

Bonding of Molybdenum(V) to Poly(ethylene-*co*-methacrylic acid) Ionomers from X- and W-Band ESR and IR Spectroscopies[†]

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The bonding of Mo^V dispersed in poly(ethylene-*co*-methacrylic acid) (EMAA) ionomers was deduced from ESR measurements at X (9.5 GHz) and W (95 GHz) frequencies, spectral simulations, and FTIR spectra and compared with previous results for Mo^V in polyacrylic acid (PAA) and in perfluorinated ionomers ("Nafion") that contain sulfonic acid groups. Molybdenum dispersed in EMAA ionomers was obtained by grafting the ionomer with gaseous MoCl₅ in the absence of air, to prevent oxidation to Mo^{VI}. This method produced both physically and chemically bonded Mo^V species, and the ratio of the two species depended on the temperature of MoCl₅ during grafting. The type of ligands was deduced from the *g*-values, and the hyperfine splittings of magnetic Mo nuclei (*I* = 5/2). The major species detected at the lower grafting temperature was Mo^V bonded to five chlorine ligands and to an oxygen ligand from a carboxylic group of the ionomer. Heating in vacuum to 400–500 K ("activation") led to the gradual replacement of the chlorine ligands by oxygen ligands and to the removal of some molybdenum. The nature of the oxygen ligands was deduced from FTIR spectra and depends on the methacrylic acid (MAA) content in the ionomer: in Mo/EMAA samples activated at ≈400 K, molybdenum is bonded to the substrate by bidentate carboxylic groups in the ionomer containing 1.3 mol % MAA and by monodentate carboxylic groups for an MAA content of 11.2 mol %. Exposure of Mo/EMAA samples to ethanol vapor resulted in an increase in the total ESR signal intensity and in the solubilization of ESR-silent Mo^V species; at 300 K the ESR spectra are isotropic, in contrast to the anisotropic signals observed at the same temperature in the absence of solvents. For water as adsorbate, two Mo^V species differing in line widths were detected and assigned to Mo^V species located in the water pools of the ionomer and in the interior of the nonpolar domains, respectively. This result is in support of the model proposed for EMAA ionomers swollen by water, which was based on ESR spectra of amphiphilic spin probes. The bonding of Mo^V to EMAA ionomers is similar to that described previously for Mo/PAA and different from that in Mo/Nafion, indicating that the determining factor is the type of acid in the ionomers. Small differences between the Mo/EMAA and Mo/PAA systems were assigned to the different distribution of carboxylic groups in the polymer.

I. Introduction

Molybdenum catalysts on oxide supports occupy a central place in many catalytic processes, due to the ability of molybdenum centers to participate in redox and ligand exchange reactions.^{1,2} Recent analyses of the catalytic products led to the conclusion that in a number of systems "activation" of the catalyst on heating above ambient temperature is due to the replacement of the initially present halogen (chlorine in most cases) ligands by oxygen ligands.^{1–5} These findings also imply that the catalytic activity can be predicted if details on the local environment of the catalytic center and the type of ligands are known.

One way to elucidate the immediate environment of catalytic centers based on molybdenum during sample preparation and catalysis is via the electron spin resonance (ESR) spectroscopy of paramagnetic Mo^V. ESR spectra of Mo^V, a 5d¹ cation, consist of strong signals from nuclei with *I* = 0 (⁹²Mo, ⁹⁴Mo, ⁹⁶Mo, ⁹⁸Mo, and ¹⁰⁰Mo, total natural abundance 74.32), from which the *g*-tensor components can be deduced. The *g* values reflect

the symmetry of the catalytic site, the type of ligand (through the spin–orbit coupling λ_L of the ligand), and the changes that occur during reaction.^{4–14} Additional structural information can be obtained from an analysis of the hyperfine splittings from Mo nuclei with *I* = 5/2 (⁹⁵Mo and ⁹⁷Mo, natural abundances 15.78% and 9.69%, respectively); these nuclei have similar nuclear magnetic moments, and separate signals are usually not detected in ESR spectra. Coupled with powerful simulation programs,^{12,15} many complex ESR spectra consisting of contributions from several molybdenum centers have been interpreted.

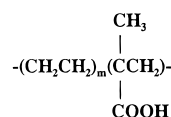
ESR spectra, simulations, and Fourier transform infrared (FTIR) spectroscopy have been used to determine the ligands coordinated to the catalytic center for molybdenum catalysts on polymeric supports such as polyacetylene, polypyrrole, and polyaniline;^{3,4} on poly(acrylic acid) (PAA) matrices;⁵ and on perfluorinated ionomers containing sulfonic groups (Nafion).^{6,7} The decrease and even disappearance of the ESR signals are also important indications of the ligand exchange reactions that take place.

In this paper we present a study of Mo^V dispersed in poly(ethylene-*co*-methacrylic acid) (EMAA) ionomers, Chart 1, in the dry state and in the presence of water and ethanol as adsorbates. The main objectives of this study were to identify the type of bonding between Mo^V, the polymer, and the adsorbates for different activation conditions and to compare

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CHART 1: EMAA Ionomer, Acid Form

with the results for Mo^V in PAA and Nafion. Because EMAA ionomers are available in a range of methacrylic acid (MAA) contents, this study made possible the comparison of Mo^V bonding in EMAA ionomers with various compositions. Of great interest was to examine to what extent the bonding of molybdenum to the support is determined by the presence of ionic and nonpolar domains in the ionomers¹⁶ and to analyze the results in view of the models proposed for EMAA ionomers from ESR studies of amphiphilic spin probes.^{17,18}

While most of the conclusions from the present study are based on ESR spectra at X band, important additional details and clarifications were obtained by FTIR spectroscopy and by ESR measurements at W band (95 GHz). To the best of our knowledge this is the first study of molybdenum centers using high-frequency ESR spectroscopy.

