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Polymer 44 (2003) 695–701

polymer

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ESR spectra of spin probe in PPO membrane

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Received 2 August 2002; received in revised form 30 October 2002; accepted 1 November 2002

Abstract

Poly(phenylene oxide) (PPO) polymer's membranes (dense) were prepared by blending spin probes (TEMPO, 5-, 12- and 16-doxylstearic aid) in the casting solution used for the preparation of membranes. It was noticed that the shape and size of the probe influence the ESR spectra of the NO· radical in the poly(phenylene oxide)membrane. Unexpectedly, from the shape of the ESR signal it was noticed that of the NO· radical of TEMPO in PPO membrane was more mobile than in water media. However, the motion of the NO· radical of 16-doxylstearic acid was higher than NO· of 5- and 12-doxylstearic acid when the radicals were in the PPO membrane. This could be due to the inductive effect from COOH group. The *Hamiltonian* parameters of the ESR signal indicated that all the probes were not randomly distributed in PPO membrane, but some probes were in orderly fashion.
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Keywords: Poly(phenylene oxide); 2,2,6,6-tetramethyl-1-piperidinyloxy free radical; 5-, 12- and 16-doxylstearic acid

1. Introduction

The application of electron resonance (ESR) method to study synthetic polymers is still in an infant stage. Stone's school [1] was the first who introduced the paramagnetic nitroxide radical into the polymer (synthetic polypeptides). Russian researchers had been foremost in application of spin probes [2]. Törmälä et al. [3,4] and Bullock et al. [5,6] tried to explore further the application of nitroxide radical in a study of synthetic polymers. Spin labeling in synthetic polymers is discussed by Miller [7].

The introduction of stable free radical ('spin label') enables one to use ESR spectroscopy to study specific environments within the synthetic membrane. There are many methods for doping spin probe into polymer. In most cases, doping is done by removing the solvent from the nitroxide and polymer solution cast into a film. A potential problem with any method is the inhomogeneous distribution of nitroxide in the film. This includes portioning between amorphous and crystalline regions in semi-crystalline polymer, portioning between different monomeric units of copolymers, particularly block polymers.

The spin Hamiltonian that adequately describes the ESR spectrum of nitroxide radical is

$$\mathbf{H} = \beta_0 \mathbf{H}|\mathbf{g}|\mathbf{S} + \mathbf{S}|\mathbf{A}|\mathbf{I}$$

where β_0 is the electron Bohr magneton, **H** is the external field, $|\mathbf{g}|$ and $|\mathbf{A}|$ are the g-value and the electron–nuclear hyperfine tensors, **S** and **I** are the electron and nuclear spin operators. A detailed discussion of this Hamiltonian (for a nuclear spin of 1) had been published by Libertini and Griffith [8]. The ESR spectrum of such system of oriented nitroxide radicals consists of three lines, separated by the hyperfine splitting $|\mathbf{A}|$ and centered at field (H) which is inversely proportional to the g-value parameter. Both $|\mathbf{g}|$ and $|\mathbf{A}|$ depend on the direction of the external field relative to the principal axes of the $|A|$ and $|g|$ tensors. The $|\mathbf{g}|$ and $|\mathbf{A}|$ component do not vary greatly from one spin label to another.

Due to the ease of sample preparation, the spin probes have received much more attention. The most important use of nitroxide spin labels is as a monitor of motion. Molecular motion is of interest over an extremely wide range of conditions, from external rotation in dilute polymer solution to motion in crystalline and amorphous bulk material. A sufficiently wide variety of nitroxide free radicals are

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PII: S0032-3861(02)00827-3

available to make nitroxides competitive. Free radical tumbles in water or other non-viscous solvents and gives highly symmetric spectra. If the viscosity of the solution is increased, the rotational motion of nitroxides decreases and the spectra become increasingly asymmetric. Very high asymmetric spectra are obtained for powder spectrum, the rigid glass spectrum or polycrystalline spectrum. Thus, all nitroxide radicals in water or in non-viscous solvents give symmetric spectra. No appreciable change could be observed due to nitroxide bearing molecule either in water or in polymeric solution. However, nothing has been reported the effect of group bearing molecule on the nitroxide radical in highly viscous or in solid polymers.

