Table IV
Effect of Casting Solvent on Spherical Microdomain of SI-21[a]

solvent	solubility parameter,[b] $(cal/cm^3)^{1/2}$	domain radius $\bar{R}$, nm	interfacial thickness ΔR, nm
toluene	8.9	17.1	2.0
methyl ethyl ketone	9.3	16.4	1.8
isopropyl acetate	8.4	16.5	1.8

[a] Solubility parameters for polyisoprene and polystyrene are 8.1 and 9.1 $(cal/cm^3)^{1/2}$. [b] From "Polymer Handbook".

Both the domain radius and the interfacial thickness are almost independent of the solvents used in this experiment for this particular block polymer. IPA is good solvent for polyisoprene in comparison to toluene and MEK. The values of $\bar{R}$ are again much less than the predicted values so that the nonequilibrium effect seems to be significant for these solvents also. The interfacial thickness ΔR also is independent of the solvent used. Thus the effect of solvent on the microdomain structure, if any, seems to vanish as the concentration increases.

IV. Concluding Remarks

For the particular polymer–solvent combinations studied in this work the solvent effects seem to vanish as concentration of the polymer increases, resulting in the final morphology in the solid state being hardly affected by the casting solvent. The solubilization of the homopolymers HPS and HPI into the SI block polymer domains is quantitatively studied. In the ternary blends of HPS, HPI, and SI, both the interdomain distance $\bar{D}$ and the radius $\bar{R}$ increase with increasing homopolymer volume fraction ψ_H, the result of which is interpreted as the ratio N_b/N_{b0} being increased with ψ_H (N_b and N_{b0} being the number of the block polymer chains per domain with and without homopolymers blended). On the other hand, in the binary blends of HPS and SI, $\bar{D}$ increases but $\bar{R}$ decreases with ψ_H, the results of which are interpreted as the ratio N_b/N_{b0} being decreased with ψ_H. Further investigation is required to clarify the change of the ratio N_b/N_{b0} and to separate equilibrium and nonequilibrium effects on that ratio. Upon blending of the homopolymer, the long-range order of the microdomains tends to be lost. The characteristic thickness of the interfacial region between the two coexisting phases is hardly changed over the amount of homopolymers blended in the study. Finally, we solved the uncertainty involved in subtracting the background scattering I_b (arising from thermal diffuse scattering within each phase) in the evaluation of the interfacial thickness ΔR. We found that the background scattering from the block polymers and their ternary and binary mixtures with the homopolymers are a weighted average of those from corresponding homopolymers. We were able to calculate and subtract the background scattering by using the additivity law.

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Viscoelastic Properties of Aromatic Ionomers

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ABSTRACT: The dynamic mechanical properties and stress relaxation behavior in the solid state are studied for two aromatic ionomers. The ionomers are potassium salts of carboxylated-phenylated polyphenylenes. Mechanical loss tangent measurements indicate that the glass transition temperature is of the order 300 °C for both ionomers. The stress relaxation behavior in the primary transition is typical of an ionomer; i.e., a broad distribution of relaxation times is observed. It is concluded that even at temperatures higher than 300–320 °C, ionic interactions still persist and strongly influence the viscoelastic properties of the aromatic polymers. Some experiments on the dynamic mechanical properties of the aromatic ionomers at low temperatures are also reported.

Introduction

It is well-known that the presence of ions in polymers exerts a significant influence on the solid-state properties. In particular, the structure and the viscoelastic properties of ionomers often exhibit very complex behavior when ions are incorporated into the material. Consequently, a num-

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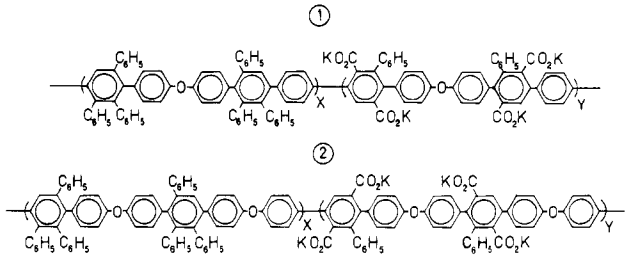

Figure 1. Structural formulas for aromatic ionomers 1 and 2.

