are needed to fully characterize a gel structure. These are the power law exponent and the gel strength.

It should again be emphasized that the above results apply at the gel point of model cross-linking polymers at temperatures far above vitrification. The prepolymers consisted of large bifunctional molecules, however, with an initial molecular weight well below the critical mass for entanglements, and of small trifunctional cross-linker molecules.

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Registry No. (PPO)(DRF) (block copolymer), 112320-36-2; DRF, 4151-51-3.

References and Notes

(1) Chambon, F.; Winter, H. H. *Polym. Bull. (Berlin)* **1985**, *13*, 499.
(2) Winter, H. H.; Chambon, F. *J. Rheol.* **1986**, *30*, 367.
(3) Chambon, F.; Petrovic, Z. S.; MacKnight, W. J.; Winter, H. H. *Macromolecules* **1986**, *19*, 2146.
(4) Chambon, F.; Winter, H. H. *J. Rheol.*, **1987**, *31*, 683.
(5) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(6) Feger, C.; Molis, S. E.; Hsu, S. L.; MacKnight, W. J. *Macromolecules* **1984**, *17*, 1830.
(7) Feger, C.; MacKnight, W. J. *Macromolecules* **1985**, *18*, 280.
(8) Chambon, F. Ph.D. Thesis, University of Massachusetts, 1986.
(9) ASTM-D 1938-74.
(10) Treloar, L. R. G. *The Physics of Rubber Elasticity*, 3rd ed.; Clarendon: Oxford, 1975.
(11) Leung, Y. K.; Eichinger, B. E. *J. Chem. Phys.* **1984**, *80*, 3877, 3885.
(12) Tung, C. Y. M.; Dynes, P. J. *J. Appl. Pol. Sci.* **1982**, *27*, 569.
(13) Clerc, J. P.; Tremblay, A. M. S.; Albinet, G.; Mitescu, C. D. *J. Phys., Lett.* **1984**, *45*, L913.
(14) Clerc, J. P.; Giraud, G.; Laugier, J. M.; Luck, J. M. *J. Phys. A: Math. Gen.* **1985**, *18*, 2565.
(15) Winter, H. H. *Progr. Colloid Polym. Sci.*, in press.
(16) Coniglio, A.; Daoud, M. *J. Phys. A: Math. Gen.* **1979**, *12*, L259.
(17) Durand, D.; Delsanti, M.; Adam, M.; Luck, J. M. *Europhys. Lett.* **1987**, *3* (3), 297.
(18) Muthukumar, M. *J. Chem. Phys.* **1985**, *83*, 3161.
(19) Cates, M. E. *J. Phys. (Les Ulis, Fr.)* **1985**, *46*, 1059.
(20) Muthukumar, M.; Winter, H. H. *Macromolecules* **1986**, *19*, 1284.
(21) Hess, W.; Vilgis, T.; Winter, H. H. *Macromolecules*, in press.

H. Henning Winter,* Paul Morganelli, and Francois Chambon

Polymer Science and Engineering Department and Chemical Engineering Department University of Massachusetts Amherst, Massachusetts 01003

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Electron Nuclear Double Resonance from Paramagnetic Centers in Ionomers. Titanium(III) in Nafion

The presence of ions and of the polymer network in ionomers is believed to lead to segregation into polar and nonpolar regions and to ionic clustering.[1] Electron spin resonance (ESR) spectroscopy has been used in recent years in order to study the process of clustering of the ionic species in the polar phase of ionomers. In our studies[2] we have deduced the immediate environment, within about 0.3 nm, of the paramagnetic Cu(II) and Ti(III) in the perfluorinated ionomer membranes known as Nafion. We have been able to detect cations ligated to the oxygen atoms from the solvent and from the sulfonic groups of the polymer network. In addition, we have identified Cu(II)–Cu(II) and Ti(III)–Ti(III) dimers, based on the detection of the spin-forbidden half-field transition. The signal from the dimers appears even at low cation concentrations, compared with the concentration needed for complete neutralization of all the sulfonic groups in the ionomer. We have suggested that clusters are formed from the association of these dimeric species.

