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ESR of Spin-Labeled Cross-Linked Perfluoro Polyethers and Properties of Adsorbed Water

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ABSTRACT: Cross-linked perfluoro polyethers showed properties such as glass transition temperatures and thermal stability, as determined by DSC and TGA, which are typical of usual perfluorinated polymers. These products were studied by ESR in the form of their spin-labeled adducts and after swelling with water solutions containing small nitroxide radicals. The analysis of the ESR line shapes revealed a relatively high flexibility of the perfluoro ether backbone. Formation of water pools in the polymer network was suggested on the basis of the ESR results, and the rheological properties of the swelling water were similar to those of water adsorbed in other perfluorinated ionomers.

Introduction

Electron spin resonance (ESR) spectroscopy has been widely applied to the characterization of synthetic polymer systems above and below their glass transition temperature, T_g.[1] Nitroxide radicals are the most used paramagnetic units, and they are largely employed as monitors of the polymer motion. These radicals are used either covalently bound at known sites in the polymer or as spin probes randomly distributed throughout the polymer.

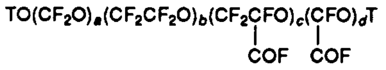
Perfluorinated compounds are receiving increasing attention both as fine chemicals and as specialty products for their use in a variety of devices.[2,3] Particular attention has been devoted to perfluorinated ionomers which contain a fluorocarbon polymer backbone with pendant ionic groups forming ionic clusters.[3,4] The best known of these ionomers is certainly the tetrafluoroethylene-sulfonated perfluorovinyl ether copolymers Nafion (Nafion is a trademark of E. I. du Pont de Nemours & Co.). The structure and properties of this class of compounds have been extensively discussed in the literature.[2,5–8] Various information on the structural and dynamic properties of transition-metal complexes and organic radicals incorporated into Nafion has been obtained by ESR and ENDOR.[9–19] ESR has also been used in a study of the aggregation properties in solution of a perfluoro polyether (PFPE) carboxylate surfactant[20] produced by Montefluos. PFPE compounds have a more flexible structure than Nafion polymers because of the presence of ether bridges in the main chain; the hydrophobicity is, however, almost the same. Perfluorocarbons are usually crystalline solids for molecular weights of over about 1000, whereas PFPE polymers exist as liquids over broad ranges of temperature and molecular weights. The typical structural flexibility is also maintained after functionalization.

In this paper we describe an ESR study on functional perfluoro polyether whose molecular features differ from those of the usual PFPE in the sense that cross-linking among polymer chains leads to ionomeric substances with structural analogies with Nafion. These cross-linked products may act as ion-exchange resins for fixing metal cations, as catalyst carriers, as a membrane for ion exchange, and in electrolytic processes.[21–22]

The polymers were labeled with a nitroxide radical and studied as a function of the degree of cross-linking to obtain information on the dynamics of the lateral chains and on the water pools formed after water swelling. The physical status of the adsorbed water was further studied by using small nitroxide molecules.

Experimental Section

Materials. The perfluorinated polyethers (PFPE) were obtained by the cross-linking of the following polyfunctional polymer precursor under UV treatment at temperatures near room temperature[21]



$$\mathrm{TO(CF_2O)_{\mathit{a}}(CF_2CF_2O)_{\mathit{b}}(CF_2\underset{\displaystyle COF}{\underset{|}{C}}FO)_{\mathit{c}}(\underset{\displaystyle COF}{\underset{|}{C}}FO)_{\mathit{d}}T}$$

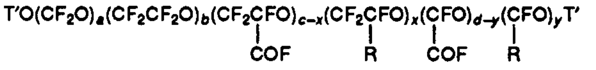
1

where T was CF_2COF with only traces of CF_3. The synthesis of this precursor was carried out by UV irradiation at 233 K of a mixture of tetrafluoroethylene and hexafluorobuta-1,3-diene in the presence of oxygen,[22] which afforded an intermediate that was subsequently converted to 1. From vapor pressure osmometry (VPO) a mean MW of 1750 was obtained. After hydrolysis of the –COF groups, the acid titration of the resulting –COOH groups gave an EW of 260, corresponding to an average of 6.7 COF groups/chain. The coefficients *a*–*d* in formula 1 were determined from ^{19}F NMR spectra[23] (Table I) to be

$$a = 5.5 \qquad b = 6.9 \qquad c = 4.2 \qquad d = 0.45$$

The discrepancies in the molecular weights obtained from VPO and calculated from the NMR-determined coefficients were in the limits of the MW of polymers usually obtained from different sources.[24]