II. Experimental Section

Materials. The EMAA ionomers in the acid form, as membranes containing 1.3% and 11.2% MAA, were prepared in the laboratories of DuPont-Mitsui Polychemicals Co. Ltd., Chiba, Japan.^{17–19} The equivalent weights (weight of ionomer containing one carboxylic group) were 2220 and 308 and correspond respectively to 17 and 153 CH₂ groups between carboxylic groups. MoCl₅ (99.9%) was from Aldrich. Ethanol (EtOH) was dried with molecular sieves (type 3A from Fisher) and kept in a glovebox in a nitrogen atmosphere.

Sample Preparation. The EMAA membranes were cut into small pieces, typically 2 × 6 × 0.3 mm, and dried at 450 K for 40 min under dynamic vacuum ((6–9) × 10^{–5} Torr). This procedure allowed the removal of water from the membranes without converting the carboxylic groups to the corresponding anhydride.²⁰ The Mo/EMAA samples were prepared using the grafting method, by treating the ionomer with MoCl₅ in the vapor phase. Two procedures were used for sample preparation: (1) Contact between MoCl₅ (at ambient temperature) and the ionomer (at 400 K) was maintained for 50–120 h. At 300 K the partial pressure of MoCl₅ is 8 × 10^{–3} Torr and that of Cl₂ is 2 × 10^{–4} Torr.²¹ Samples thus prepared were labeled Mo/EMAAL-*x*, where *x* is the molar MAA content of the ionomer. (2) Both MoCl₅ and the ionomer were at 400 K, and contact was maintained for 20–40 h. At 400 K the partial pressures of MoCl₅ and Cl₂ are 5 and 0.6 Torr, respectively.²¹ Samples thus prepared were labeled Mo/EMAALH-*x*. Some samples were prepared by treating the ionomer with a solution of MoCl₅ in cyclohexane, but this method was abandoned because of the weak ESR signals.

Thermal treatment (“activation”) of the samples was carried out in the temperature range 400–525 K for 30 min unless specified otherwise. The intensities of ESR spectra before and after activation were directly compared because the same samples were used and placed in the same position in the ESR resonator. All steps of sample preparation were carried out in vacuum or in a glovebox flushed with nitrogen, in order to prevent oxidation of Mo^V to Mo^{VI}.

Chemical Analyses. The molybdenum and chlorine contents in a Mo/EMAAL-1.3 sample before activation and after activation at 475 K for 30 min were determined (Galbraith Laboratories, Inc., Knoxville, TN).

Adsorption Experiments. Water and ethanol were degassed by the freeze–pump–thaw technique. The Mo/EMAA samples were activated in the temperature range 400–525 K in vacuum prior to admission of the adsorbate and exposed to water vapor (25 Torr) and ethanol vapor (70 Torr).

Spectroscopic Measurements. ESR spectra at X band were measured with a Bruker ECS106 spectrometer operating at 9.7 GHz (empty cavity at ambient temperature) and 100 kHz modulation, and equipped with the ESP 3240 data system for acquisition and manipulation, and with the ER4111 VT variable-temperature controller. The microwave frequency was measured with the Hewlett-Packard 5350B microwave frequency counter. DPPH (2,2-diphenyl-1-picrylhydrazyl) was used for field calibration (*g* = 2.0036). Spectra were recorded with 4 G modulation amplitude, 2048 points, and microwave power of 2 mW in the range 3000–4000 G (*g* ≈ 2 region) and 20 mW in the range 1500–1900 G (for dimeric species).

The experiments at high frequency (W band) were performed with the spectrometer built and located at the EPR Center, University of Illinois at Urbana–Champaign.²² The microwave source was a Gunn oscillator (ZAX Millimeter Wave Corp., San Dimas, CA) with a power output of 35 mW at 94.3 GHz. The microwave frequency was measured by a source-locking counter (model 578 from EIP Microwave Inc, San Jose, CA). The magnetic field was supplied by a Varian (Palo Alto, CA) XL-20 superconductive magnet. The magnetic field scan was 1100 G with the solenoid coil placed inside the room-temperature bore of the magnet. The cylindrical TE_{01n} (*n* = 2 or 3, depending on tuning) cavity was used. The quartz capillary (diameter 1 mm, length 25 mm) containing the sample was coaxial with the cavity and did not change significantly the *Q* factor of the resonator. Spectra were recorded with a magnetic field modulation of ≈100 kHz, 1 G modulation amplitude, and microwave power attenuation in the range 13–16 dB. The *g* standard was an aqueous solution of 0.8 mM 4-oxo-TEMPONE. Additional details on the high-frequency ESR spectrometer have been published.²²

FTIR spectra were measured with the Nicolet IMPACT4000 spectrometer equipped with the OMNIL data system for acquisition and manipulation. Typical spectra were recorded in the 400–4000 cm^{–1} range with 2 cm^{–1} resolution. The thickness of the films measured was ≤0.1 mm.

Simulations. ESR spectra were simulated with the program SIM14A.¹⁵ The original program was modified by introducing optimization procedures: grid search with adjustable step, the Nelder-Mead simplex method with no restrictions on the range of the ESR parameters and a maximum of 20 optimization parameters, and Monte Carlo.¹² The program calculates the energy levels of the spin system to second order and the transition probabilities to first order. Simulations were performed in two steps: the initial parameters were first deduced by the simplex minimization method and then refined by grid search, using grid widths of 0.0005–0.0010 for *g* values, 2 G for A_{||}, 1 G for A_⊥, and 1 G for the line width. Typically one spectrum was calculated in 5–7 s on a personal computer equipped with a Pentium 100 processor.

III. Results

ESR Spectra of the Mo/EMAAL System. ESR spectra were measured in the temperature range 125–350 K at X band and at ambient temperature at W band, as a function of the activation temperature (up to 525 K) and MAA content in the ionomer (1.3 and 11.2 mol %).