ber of studies dealing with the structure and the rheological properties of ionomers, primarily those based on ethylene,[2-9] styrene,[10-16] and the rubbers,[17-20] have appeared during the past 15 years. The majority of these studies indicate that the observed changes in properties are due to ion aggregation. For styrene-based and ethyl acrylate-based ionomers, it has been proposed that at least two types of aggregates are formed, i.e., multiplets consisting of a few ion pairs, and larger clusters containing ionic groups as well as organic material. These ionomers are thus to be regarded as microphase-separated materials where ion-rich regions (clusters) are immersed in a matrix of low ion content, i.e., containing mainly multiplets. Thus, it is not surprising that this aggregation of ions has a strong impact on the physical properties of the ionomers. In this presentation no extensive review of the literature concerning the ion-containing polymers will be given; only features having a direct bearing on the present study will be mentioned. A detailed description of the structure and the properties of ionomers can be found in two recent books[21,22] dealing with the subject.

Most studies of the viscoelastic properties of ionomers have been devoted to materials for which the glass transition temperatures or melting temperatures range from well below room temperature up to ca. 150 °C.[21,22] Dynamic mechanical measurements reveal two loss tangent peaks in the glass transition region for the styrene-,[14] ethyl acrylate-,[23] and ethylene-based ionomers.[4] Both peaks move to higher temperatures with increasing ion content. The lower peak has been assigned to the glass transition of the ion-poor matrix while the upper peak has been associated with the glass transition of the ionic clusters. The presence of ions also results in a broadening of the distribution of relaxation times (as determined from stress relaxation) and, above a certain ion concentration, in the breakdown of time–temperature superposition. The critical ion content is ca. 6 mol % for the styrene ionomers[12] and 12–15 mol % for the ethyl acrylate ionomers.[24] The breakdown of time–temperature superposition reflects the existence of a secondary mechanism, probably associated with the clustered regions.[12,13]

The aim of the present work was to explore, on a preliminary basis, whether the ionic interactions which give rise to the viscoelastic behavior described above are present also in materials of a very high glass transition temperature. Longworth et al.[6] found that a small-angle X-ray scattering peak, related to ionic interactions, persisted to very high temperatures, but to what extent this has a bearing on the visoelastic properties is not known. Aromatic ionomers seem to be an excellent choice for a study of this type since their glass transition temperatures (T_g) far exceed those of styrene-based ionomers, which is the amorphous system which has been studied in greatest detail to date. The two aromatic ionomers studied here were chosen from a series of recently synthesized carboxylated–phenylated polyphenylenes in their potassium salt form.[25-27] The structural formulas of the materials are

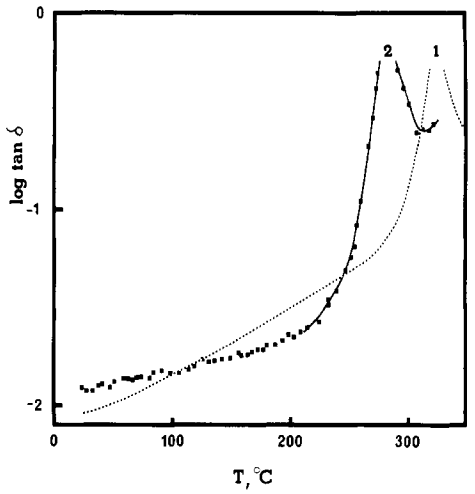

Figure 2. Mechanical loss tangent vs. temperature for the aromatic ionomers: dashed line, ionomer 1; solid line, ionomer 2. For the sake of clarity the experimental points are only shown for one curve.

shown in Figure 1, and the ionomers will hereafter be referred to as "polymer 1" and "polymer 2", respectively. The ratio x:y denotes the mole percent of each repeat unit. In this work only the 80:20 random copolymers were studied, because of sample availability. The synthesis and characterization of the aromatic ionomers have been described in detail earlier[25,27] and will not be included here.

Experimental Section

A. Sample Molding. Between 0.5 and 0.8 g of polymer was weighed into a mold, which then was heated to 250–285 °C. When the desired temperature was reached, a load of ca. 20 000 lb was applied and maintained for 20 min. The sample was removed from the mold after it had cooled down to room temperature. Prior to testing, the samples were dried at ca. 200 °C under vacuum. Typical dimensions of the samples were 4 × 0.6 × 0.25 cm.