The structure of polymer in a membrane depends to a large extent on structural arrangements and mobility of polymer molecules in a lacquer or in a solution during evaporation of the solvent. Kim et al. [9] studied the segmental mobility and free-volume decay of poly(methyl methacrylate) using TANOL as a probe. At 190 °C, the tumbling of the radical in polymer was almost free of hindrance. They suggested that rotational barriers are due to bulky side group at lower temperatures (20 °C). Kusumoto [10] suggested that at low temperatures, the probe in the polymer may experience hindered rotation in a micro cavity of the polymer matrix, and also the rotational behavior is strongly influenced by the specific shape and size of the probe.

Hachisuka et al. [11] clarified that unrelaxed volume and/or micro voids content is the characteristics of the equilibrium nature of glassy polymers. Tsujita et al. [12] studied the sorption behavior of quenched PPO membranes and analyzed by dual mode sorption model. The increase in sorption in quenched membrane was interpreted in terms of increasing micro voids content.

In this paper, we are reporting the effect of spin probe size (radical bearing molecule) in PPO membrane on the shape of ESR signal of NO˙ radical at room temperature.

2. Experimental

The technique for the ESR measurements is given elsewhere [13,14]. General Electric supplied PPO and its intrinsic viscosity was 1.5 dl g^{-1} (at 25 °C in chloroform). The concentration of PPO solution was 2 wt% in 1,1,2-trichloroethylene (BDH), which was used for membrane casting. The spin probes used in the present ESR study were 2,2,6,6-tetramethyl-1-piperidinyloxy free radical (TEMPO), 5-, 12- and 16-doxylstearic acid and were supplied by Sigma. The concentration of free radical in the casting solution was 0.002 wt% of PPO. The spectral line shapes did not depend on the probe concentration in the range of concentration used here. The orientation of the membrane (inside the cell) is specified by the angle, θ, between the external field direction and the direction normal to the surface of the membrane. The designations parallel (‖) and perpendicular (⊥) corresponding to $\theta = 0$ and 90°, respectively. The two values of A (hyperfine splitting) and g calculated under these two conditions are designated as $A_{\|}$ and $A_{\perp}$, and $g_{\|}$ and $g_{\perp}$, respectively.

The method used for casting the membrane was similar to that described elsewhere [13]. The 3 ml casting solution was spread smoothly over a glass plate inside an O-ring made of aluminum for molding. Membranes were dried at room temperature for 24 h. Prior to use, the membrane was further dried for 72 h in vacuum to remove last traces of solvent. All the measurements were made at room temperature

3. Results and discussion

Fig. 1 shows the ESR spectra of TEMPO solution in water (0.02 wt%). The spectra consist of three symmetric peaks, since the NO˙ radical of TEMPO is freely mobile in the solution. The spectra are isotropic (symmetric) and the value of Hamiltonian parameter $|A|$ (distance between two peaks) is 17 G. All three peaks are almost equal in height and symmetric. If the viscosity of the solution is increased, the rotational motion of the nitroxides decreases and the spectra become increasingly asymmetric as shown in Fig. 2 [15]. The bottom spectrum of Fig. 2 is the limiting case approached as the viscosity becomes very large. Fig. 2(d) is frequently referred to as the powder spectrum, the rigid glass spectrum, or the polycrystalline spectrum. Between the two limits of very rapid motion and a rigid glass, the spectra are quite complex [15].

