Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Restriction of Spin Probe Motions in Polymer Composites Due to Chemical Factors

J. Tiňo[a]; P. Mach[a]; Z. Hloušková[a]; I. Chodák[a]
[a] Polymer Institute Slovak Academy of Sciences, Bratislava, Slovak Republic

To cite this Article Tiňo, J. , Mach, P. , Hloušková, Z. and Chodák, I.(1994) 'Restriction of Spin Probe Motions in Polymer Composites Due to Chemical Factors', Journal of Macromolecular Science, Part A, 31: 10, 1481 — 1487
To link to this Article: DOI: 10.1080/10601329409350105
URL: http://dx.doi.org/10.1080/10601329409350105

J.M.S.—PURE APPL. CHEM., A31(10), pp. 1481–1487 (1994)

RESTRICTION OF SPIN PROBE MOTIONS IN POLYMER COMPOSITES DUE TO CHEMICAL FACTORS

J. TIŇO, P. MACH, Z. HLOUŠKOVÁ, and I. CHODÁK

Polymer Institute
Slovak Academy of Sciences
842 36 Bratislava, Slovak Republic

ABSTRACT

Hyperfine splitting constants of the nitroxyl radical, with and without hydrogen bonds to the surrounding molecules, have been calculated using the UHF method on a 6-31G* base. In polyethylene filled with silica, hydrogen bonds are formed between nitroxyl radicals and —OH groups of the filler. The formation of hydrogen bonds leads to a change in the A_{ZZ} value from 3.33 mT for an isolated nitroxyl radical to 3.83 mT for a radical with a hydrogen bond. The relevant values as measured experimentally are 3.4 and 4.0 mT, respectively. The same procedure was used to calculate the theoretical A_{ZZ} value for a nitroxyl radical interacting with polyamide via a hydrogen bond. The value was found to be 3.63 mT (experimental value = 3.6 mT). Hydrogen bond formation results in a restricted motion of the nitroxyl radical in a polymeric medium.

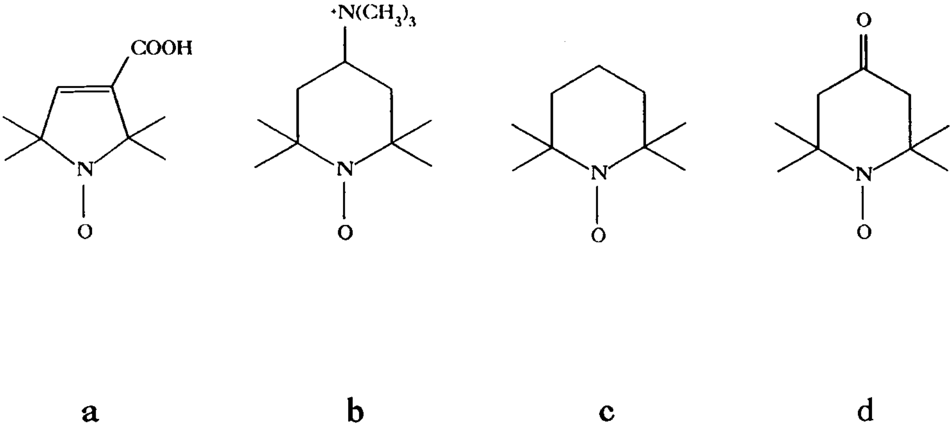
INTRODUCTION

When investigating the molecular mobility in polymer systems using the spin probe method, interaction of the probe with the medium is very often observed [1–5]. The hydrogen bond is one of the possible modes of interaction if the conditions for its formation are met. If the nitroxide spin probe forms a hydrogen bond (with the medium), the electronic structure of the probe and consequently the spin distribution are changed. As a consequence the nitrogen hyperfine splitting (hfs) constant, a_N, [$a = 1/3\ (A_{xx} + A_{YY} + A_{ZZ})$] is also changed [4]. The change of hfs constants is also observed in polar medium. Due to the high dielectric constant of the medium, the formation of a pseudoionic resonance structure of the probe is favored and, consequently, the hfs constant a_N increases [2, 3, 5]. This situation can be illustrated by the behavior of 3-carboxy-2,2,5,5-tetramethylpyrroline-1-oxyl (Structure a in Scheme 1).

The a_N constant of Structure a is 1.61 mT in water and 1.41 mT in cyclohexane [3]. Changes of the hfs constant a_N of 4-(trimethyl ammonium)-2,2,6,6-tetramethylpiperidinyl-1-oxyl iodide (b) in micellar medium were described by Ottaviani et al. [2]. During micelle formation the spin probe is transferred from water to the less polar solvent, resulting in a decrease of the a_N value from 1.69 mT (measured in bulk water) to 1.59 mT.