It must be stressed that it was necessary to mold the samples at a rather low temperature, i.e., close to their T_g, in order to avoid decomposition or cross-linking. This has been pointed out before.[26] In spite of this, it cannot be excluded that some minor degradation may have occurred during the molding since some of the samples darkened very slightly. It is, however, felt that this does not influence the overall viscoelastic behavior of these ionomers. The samples were opaque and brownish, but of a uniform color, suggesting that the molding process, in spite of its low temperature, did not leave any powdery heterogeneities near the surface. Fracture surfaces were clean and glassy. Attempts to cast films from solution, while yielding uniform samples, resulted only in very thin specimens, far too thin for purposes of the present study.

B. Dynamic Mechanical Properties. Dynamic mechanical measurements from room temperature up to ca. 350 °C were performed under vacuum with a torsion pendulum described earlier.[28] In the glassy region the data were obtained at ca. 2–3 Hz and in the low-modulus region in the region 0.1–0.5 Hz. The dynamic mechanical properties at low temperatures were studied with the torsion pendulum at frequencies of ca. 1–3 Hz and with a vibrating reed device[29] at higher frequencies. Heating or cooling rates were always less than 1 °C/min.

C. Stress Relaxation Behavior. Stress relaxation experiments were performed in a nitrogen atmosphere, using a high-temperature stress relaxometer similar to that described earlier.[30] The stress at constant strain was measured for up to ca. 6×10^3 s for a series of temperatures above and below the glass transition temperature. The temperature variation during a run was below ±0.2 °C. For measurements in the glassy region the experiments were performed in the bending mode, while for lower values of the modulus (below 5×10^8 dyn/cm^2) stretching was employed.

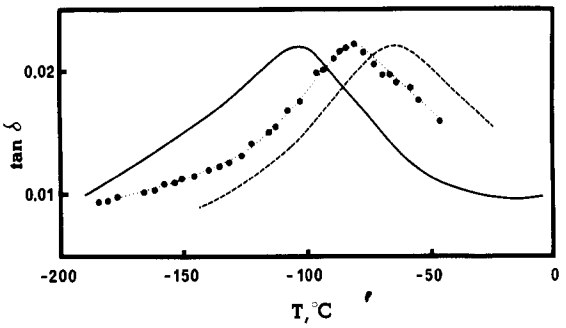

Figure 3. Loss tangent vs. temperature for ionomer 1 at low temperatures: solid line, result obtained using the torsion pendulum (frequency corresponding to the peak is ca. 1.6 Hz); dotted line, result obtained using the vibrating reed (frequency at the peak ca. 390 Hz); dashed line, result obtained using the vibrating reed (frequency at the peak ca. 2440 Hz). For the sake of clarity the experimental points are only shown for one curve.

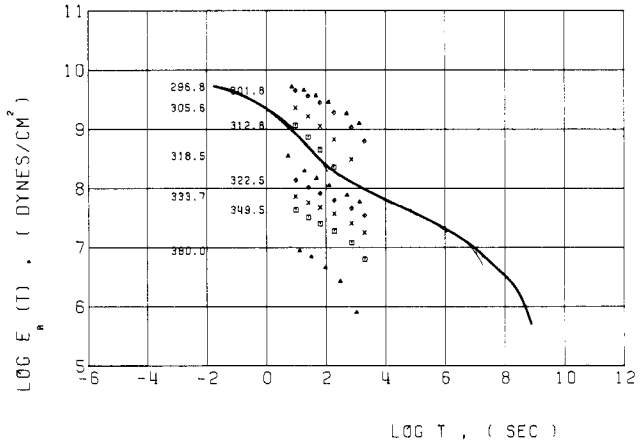

Figure 4. Original stress relaxation curves at different temperatures and master curve for ionomer 1. $T_{ref} = T_g$.

Results

A. Dynamic Mechanical Properties. In Figure 2 the loss tangent vs. temperature is shown for the two aromatic ionomers. The peak temperatures are 314 and 278 °C for polymers 1 and 2, respectively, which are close to the glass transition temperatures reported earlier (312 and 279 °C).[25] At temperatures higher than ca. 350 °C the samples got progressively darker and no measurements were made above that temperature.

The loss tangent at low temperatures (from ca. −190 to 0 °C) for polymer 1 is shown in Figure 3 for three different frequencies. The low-frequency curve was determined with the torsion pendulum and the other two with the vibrating reed. A single, rather broad peak is observed for all three frequencies. For polymer 2 a similar peak is observed at approximately the same temperature and with the same intensity. When the frequency corresponding to the peak temperature is plotted vs. $10^3/T$, where T is the peak temperature (in Kelvin), for both polymers 1 and 2, one line is obtained with an activation energy of 13 ± 2 kcal/mol. Obviously the same low-temperature mechanism is operative in both polymers.