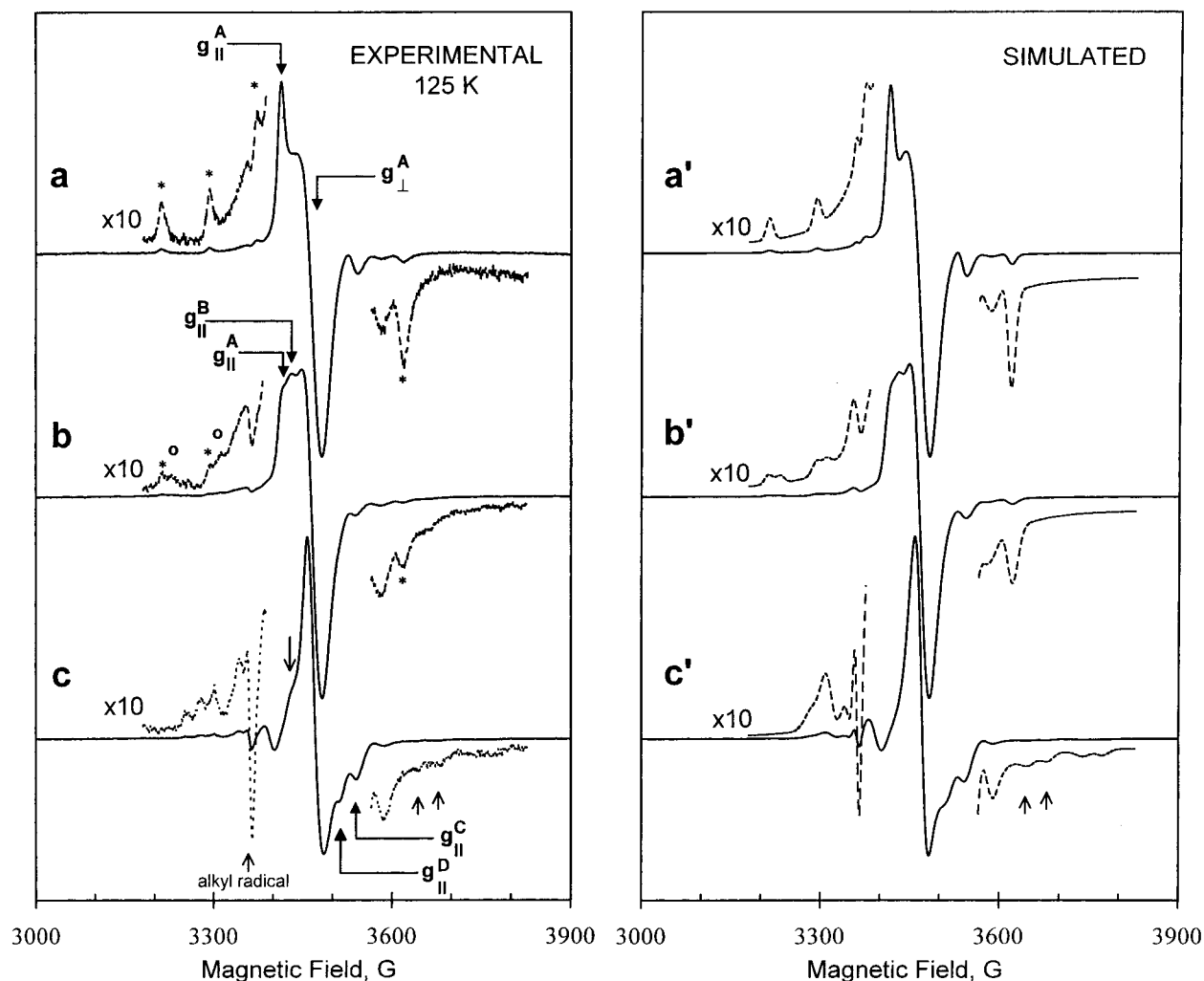


Figure 1. Experimental X-band ESR spectra at 125 K and corresponding simulated spectra of Mo/EMAAL-1.3 before thermal treatment (a, a') and after activation at 400 K (b, b') and at 475 K (c, c'). Vertically expanded ($\times 10$) portions of spectra are also shown. (a) $g_{||}$ and g_{\perp} values (arrows) and four of the signals from the parallel sextet (asterisks) of Mo(A). (b) $g_{||}$ values for Mo(A) and Mo(B) (arrows), three of the signals from the parallel sextet of Mo(A) (asterisks), and two of the signals from the parallel sextet for Mo(C) and Mo(D) (circles). (c) $g_{||}$ values for Mo(C) and Mo(D) (long arrows) and one each of the signals from the parallel sextet for Mo(C) and Mo(D) (short arrows). Upward arrow points to the signal from the alkyl radicals at $g = 2.0030$. The microwave frequency was 9.4201 GHz. Spectra were simulated assuming the presence of species Mo(A) in (a'), Mo(A) plus Mo(B) in the ratio 3:7 in (b'), and Mo(C) plus Mo(D) in the ratio 6:4 in (c').

TABLE 1: ESR Parameters for Mo^V Centers

species	$g_{ }$	g_{\perp}	$A_{ }$ (G)	A_{\perp} (G)	$\Delta H_{ }$ (G)	ΔH_{\perp} (G)	line shape	comments
Mo(A)	1.970	1.938	81.0	37.5	12.2	26.5	Gaussian	this study
Mo(B)	1.963	1.938	≈ 78	≈ 36	14.5	28.6	Gaussian	this study
Mo(C)	1.902	1.947	94.3	40.0	21.9	24.0	Gaussian	this study
Mo(D)	1.918	1.942	78.5	36.6	24.4	20.0	Gaussian	this study
Mo(EtOH)	1.967	1.937	≈ 81	≈ 37				this study
Mo(A)/PAA	1.967	1.937	81.9	36.7				ref 5
Mo(B)/PAA	1.957	1.934	82.0	≈ 37				ref 5
Mo(C)/PAA	1.902	1.946	94.3	40.0				ref 5
Mo/DMF	1.968	1.937	81.9	36.7				ref 5
Mo(A')	$g_{iso} = 1.952$							this study
Mo(dimer-I)	$g_{iso} = 3.865$				$\Delta H_{iso} = 14.7$		Gaussian	this study
Mo(dimer-II)	$g_{iso} = 4.081$				$\Delta H_{iso} = 31.3$		Lorentzian	this study
Mo(W-I)	$g_{iso} = 1.948$		$A_{iso} = 51.6$		$\Delta H_{iso} = 10.2$		Gaussian	this study
Mo(W-II)	$g_{iso} = 1.946$		$A_{iso} = 51.0$		$\Delta H_{iso} = 28.5$		Lorentzian	this study
Mo/cyclohexane	$g_{iso} = 1.953$		$A_{iso} = 52.0$					ref 5

