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PHYSICAL PROPERTIES AND STRUCTURE OF ION-CONTAINING
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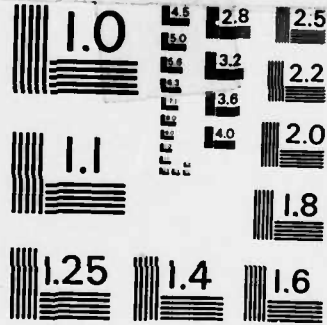
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on Nafion membranes.



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Physical Properties and Structure of Ion-Containing Polymers

Final Report

Submitted by Dr. A. Eisenberg

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FOREWORD

It is widely recognized that the incorporation of ions into organic polymers modifies their properties dramatically. For over twenty years now, increasing efforts have been devoted to the determination of structure-property relationships in these materials in bulk, as well as to the elucidation of the structures of the various types of ionic aggregates which are formed. While the latter effort has not resulted in an unambiguous elucidation of the aggregate structures, the structure-property studies have revealed a wealth of information which might be of great potential industrial as well as academic significance. The literature, as of 1976, is summarized in a monograph (1) on this subject; an earlier book (2) contains a series of review articles on special topics within the field; in addition several conference or workshop proceedings have appeared during the past ten years (3-7).

Several examples may be introduced to illustrate the dramatic changes in properties resulting from the incorporation of small amounts of ionic groups into various polymers. The industrial potential which some of these changes represent will also be mentioned.

The presence of ca. 9 mole % of sodium methacrylate comonomer in polystyrene of molecular weight of about 100,000 g raises the T_g of the copolymer by about 30°C. More importantly however, at 180°C the modulus of this material is around 10^9 dynes/cm²; polystyrene is an oil at the same temperature. This increase in

modulus may not be accounted for by the observed increase in T_g alone. Thus, while the material is a random copolymer containing only 9% of the second monomer, it behaves like a phase separated block copolymer containing ca. 60-70% of a "hard" phase of a T_g of ca. 200°C (9).

The incorporation into polytetrafluoroethylene of short perfluoro(propylene oxide) side chains terminated by sodium sulfonate or carboxylate end-groups yields a permselective membrane (Nafion, Flemion) possessing a very high diffusion coefficient for small cations, a high diffusion coefficient for water, but a very low one for anions. Because of its high chemical stability in the presence of alkali and chlorine at temperatures around 80°C, as well as the other properties mentioned above, this ionomer is now in the process of revolutionizing the industrial production of chlorine (7).

Another interesting development involves the aromatic ionomer membranes (10), which couple high water transport and ionic conductance with excellent stability in the presence of concentrated potassium hydroxide and an oxygen pressure of 30 atm. at 180°C. These materials show promise for use as separators in the production of hydrogen.

The presence of magnesium methacrylate in a polyethylene copolymer raises the T_g by ca. 10°C per mole %. In the polyphosphates, the T_g of $(HPO_3)_x$ which lies at -10°C, rises to 520°C when the polyacid is neutralized with Ca^{++} (1).

Polyethylene copolymers containing 3 to 5 mole % of partly

neutralized acrylic or methacrylic acid (Surlyns) are characterized by a vastly superior melt strength and enhanced mechanical properties, over those of the polyethylene homopolymer. It has, among others, revolutionized the manufacture of golf balls by providing optimum coefficients of restitution with excellent low temperature properties (11). The material has also found extensive use in packaging and tie coat applications (2).

The sulfonation of ethylene-propylene copolymers containing a small amount (about 1%) of copolymerized norbornadiene yields a material which, in the presence of additives such as zinc stearate, behaves like a thermoplastic elastomer, i.e. an injection moldable rubber (12). As can be imagined, this development is of great potential industrial significance, and is undergoing extensive field testing at this time.

The study of the modifications of the properties of polymer by the introduction of ionic groups is fundamental in understanding the behavior and function of ionic species in polymers. This report deals with attempts that have been made in this laboratory over the past six years under ARO sponsorship to shed some light on various aspects of this field.

Statement of the problem studied

A better understanding of the influence of ionic groups on the properties of polymers may be obtained by an investigation of the factors influencing the formation of the aggregates accompanied by fundamental studies on the nature of these aggregates.

