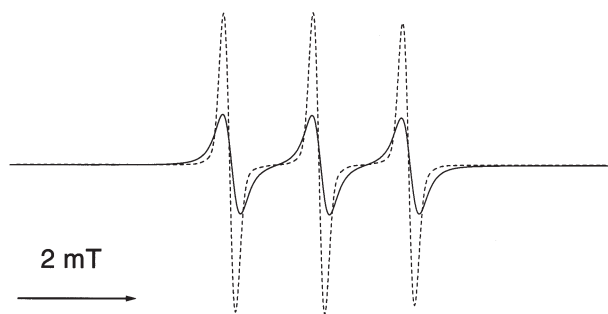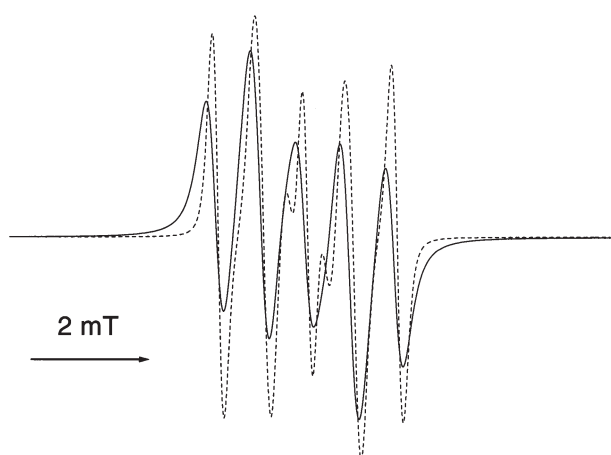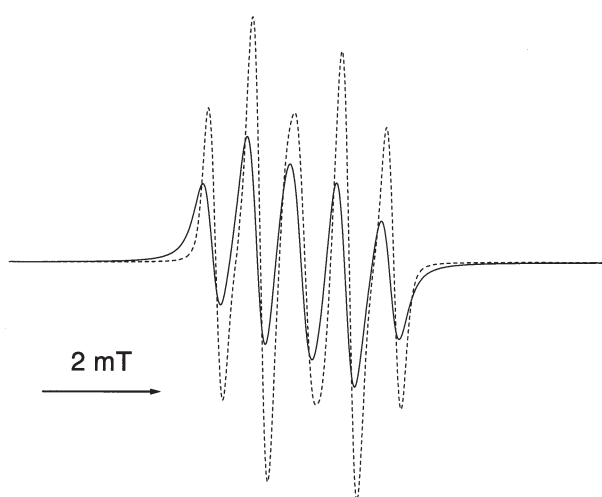

Fig. 1. EPR spectra of monoradical probe *III* in benzene solution before —— and after deaeration − − −. Concentration of probe is 9.89×10^{-4} g dm⁻³.

Table 1. Integral Values, Relative Concentrations, and Splitting Constants

Probe	Integral	Concentration	Integr./conc.	c_r	a_N
		g dm^{-3}	g dm^{-3}	%	mT
I	1.0493×10^7	0.995×10^{-3}	1.05504×10^{10}	86	1.53
II	1.1864×10^7	1.02×10^{-3}	1.15758×10^{10}	95	1.53
III	1.1141×10^7	0.989×10^{-3}	1.12638×10^{10}	92	1.53
IV	1.0873×10^7	0.996×10^{-3}	1.09129×10^{10}	89	1.53
V	8.8973×10^6	0.999×10^{-3}	8.999×10^9	74	1.53
VI	1.1650×10^7	0.992×10^{-3}	1.17404×10^{10}	96	1.54
VII(standard)	1.2065×10^7	0.99×10^{-3}	1.22243×10^{10}	100	1.53
VIII	9.3365×10^6	0.98×10^{-3}	9.52704×10^9	78	1.53
IX	1.1616×10^7	1.01×10^{-3}	1.14655×10^{10}	94	1.53
X	1.2326×10^7	0.984×10^{-3}	1.25201×10^{10}	102	1.54
XI	1.2077×10^7	1×10^{-3}	1.20421×10^{10}	98	1.53
XII	1.1427×10^7	0.99×10^{-3}	1.15394×10^{10}	94	1.53
XIII	1.0637×10^7	1.01×10^{-3}	1.05223×10^{10}	86	1.53
XIV	1.0686×10^7	0.999×10^{-3}	1.07007×10^{10}	87	1.53
XV	2.3326×10^7	0.995×10^{-3}	2.34369×10^{10}	192	0.75
XVI	2.1412×10^7	1×10^{-3}	2.13821×10^{10}	175	0.76
XVII	2.9905×10^7	1.01×10^{-3}	2.96165×10^{10}	242	0.57