The ESR spectra of the TEMPO doped PPO membrane prepared at room temperature (22 °C) (Gain = 4×10^4) are given in Fig. 3. Spectra in Fig. 3(a) and (b) are recorded when the magnetic field was perpendicular ($\theta = 90°$) and parallel ($\theta = 0°$) to the membrane, respectively. Both spectra are isotropic and suggest that the nitroxide radicals are tumbling very fast, which are unexpected, as the PPO should be having as a rigid phase. The Hamiltonian parameter and other ESR measurements are given in Table 1. On comparing Fig. 3(a) and (b) and Table 1, it

Table 1
Hamiltonian parameters A and other ESR parameters of NO˙ radical from TEMPO in PPO membrane

PPO membrane	θ (degree)	b^a/a^b ratio[c]	b^a/c^d ratio[c]	A (G)	Width of peaks (G)		
					A	B	C
Dry	90	1.37	1.71	15	3.5	3.5	4
Dry	0	1.33	1.80	15.5	4	4	4.5

[a] Height of the middle line B.
[b] Height of the first line A (lower magnetic field).
[c] Arbitrary unit.
[d] Height of the third line C (higher magnetic field).

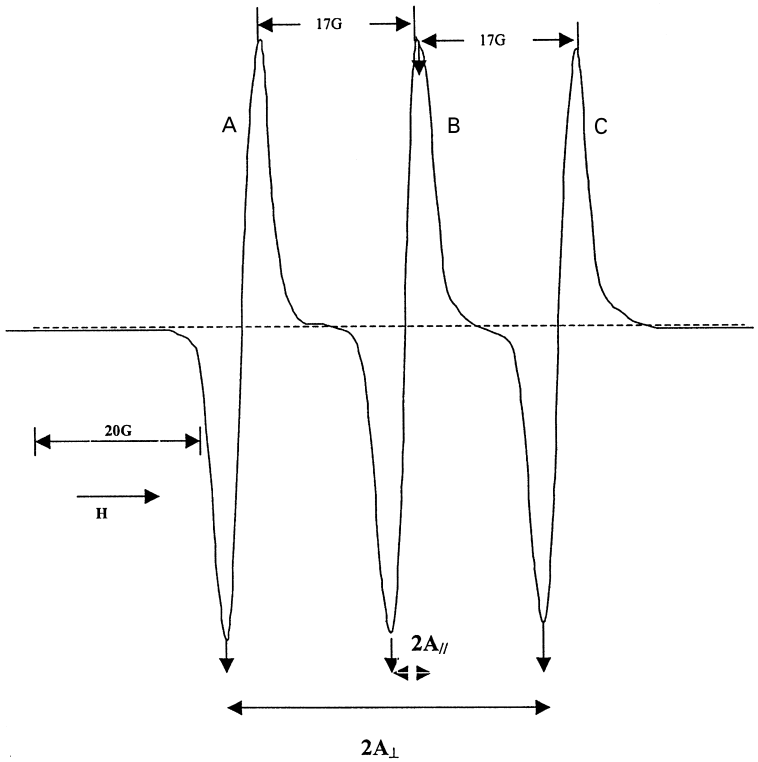


Fig. 1. ESR spectra of TEMPO solution in water (0.02 wt%).

seems they are slightly different with each other, which indicates that the nitroxide radicals may not be randomly distributed in the PPO membrane. In other words, radicals in the PPO membrane could be in some orderly fashion. PPO is a semi-crystalline polymer [16] and hydrophobic. The narrow line spectra and small Hamiltonian parameter $|A|$ are interpreted to arise from free tumbling, and the broad lines and large $|A|$ are believed to result from highly restricted motion. Narrow line spectra shown in Fig. 3(a) and (b) suggest that the rotational motion of NO˙ radical in PPO membrane is fast. In TEMPO containing PPO the value of $|A|$ (15 G) is less than in water (17 G), which suggests that in the PPO membrane the motion of the radical is faster than in water media. The ESR spectra of Fig. 3(a) and (b) seems to be simulated nitroxide spectra, i.e. single crystal spectra