X-Band ESR spectra at 125 K of Mo/EMAAL-1.3 before and after heat treatment are presented in Figure 1. The ESR spectrum measured before activation (Figure 1a) consists of the main signal from molybdenum isotopes with $I = 0$ and hyperfine lines from ^{95}Mo and ^{97}Mo with $I = 5/2$. The simple spectrum can be interpreted in terms of a single species, Mo(A). The main signal is typical of a Mo^V complex with $g_{||} > g_{\perp}$; the positions of $g_{||}^A$ and g_{\perp}^A are indicated by the downward arrows. Four of the six lines of the parallel component are indicated by

asterisks in the vertically expanded portions of the spectrum. The weaker hyperfine lines belong to the perpendicular sextet. The simulated spectrum based on these observations and shown in Figure 1a' is in excellent agreement with experiment; the magnetic parameters for Mo(A) are listed in Table 1.

Important changes occurred after activation at 400 K, Figure 1b. The Mo(A) species is still detected and is indicated by its $g_{||}^A$ (arrow) and parallel hyperfine lines (asterisks). In addition, a second species, Mo(B), appears and is shown by its $g_{||}^B$ value

(arrow) and two of the six parallel signals (circles). The ESR signal was simulated by contributions from Mo(A) and Mo(B) in an intensity ratio 3:7, Figure 1b'. Because of the superposition of two components in Figure 1b, the magnetic parameters for Mo(B) given in Table 1 have a larger margin of error compared to Mo(A).

The intensity of the ESR spectrum after activation at 475 K was only $\approx 50\%$ of the initial intensity. The ESR line shape, Figure 1c, is complex, but the main line for nuclei with $I = 0$ is typical for Mo^V complexes with $g_{\parallel} < g_{\perp}$. In analogy with previous results,^{5,7} the g_{\parallel} values of two new species, Mo(C) and Mo(D), are identified, and shown by arrows in Figure 1c. The intensity ratio of the indicated signals varies slightly with the conditions used for sample preparation, a clear proof that the signals are from different species and not from one species with rhombic symmetry. Two hyperfine lines belonging to the parallel component, one each for species Mo(C) and Mo(D), are indicated in the vertically expanded spectrum. The spectrum was simulated, Figure 1c', by contributions from Mo(C) and Mo(D) in the ratio 6:4. The magnetic parameters for Mo(C) and Mo(D) deduced from the simulation are given in Table 1. The shoulder observed in the experimental spectrum and indicated by the downward arrow in Figure 1c is not reproduced by the simulation, most likely because small amounts of species Mo(A) or/and Mo(B) are still present after the high-temperature activation. The sharp signal at $g = 2.0030 \pm 0.0003$, clearly seen after the high-temperature activation and shown by the upward arrow in Figure 1c, has also been detected in the Mo/PAA and Mo/Nafion systems and is similarly assigned to alkyl radicals formed by polymer degradation; this signal was added in the simulation of the spectrum given in Figure 1c'. Activation at 525 K caused a decrease of the overall intensity, but no major spectral changes in the line shapes were detected.

ESR spectra of Mo/EMAAL measured as a function of temperature change gradually above 250 K, and the total signal intensity decreases. The spectrum at 300 K for the sample before activation is shown in Figure 2 (top). The hyperfine splittings are identical to those presented in Figure 1a, indicating the contribution from Mo(A); an additional, probably isotropic, component is also seen on close inspection, and the downward arrow points to its g_{iso} value (1.952); this is species Mo(A'). The W-band ESR spectrum recorded at ambient temperature and shown in Figure 2 (bottom) after baseline correction reflects the g -tensor anisotropy for Mo(A); the hyperfine splittings are buried in the broad signals.

ESR Spectra of Mo/EMAAL. X-band ESR spectra at 125 K of Mo/EMAAL-1.3 are shown in Figure 3a (before activation) and in Figure 3b,c for activation temperatures of 400 and 475 K, respectively. The complex spectra shown in Figure 3a,b represent a superposition of several molybdenum species; the main signal suggests the presence of species with $g_{\parallel} > g_{\perp}$ (mostly chlorine ligands) and $g_{\parallel} < g_{\perp}$ (oxygen ligands). The spectrum detected after activation at 475 K (Figure 3c) is better resolved. The downward arrow points to the g_{\parallel} value for species with $g_{\parallel} > g_{\perp}$, and upward arrows point to g_{\parallel} values for species with $g_{\parallel} < g_{\perp}$, Mo(C) and Mo(D). Inspection of the hyperfine splittings at high vertical expansion showed hyperfine lines predominantly from Mo(C) and Mo(D). For these reason the ESR spectrum was simulated (dotted line in Figure 3) by a superposition of signals from Mo(C) and Mo(D) in the ratio 4:6. Numerous simulations showed that the contribution of species Mo(A) and Mo(B) is $\leq 10\%$ of the total intensity. The most pronounced effect of activation at 525 K was a decrease of the overall spectral intensity.