A significant part of the work done in this laboratory has concentrated on structure-property relationships in ionomers. An investigation of the influence of the type, position and sign of the ionic group as well as the dielectric constant and glass transition temperature of the backbone on the properties of the parent polymer was undertaken. The interactions between ionomers and polar and non-polar plasticizers was examined. The kinetics of ion-hopping in ionically terminated star-fish polymers were studied by stress-relaxation.

A study of the effect of the placement of the ionic groups along the chain was undertaken by comparing the properties of random and ABA block copolymers of styrene and N-methyl-4-vinylpyridinium iodide copolymers. In addition, work of more applied nature was undertaken by the investigation of polymer miscibility enhancement by ionic interactions. Finally, several studies were performed on Nafion, a perfluorinated ionomer of interest to the chlor-alkali and other industries.

Summary of Results Obtained

This section will be divided into 4 sub-sections to better describe the progress that has been achieved in our understanding of the effect of ions in polymers. These will be:

- A- Structure-Property Relationships
- B- Blends
- C- Ionomeric Blocks
- D- Membranes

A- Structure-Property Relationships

To obtain a greater variety of ionic polymers for which physical data can be collected, various ionomers were synthesized and studied in this laboratory over the last six years. These include:

-Carboxylated Styrenes: A technique for the homogeneous lithiation and subsequent carboxylation of high molecular weight polystyrenes containing up to 14 mole % p-bromostyrene was developed. Thus, poly (styrene-co-p-bromostyrene)s were reacted in dilute THF solution with large stoichiometric excesses of n-butyllithium with no precipitation of ionomer and subsequently carboxylated with anhydrous carbon dioxide or dry ice. By this technique polystyrenes in which up to 100% of the original bromine groups had been replaced by carboxyl functionalities were obtained. The effect of up to 7.82 mole % ionic groups on the stress relaxation and dynamic mechanical (torsion pendulum)

properties of poly(styrene-co-sodium styrene-p-carboxylate) was studied. The results obtained were compared with those reported elsewhere for polymers containing the same ionic groups at a different position on the polystyrene backbone (styrene-sodium methacrylate copolymers) and with polymers containing different ionic groups at the same position (styrene-sodium styrene-p-sulfonate copolymers). The results of these comparisons show that positioning of ionic groups affects the size of ionic aggregates formed while their type dictates the strength of the forces within the aggregates. (Papers 21 and 27).

-Styrene-4-Vinyl Pyridine copolymers: The effect of the sign of the ionic group was investigated by looking at random copolymers of styrene and N-methyl-4-vinylpyridinium iodide. Their thermal (DSC) and dynamic mechanical (torsional pendulum) properties were examined. Whereas the increase in the glass transition temperature with ion-content was found to be similar to those obtained for styrene ionomers bearing a negative ionic group, their dynamic mechanical properties were quite different: the second loss tangent peak usually encountered in ionomeric systems was absent and the variation of the storage modulus G' with temperature did not show the change in slope with ion-content exhibited by the other systems. In fact, the G' curves are similar to that of polystyrene except for a shift to higher temperatures reflecting the higher T_g 's of the ionomers.

-Styrene-4-hydroxystyrene copolymers: Polystyrene-co-4-methoxy-styrene was prepared by random radical copolymerization of

4-methoxystyrene and styrene.

Dimethylation of the copolymer led to formation of polystyrene-co-4-hydroxystyrene, which was then neutralized by sodium naphthalenide. The sodium salts of polystyrene-co-4-hydroxystyrene were then studied by DSC and torsion pendulum. Two loss tangent peaks were observed for the salts, the positions of which increased with increasing salt content.

-Sulfonated isoprenes: Acetyl sulfate was used as sulfonating agent for the sulfonation of cis-1,4-polyisoprene. IR and NMR spectra showed that the sulfonation was accompanied by extensive cyclization. A series of DSC and loss tangent studies of both the sodium salts and the methyl esters were undertaken. It was found that cyclization exerts a profound influence on the microbrownian segmental motion of the hydrocarbon matrix and is the dominant factor in raising the glass transition temperatures. However, the differences in the mechanical properties between salts and esters suggested that the presence of ions did influence the melt viscosities and shear moduli of the sulfonated cyclized rubbers; this influence could be minimized by esterification or water absorption. It was seen that the ionic effects in these materials are quite typical of those encountered in a wide range of other ionomers. (Paper no. 14).