B. Stress Relaxation Behavior. Figure 4 shows the original stress relaxation curves and the resulting master curve for polymer 1. The glass transition temperature, i.e., the loss tangent peak temperature, is taken as the reference temperature for construction of the master curve. Evidently the time–temperature superposition principle is valid over the temperature range investigated. The master curve for polymer 2 (Figure 5) is similar to that of polymer

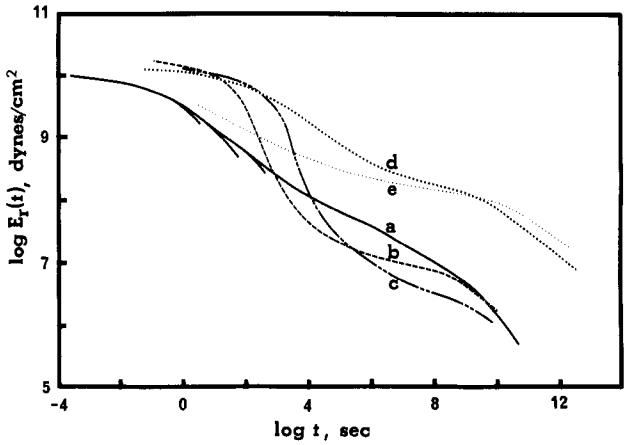

Figure 5. Master curves for (a) aromatic ionomer 2, (b) poly(2-methyl-6-phenyl-*p*-phenylene oxide),[31] (c) polystyrene,[12] (d) a 6.2 mol % St–NaMA copolymer,[12] and (e) a 12 mol % EA–NaA copolymer.[24]

1. Some minor deviations from time–temperature superposition are observed for stress relaxation runs below T_g, as indicated in Figure 5, but above T_g the individual curves are superimposable. Figure 5 also contains, for the sake of comparison, master curves for polystyrene,[12] a styrene–sodium methacrylate (St–NaMA) copolymer containing 6.2 mol % ions,[12] poly(2-methyl-6-phenyl-*p*-phenylene oxide),[31] and an ethyl acrylate–sodium acrylate (EA–NaA) copolymer containing 12 mol % ions.[24] From Figures 4 and 5 it is obvious that the aromatic ionomers relax more slowly in the primary transition region than the two nonionic polymers shown in Figure 5, the behavior of the aromatic ionomers being similar to that of the styrene and ethyl acrylate ionomers. A weak inflection point around 10^8 dyn/cm^2 is also observed in the master curves for both the ionomers.

At this point it should be stressed that the stress relaxation curves obtained around 350 °C and above should not be taken too literally since the specimens became very dark due to degradation or cross-linking. This does not, however, affect the major conclusions arrived at below.

The shift factors used for constructing the master curves for the aromatic ionomers can approximately be fitted to a WLF equation with $c_1 = 14$ and $c_2 = 65$ for ionomer 1 and $c_1 = 16$ and $c_2 = 64$ for ionomer 2. However, if the shift factors ($\log a_T$) are plotted vs. the reciprocal temperature, each curve can be described by two straight lines (not shown). This is not an uncommon situation; the same behavior was observed for the ethyl acrylate-based ionomers.[24] Calculation of the activation energy (E_a) at T_g yields the same result (330–340 kcal/mol) using either the WLF equation or the Arrhenius expression for both the aromatic ionomers.

Figure 6 shows the 10-s modulus vs. temperature for the aromatic ionomers 1 and 2, polystyrene,[12] and a St–NaMA copolymer containing 6.2 mol % ions.[12] As expected, the modulus–temperature curves are not as steep for the aromatic ionomers as for the pure polystyrene. Again, the behavior is similar to that of an ionomer.