After UV treatment, the cross-linking occurred through loss of –COF groups and was followed by coupling of the fluorocarbon chains to give products with the structure[25–27]



$$\mathrm{T'O(CF_2O)_{\mathit{a}}(CF_2CF_2O)_{\mathit{b}}(CF_2\underset{\displaystyle COF}{\underset{|}{C}}FO)_{\mathit{c-x}}(CF_2\underset{\displaystyle R}{\underset{|}{C}}FO)_{\mathit{x}}(\underset{\displaystyle COF}{\underset{|}{C}}FO)_{\mathit{d-y}}(\underset{\displaystyle R}{\underset{|}{C}}FO)_{\mathit{y}}T'}$$

where T′ = CF_2COF or CF_2R and R is the cross-linking site. Two differently cross-linked polymers were obtained as a function of the treatment times: PFPE-65, with EW = 750, and PFPE-75, with EW = 1040. The cross-linking degrees were 65% and 75%, respectively. These values were calculated simply from the differences between the EW before and after the cross-linking treatment.

The compounds were hydrolyzed with water and used as the sodium salt of the corresponding carboxylates. Sodium salts were obtained by ion exchange in concentrated NaCl solutions.

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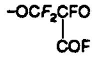
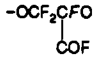
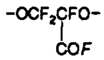
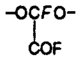
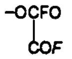
Table I
Assignment of the NMR Peaks of PFPE[23]

chemical shift (ppm; ref, $CFCl_3$)	assignt
+14	$-CF_2CO\mathit{F}$
-51.9	$-OCF_2CF_2OC\mathit{F}_2OCF_2CF_2O-$
-53.6	$-OCF_2OC\mathit{F}_2OCF_2CF_2O-$
-55.3	$-OCF_2OC\mathit{F}_2OCF_2O-$
-89	$-OCF_2CF_2OC\mathit{F}_2CF_2O-$
-90.5	$-OCF_2OC\mathit{F}_2CF_2O-$
-84, -90[a]	 $-OC\mathit{F}_2\underset{\substack{\vert\\ COF}}{C}FO-$
-130, -132[a]	 $-OCF_2\underset{\substack{\vert\\ COF}}{C}\mathit{F}O-$
+26.3	 $-OCF_2\underset{\substack{\vert\\ CO\mathit{F}}}{C}FO-$
-90, -100[a]	 $-O\underset{\substack{\vert\\ COF}}{C}\mathit{F}O-$
+23.5	 $-O\underset{\substack{\vert\\ CO\mathit{F}}}{C}FO$

[a] The relatively broad chemical shift ranges reflected the substituent variation flanking the ether oxygen atoms.

All products were waxy, white, hygroscopic, insoluble in the usual solvents, unmoldable, and only susceptible to swelling in solvents, depending on the cross-linking degree. To avoid moisture adsorption, the samples were stored in a $CaCl_2/SiO_2$ desiccator.

The nitroxides 4-amino-2,2,6,6-tetramethylpiperidin-1-oxyl (Tempamine), 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (Tempol), and 4-(trimethylammonio)-2,2,6,6-tetramethylpiperidin-1-oxyl ($TempTMA^+$) were purchased from Molecular Probe, Eugene, OR, and used without further purification.

Spin Labeling. Spin labeling of PFPE (SL-PFPE) was carried out by reaction of Tempamine with the methyl esters of the PFPE compounds. The esters were prepared by stirring of 500 mg of nonhydrolyzed PFPE with a CF_2ClCF_2Cl/CH_3OH, 80:20 (v/v), mixture, according to the procedure commonly used for the preparation of perfluorocarbon derivatives.[28] The products were repeatedly washed with methanol to completely remove HF and treated with a 5×10^{-3} mol/L Tempamine solution in anhydrous ethanol in an amount corresponding to 40% of the esterified perfluoroacyl groups. From the adsorbance at 242 nm of the unreacted nitroxide in the mother liquor, the PFPE spin labeling was determined to be >95%.