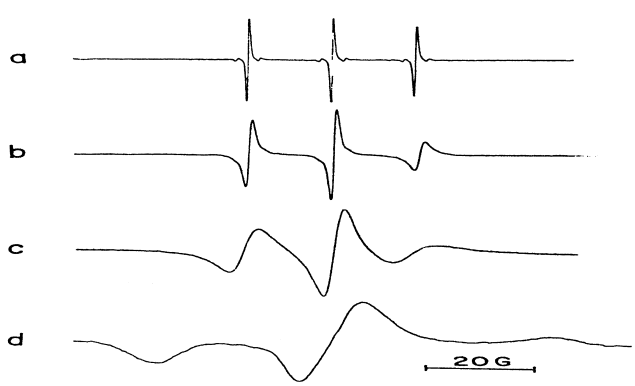


Fig. 2. X band of ESR spectra of nitroxide dissolved in ethylene glycol at (a) 25°, (b) −25°, (c) −80° and (d) −150° [8].

with the magnetic field oriented along each of the principal axes, x, y and z [17]. However, it is not a perfect single crystal spectra as the height of three hyperfine structures (HFS) are not equal. It seems that there is little hindrance in the mobility. But the rate of tumbling of the radical is very high.

Fig. 4 (a) and (b) shows the ESR spectra of NO˙ radical when 5-doxylstearic acid was in PPO casting solution instead of TEMPO. Spectra in Fig. 4(a) and (b) are recorded when the magnetic field was perpendicular ($\theta = 90°$) and parallel ($\theta = 0°$) to the membrane, respectively. Both spectra are asymmetric.

These spectra are different than the ESR spectra of PPO membrane doped with TEMPO. However, spectra Fig. 4(a) and (b) are also slightly different in shape when the same probe was added to in the casting solution of PPO having higher molecular weight (intrinsic viscosity 1.79 dl g^{-1} at 25 °C in chloroform) [13,14]. On comparing Fig. 4(a) and (b), it seems they are different from each other, which indicates that the nitroxide radicals are not randomly distributed in the PPO membrane. In other words, radicals are in the PPO membrane in some orderly fashion. However, the difference is quite significant. It could be possible that a part of the free radicals in PPO is in orderly fashion and the rest is distributed randomly. The spectra Fig. 4(a) and (b) are similar to the spectra reported by Törmälä et al. [3] and Khulbe et al. [13,14].

On comparing the Figs. 3 and 4, it seems that the molecular weight of the nitroxide bearing molecule or

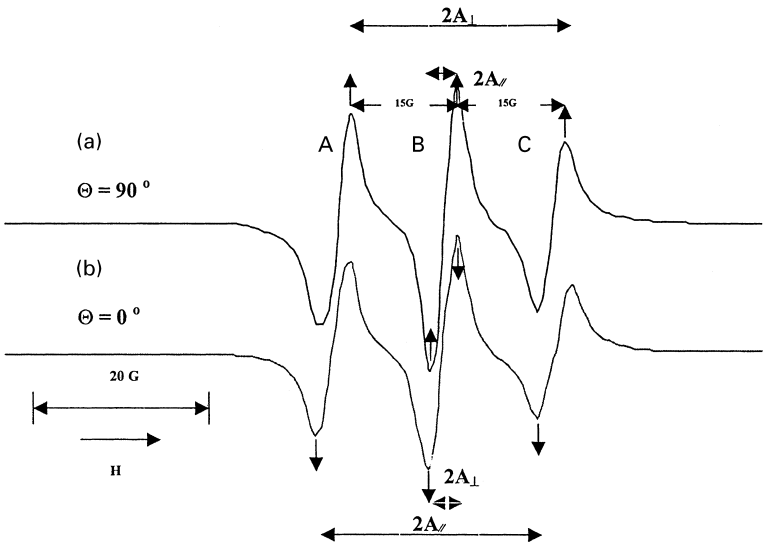


Fig. 3. ESR spectra of TEMPO doped in PPO membrane at room temperature (22 °C) and membrane orientation in the magnetic field: (a) $\theta = 90°$; (b) $\theta = 0°$.

macromolecule plays a part in the mobility of the radical when the nitroxide bearing molecule or macromolecule is doped in the polymer. The molecular weight of TEMPO is 159 while the molecular weight of the 5-doxylstearic acid is 365.