Discussion

A. Dynamic Mechanical Properties. 1. High Temperatures. The agreement between the position of the tan δ peaks obtained here and the glass transition temperatures determined earlier for the aromatic ionomers[25] is excellent. As expected, the five phenyl groups in the backbone between the ether linkages in polymer 1 result in a higher T_g compared to that for polymer 2, which

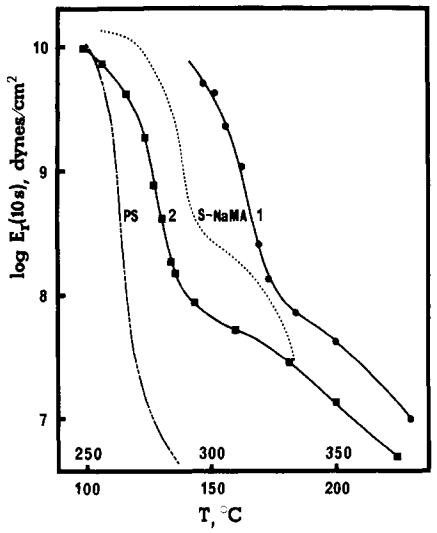

Figure 6. 10-s modulus vs. temperature for the aromatic ionomers 1 (●) and 2 (■) and for polystyrene[12] and the 6.2 mol % St-NaMA copolymer.[12] Note that the upper temperature scale applies to the aromatic ionomers while the lower applies to the styrenes.

only contains three phenyl groups and thus has a less rigid main chain. In ref 25 the T_g values for the corresponding nonionic ethyl ester precursors are given as 278 °C for polymer 1 and 257 °C for polymer **2**. Thus, the presence of ions substantially increases the glass transition temperatures of the aromatic ionomers. Unfortunately, no dynamic mechanical measurements (or stress relaxation experiments) on the precursors or the corresponding acids could be performed since the present molding technique resulted in degradation or cross-linking of the samples.

To compare further the aromatic ionomers with the styrene ionomers, it is useful to calculate the mole percent ions per backbone phenyl group. For the aromatic ionomers studied here the result is ca. 13 mol % ions. The increase in T_g due to the presence of ions is 34 °C for polymer 1 and 22 °C for polymer **2** (calculated as the difference in T_g between the salt and the nonionic precursor). The increase in T_g is thus roughly 2.6 °C/mol % ions for ionomer 1 and 1.7 °C/mol % for ionomer **2**. Both of these values are comparable to those obtained for other ionomers (1.3–9.7 °C/mol %).[22]

As has been mentioned before, the aromatic salts began to darken somewhat below 350 °C; thus it was not possible to continue the measurements to higher temperatures to find if a high-temperature peak corresponding to the glass transition of the clustered material exists.

2. Low Temperatures. For both aromatic ionomers, a low-temperature peak was observed with the torsion pendulum at ca. −110 °C. The activation energy was 13 ± 2 kcal/mol. Comparing this result with that obtained by Eisenberg and Cayrol[31] for unsubstituted and methyl- or phenyl-substituted poly(phenylene ethers), it seems likely that the low-temperature peak is associated with the hindered torsional oscillation of the pendant phenyl groups. Another possible mechanism would be hindered torsional oscillation of the backbone,[31] but considering the size of the groups, this appears less likely in this case. It can be mentioned that an increase in activation energy for the backbone oscillation from 12 to 23 kcal/mol was noted when the unsubstituted poly(phenylene ether) was changed to the phenyl-substituted one.[31]

B. Stress Relaxation Behavior. From Figures 5 and 6 it is obvious that the stress relaxation behavior of polymers 1 and **2** is rather similar to that of a St-NaMA copolymer or an EA-NaA copolymer. Compared to the nonionic polymers, the aromatic ionomers have a substantially broader distribution of relaxation times. It may be noted that phenyl rings in the backbone do not by themselves slow down the relaxation rate in the transition region (cf. curves a and b in Figure 5). In fact, the master curves for pure polystyrene and the substituted poly(phenylene ether) in Figure 5 are very similar. Furthermore, since the master curves of ionomer **1**, which contains five phenyl groups between the ether linkages, and ionomer **2**, containing three phenyl groups, are very similar, the decrease in relaxation rate cannot be due to the existence of an aromatic sequence in the backbone. It is now very plausible that the slowing down of the relaxation rate (broadening of the distribution of relaxation times) for the aromatic ionomers is due to the presence of ions. Thus ionic interactions still exist even at these very high temperatures, at least in these polymers, and they influence the viscoelastic properties appreciably.