Sample Handling. The dry SL-PFPE samples were directly inserted in quartz capillaries of 2 mm i.d. The preparation procedure and the handling of the water containing samples were as previously reported.[18,19]

Techniques. The ESR spectra were obtained with the aid of the Bruker 200DD ESR spectrometer operating at X band (~9.5 GHz). Instrumental settings were such as to avoid signal saturation and overmodulation. The temperature was varied by using the Bruker ST100/700 variable-temperature accessory.

The NMR spectra were recorded with a Varian 200 spectrometer using $CFCl_3$ as internal reference standard.[23]

The Perkin-Elmer DSC 2C differential scanning calorimeter was used to determine the glass transition temperature, T_g, of the cross-linked samples, using a heating rate of 20 K/min and the base-line deviation method.

The Du Pont Model 9900 TGA instrument was used for thermogravimetric analysis. The heating rate was 10 K/min.

Results and Discussion

The T_g values of the cross-linked PFPE as measured by DSC were as follows: PFPE-65, 160 K; PFPE-75, 175 K. These values were in the expected range using as reference those reported for linear-chain perfluoro polyethers HFP- and TFE-Fomblin (Montedison registered trademark).[29]

Figure 1 shows the TGA behavior of PFPE-75. A similar pattern was obtained for PFPE-65. Thermal stability was noted up to 498 K, with a weight loss of 10.2% (2.02% at 396 K, due simply to water depletion). Above 500 K decarboxylation occurred with increasing weight loss, which was about 50% at 610 K.

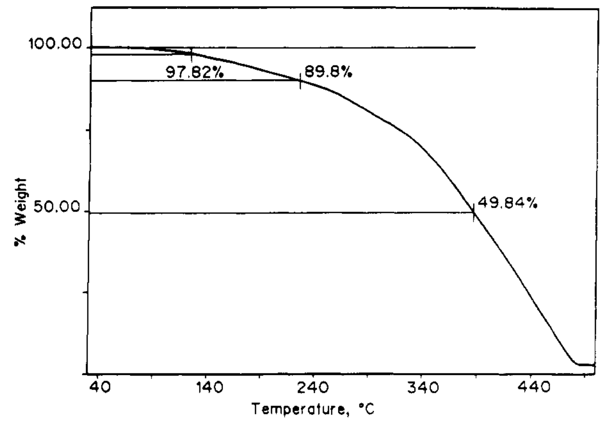


Figure 1. Thermal gravimetric analysis of PFPE-65. Heating rate: 10 K/min.