-Ethyl acrylate-vinylpyridine copolymers: Ethyl acrylate based copolymers containing from 0 to 20 mole % of 4-vinylpyridine or 2-methyl-5-vinylpyridine co-units were synthesized and characterized. Those polymers were then quaternized using methyl

iodide in order to get two series of ionomers. A study of their thermal and dynamic mechanical properties was completed.

-Quaternized poly(4-vinyl pyridine): Quaternization effects on the glass transition temperature of poly(4-vinyl pyridine) were studied by DSC. An attempt was made to study the effect of plasticizers on the properties of completely quaternized poly(4-vinyl pyridine).

The water sorption behaviour of styrene-methacrylic acid copolymers and of their sodium salts was studied as a function of concentration of ionic groups and nature of the sample. The influence of thermal history was also examined. The salt forms of the copolymers were found to have a greater hydration capacity than the acids, the hydration capacity increasing with ion content for the salts. The hydration energy of the acid forms was found to be in the vicinity of the liquefaction energy of water whereas the energy for the salt forms became much lower than that value, with increasing water content. This decrease in energy has been attributed to a rearrangement of the cluster structure to accomodate more water molecules. (Paper no. 22).

Dielectric studies were performed on a styrene ionomer in view of understanding the behavior of the carboxylate group in a styrene matrix. Specifically, dielectric and conductivity measurements were carried out on styrene-methacrylic acid copolymers and their salts in the glass transition region, stressing the comparison of polymers neutralized to different extents. A simple monomer-dimer equilibrium between carboxylic

acid groups is applicable to the pure acid polymers, which explains the increase of both the glass transition temperature and of the dielectric strength with concentration of methacrylic acid. The dielectric data indicated that very few sodium carboxylate groups can dissolve in the matrix of the pure salt, whereas the presence of carboxylic acid groups in partly neutralized polymers enhanced the dissolution of the salt groups in the matrix. Considerable differences were observed between the partly neutralized polymer and the blend consisting of pure acid and pure salt copolymers, which suggests that exchange of cations between acid and salt groups is quite slow even at high temperatures. The conductivity of the ionomers appears to be related to the diffusion of carriers through the matrix. (Paper no. 8).

The viscoelastic properties of various ionomers were also examined. Ethyl acrylate ionomers were studied by stress relaxation. The results were compared with those for the styrene ionomers studied previously. The behavior of the two systems was qualitatively similar, although significant quantitative differences exist. Specifically, the onset of thermorheological complexity was found here at 12-16 mole % of ions, while in styrene it is observed at ca. 6 mole %. Furthermore, the modulus-temperature plots showed great similarity if the acrylate samples were compared with the styrenes containing about half as many ions. Other properties showed similar trends. The increased dielectric constant of the acrylates

is believed to be responsible for the observed differences in the two systems. The effect of a change in counterions was also studied to some extent. The onset of thermorheological complexity is seen to be qualitatively related to the size and charge of the cation. (Paper no. 5).

The solid-state viscoelastic properties of polystyrene containing randomly distributed groups of styrene-p-sodium sulfonate were studied and compared with the corresponding properties of copolymers of styrene and sodium methacrylate (S-NaMA). The viscoelastic behavior in the primary transition region of these two ionomers is very similar. As for the S-NaMA copolymers, it is proposed that sulfonated polystyrene is composed of ion-rich regions (clusters) immersed in a matrix of low ion concentration. Two peaks were observed in the plot of mechanical loss tangent versus temperature for the sulfonated material. The lower peak was assigned to the glass transition of the ion-poor matrix and the upper to the glass transition of the clustered regions. As for some other ionomers, the presence of ions was found to slow down the stress relaxation rate, giving a broad distribution of relaxation times. Above certain ion concentration, the sulfonated polystyrenes were thermorheologically complex owing to the onset of a secondary relaxation mechanism associated with the ion-rich regions. (Paper no. 11).

The dynamic mechanical properties and stress relaxation behavior in the solid state were studied for two aromatic ionomers, potassium salts of carboxylated-phenylated polyphenylenes.