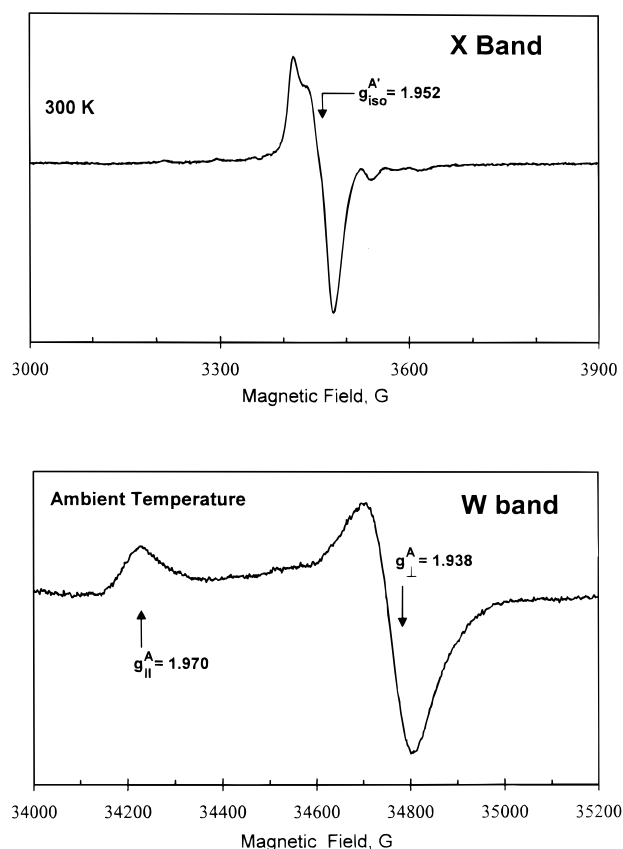


Figure 2. ESR spectra of Mo/EMAAL-1.3 before thermal treatment: (top) at 9.4182 GHz (X band); arrow points to the g_{iso} for Mo(A'); (bottom) at 94.283 GHz (W band); the g -tensor values for Mo(A) are shown by arrows.

The inset in Figure 3 presents the experimental spectrum at 125 K for the Mo/EMAAL-1.3 sample after vacuum treatment at ambient temperature for 30 min, recorded with 20 mW microwave power in the magnetic field range 1500–1900 G. This spectrum shows the presence of two dimeric species and was simulated by contributions from Mo(dimer-I) and Mo(dimer-II) (Table 1). These signals became weaker after activation at 400 K and disappeared upon activation at 450 K for 30 min or longer.

Adsorption of Ethanol. Contact of Mo/EMAAL samples activated at 475 K for ≈ 15 h with ethanol vapor (70 Torr) for 14 h caused gradual changes in the line shape and an increase of signal intensity. X-Band ESR spectra of Mo/EMAAL-1.3 at 125 and 300 K are shown in Figure 4. After ethanol contact the relative intensity of the ESR spectrum measured at 125 K was higher by a factor of 4 compared to the original spectrum; at 300 K the increase in intensity was even more pronounced. These ESR spectra reflect the dominant presence of species Mo(EtOH) with parameters similar to Mo(A), Table 1. Simulations (not shown) suggest also the presence of species Mo(C) and Mo(D), with a relative intensity of $\approx 20\%$ at 125 K and $\approx 5\%$ at 300 K.

Adsorption of Water. In Figure 5 (top) we present the ESR spectrum at 300 K for Mo/EMAAL-11.2 activated at 400 K, followed by contact with water vapor (25 Torr) for 1 day. The spectrum is symmetrical, and the central signal consists of a narrow signal superimposed on the broader signal shown by the arrows. For this reason the spectrum was simulated by assuming a superposition of two isotropic signals, Mo(W-I) and Mo(W-II) (Table 1). In Figure 5 (bottom) we present the superposition of the two spectral components in (a) and also

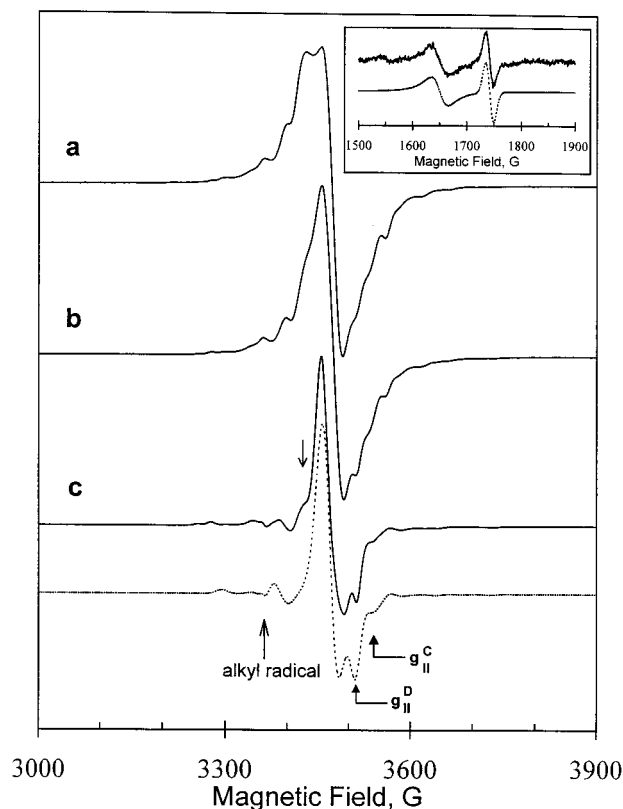


Figure 3. X-band ESR spectra at 125 K of Mo/EMAAL-1.3 before thermal treatment (a) and after activation at 400 K (b) and at 475 K (c). Downward arrow points to the $g_{||}$ value for species with $g_{||} > g_{\perp}$, and upward long arrows to $g_{||}$ values for Mo(C) and Mo(D). The microwave frequency was 9.4201 GHz. The upward arrow in (c) points to the signal from alkyl radicals at $g = 2.0030$. The simulated spectrum (dotted line) is based on contributions from species Mo(C) and Mo(D) in the ratio 4:6. Inset: The spectrum before thermal treatment recorded in the region of dimeric species, with a microwave power of 20 mW, and the corresponding simulated spectrum 24 (dotted line).