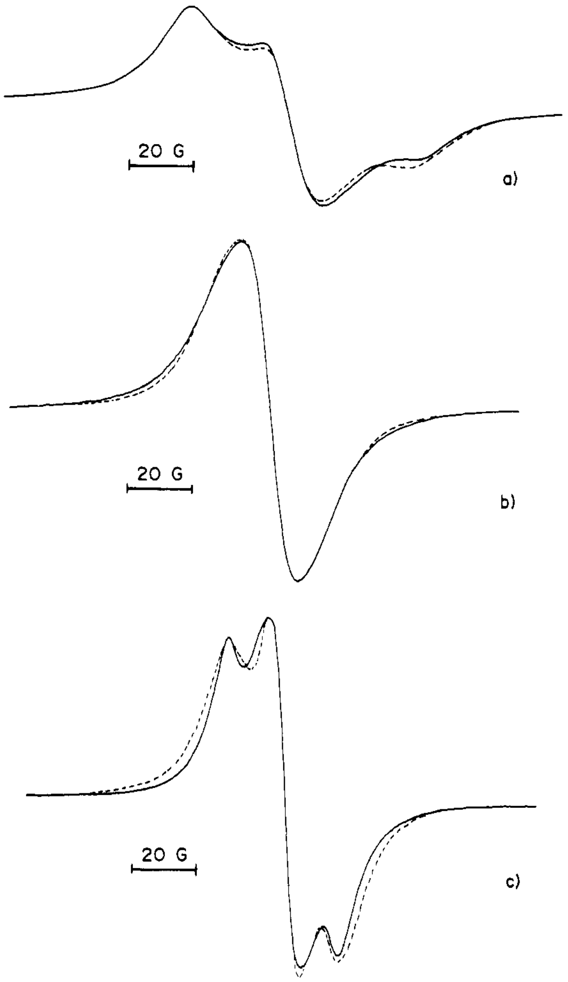


Figure 2. Experimental (full lines) and computed (dashed lines) ESR spectra (T = 298 K) of dry (a) and water-swollen spin-labeled (b) PFPE with a cross-linking degree of 65%. (c) Experimental and computed spectra of water-swollen SL-PFPE with a cross-linking degree of 75%.

Figure 2a shows the ESR spectrum at room temperature of the SL-PFPE-65, which was kept for 7 days in a $CaCl_2/SiO_2$ desiccator and 3 days in an oven at 323 K under moderate depression. More prolonged drying treatment did not significantly alter the line shape. The spectrum was a typical slow-motion ESR spectrum[30,31] whose hyperfine components were broadened by spin–spin effects, that is, dipole–dipole interaction and Heisenberg spin exchange.[32,33] The signal could be reproduced by using the procedure reported by Schneider and Freed[31] (dashed line in Figure 2a). The input magnetic parameters for the **g** and A tensor components that gave the best fit were

$$g_{xx} = 2.0088 \qquad A_{xx} = 6.5\ \mathrm{G}$$

$$g_{yy} = 2.0072 \qquad A_{yy} = 7.5\ \mathrm{G}$$

$$g_{zz} = 2.0035 \qquad A_{zz} = 33.6\ \mathrm{G}$$

$$T_{2,0} = 13\ \mathrm{G}$$

with isotropic correlation time $\tau = 5 \times 10^{-7}$ s, which indicated a relatively high degree of flexibility. Introducing small anisotropies in the rotational diffusion coefficients[30] did not significantly alter the line shape. The residual linewidth $T_{2,0} = 13$ G included the line broadening due to spin–spin interactions.

The presence of strong spin–spin interactions was proved after swelling the polymer with water. The line shape was reduced to a single, exchanged narrowed line with ΔB = 18.2 G (Figure 2b). This line resembled those given by pore nitroxides (ΔB = 16–20 G, depending on the nitroxide). A computer program based on the modified Bloch equations including the Heisenberg spin exchange[34,35] reproduced perfectly the line shape (dashed line in Figure 2b). The best fit was obtained assuming $\Delta B(m_\mathrm{I}{=}1) = 10$ G, $\Delta B(m_\mathrm{I}{=}0) = 6$ G, and $\Delta B(m_\mathrm{I}{=}{-1}) = 10$ G, $\langle A_\mathrm{N} \rangle = 14.5$ G, and ω_exc = 20 MHz. The same signal shape as in Figure 2a was reproduced by simple drying of the water-containing SL-PFPE-65 sample for 2 days in the desiccator.

The same treatment as above carried out on SL-PFPE-75 gave similar results, the most significant difference being a decrease in the Heisenberg spin-exchange frequency. Desiccated samples gave rise to slow-motion spectra with the same mobility as PFPE-65, and water-swollen samples showed a partial resolution of the hyperfine components in the liquidlike signal (Figure 2c), which was simulated assuming ω_exc = 10 MHz.

Assuming water pool formation for both PFPE-65 and PFPE-75 on the basis of the molecular analogies with the perfluorinated ionomer Nafion, the calculated exchange frequencies agreed with a significant protruding into water pools of the nitroxide moieties of the spin-labeled fluorocarbon chains. The higher value of ω_exc of SL-PFPE-65 meant smaller distances among –NO groups, which therefore moved in a more restricted space than those in SL-PFPE-75. This was attributed to the different degrees of cross-linking, which led to different sizes of the water pools, in that the smaller holes available for water adsorption, the lower the degree of cross-linking. A slightly more extensive spin labeling was obtained with PFPE-65 than with PFPE-75 since a larger number of functional groups were available for spin labeling in the former. This might also lead to shorter average distances among –NO units, which would, however, only partially explain the doubling of the exchange frequency.