Mechanical loss tangent measurements indicated that the glass transition temperature is of the order 300°C for both ionomers. The stress relaxation behavior in the primary transition was typical of an ionomer; i.e., a broad distribution of relaxation times was 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 were also reported. (Paper no. 10).

A study of the effects of polar and non-polar plasticizers in ionomers, using the torsion pendulum, has been completed. Specifically, styrene ionomers with 2, 5 and 8 mole % of sodium neutralized methacrylic acid co-units were plasticized by varying amounts (<50 weight %) of diethylbenzene. Torsional pendulum results showed that the matrix glass transition temperature and the transition due to the ionic regions of the polymer were equally plasticized. In contrast, results for a styrene ionomer with 5 mole % of sodium neutralized sulfonic acid showed no plasticization effect on the ionic transition. The ionic peak in both types of styrene ionomers was destroyed with the incorporation of glycerine, a polar plasticizer.

A melt rheology study, using the Rheometrics Mechanical Spectrometer in the dynamic mode, of the 5% carboxylic styrene ionomer plasticized to varying extents (25-60 wt. %) by a styrene oligomer (800 MW) was begun.

Dynamic melt rheology results for a copolymer of styrene and 4-vinyl-pyridine (2, 5, 7 and 9 mole % of the latter) and the corresponding methyl iodide salts were gathered. As had been indicated already by torsional pendulum studies, the melt rheology shows no clear evidence of ionic aggregation in those ionomers, except for a somewhat slower decrease of the modulus in the flow region. Otherwise the various curves can be superimposed by merely shifting along the frequency axis using the corresponding glass transition temperature as a reference.

Ionic interactions can also be seen in non-ionic parent polymers. In this context, the effect of a perchlorate salt on the viscosity of a polar homopolymer was investigated. The viscosity enhancement in low molecular weight poly(ethylene oxide) and poly(propylene oxide) resulting from dissolution of LiClO_4 was measured as a function of molecular weight and salt content. It was shown that on a $\log \eta$ vs. temperature plot, the viscosities for various salt contents yield lines of identical shape that can be superimposed by simple shifts along the temperature axis to yield a master curve for each molecular weight. Furthermore, by additional vertical shifting one can obtain a single master curve for all molecular weights and salt contents studied here, for each of the two families of polymers. Between about 3 and 13 mole % the increase in viscosity is attributable mainly to the increase in the glass transition temperature. Below that region another mechanism must be operative, since the glass transition rose only very slowly

while the viscosity rose appreciably. (Paper no. 6).

Work of a more fundamental nature was undertaken in two collaborative efforts. Small-angle neutron scattering test experiments were performed on two ion-containing polymer systems - the styrene-sodium methacrylate copolymers and the Nafions (copolymers based on the perfluoroethylene backbone with side chains containing a terminal sulfonic acid group). Evidence for ion aggregation was found in the styrene copolymers for ion concentrations of 3.8, 7.2, and 10 mole %. No appreciable changes in the radius of gyration were observed in the acid and salt copolymers; however, for the 10% salt sample extrapolation to zero concentration was found to be impossible. Clustering of absorbed water was observed in the hydrated Nafion samples in both the acid and sodium salt forms. (Paper no. 7).

Thanks to collaboration with professor Kennedy's group at Akron, ion-hopping kinetics were studied by using the 3-arm star polyisobutylene-based model ionomers. It was found that polymer chains of 3-arm star PIB ionomer are crosslinked by chemical trifunctional linkages and that ionic aggregates exist mostly as multiplets in the middle of the chains. The kinetic constant for this system was obtained as $k = 7.11 \times 10 \exp(-94,100/RT)$ by stress relaxation.

Raman spectroscopy was used for the first time to show the presence of multiplets and clusters of ion pairs in ethyl acrylate-sodium acrylate, styrene-sodium methacrylate and styrene-sodium-p-styrene carboxylate ionomers and to determine the