The chemical structures of the TEMPO and 5-doxylstearic acids are given in Fig. 5. From the above study, it seems that the shape of the ESR spectra of NO˙ radical in PPO membrane depends on the rigidity of the polymer and on the molecular weight or the chemical structure of the radical bearing molecule.

When a nitroxide-bearing molecule is covalently attached to another molecule or macromolecule, it is considered to be spin labeled. However, the presence of the nitroxide grouping will not significantly perturb the behavior of the spin labeled molecule in the system under study. On the other hand, a nitroxide-containing molecule, which is covalently attached to molecules of the system under study, is considered to be spin probe. The ESR spectra of TEMPO in PPO is symmetric (similar as ESR spectra of TEMPO in water) and tumbling faster than in water. The environment of the free radical in PPO is different (void space) than the environment in water. Thus, it could be possible that TEMPO in PPO is acting as a spin probe and doxylstearic acids are as spin label.

Figs. 6(a), (b) and 7(a), (b) show the ESR spectra of NO˙ radical when 12-doxylstearic acid and 16-doxylstearic acid radicals were doped in the PPO casting solution, respectively. On comparing these results it suggests that 12-doxylstearic acid and 5-doxylstearic acid have similar NO˙ ESR spectra, while NO˙ spectra obtained either from TEMPO or 16-doxylstearic acid in the PPO membrane are different. From Fig. 7(a) and (b), it seems that the ESR spectra of NO˙ radical is almost isotropic, similar to those obtained from TEMPO. Moreover, the NO˙ radical of TEMPO in the PPO membrane is highly mobile. On

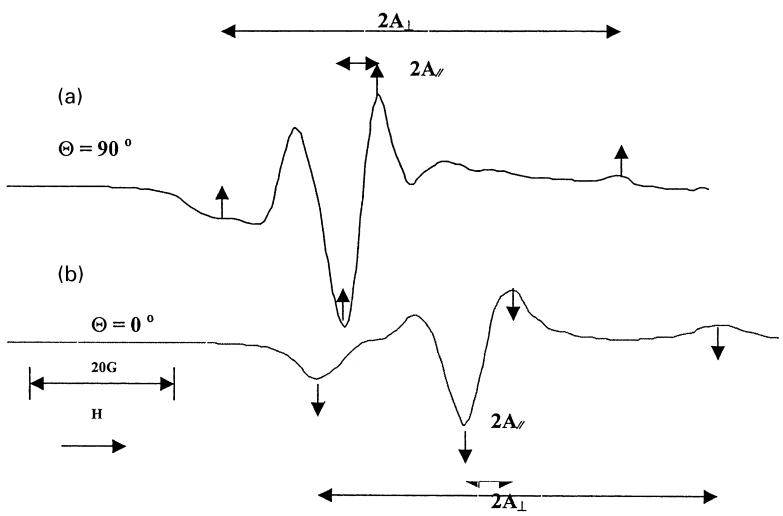
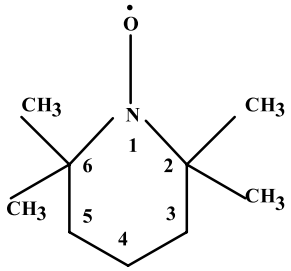
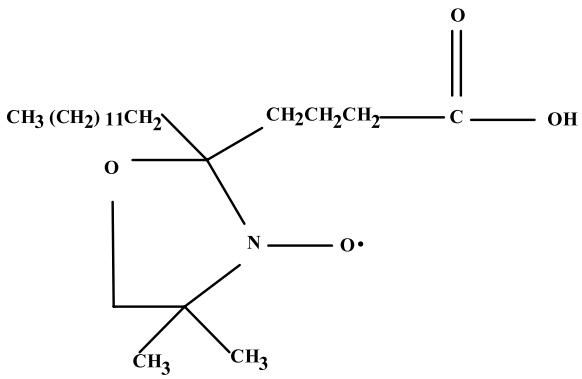


Fig. 4. ESR spectra of 5-doxylstearic acid doped in PPO membrane at room temperature (22 °C) and membrane orientation in the magnetic field: (a) $\theta = 90°$; (b), $\theta = 0°$.