Determination of the cluster size is important for an accurate model of phase separation in ionomers. This implies measurement of the structure around the cation in the second solvation shell, to about 0.5 nm and even further, to the regions occupied by the organic network. At these distances the interactions of the nuclei with the paramagnetic centers are too weak to be measured by ESR, because the line widths detected in the solid state are inhomogeneously broadened and the signal is a convolution of many small interactions.

The resolution in magnetic resonance experiments is considerably enhanced by using multiple-resonance techniques. Of these techniques, electron nuclear double resonance (ENDOR) has increased resolution compared to ESR and increased sensitivity compared to NMR. The ENDOR signal is obtained by monitoring the change in the intensity of a partially saturated ESR signal while sweeping the nuclear transitions by an radiofrequency (rf) field which is typically in the range 2–50 MHz. The ENDOR effect is very sensitive to the relaxation paths in the spin system and it is usually difficult to predict the temperature corresponding to a maximum signal.[3]

In this paper we present the first application of ENDOR for the study of ionomers. ^1H and ^2H, and ^{19}F ENDOR signals were obtained in the temperature range 4–20 K in Nafion containing the paramagnetic cation Ti(III). To the best of our knowledge this is the first detection of ENDOR signals of these nuclei from a Ti(III) center surrounded by oxygen ligands.[4] The significance of the results and the information that can be obtained will be discussed. Extension of this method to other systems will be suggested.

Experimental Section. Nafion-H powder (Scientific Polymer Products) with an equivalent weight of 1100 g/mol of SO_3H was used without further purification. Methanol (Fisher) and deuteriated methanols (Norell Chemical Co.) were dehydrated by using molecular sieves Type 3A from Kodak. The deuterium enrichment of CH_3OD and CD_3OD was 99%. Methanol solutions of $TiCl_3$ from Aldrich, in the concentration range 0.04–0.10 M, were used to exchange 30–40% of the SO_3H groups of the ionomer, based on three sulfonate groups per Ti(III). More details on the experimental procedure have been published.[2c]

ESR and ENDOR spectra at X-band were measured with Bruker 200D SRC spectrometers in Detroit and Linkoping operating at 9.7 GHz. ESR spectra at 100 K were obtained by using the Bruker variable-temperature ER 4111 VT unit. ENDOR spectra were obtained in Linkoping with the Bruker ENDOR attachment equipped with the Aspect 2000 computer. The magnetic field was measured by using the Bruker ER 035 NMR Gaussmeter and the microwave frequency was measured with an EIP Model 548 A microwave frequency counter. The maximum rf power of the ENDOR unit is 100 W. In all ENDOR experiments helium was used as the coolant in a flow cryostat from Oxford Instruments.

Results and Discussion. The samples measured were Nafion containing Ti(III), swollen by CH_3OD and by CD_3OD. The samples are designated Ti/Nafion/CH_3OD and Ti/Nafion/CD_3OD, respectively.

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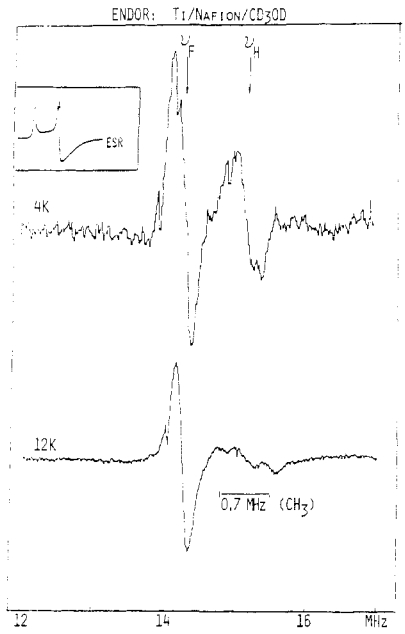

Figure 1. ENDOR from Ti/Nafion/CD_3OD at 4 and 12 K. The position of the external field is indicated by the arrow in the ESR spectrum. The rf power is 80 W and the microwave power is 6.3 mW. The spikes observed are due to the rf synthesizer.