relative concentrations of ion pairs in these different kinds of sites. The Raman spectra of a series of ethyl acrylate-sodium acrylate copolymers with sodium acrylate contents varying from zero to 100 mole % were measured in the $425-100\text{ cm}^{-1}$ region at room temperature, 150, 200, and 250°C. The bands observed at 246 and 175 cm^{-1} were attributed to ion multiplets and clusters, respectively. At all four temperatures investigated, the intensities of the multiplet and cluster bands increased steadily with increasing sodium acrylate content up to ca. 10 and 35 mole %, respectively, and thereafter remained essentially composition invariant. With increasing temperature, the multiplet band intensity increased while the cluster band intensity decreased throughout the complete composition range studied. A similar variable-temperature Raman study was also carried out for a series of styrene-sodium methacrylate ionomers. In this series the bands appearing at 254 and 166 cm^{-1} attributed to ion multiplets and clusters, respectively. The intensities of these bands showed practically no variation with temperature. Finally, the infrared and Raman spectra of a series of styrene/sodium p-styrene carboxylate ionomers with sodium p-styrene carboxylate contents varying from zero to 13.6 mole % were recorded, and some vibrational assignments proposed. The bands appearing in the Raman spectra at 248 and 158 cm^{-1} were attributed to ion multiplets and clusters, respectively. The relative intensities of these two bands were used to determine the relative concentrations of ion pairs in these two different

kinds of sites, and were found to be invariant over the range of -258 to 250°C. The results of these studies indicate that the variation with temperature of the ion contents in multiplets and clusters is strongly dependent on the proximity to the glass-transition temperature. Furthermore, it is seen that the total amount of ions in clusters or multiplets depends on the dielectric constant of the polymer, a high dielectric constant favoring multiplets at the expense of clusters. (Papers 1, 3, 4, 9).

B- Blends

The introduction of specific interactions in polymer pairs can lead to enhanced miscibility. These can be ionic in nature, as in ion-ion and ion-dipole interactions. Both types were studied in this laboratory.

Interactions between anions on one polymer chain with cations on another rendered miscible otherwise immiscible polymer pairs. These interactions were introduced into the polymers in a novel fashion by incorporating sulfonic acid groups onto one polymer and amino groups onto the other. Specifically, when 5 mole % of $\text{-SO}_3\text{H}$ groups were attached to polystyrene, and 5 mole % of vinyl pyridine were copolymerized with ethyl acrylate, proton transfer occurred upon mixing, and the pairwise attractive interactions between the resultant ions compatibilized the blend. The same was observed for the styrene-vinyl pyridine and sulfonated polyisoprene polymer pair. In this system, removal of the ionic interactions through esterification destroyed the miscibility, demonstrating that these are indeed responsible for the miscibility

enhancement. (Dynamic mechanical and optical properties were used as a measure of compatibilization). (Papers 15, 16, 18).

One final variation on this theme concerns blending polyurethanes, which possess an amine functionality, with sulfonated polystyrene. In one study, blends were prepared from polyurethanes containing a tertiary amine in the chain extender, with lightly sulfonated polystyrenes. In the absence of polystyrene, the polyurethanes are not phase separated. Addition of the sulfonated polystyrene led to a blend of the latter with the hard segments in one phase with the exclusion of the soft segments into a separate phase. The degree of phase purity of the soft segments increased with increasing sulfonate content at a constant styrene concentration, or with increasing styrene content at a constant sulfonate concentration in the styrene. Blend formation was confirmed in a study involving the mixing of a polyurethane containing hard segments without any soft segments, which led to a one-phase system at a high enough sulfonated polystyrene content. In a further study, blends were prepared from two kinds of urethane elastomers, containing 1,4-butanediol or 3,3'-dichloro-4,4'-diamino-diphenyl-methane as chain extenders, with lightly sulfonated polystyrenes. Dynamic mechanical studies showed that strong interactions occur between the sulfonic acid and the urethane or urea moieties on the polyurethane chains. These strong interactions were clearly seen in the composition dependence of the loss tangent peaks (due to the glass transitions) for both the high temperature and

the low temperature glass transitions of the blends. They were further confirmed by model studies. (Papers 24, 25).

It was found that ion-dipole interactions can lead to considerable miscibility enhancement in the styrene ionomer/poly(alkylene oxide) systems. The miscibility enhancement in these systems was compared to that due to hydrogen bonding, and the influence of molecular weight and of ionic content on miscibility was also studied. In addition to the styrene/alkylene oxide system, ion-dipole interactions were found to be effective in enhancing the miscibility in many ionic polymer/polar polymer pairs. The ionomers used in this study were styrene lithium methacrylate and ethyl acrylate copolymers, while polyethers, polysulfide, polyesters, polyimine, and substituted polyethylenes served as polar polymers. (Paper No. 23).