TEMPO (2,2,6,6-Tetramethyl-1-piperidinyl-oxy)
(F.W.=156.25)



5-Doxylstericacid (F.W.=384.59)

Fig. 5. Chemical structure of TEMPO and 5-doxylstearic acid.

comparing ESR spectra of 5- and 12-doxylstearic acid, when the ESR was run at $\theta = 0$ and 90°, it seems that these probes are also in an orderly fashion in the polymer. The molecular motion increases as the label is moved further from the carboxyl end.

From Figs. 4, 6 and 7 it seem that the mobility of the radical of 16-doxylstearic acid is maximum in comparison

Table 2
Width of the middle peak B (ΔH)

Spin probe	θ (degree)	ΔH, width of peaks (G)
TEMPO	0	3.5
	90	4
5-doxylstearic acid	0	4.5
	90	7.5
12-doxylstearic acid	0	4
	90	7
16-doxylstearic acid	0	3.5
	90	5

with 5- and 12-doxylstearic acids. From Table 2, it seems that the width of the middle line 'B' in the ESR spectra of the studied spin probes in the PPO membrane is in the following order:

5-doxylstearic acid > 12-doxylstearic acid

> 16-doxylstearic acid > TEMPO

It should be noted that the mobility of the NO˙ radical of the probes in PPO polymer is in the reverse order.

A similar effect was observed by Jost et al. [18] when they examined motion and orientation in lipid bilayer structure by using these probes. The increased motion as the label is translated toward the hydrocarbons end reflects a corresponding increase in the fluidity of the phospholipid chains. They interpreted that this could be due to the polar group to anchor the lipid chains at one end, allowing progressively more molecular motion along the hydrocarbon chains. It could be also due to the *inductive effect* of COOH group. The effect decreases with distances from acidic group [19].

An analysis based on the assumed axial symmetry of

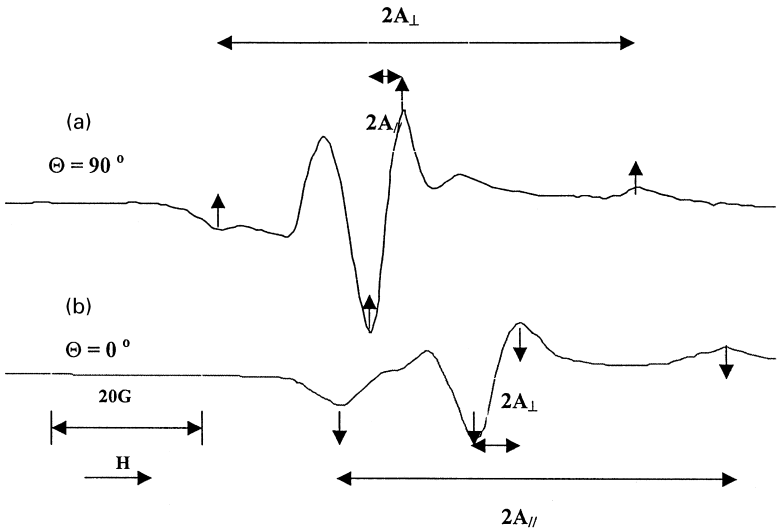


Fig. 6. ESR spectra of 12-doxylstearic acid doped in PPO membrane at room temperature (22 °C) and membrane orientation in the magnetic field: (a) $\theta = 90°$; (b) $\theta = 0°$.