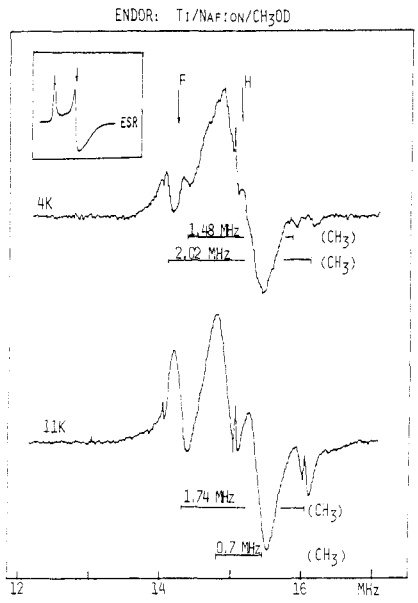

Figure 2. ENDOR from Ti/Nafion/CH_3OD at 4 and 11 K. The position of the external field is indicated by the arrow in the ESR spectrum. The rf power is 80 W; the microwave power is 20 mW at 4 K and 6.3 mW at 11 K. The spikes observed are due to the rf synthesizer.

The ESR spectrum from Ti(III) is relatively simple because only g anisotropy is detected. The g values measured at 100 K, $g_{\parallel} = 1.989$ and $g_{\perp} = 1.878$, correspond to a trigonally distorted octahedral symmetry.[2] ESR spectra are shown in the small insets in Figures 1–3. ENDOR spectra were observed while monitoring the perpendicular ESR transition, as indicated in the insets.

ENDOR spectra from Ti/Nafion/CD_3OD are shown in Figure 1. The signals at 4 K are centered on the free nuclear frequencies of ^{19}F and H; at the measuring magnetic field of 3550.6–3546.8 G, these frequencies are 14.2 and 15.1 MHz, respectively. These signals are the fluorine and proton matrix ENDOR; the ENDOR effect is due in this case to the interaction of the paramagnetic center with nuclei by dipolar interaction only, with no isotropic hyperfine splitting.[5] The H-matrix ENDOR signal is weaker and is due to incomplete deuterium enrichment. Both matrix ENDOR lines are very narrow; the peak-to-peak derivative width is 0.23 MHz for both nuclei. At 12 K the relative intensity of the two signals changes dramatically, most likely due to a different temperature dependence of the relaxation processes responsible for the ENDOR effect. The line width of the F-matrix line decreases to 0.21 MHz and that of the H-matrix line increases to 0.33 MHz. At 18 K the proton matrix signal disappears completely. A weak proton doublet with a separation of 0.7 MHz is detected and is assigned to the methyl protons.

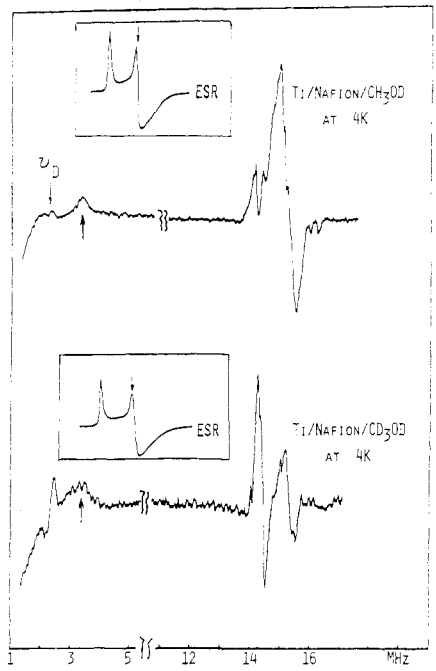

Figure 3. ENDOR from Ti/Nafion/CH_3OD and Ti/Nafion/CD_3OD at 4 K. The position of the external field is indicated by the arrow in the ESR spectrum. The rf power is 80 W; the microwave power is 20 mW and 6.3 mW, respectively. Upward arrow in the ENDOR spectra at 3.5 MHz indicates the splitting from the deuterium in the OD group. The spikes observed are due to the rf synthesizer.