Figure 3 shows the ESR spectra at different temperatures of a 10^{-3} mol/L water solution of Tempol and TempTMA$^+$ adsorbed on PFPE-75. The ESR signals were due to radicals with correlation times in the fast-motion domain. These signals maintained their overall shape in the temperature range 260–340 K and changed to a slow-motion shape below 250 K, well above the glass transition temperature. This was the typical ESR line-shape behavior previously reported for water adsorption on silica gels, zeolites, and Nafion.[18,36–38] It was interpreted assuming that the water adsorbed on porous supports or confined to restricted spaces, as the water pools in the PFPE should be, does not suddenly crystallize under cooling but undergoes progressive immobilization from liquidlike to glassy-like motion.

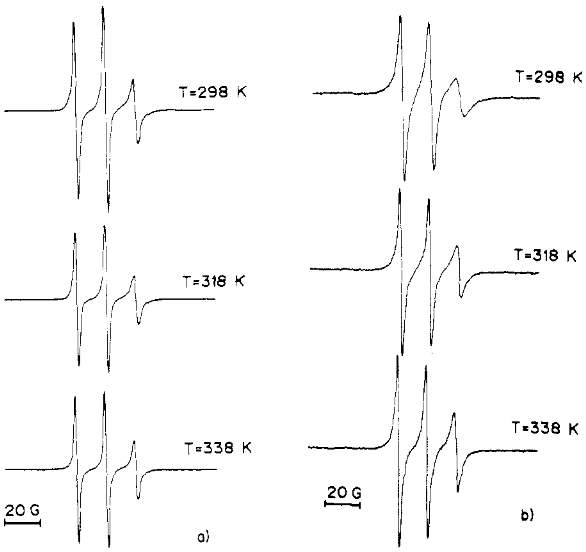


Figure 3. ESR spectra at different temperatures of 10^{-3} mol/L water solutions of Tempol (a) and TempTMA$^+$ (b) adsorbed onto PFPE-75.

A careful analysis of the line shapes of the liquidlike signals revealed that they were not due to a single set of radicals with the same relaxation rate. This is a well-documented situation in the ESR of synthetic polymers, and it has been found with both spin labels and spin probes. Brown and Sandreczki,[39] in agreement with the arguments of Veksli and Miller,[40,41] suggest bimodal or broad monomodal distribution for the motional correlation times of spin labels and spin probes in an amine-cured epoxy resin as a function of solvent plasticizer content. Fitting of the experimental signals with line shape computed on the basis of programs that gave the ESR patterns expected from the accepted relaxation mechanisms in the fast narrowing region[30,31] failed to be accurate. For instance, Figure 4 compares the experimental 298 K signals of Tempol (Figure 4a) and TempTMA$^+$ (Figure 4b) with the spectra computed with different procedures. The dashed lines in both parts a and b of Figure 4 were computed as a sum of Lorentzian lines with widths corresponding to the peak-to-peak separations, i.e. regardless of the relaxation mechanisms governing the line shape.[35] The agreement was poor, particularly in the Tempol case. This was improved by using a line-shape calculation arising from anisotropic motion, i.e., assuming anisotropic diffusion along the z axis with respect to x and y axes[30] (dotted line in Figure 4a). This shape was calculated with Brownian diffusional coefficients $D_\perp = 1.76 \times 10^{8}\ \mathrm{s}^{-1}$ and $D_\parallel = 1.76 \times 10^{9}\ \mathrm{s}^{-1}$ ($\tau_\perp = 9.5 \times 10^{-10}$ s and $\tau_\perp = 9.5 \times 10^{-11}$ s, respectively). The **g** and A components were as follows:

$$g_{xx} = 2.0095 \qquad A_{xx} = 6.6\ \mathrm{G}$$

$$g_{yy} = 2.0065 \qquad A_{yy} = 7.8\ \mathrm{G}$$

$$g_{zz} = 2.0027 \qquad A_{zz} = 36.2\ \mathrm{G}$$

Spectral line shapes similar to that given by the TempTMA$^+$/PFPE system reported, for instance, by Schlick and co-workers[42] in a study of phase separations