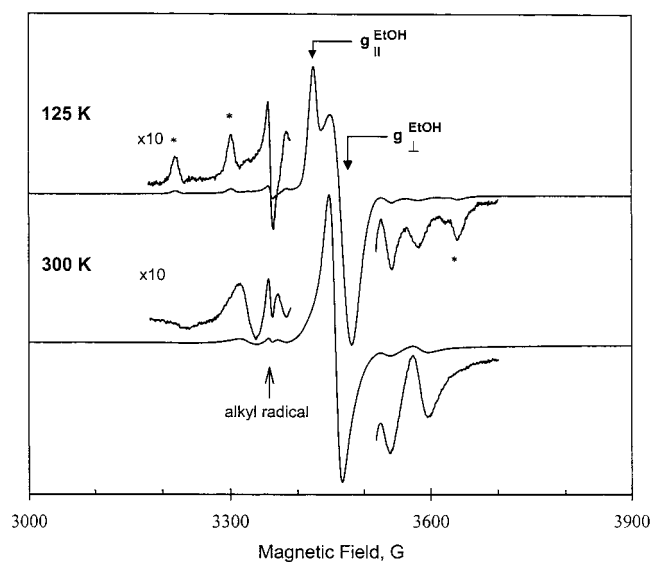


Figure 4. X-band ESR spectra at 125 and 300 K of Mo/EMAAL-1.3 after activation at 475 K for 15 h and exposed to ethanol vapor (70 Torr) for 14 h. Vertically expanded portions of the spectra are also shown. Arrows point to the g -tensor values and asterisks to parallel signals for species Mo(EtOH); the alkyl radical position is also displayed. The microwave frequency was 9.4200 GHz at 125 K and 9.4192 GHz at 300 K.

each component separately, Mo(W-I) in (b) and Mo(W-II) in (c). The major difference between the last two signals is the

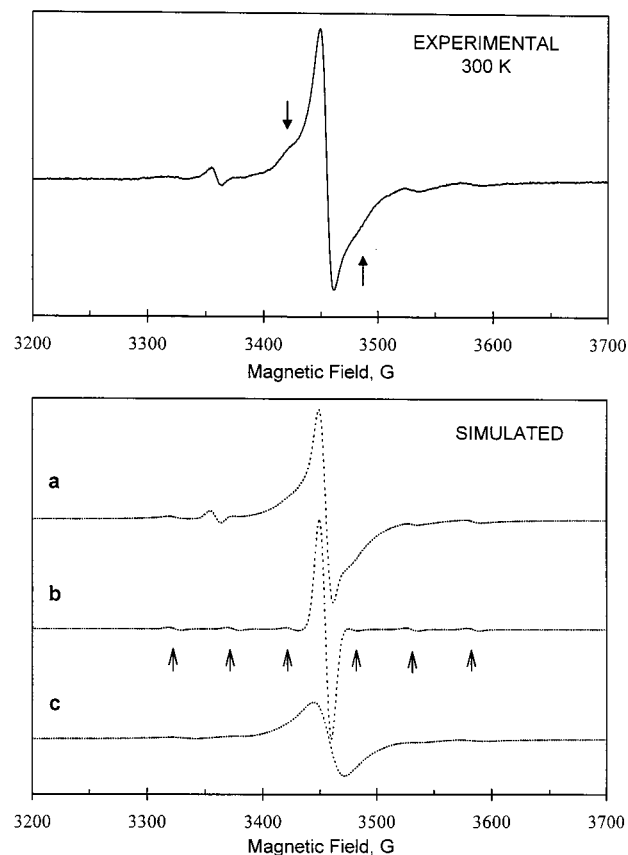


Figure 5. Experimental (—) X-band ESR spectra at 300 K of Mo/EMAAL-11.2 after activation at 400 K and exposure to water vapor (25 Torr) for 1 days. Arrows point to the Mo^V signal with broader lines. The microwave frequency was 9.4173 GHz. The simulated (---) spectrum shown in (a) is a superposition of signals from species Mo(W-I) and Mo(W-II) in the ratio 5:95; Mo(W-I) is shown in (b), and Mo(W-II) in (c). The six arrows point to the isotropic hyperfine sextet from the Mo^V nuclei with $I = 5/2$.

line width: 10.2 and 28.5 G, respectively. Activation at 500 K followed by exposure to water vapor caused only minor changes in the line shapes and a large decrease of the overall intensity over 2 days.

Mo Content in EMAA Ionomers. The Mo content determined by chemical analysis is 0.025 wt % (molar ratio [COOH]/[Mo] = 173) before activation, in agreement (within a factor of ≈ 2) with the Mo content determined by ESR, by comparing intensities at 125 K of a Mo/EMAAL-1.3 sample with a known solution of MoCl₅ in ethanol. This agreement seems to indicate that all Mo present in the ionomer is paramagnetic, as expected from treatment of MoCl₅ in vacuum or under nitrogen.

The chemical analysis also indicated that the Mo content decreases by 16% after activation at 475 K for 30 min; the ESR intensity after this activation decreased by 50%. We conclude therefore that the amount of ESR-silent species is $\approx 34\%$.

The chlorine content also decreases after activation, from 0.44 to 0.38 wt %; to our surprise, however, the molar ratio [Mo]/[Cl] $\approx 1/50$ in both cases, indicating bonding of chlorine to the polymer, possibly by replacement of hydrogen from CH₂ groups.

FTIR Spectra. The spectral region of interest is 1400–1800 cm⁻¹, where the signals corresponding to the C=O vibration in monodentate and bidentate carboxylic groups are expected at ≈ 1700 and ≈ 1500 cm⁻¹, respectively. The EMAA and Mo/EMAAL samples were compared by normalizing the spectra to the same intensity of the band at 1450–1470 cm⁻¹, which is not expected to vary with incorporation of molybdenum.