ENDOR spectra from Ti/Nafion/CH_3OD are shown in Figure 2. At 4 K the proton matrix ENDOR signal is dominant. In addition, two proton doublets with splittings of 2.02 and 1.48 MHz are detected. At 11 K two proton doublets with splittings of 1.74 and 0.7 MHz are indicated. By comparison with the proton splittings in Figure 1, these splittings are assigned to methyl protons. The signals assigned to the methyl protons have been detected by saturating the perpendicular ESR signal. Normally this procedure can be used to select the corresponding hyperfine components in the ligands. For the methyl protons, however, this method is not easy to apply because there are *three* interacting protons with different principal values and directions of the hyperfine tensor. It is also easy to see that these directions are not expected to coincide with the molecular axes, which define the principal directions of the g tensor. In spite of these complications, some deductions can be made, from the *averaged* hyperfine splittings shown in Figure 2, at 11 K. Due to motional averaging, the hyperfine tensor seems to be axially symmetric, with $A_{\parallel} = 1.74$ MHz and $|A_{\perp}| = 0.7$ MHz. The tensor (1.74, –0.7, –0.7) in megahertz can be decomposed to give $a_{iso} = 0.11$ MHz and a dipolar tensor of (1.63, –0.82, –0.82) in megahertz. The sign of the tensor components has been chosen so as to obtain a minimum value of a_{iso}.[6] If we assume that the three protons of the methyl group

have similar values of a_{iso} and that the value of 2.02 MHz represents a maximum value of the hyperfine tensor for one of the protons (the closest to the cation), the maximum principal value of the *dipolar* tensor for this proton is 1.91 MHz. This value corresponds to a distance of 0.43 nm between this methyl proton and Ti(III).

In Figure 3 we present ENDOR spectra from the two samples studied at 4 K, in the rf frequency range 1–17 MHz. In addition to the high-frequency signals shown in Figures 1 and 2, we observe a signal corresponding to the free nuclear frequency of the ^2H nucleus, at 2.3 MHz. This signal is stronger in the sample prepared from fully deuteriated methanol and represents the D-matrix ENDOR line. An additional signal at 3.5 MHz is assigned to the deuterium of the OD group in deuteriated methanol. This splitting translates into a hf of 2.4 MHz from deuterons and of 15.6 MHz from protons (because of a ratio of 6.51 between the magnetic moments of H and D nuclei). This large splitting explains the considerable narrowing of the ESR from the Ti(III) center upon deuteriation of methanol.[2]

Of great interest for ionomer research is determination of the Ti–F distance. To the best of our knowledge, the width of the matrix ENDOR line from fluorine nuclei is the narrowest such line reported in the literature.[7]

For nuclei situated at distances larger than about 0.5 nm from the paramagnetic center, the ENDOR response seems to be dominated by an angularly independent nuclear spin–lattice relaxation mechanism which is due to spin diffusion.[8] For a nuclear spin–lattice relaxation time T_{1N} independent of orientation, the matrix ENDOR line shape has been studied[9] as a function of the relative magnitudes of the nuclear spin-packet line width $(T_{2N})^{-1}$ and the electron–nuclear dipolar interaction parameter α, where $\alpha = g_e\beta_e g_N\beta_N/2r_N^3$ and r_N is the closest distance of the nuclei to the paramagnetic center. When $(T_{2N})^{-1}$ is similar to or larger than α, the matrix ENDOR line consists of a single line centered at the free nuclear frequency ν_N. Doublets at $\nu_N \pm \alpha$ and $\nu_N \pm 2\alpha$ are expected when the electron–nuclear dipolar interaction is larger than $(T_{2N})^{-1}$.

For the fluorine matrix ENDOR line measured in this study, no doublet splitting has been detected. The value of the fluorine spin–spin relaxation time T_{2F} has been measured in NMR studies of various Nafion samples and this value was found to be in the range 10–15 μs at 173 K, the lowest temperature measured,[10,11] corresponding to a spin-packet line width of 0.07–0.1 MHz. Therefore we can assume that $(T_{2F})^{-1}$ is of the same magnitude as α and that the peak-to-peak derivative line width is $2\alpha + (T_{2F})^{-1}$. From the experimental line width of 0.23 MHz and the expression $r_F^3 = 35.59/\alpha$, we deduce that r_F is in the range 0.76–0.82 nm. In the expression for r_F, α is in kilohertz and r_F is in nanometers. In deriving this expression we have used the isotropic g value of 1.915 for the Ti(III) paramagnetic center. This method for calculation of the Ti–F distance is in accord with the ENDOR response model of Iwasaki et al.[12]

Preliminary simulations of the fluorine matrix ENDOR signal were also performed by using an ENDOR model which specifically includes all relaxation paths,[8,13] with T_{1E} in the range 100–700 μs and T_{2E} in the range 0.6–1.2 μs (deduced from electron spin echo experiments[14]), T_{1F} in the range 0.4–1.5 s, and T_{2F} in the range 10–15 μs.[10,11] The simulations seem to indicate a value of r_F in the range deduced from the simpler model used above. More simulations are planned, in order to ascertain the effect of the experimental parameters, such as microwave and radiofrequency fields, on the experimental line shape.