The similarity between the 6.2 mol % St-NaMA ionomer or the 12 mol % EA-NaA ionomer and the aromatic ionomers (Figure 5) may not be a coincidence since it was earlier found that the aromatic ionomers contained ca. 13 mol % ions per pendant phenyl group. The inflection point in the master curves for the aromatic ionomers occurs at a modulus value which is lower than the corresponding value for a St-NaMA copolymer[12] but rather close to that of an ethyl acrylate-based ionomer of the same ion concentration.[24] This behavior may perhaps be expected since the existence of an ether linkage in the backbone of the aromatic ionomers increases the dielectric constant of the materials compared to that of the styrene ionomers. A higher dielectric constant would result in a lower cluster content. Furthermore, as for the ethyl acrylate-based ionomers[23,24] a higher ion concentration than that found in styrene would be needed to achieve the same effects on the physical properties. This again illustrates how the rheological behavior of the aromatic ionomers is influenced by the presence of ions and that there exist far-reaching similarities between different ionomer families.

In contrast to the styrene ionomers above 6 mol % of ions, no deviations from time–temperature superposition were observed, at least not above T_g for the time regions covered by the individual runs. This does not, of course, exclude the possibility of thermorheological complexity at higher ion concentrations. As mentioned above, the aromatic ionomers probably have a higher dielectric than the styrene ionomers. As in the ethyl acrylate ionomers,[24] this would result in a breakdown of time–temperature superposition only at ion concentrations appreciably higher than was found for the styrene ionomers.

It is also possible that the lifetime of the clusters is very short at the high temperatures of this study and as a result of this, the materials might remain thermorheologically simple at all ion concentrations. The broadening of the distribution of relaxation times would then be mainly due to the cross-linking action of the multiplets. However, recent Raman spectroscopic studies[32] of St-NaMA and EA-NaA ionomers indicate that the clusters are stable up to temperatures far above T_g, leaving this possibility less likely. Unfortunately, Raman spectroscopy could not be used for the aromatic ionomers due to heavy fluorescence.[33]

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Plasma Polymerization of Ethylene and the Series of Fluoroethylenes: Plasma Effluent Mass Spectrometry and ESCA Studies

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ABSTRACT: The plasma polymerization of ethylene and the series of fluorinated ethylenes has been investigated in a capacitively coupled, low-pressure radio-frequency system. ESCA analysis of the polymer films allowed the relative concentrations of CF_3, CF_2, CF, and carbon not directly attached to fluorine to be determined. The structures and stoichiometries of the films were found to exhibit distinct trends depending on the injected material. The neutral species in the effluents of the plasmas were analyzed by mass spectrometry and this data coupled with the ESCA data allowed the primary precursors to polymerization to be identified. In going along the series from ethylene to tetrafluoroethylene the relative importance of acetylene in the plasma steadily decreases while that of difluoroacetylene increases. The relative importance of fluoroacetylene exhibits a maximum at the isomeric difluoroethylenes. Methylene plays an important role in the ethylene plasma while the relative importance of difluorocarbene increases along the series until for tetrafluoroethylene the plasma reactions are dominated by $:CF_2$ and CF_2CF_2 itself. We believe that plasma polymerization proceeds via a plasma-induced mechanism involving the unchanged injected material and a second mechanism involving the initial formation of these other precursors in the plasma.

Introduction

In previous papers[1,2] we have shown how the ESCA investigation of plasma-polymerized films, coupled with direct mass spectrometric sampling of the low molecular weight neutral products in the plasma effluent, provides a new dimension to the investigation of structure and polymerization mechanism for plasma-polymerized materials. In those investigations[1,2] involving the synthesis of metal-containing plasma-polymerized fluoro polymers, detailed information was derived concerning both the state of the metal and the structure of the polymer matrix. The mass spectrometric studies allowed the primary precursors of the polymerization to be identified.

In this paper we present a study of the plasma polymerization of ethylene and the series of fluorinated ethylenes: fluoroethylene, 1,1-difluoroethylene, *cis*- and *trans*-1,2-difluoroethylenes, trifluoroethylene, and tetrafluoroethylene. For comparison purposes we also include the results from an experiment involving the formation of a plasma-polymerized film produced by argon plasma sputtering of a poly(tetrafluoroethylene)-coated excitation electrode and subsequent condensation of the sputtered species on a substrate after they have traversed the plasma. The motivation for this investigation lies in the increasing interest in fluorinated plasma polymers and how fluorocarbon systems differ from hydrocarbon and fluorohydrocarbon plasmas. In addition, this work has provided valuable background data for our investigations of simultaneous etching and polymerization in plasmas excited in mixtures of fluorocarbons and hydrogen.[2]

In a previous publication,[3] Kay and co-workers have shown how a definite correlation exists between the polymer deposition rate and the sum of the partial pressures of all unsaturated neutral species in a tetrafluoro-

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