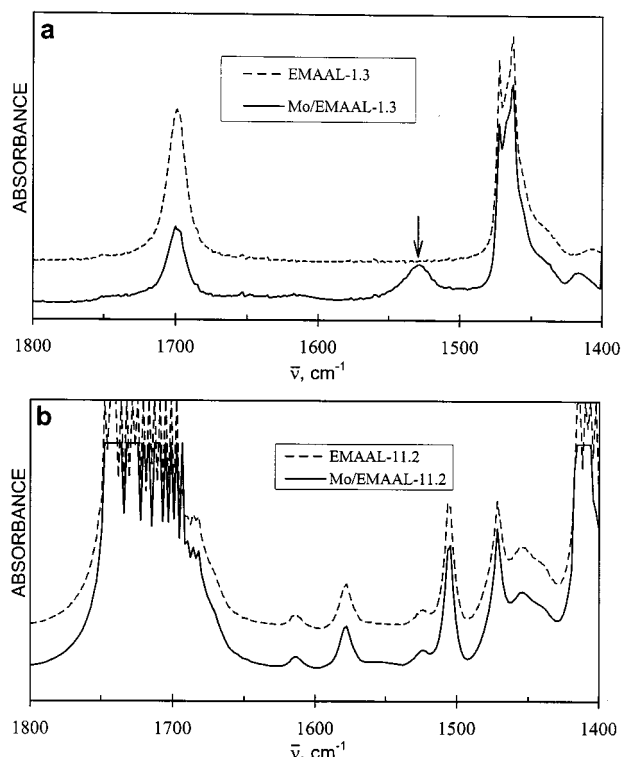


Figure 6. FTIR spectra of EMAAL-1.3 and Mo/EMAAL-1.3 activated at 373 K (a) and of EMAAL-11.2 and Mo/EMAAL-11.2 activated at 373 K (b). The arrow in (a) points to the C=O vibration of the *bidentate* carboxylic group (see text).

The IR spectrum of EMAAL-1.3 consists of one band at 1700 cm^{-1} , as shown in Figure 6 (top). For Mo/EMAAL-1.3, an additional signal appears at 1530 cm^{-1} (indicated by the downward arrow in Figure 6a), and the intensity of the signal at 1700 cm^{-1} decreases. The signal at 1700 cm^{-1} was out of range for the EMAAL-11.2 sample, even for very thin films. The IR spectrum of Mo/EMAAL-11.2 is similar to that of the original membrane (Figure 6, bottom).

IV. Discussion

In this section we will identify the type of bonding of Mo^V to the ionomer support from an analysis of the magnetic parameters and by comparison with results obtained in PAA⁵ and Nafion⁷ systems; we will attempt to assess the effect of synthetic details on the bonding; and we will consider the effect of adsorbates (ethanol and water) and of methacrylic acid content.

Mo^V in EMAAL Ionomers. Two major species were identified in Mo/EMAAL samples immediately after synthesis: species Mo(A) and Mo(A'). Mo(A) is almost identical to Mo-(A)/PAA,⁵ and its g values ($g_{\parallel} > g_{\perp}$) indicate the presence of chlorine ligands in the first coordination sphere of the cation.^{9,11} Therefore we assign Mo(A) to Mo^V attached to five chlorine ligands and to a carboxylic group via a monodentate bond, as $-\text{COO}-\text{MoCl}_5$. Mo(A') is assigned to physically adsorbed MoCl_5 based on the value of $g_{\text{iso}} = 1.952$, which is close to that measured for MoCl_5 in cyclohexane ($g_{\text{iso}} = 1.953$, Table 1), where no coordination of the solvent to molybdenum is expected. This signal was not detected at W band (Figure 2), for two possible reasons: the lines are broader and the dynamical regime is shifted to higher temperatures at the higher frequency. For an activation temperature above 400 K Mo(A') was not detected; we propose that this behavior is due to the formation of ESR-silent species and desorption of molybdenum species.

This conclusion is supported by the chemical analyses and by the experiments with ethanol as adsorbate (*vide infra*).

Activation of Mo/EMAAL samples at 400 K leads to the appearance of species Mo(B). Based on the decrease of g_{\parallel} (compared to Mo(A)), we conclude that this species is formed by replacement of a Cl ligand and attachment of Mo^V to the ionomer via a bidentate carboxylic group, as deduced in Mo/PAA. Activation at 475 K leads to the detection of two additional species, Mo(C) and Mo(D), both with $g_{\parallel} < g_{\perp}$, a clear indication for further replacement of the chlorine ligands by oxygen ligands from the carboxylic groups of the ionomer. Mo-(C) has magnetic parameters similar to Mo(C)/PAA (Table 1), which was assigned to Mo^V bonded to one bidentate and four monodentate carboxylic groups. We can only speculate on the ligand arrangement in Mo(D); one possibility is a different distribution between mono- and bidentate carboxylic ligands, which can lead to changes in the symmetry of the complex. The decrease in the signal intensity after activation at 525 K can be explained by assuming the transformation of the paramagnetic species to ESR-silent species, as a result of aggregation, and/or to the removal of molybdenum as a result of the degradation of the carboxylic groups.

The ESR spectra of Mo/EMAAL before and after activation at 400 K are a superposition of several components representing chemically and physically adsorbed molybdenum species, and a detailed analysis by simulations is not possible. The low-resolution points to interaction between paramagnetic centers as a line-broadening mechanism. The presence of the dimeric species shown in the inset of Figure 3 also supports the idea of proximal paramagnetic cations. After activation at 475 K the spectra are amenable to analysis and were simulated by a superposition of signals from species Mo(C) and Mo(D) in the ratio 4:6 (Figure 3). Changes in the ESR spectra and the decrease of the overall signal intensity after activation at 475 and 525 K are due to aggregation of weakly adsorbed Mo^V species; the weakening of the dimer signal upon activation at 400 K and its disappearance at an activation temperature of and above 450 K are in support of this conclusion.

Ethanol and Water Adsorption. The line widths and intensity changes in the ESR spectra due to adsorbates are helpful in determining the type of Mo^V coordination and its bonding to the polymeric support.