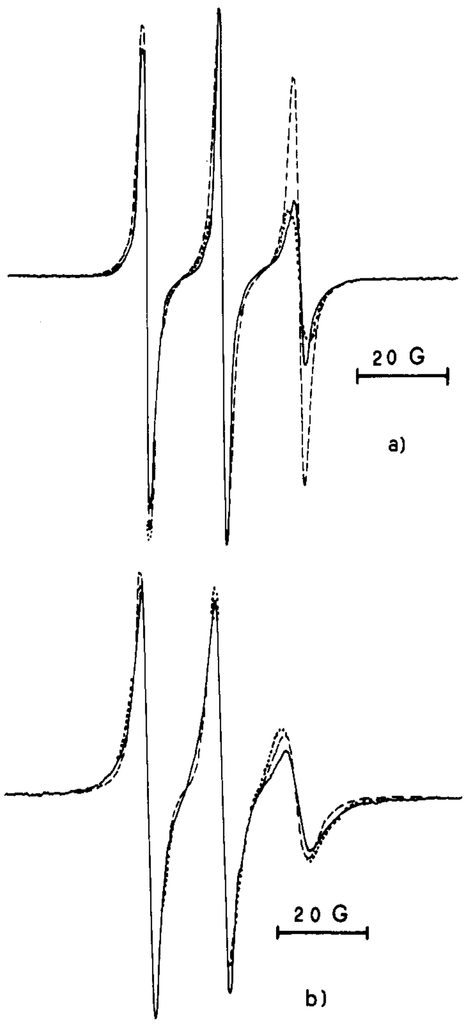


Figure 4. ESR spectra (full lines) at 298 K of 10^{-3} mol/L water solutions of Tempol (a) and TempTMA$^+$ (b) adsorbed onto PFPE-75 as compared with the line shapes (dashed lines) computed as a sum of Lorentzian lines with the peak-to-peak separations of the experimental signals and with the line shapes (dotted lines) computed for probes in anisotropic motion (see text for details).

in interpenetrating poly(vinyl chloride) and cross-linked polyurethane polymers. The experimental patterns are fitted with spectral shapes computed by using a distribution of g_{iso} and A_{iso} values, which reflects the heterogeneity in the local environments. On the other hand, the calculation used for very anisotropic motion such as that observed in spin-labeled poly(methyl methacrylate)[43] or in oriented systems[44,45] led to a relatively good fit as shown in the dotted line in Figure 4b. The order parameter,[30] S, was assumed to be 0.8 with the following magnetic parameters:

$$g_{zz} = 2.0098 \qquad A_{xx} = 8.84\ \mathrm{G}$$

$$g_{yy} = 2.0075 \qquad A_{yy} = 8.84\ \mathrm{G}$$

$$g_{zz} = 2.0037 \qquad A_{zz} = 32.12\ \mathrm{G}$$

The large motional anisotropy was ensured by $N = D_{zz}/D_{xx} = 40$; i.e., $D_{zz} = 3.5 \times 10^9\ \mathrm{s}^{-1}$ ($\tau_{\parallel} = 4.75 \times 10^{-11}$ s) and $D_{xx} = 8.8 \times 10^7\ \mathrm{s}^{-1}$ ($\tau_{\perp} = 1.9 \times 10^{-9}$ s). However, at present we have no convincing proof of an orientational order in our samples. In addition a reasonable degree of polydispersity was expected for the investigated products. We therefore suggest that the situation described by Schlick et al.[42] could also apply to our systems. In conclusion, the experimental line shapes could not be simulated with a reasonable accuracy if singly relaxing radicals are accepted. This meant that the experimental lines arose from radicals with different relaxation rates; i.e., the nitroxides sensed different motional regions, most of which were in the fast-motion domain.[39] This occurred in both cases and in the entire temperature range of liquidlike spectra. An accurate determination of the correlation times for the modulation of the magnetic anisotropies, τ, and of their activation energies was therefore prevented, and this obstacle could not be overcome because the distribution of the differently relaxing sites was not known. This was in line with the proposed model of water pools, in which different interactions of the probes with both pendant ionic groups and fluorocarbon chains were expected.