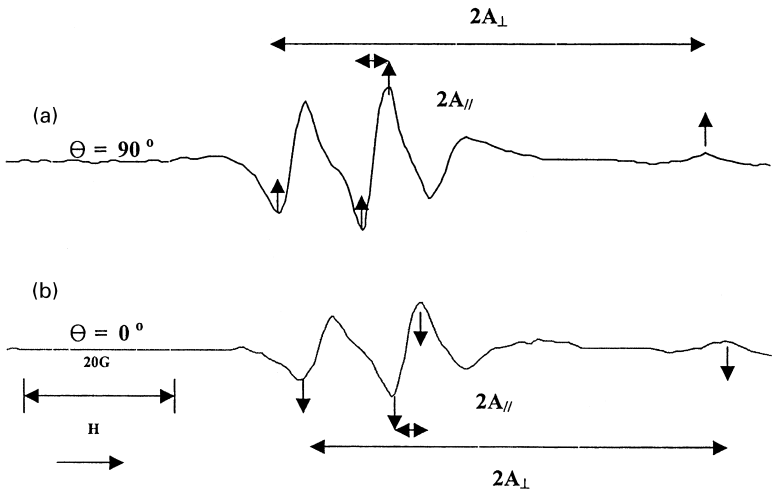


Fig. 7. ESR spectra of 16-doxystearic acid doped in PPO membrane at room temperature (22 °C) and membrane orientation in the magnetic field: (a) $\theta = 90°$; (b) $\theta = 0°$.

these spectra was carried out according to Edelstein et al. [20]. It is known that the two outermost peaks of the 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 $|g|$ and $|A|$, obtained by the above method together with the known relationship $|g| = (g_{\|} + 2g_{\perp})/2$ and $|A| = (A_{\|} + 2A_{\perp})$, give the values for the parameters of the spin, which are given in Table 3.

From Table 3, it seems that the ESR parameters (Hamiltonian parameters of the NO˙ radical in the PPO membrane polymer) depend on the specific site of the NO˙ in the stearic acid molecule and $g_{\perp}$ is always greater than $g_{\|}$.

Poly(phenylene oxide) is a semi-crystalline polymer. Ilinitch et al. [21] suggested that the free volume of poly(phenylene oxide)s contains a three-dimensional network of intermolecular micro cavities. They also suggested the 'throat and cavity' model for intrinsic micro porosity for PPO membranes and measured the diameters of pore throats to be in the range of ca. 0.4 nm at 77 K. The spin probes may be located in these pores.

From the above results, it seems that the presence of the micro cavity (free volume) and the shape and the size of the probe, all are playing part in the shape of ESR spectra of NO˙ radical in the polymer. As the TEMPO size is smaller than the other used probes, and the size of micro cavity (individual free volume) is quite large, the NO˙ radical is tumbling very fast in those micro cavities. Other probes, the sizes of which are larger than TEMPO could not tumble in the micro cavity very fast. These studies can give a clue to find the size of micro cavity in polymeric membranes.

4. Conclusions

From the above study the following conclusions can be drawn:

1. The ESR spectra of NO˙ radical in PPO membrane depend on the molecular weight and the chemical structure of the radical bearing molecule. However, the rigidity of the PPO material or its conformation has no effect on the ESR spectra of TEMPO.
2. The rate of tumbling of NO˙ radical of TEMPO in PPO is more than in water. The shape of the ESR spectra of

Table 3
Hamiltonian parameters of ESR spectra of PPO membranes doped with different spin probes

Spin probe	θ (degree)	$g_{\|}$	$g_{\perp}$	$A_{\|}$ (G)	$A_{\perp}$ (G)	$\|A\|$ (G)	$\|g\|$
TEMPO	90	2.004	2.0049	15	2	6.3	2.0046
	0	2.0035	2.0041	15.5	2	6.5	2.0038
5-doxylstearic acid	90	2.005	2.0052	25	2	9.1	2.0051
	0	1.9919	1.9950	25.8	3.5	11.3	1.9939
12-doxylstearic acid	90	1.9947	1.9992	32	2.25	11.41	1.9973
	0	1.9857	1.9887	28.5	3.5	11.84	1.9877
16-doxylstearic acid	90	1.9918	1.9990	35	2	13	1.9972
	0	1.9897	1.9973	34.5	2.5	13.16	1.9947

TEMPO in PPO membrane is similar to the ESR spectra of a single crystal of TEMPO.

3. On doping the different probes in PPO by mixing them in the casting solution, it seems that all molecules of probes were not distributed in the membrane randomly, but some may be in orderly fashion.

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