Fig. 2. EPR spectra of biradical probe *XV* in benzene solution before —— and after deaeration – – –. Concentration of probe is 9.95×10^{-4} g dm^{-3}.

Fig. 3. EPR spectra of biradical probe *XVI* in benzene solution before —— and after deaeration – – –. Concentration of probe is 1×10^{-3} g dm^{-3}.

the polarity of the solvent and in benzene these values are in the range 1.46—1.7 mT for different nitroxyl radicals [15—18].

The spectra of probes *XV* and *XVI* (biradicals) represent quintets (5 peaks, $n = 2$) (Figs. 2 and 3). The theoretical ratio of peaks integrals for these probes with two equivalent N atoms is 1:2:3:2:1. The spectrum of probe *XVII* (triradical) is septet (seven peaks, $n = 3$) and the theoretical ratio of peaks integrals is 1:3:6:7:6:3:1. In the case of the probe *XVI* the experimentally measured integral ratios are close to the theoretical values (1:1.8:2.8:1.8:1). The comparison of the simulated and experimentally measured spectra of compound *XVI* (Fig. 4) shows a good agreement, too. On the other hand, in the case of probes *XV* and *XVII* (Fig. 5) the integrals of

peaks differ significantly from the theoretically predicted ones (probe *XV* – 1:1.8:2.4:1.7:1, probe *XVII* – 1:0.9:1.6:2.2:1.5:0.9:1). The reason for this difference is probably the fact that the paramagnetic centres are not equivalent and/or due to the presence of paramagnetic phosphorus. The number of lines corresponds well to the theoretically predicted ones in all cases.

The influence of dissolved oxygen on the EPR spectra is a well-known phenomenon. Due to the paramagnetism of oxygen molecules, their collisions with the free radical centres contribute to the magnetic relaxation of radicals and so to the increasing of EPR line width. The measure of line widths is proportional to the frequency of the collisions. Removing the oxygen
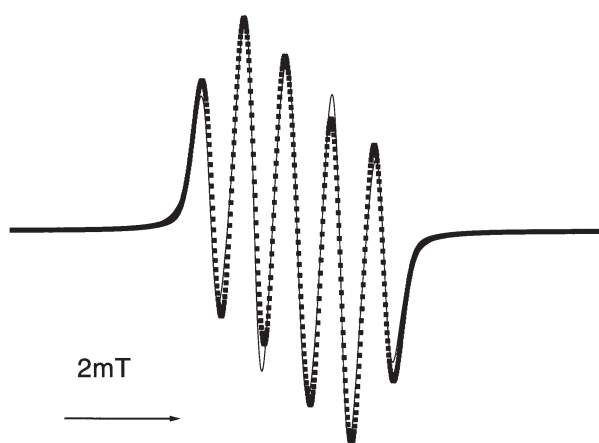
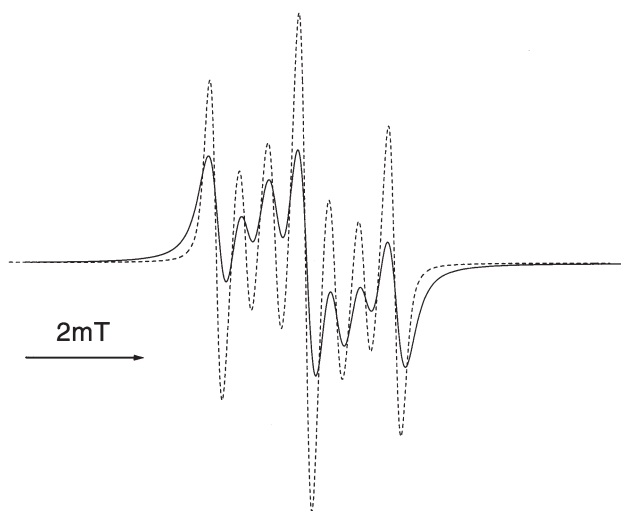**Fig. 4.** EPR spectra of biradical probe *XVI* in benzene: experimental spectrum —— and simulated spectrum ■ ■ ■.