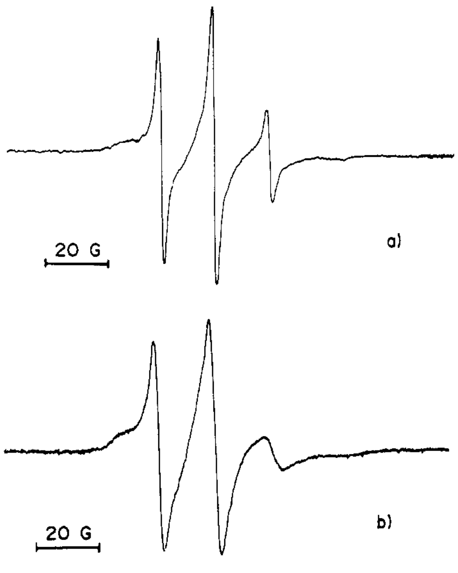


Figure 5. ESR spectra at 298 K of 10^{-3} mol/L water solutions of Tempol (a) and TemTMA$^+$ adsorbed onto PFPE-65.

In the case of PFPE-65, the ESR signals from both Tempol and TempTMA$^+$ (Figure 5) were superimpositions of a liquidlike and a slow-motion signal, with the relative intensity of the second signal increasing with decreasing temperature. Below 250 K the slow-motion signal was the only one observed in this case, regardless of the nature of the probe used. This finding has been reported in several cases of water adsorption on porous systems.[46,47] The two absorptions were due to radicals localized in regions characterized by markedly different motional properties, which closely reflected the bimodallike distribution of the correlation times discussed by Brown and Sandreczki.[39] The diffusion rate between the two sets of sites was low enough in the ESR time scale to get ESR signals that contributed separately to the overall absorption. We attributed these signals to radicals that are almost free to move in water pools and to radicals strongly interacting (for instance, through ionic interaction in the case of TempTMA$^+$) with charged sites (the $-COO^-$ groups) of the polymer network. These were present in more considerable amounts in PFPE-65 than in PFPE-75, as reported above for the spin-labeled products. Table II reports the values of the ^{14}N hyperfine coupling constants of Tempol in PFPE-75 and PFPE-65 at three different temperatures, compared with the values in bulk water and in Nafion.[18] The significant decrease in the hyperfine coupling constants in the PFPE polymers as compared with bulk water was completely in line with the findings in the Nafion membrane.[18] As in this ionomer, the lower $\langle A_N \rangle$ values than in bulk water represented a decreased water polarity; this corresponded to partially non-hydrogen-

Table II
Hyperfine Coupling Constants (in Gauss) of ^{14}N in Tempol Water Solution Adsorbed in Perfluorinated Compounds

	T = 288 K	T = 308 K	T = 328 K
Tempol/Nafion[a]	16.45	16.45	16.45
Tempol/PFPE-75	17.0	16.9	16.8
Tempol/PFPE-65	17.0	16.9	16.8
H_2O	17.3	17.2	17.1

[a] The temperature dependence of A_N was in the limit of the experimental errors.

bonded water, which was exposed mainly to the hydrophobic fluorocarbon chains penetrating into the water pool.[48-50] The polarity sensed by nitroxides inserted into the PFPE was almost independent of the degree of cross-linking, as suggested by the same values of $\langle A_N \rangle$ in PFPE-65 and PFPE-75. Results with the same general trend were also found with the positive radical; however, the electrostatic interactions of this radical with the charged groups in the molecular skeleton of the cross-linked polymers prevented us from obtaining other than qualitative information.

Conclusion

The analysis of the ESR spectra of cross-linked perfluoro polyethers either as spin-labeled adducts or after the adsorption of aqueous solutions of nitroxide radicals suggested a relative flexibility of the molecular backbone with formation of holes in which water could be positioned. The sizes of these holes and their properties depended on the degree of cross-linking. The rheology and the polar properties of adsorbed water were in line with those observed for water adsorbed on several porous supports including the perfluorinated ionomer Nafion.

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