Substantial changes of the hfs constant in di-*tert*-butylnitroxide (DTBN) were observed by Lozos and Hoffman [4] when investigating by EPR the DTBN radical adsorbed on silica and alumia. In toluene the A_{ZZ} value was found to be 3.46 mT, in silica 3.86 mT. The latter value is similar to the A_{ZZ} value found in phenol (3.83 mT). The authors concluded that the observed phenomena are caused by the formation of hydrogen bonds.

We have observed a similar shift of the A_{ZZ} component of a hyperfine splitting tensor of the probe TEMPO (c) when investigating its EPR spectra in silica-filled polyethylene [6]. In unfilled polyethylene, $A_{ZZ} = 3.4$ mT, which increased up to 4.0 mT if 16.6 vol% silica was added. Considering the structure of the filler, it is assumed that the observed increase is caused by hydrogen bond formation between the spin probe and the OH moieties present on the filler surface. This suggestion has to be taken into account if the molecular mobility of polymers is investigated by the spin probe method since the shape of the EPR spectrum is dependent on the rotational state of the probe. If there are only weak interactions between the probe and the medium, probe rotation is directly related to the motional state of the polymeric system [7, 13, 14]. If strong interaction plays a role due to a hydrogen bond formation, the mobility of the probe is modified significantly. Therefore, it is important



SCHEME 1.

to explain the reason for the change of hfs constants of spin probes used for the study of molecular mobility. A useful procedure is a comparison of theoretical and experimental hfs constants of either isolated or hydrogen-bond-linked probes. Such a comparison can be made by using quantum chemical calculations of hfs constants. The ab initio UHF method was used in this paper.

EXPERIMENTAL

Low density polyethylene (Bralen RA 2-19, Slovnaft, Bratislava) and particulate silica (Ultrasil VN3, Degussa, surface area 139 m^2) were used as the matrix and filler. The samples were prepared in a Plastograph Brabender internal mixer at 155°C for 5 minutes at 75 rpm. The slabs, 0.5 mm thick, were compression molded at 180°C for 2 minutes. Identification of the samples is given in Table 1.

The spin probe TEMPO was introduced into Samples A–E by vapor diffusion at 70°C for 4 hours. ESR spectra were recorded on a Varian E4 ESR spectrometer equipped with a temperature control operating in temperature range −150 to 150°C.

RESULTS AND DISCUSSION

The spectra of the probe TEMPO were measured in unfilled polyethylene (Sample A), in polyethylene–silica mixtures with different silica contents (Samples B–E), and in nylon. The characteristics of ESR spectra and the relations between probe mobility and composite structure were discussed elsewhere [6]. In this paper, differences in the spectra as related to silica content in the samples will be considered.

At 123 K the A_{ZZ} parameter is equal to 3.4 mT for Sample A and 3.3 mT for Samples B and C (Table 2). ($2A_{ZZ}$ is the peak-to-peak separation of the rigid limit spectrum; $2A'_{ZZ}$ is the peak-to-peak separation at higher sample temperatures.) These values correspond with the published data of other authors. For example, an A_{ZZ} value of 3.46 mT has been published for di-*tert*-butyl nitroxide (DTBN) in toluene [4]. Törmälä [7] gives two values (3.1 and 3.3 mT) for the Probe Id (Scheme 1). Generally, hfs constants depend on the chemical nature of the medium in which the probe is dispersed [1–5].

TABLE 1. The LDPE-Based Composites with Various Silica Contents

	Sample				
	A	B	C	D	E
Ultrasil, vol%	0	4.7	9.1	16.6	25.9

TABLE 2. A_{ZZ} Values for the Probe TEMPO Measured in LDPE/Silica Composites and in Nylon at 123 K, and Corresponding T_{50G} Values

	A_{ZZ}, mT		
Sample	Experimental	Calculated	T_{50G}, K
A	3.4	3.33[a]	218
B	3.3		190
C	3.3		198
D	4.0	3.83[b]	295
E	4.0	3.83[b]	303
Nylon	3.5	3.63[b]	330

[a] The calculated value for the dimethyl nitroxyl radical without the H-bond (see text).

[b] The calculated value for the dimethyl nitroxyl radical with the H-bond (see text).

The A_{ZZ} component of the hfs constant changed significantly during our measurements if the probe was inserted in an environment susceptible for hydrogen bond formation. Such an environment can be formed in polyethylene by the addition of 16.6 vol% or more of silica containing OH groups on the surface. In this case the A_{ZZ} value rises to 4.0 mT at low temperatures (Table 2, Fig. 1).