Fig. 5. EPR spectra of triradical probe *XVII* in benzene solution before —— and after deaeration – – –. Concentration of probe is 9.89×10^{-4} g dm^{-3}.

from the probe the lines become narrower (Figs. 1—3).

The dissolved air was removed from the probes utilizing the cyclic freeze-thaw technique. The probe was frozen with liquid nitrogen and the space above the probe was evacuated to 3—5 Pa. After then the valve between probe and vacuum pump was closed and the probe was tempered to room temperature. The process was repeated for several times. The signal of evacuated probes was narrower (0.21—0.28 mT) compared with the original ones. On the other hand, the hyperfine splitting constant was unchanged (1.53 mT). The signal of probes *I—XIV* was triplet with lines of equal intensity. The comparison of signal of probe *III* before and after removing of the dissolved air is shown in Fig. 1. In the case of probe *XV* (biradical) the number of lines is five, but the ratio of integrals

does not correspond to the expected ones. In that case we were not able to determine satisfactorily the ratio of lines. The spectra of this probe before and after removing of air are shown in Fig. 2. In the case of the second biradical – probe *XVI*, the values of lines integrals correspond approximately to the expected ratio (1:2:3.2:1.9:1) before and after removing of dissolved air (Fig. 3). We did not find the theoretically expected integral value ratios either for the spectra of triradical – probe *XVII* (1:1.1:1.9:2.5:1.8:1.1:1.1). The spectrum of the probe before and after removing of air is shown in Fig. 5.

The EPR spectra of probes *I—VI* in iPP matrix were measured at room temperature. To determine the possible influence of the polarity of polymer matrix on the EPR spectra we measured the spectra of some probes listed in Formula 1 in PVC matrix, too. The measured spectra are well-known spectra of NO$^\bullet$ radicals in solid polymer matrix or in liquids at low temperature, where the free rotation of molecules is significantly hindered [16]. Due to this fact the spectra in polymer matrix were anisotropic contrary to the isotropic spectra of the same probes in solution at room temperature.