Finally, a study was made of blends of PVC with poly(ethyl acrylate). Blends of poly(vinyl chloride) and polyethyl acrylate-co-4-vinyl pyridine of different 4-VP contents (2 to 14 mole percent) were prepared. These were found to be partially miscible as evidenced from the presence of a single, though broad, tangent delta peak obtained from torsion pendulum experiments. Thus, the presence of 4-vinyl pyridine enhances miscibility in the otherwise immiscible poly(vinyl chloride)/poly(ethyl acrylate) system. Several possible types of interactions which might exist between these two polymers, such as ion-dipole, crosslinking, charge-transfer hydrogen-bonding

and dipole-dipole, were explored. From ultraviolet, conductance, infrared and solubility studies, it was shown that hydrogen-bonding or dipole-dipole (or possibly a combination of the two) interactions were the most likely in this system. These interactions had been suggested previously for other systems by various investigators. (Paper no. 26).

C- Ionomeric Blocks

In order to determine the influence of the placement of the ions on the chain, a comparison of the thermal and dynamic mechanical properties of random and block copolymers of styrene and N-methyl-4-vinylpyridinium iodide was undertaken. The random copolymers were synthesized by free-radical bulk copolymerization; their properties have been outlined above.

The block copolymers are synthesized by living anionic polymerization. The use of this polymerization technique required the building and the redesigning of a sophisticated vacuum line. This line now allows the routine production of 50 to 80 gram batches of monodisperse ($M_w/M_n = 1.07$) polystyrene. A new device designed in this laboratory also permits the synthesis of block copolymers of 4 different 4-vinylpyridine contents in a single run, from the same batch of styrene middle block.

D- Membranes

Several studies were performed on Nafion membranes. In one of these, the dynamic mechanical properties of Nafion precursor were determined as a function of the degree of

conversion to the sodium ionomer, and those of the acid as a function of the degree of conversion to the cesium salt. A run was also made on the barium neutralized material, as well as on a remolded sample of a partly converted precursor. The precursor shows four dispersions which (in order of decreasing temperature) are identified with the glass transition, motions of the ether side chains, CF_2 groups in the backbone, and pendant SO_2F groups. Four relaxation regions are also seen in the ionomer, which are identified with the glass transition of the ionic regions and of the matrix, as well as with motions of the ether side chains and the backbone CF_2 groups. While the polymers in the acid and the salt forms are compatible, as seen by the gradual movement of the ionic glass transition peak to higher temperatures with increasing degree of neutralization, the salt and the precursor are not compatible. In the barium salt, the ionic glass transition peak occurs at a temperature close to the melting point of the crystalline regions, and most likely contains a contribution from that process also. (Paper no. 17).

Mechanical properties were also investigated. That study shows that the primary relaxation or glass transition process occurring in Nafion-Na is profoundly influenced by the presence of water in the structure; this confirms the recent assignment of the primary T_g or α relaxation to the ionic groups in the polymer and represents a reversal of the original assignment. It is evident that the nature of the cation is not important

in under-water stress relaxation, in marked contrast to the behavior observed for the Nafion polymers in the dry state. Amorphous Nafion-Na has a lower modulus than semicrystalline Nafion-Na in under-water as well as dry state and under-methanol stress relaxation tests, and both semicrystalline and amorphous Nafion-Na relax faster under-water than in the dry state. Increased swelling in methanol, as compared to water, leads to a lower modulus for Nafion-Na, but not to higher relaxation rates in the under-methanol stress relaxation experiments. This clearly indicates that methanol also interacts with the interfacial region or with the fluorocarbon matrix in Nafion-Na, not just with the ionic regions. (Paper no. 20).

In another study, it was shown that stress relaxation occurred much more rapidly when a current was passing through the membrane than in the absence of current. A new instrument had to be designed and built for this work, and the effect was labeled as electrorheological. (Paper no. 19).

Finally, a review was written on the mechanical properties of the Nafions. (Paper no. 13).

GENERAL

A review was written on the changes in our understanding of clustering in ionomers. (Paper no. 2).

ACKNOWLEDGEMENT

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SUBMITTED COMPLETED MANUSCRIPTS

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