Ethanol adsorption on Mo/EMAAL samples activated at 475 K led to significant changes in the ESR spectra. The signal at 300 K is dominated by an isotropic component with g_{iso} and A_{iso} values similar to those of MoCl_5 in ethanol solutions; the line widths are however significantly larger, 20 G versus 8 G in ethanol solutions, probably due to hindered mobility in the presence of the ionomer.²³ The magnetic parameters and the significant increase in intensity can be explained by assuming the dissolution of ESR-silent species in ethanol; a similar process has been detected for water adsorption on Mo/SiO_2 .²⁴ The ESR spectrum at 125 K, which is dominated by the component Mo-(EtOH) with parameters typical for Mo^V surrounded by chlorine ligands (Figure 4) provides additional support for this assignment. The main difference between Mo(A) and Mo(EtOH) is the origin of the oxygen ligand: from the carboxylic group in Mo(A) and from the OH group of ethanol in Mo(EtOH). This difference leads to the important difference in dynamics: at 300 K Mo(A) is immobilized and its ESR spectrum is in the rigid limit, while the ESR spectrum of Mo(EtOH) is motionally narrowed.

Exposure of Mo/EMAAL samples activated at 400 K to water vapor (25 Torr) leads to changes in line shape and intensity.

The spectrum given in Figure 5 is isotropic; the shoulders (arrows in Figure 5) that symmetrically flank the major signal indicate a superposition of two isotropic signals with similar *g* and hyperfine splittings, but different line widths. We interpret this result in terms of *two* different environments of Mo^V, in agreement with the model of EMAA membranes swollen by water, which was proposed on the basis of ESR spectra of spin probes;^{17,18} the model has suggested the formation of reverse micelles and water pools, but also some penetration of the water into the nonpolar domains in the ionomers. Within the framework of this model, the isotropic signal with the narrower lines (Mo(W-I)) represents Mo^V solvated in the water pools, while the isotropic signal with the broader lines (Mo(W-II)) represents Mo^V solvated in the nonpolar regions.

Effect of MAA Content. FTIR spectra revealed important differences in the bonding of Mo^V with the MAA content of the ionomer. The IR spectra given in Figure 6 show for EMAA-1.3 the appearance of a band at 1530 cm⁻¹ that is typical of bonding between Mo^V and *bidentate* carboxylic group²⁵ and provides support for the assignment proposed above for the Mo-(B) species. The band at 1530 cm⁻¹ is absent in the IR spectrum of EMAA-11.2, indicating that at the higher MAA content the bonding of Mo^V is via *monodentate* bonding to different carboxylic groups. This conclusion is reasonable in view of the proximity of the carboxylic groups in EMAA-11.2 and their availability for bonding of the cation.

Comparison of Mo^V Bonding in EMAA, PAA, and Nafion. Both EMAA and PAA systems contain carboxylic groups that can bind transition metal cations. The main structural difference between the two polymers is the number of CH₂ groups between the ionic groups, which leads to the classification of EMAA as an ionomer and PAA as a polyelectrolyte. Nafion is also classified as an ionomer because the number of ionic groups is small, typically 15 mol %.

The results of this and previous studies of Mo^V species indicate that the major factor that determines the formation of the molybdenum complex is the nature of the ionic groups. The Mo/EMAA species detected before thermal treatment (Mo(A)) and after activation at 400 K (Mo(B)) are characterized by ESR parameters similar to those previously described for Mo/PAA.⁵ The Mo/EMAA signal detected after activation at 475 K (Mo-(C)) is essentially the same as that obtained in PAA at comparable conditions. Species Mo(D)/EMAA has no parallel in the PAA systems and is assigned to the different distribution of the carboxylic groups. The effect of the ionic group content in EMAA ionomers is evident in the FTIR spectra, which have shown the different bonding of Mo^V in EMAA containing 1.3 and 11.2 mol % MAA groups.

Although the main role in complex formation is played by the carboxylic groups, the results of water adsorption experiments reveal the presence of the ionic domains in EMAA, which are absent in PAA.

The Mo/Nafion system is different and has displayed complex formation between the sulfonic groups and Mo^V even without heat treatment. In spite of the similar phase separation into ionic and nonpolar domains in both Nafion and EMAA ionomers, our studies have shown that Nafion-type ionomers act as ion-selective membranes; EMAA ionomers do not act in this way because of the weak acidic properties of the carboxylic groups.

V. Conclusions

The bonding of Mo^V in poly(ethylene-co-methacrylic acid) (EMAA) ionomers was studied by ESR at X (9.5 GHz) and W (95 GHz) frequencies, spectral simulations, and FTIR, for

various preparation methods and thermal treatments. The synthetic method consisted of grafting the ionomer with gaseous MoCl₅ in an inert atmosphere.

When MoCl₅ was kept at ambient temperature during grafting, the major species detected was Mo^V bonded to five chlorine ligands and to the ionomer by an oxygen from a carboxylic group. Activation in the range 400–500 K led to the gradual replacement of the chlorine ligands by oxygen ligands from the carboxylic groups and to the loss of Mo. The nature of the oxygen ligands depends on the methacrylic acid (MAA) content in the ionomer: in Mo/EMAA samples activated at 373 K, molybdenum is bonded to the substrate by bidentate carboxylic groups in the ionomer containing 1.3 mol % MAA and by monodentate carboxylic groups for an MAA content of 11.2 mol % MAA.

Exposure of Mo/EMAA samples to ethanol and water vapor resulted in the solubilization of physically adsorbed Mo^V species by the solvents; at 300 K the dominant spectral component is isotropic, in contrast with the anisotropic signals observed at the same temperature in the absence of the solvent. For water as adsorbate, *two* isotropic Mo^V species were detected and assigned to cation locations in the water pools of the ionomer and in the interior of the nonpolar domains, respectively; this conclusion provides support for the model for EMAA ionomers swollen by water deduced from ESR spectra of amphiphilic spin probes.

The main factor determining the bonding of Mo^V to the ionomer is the type of acid groups, as seen from the similarity of complexes detected in Mo/EMAA and Mo/PAA.

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