The EPR spectra of films were measured at two molalities of labels (0.02 mol kg^{-1} and 0.002 mol kg^{-1}). The variation of labels molality did not change the shape of the spectra. The technique of films preparation, pouring the polymer solution on a glass plate and slow evaporation of solvent, does not allow to control efficiently the uniform probe concentration in the whole volume of the polymer film. For this reason the determination of probes concentration from the EPR spectra is not very precise. The EPR spectrum of a monoradical is shown in Fig. 6. All spectra of monoradical in polymer matrix are very similar as in the solution. Comparison of the spectra of probe *V* mea-
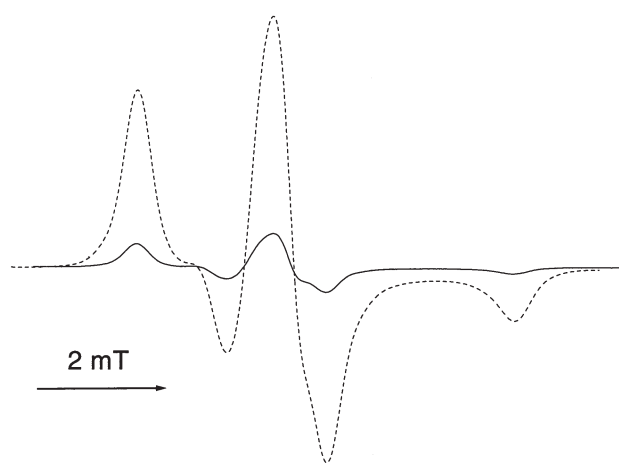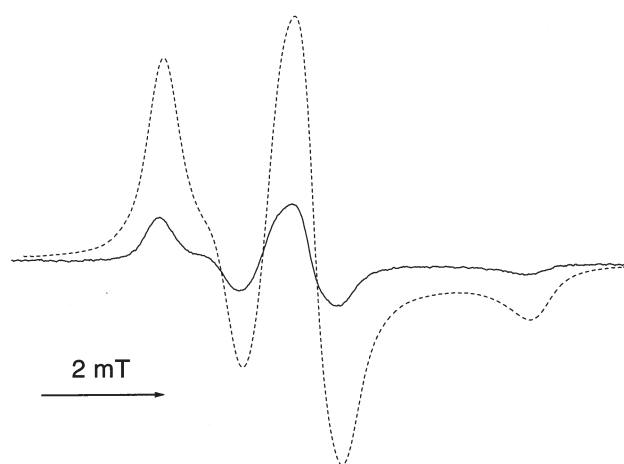

Fig. 6. EPR spectrum of probe *V* in PVC matrix at molality $m = 2 \times 10^{-3}$ mol kg^{-1} —— and $m = 2 \times 10^{-2}$ mol kg^{-1} – – –.

Fig. 7. EPR spectra of probe *VI* in iPP matrix at molality m = 2 × 10^{-3} mol kg^{-1} — and m = 2 × 10^{-2} mol kg^{-1} – – –.

sured in PVC (Fig. 6) and probe *VI* measured in iPP (Fig. 7) showed that the polarity of polymer matrix does not affect the shape of the spectra. The nitroxide radicals are chaotically oriented in the probe and the spectrum is the superposition of spectra of all possible radicals orientations in the magnetic field [15].

From the EPR measurements of dissolved probes and their comparison with an internal standard, we determined the purity of the prepared probes containing nitroxide radicals.

CONCLUSION

EPR spectra of 17 stable nitroxide radicals based on 4-substituted 1-oxyl-2,2,6,6-tetramethylpiperidine were measured. Four derivatives containing pyrene as chromophore and five other derivatives with naphthalene chromophore were used. Different types of bridge, connecting covalently the 4-substituted 1-oxyl-2,2,6,6-tetramethylpiperidine radical to chromophore were used.

In fact, no influence concerning the size of the chromophore and type of linkage on EPR spectra was observed in solution as well as in polymer matrix. Two other biradicals containing phosphorus and sulfur and one triradical containing phosphorus were investigated.

EPR spectra of probes containing one nitroxide radical provide triplet with line of equal intensity. The spectrum of both radicals was quintet and the triradical septet. In the case of biradical containing sulfur the ratio of peaks integrals corresponds well to the theoretically expected values. On the other hand, the ratio of peaks integrals differs from the theoretically expected one for biradical containing phosphorus. The

number of lines corresponds to the theoretically expected value in all cases.

The EPR spectra of probes containing pyrene and two containing naphthalene were measured in polymer matrices (iPP, PVC) at room temperature. The measured spectra are the well-known anisotropic spectra of nitroxide radicals with hindered rotations of radicals. The polarity of polymer matrix did not affect the spectra.

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