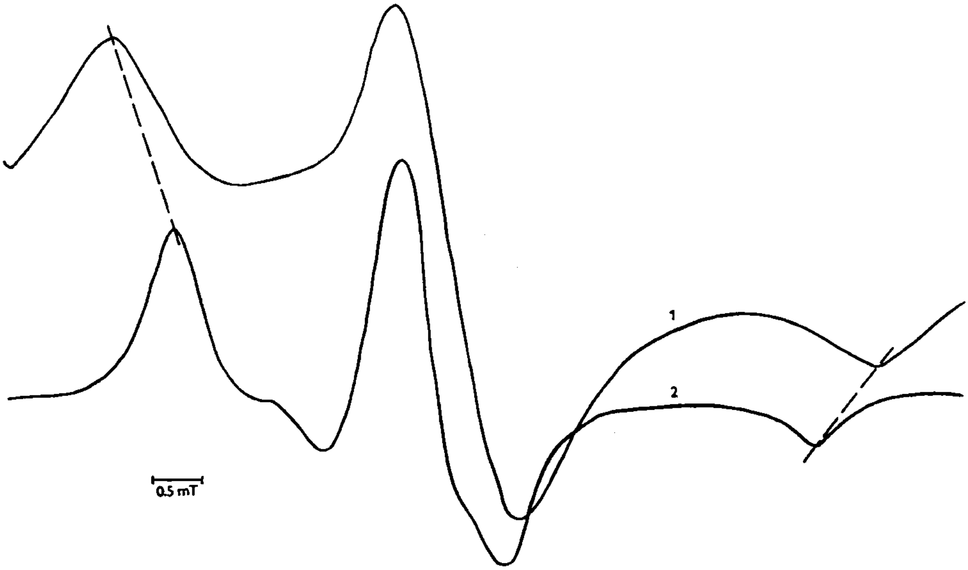


FIG. 1. EPR spectra of the spin probe TEMPO in polyethylene (1) and in polyethylene filled with 25.9 wt% of silica (2) measured at 153 K.

To understand this change in detail, a calculation by the UHF method of hfs constants was made for an isolated probe and for a probe with a hydrogen bond. The nitroxyl radical was simulated by a fragment $CH_3{-}NO^{\cdot}{-}CH_3$ while —OH moieties at the silica surface were modeled by a water molecule. The model calculation was done for computational reasons. The difference between the A_N value of DTBN (1.73 mT) and the hfs constants of the radicals Ic (1.73 mT) and Id (1.69 mT), all measured in water, is negligible, as shown in Reference 5.

It is well-known (e.g., Refs. 8 and 9) that hfs calculations have to be based on a high quality quantum-chemical method requiring both 1) a very large base of atomic orbitals and 2) inclusion of a significant part of the electron correlation. The base set used in our study (6-31G*) [10] and the UHF method describe the system more or less qualitatively. The results given in this paper have to be understood in this sense although, as seen from Table 2, theoretical data correspond very well with the experimental values. In our case, $\langle S^2\rangle_{UHF}$ (the measure of spin contamination) is 0.765 for the nitroxyl radical and 0.766 for the H-bonded nitroxyl radical. It has been shown [11] that in the case of such a small spin contamination, the UHF results are reasonable.

An energetic minimum was found for the bond between the hydrogen of the OH group and the oxygen of the nitroxyl radical. It was found that the water molecule is located approximately in the plane of the $CH_3{-}NO^{\cdot}{-}CH_3$ fragment. The distance $>NO^{\cdot}$ . . . HO— is 2.09 Å, the NOH angle is 117.8°, the CNOH torsion angle is 13.6°, and the hydrogen bond energy is 5.9 kcal/mol. Because of the base set used, it can be assumed that the latter energy is slightly overestimated (it is 120–130% of the interaction energy) [12]. The calculated A_{ZZ} values for the N atom of the $>NO^{\cdot}$ radical are 3.33 mT for the free radical and 3.83 mT if a hydrogen bond interacting with the nitroxyl radical is considered, i.e., the difference caused by hydrogen bond formation is 0.5 mT.

A little lower A_{ZZ} value was found for the experiment done in nylon (Table 2). Since another type of hydrogen bond (—O . . . H—N—) is present in this case, the calculation was also made for this case using an ammonium molecule as a model for NH moiety. As expected, the hydrogen bond calculated is weaker (3.6 kcal/mol) and the distance O . . . H is larger (2.41 Å). The NOH angle is 113.9° and the CNOH torsion angle is 26.5°. The A_{ZZ} value for the $>NO^{\cdot}$ radical with a hydrogen bond was found to be 3.63 mT. When compared with the radical without a hydrogen bond ($A_{ZZ} = 3.33$ mT), the difference is lower than that for the hydrogen bond with an OH group.