Conclusion. The results presented indicate that the double-resonance ENDOR technique can provide detailed information about the location of nuclei around the cations in ionomers, to a distance of about 1 nm. This means that the ionic regions can be defined with great accuracy by using advanced simulation methods for the ENDOR response. Additional experiments are planned to determine the effect of the paramagnetic ion concentration on the intensity and width of the fluorine matrix ENDOR line in Nafion. The method described here can be extended to other systems. For instance in ionomers with protonated chains we can completely deuteriate the swelling solvent; the proton matrix signal will represent exclusively the network nuclei and the simulation will give distances to the network. It is also possible to selectively deuteriate *portions* of the network in addition to the solvent, in order to specifically *see* parts of the chain we want to study. The method can of course be extended to other paramagnetic cations, varying the concentration and the cation charges. We are currently involved in additional ENDOR studies of ionomers.

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Registry No. Nafion-H, 63937-00-8; $TiCl_3$, 7705-07-9.

References and Notes

(1) *Perfluorinated Ionomer Membranes*; Eisenberg, A., Yeager, H. L., Eds.; American Chemical Society: Washington, DC; 1982.
(2) Alonso-Amigo, M. G.; Schlick, S. (a) *J. Phys. Chem.* **1986**, *90*, 6353; (b) *Polym. prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1986**, *27*, 337; (c) *J. Chem. Soc., Faraday Trans. 1*, in press; (d) *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28*, 363.
(3) Kurreck, H.; Kirste, B.; Lubitz, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 173.
(4) Search of ENDOR studies from the Ti(III) center revealed only a handful of references. Of these the most relevant to this study are as follows: (a) Brik, A. B.; Matyash, I. V.; Fedotov, Yu. V. *Fiz. Tverd. Tela (Leningrad)* **1977**, *19*, 71 (in Russian). (b) Labauze, G.; Raynor, J. B.; Samuel, E. *J. Chem. Soc., Dalton Trans.* **1980**, *12*, 2425. (c) Van Wezep, D. A.; Van Kemp, R.; Severts, E. G.; Ammerlaan, C. A. *J. Phys. Rev. B* **1985**, *32*, 7129. (d) Gourier, D.; Vivien, D.; Samuel, E. *J. Am. Chem. Soc.* **1985**, *107*, 7418. (e) Gourier, D.; Samuel, E. *J. Am. Chem. Soc.* **1987**, *109*, 4571.
(5) Vedrine, J. C.; Hyde, J. S.; Leniart, D. C. *J. Phys. Chem.* **1972**, *76*, 2087.
(6) Yim, M. B.; Makinen, M. W. *J. Magn. Reson.* **1986**, *70*, 89.
(7) Schlick, S.; Kevan, L. *J. Appl. Polym. Sci.* **1982**, *27*, 319.
(8) Schlick, S.; Kevan, L.; Toriyama, K.; Iwasaki, M. *J. Chem. Phys.* **1981**, *74*, 282.
(9) Leniart, D. S.; Hyde, J. S.; Vedrine, J. C. *J. Phys. Chem.* **1972**, *76*, 2079.
(10) Boyle, N. G.; McBrierty, V. J.; Douglass, D. C. *Macromolecules* **1983**, *16*, 75.
(11) Boyle, N. G.; McBrierty, V. J.; Eisenberg, A. *Macromolecules* **1983**, *16*, 80.
(12) Iwasaki, M.; Muto, H.; Eda, B.; Nunome, K. *J. Chem. Phys.* **1972**, *56*, 3166.
(13) Kevan, L.; Schlick, S.; Toriyama, K.; Iwasaki, M. *J. Phys. Chem.* **1980**, *84*, 1950.
(14) Schlick, S.; Sass, C.; Kevan, L., unpublished results.

Shulamith Schlick*
Department of Chemistry, University of Detroit
Detroit, Michigan 48221-9987

Lars Sjoqvist and Anders Lund
Department of Physics and Measurement Technology
Linkoping University, S-581 83 Linkoping, Sweden

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