A good correlation was found for calculated and measured values. However, the method is approximative and its limitations are well known. For the present discussion it is significant that the hydrogen bond effect on the A_{ZZ} values was well characterized.

From the values in Table 2, another characteristic can be deduced for spin probes forming H-bonds. The values of T_{50G} (the temperature at which $2A'_{ZZ} = 5$ mT, i.e., 50G) are closely connected with the molecular mobility in a particular polymeric system. The rotational mobility of the probe is more intensive if the free volume is increasing due to increased molecular mobility of the medium [13, 14]. A gradual change to fast rotation of the probe is characterized by a change from a broad spectrum into a sharp one with narrower line separation in the EPR spectrum. The probe motion can be hindered due to other factors, e.g., because of above-

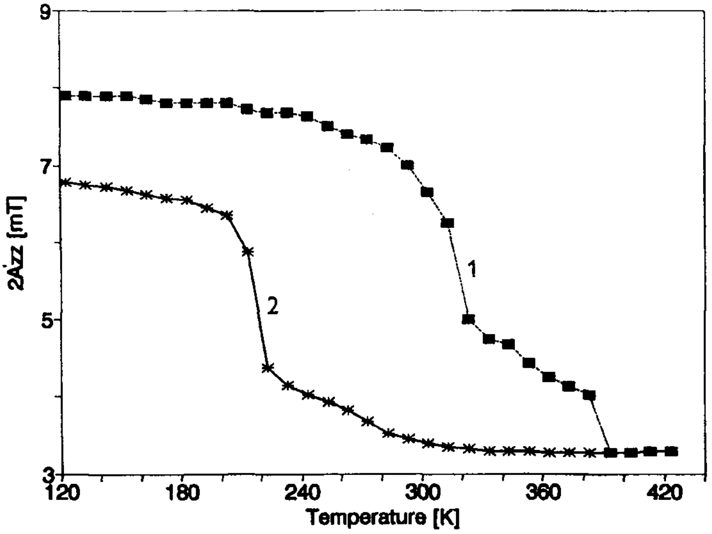


FIG. 2. The dependence of $2A'_{zz}$ value on temperature for the probe TEMPO in Samples E (Curve 1) and A (Curve 2).

mentioned interaction with the environment via the H-bond [1]. In this case the transition to fast rotation is observed at higher temperatures. The A'_{zz} parameter does not drop immediately to a standard value (see Fig. 2, Curve 1), as observed for a free-moving probe, but remains at the shifted value. This fact has to be taken into account when the mobility of a system is considered.

REFERENCES

[1] K. Hamada, T. Iijima, and R. McGregor, *Polym. J.*, *19*, 709 (1987).

[2] H. F. Ottaviani, P. Baglioni, and G. Martini, *J. Phys. Chem.*, *87*, 3146 (1983).

[3] H. Caldararu, A. Caragheorgheopol, M. Dimonie, D. Donescu, I. Dragutan, and N. Marinescu, *Ibid.*, *96*, 7109 (1992).

[4] G. P. Lozos and B. M. Hoffman, *Ibid.*, *78*, 2110 (1974).

[5] B. L. Bales, "Inhomogeneously Broadened Spin-Label Spectra," *Biological, Magnetic Resonance*, Vol. 8 (L. J. Berliner and J. Reuben, Eds.), Plenum, 1989, pp. 77–130.

[6] Z. Hloušková, J. Tiño, and I. Chodák, *Eur. Polym. J.*, *30*, 175 (1994).

[7] P. Törmälä, *J. Makromol. Sci.*, *Rev. Macromol. Chem.*, *C17*, 297 (1979).

[8] J. Tiño, V. Klimo, T. A. Claxton, and B. Burton, *J. Chem. Soc.*, *Faraday II*, *75*, 1307 (1979).

[9] T. A. Claxton, J. Tiño, and B. Burton, *Ibid.*, *76*, 1655 (1980).

[10] P. C. Hariharan and J. A. Pople, *Theoret. Chim. Acta*, *28*, 213 (1973).
[11] J. Tiňo and V. Klimo, *Collect. Czech. Chem. Commun.*, *41*, 960 (1976).
[12] P. Čársky and M. Urban, "Ab Initio Calculations," *Lect. Notes Chem.*, *16* (1980), Table 5.16.
[13] N. Kusumoto, S. Sano, N. Zaitsu, and Y. Motozato, *Polym. J.*, *17*, 448 (1976).
[14] A. T. Bullock, G. G. Cameron, and I. S. Miles, *Polymer*, *23*, 1536 (1982).