Properties of sulfonated polysulfone ionomers.

Michael A. Drzewinski
University of Massachusetts Amherst

PROPERTIES OF SULFONATED POLYSULFONE IONOMERS

A Thesis Presented

by

MICHAEL A. DRZEWINSKI

Submitted to the Graduate School of the
University of Massachusetts in partial fulfillment
of the requirements for the degree of

MASTER OF SCIENCE

May   1982

Polymer Science and Engineering

PROPERTIES OF SULFONATED POLYSULFONE IONOMERS
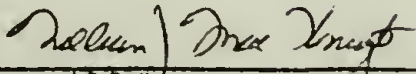
A Thesis Presented

by

MICHAEL A. DRZEWINSKI

Approved as to style and content by:

_____

Dr. William J. MacKnight, Chairperson of Committee

_____

Dr. William J. MacKnight
Department Head
Polymer Science and Engineering

ACKNOWLEDGEMENT

At this time I wish to acknowledge the advice and direction given to me by my advisor, Professor William J. MacKnight. I am indebted to him for his enthusiastic interests, support, and contributions to my education, especially in the area of ionomers. I would also like to thank at this time the Hybrid Cell Project of the Occidental Research Corporation for so graciously supplying the samples used in this study as well as for their financial support.

Many of my fellow students have helped me in completing this work as well as with other aspects of my education. I would like to particularly thank Cameron Murray for his computer assistance and expertise; Dale Handlin for his advice and experience with ionomers which are all too often uncooperative; and Don Burchell for the unselfish giving of his time in performing the FTIR Analysis.

Finally, I would like to thank all the people in my life who may have either helped or hindered my progress for they are responsible for what I am today. Last and most importantly, I would like to dedicate this work to the people most responsible for making me what I am today, my parents. For without them none of this could ever have been possible.

ABSTRACT

Properties of Sulfonated Polysulfone Ionomers

(May 1982)

Michael Anthony Drzewinski, B.S., Rensselaer Polytechnic Institute

M.S., University of Massachusetts

Directed by: Professor William J. MacKnight

The structure-property relationships of sulfonated polysulfone
ionomers were investigated. The techniques of Fourier Transform
Infrared, Differential Scanning Calorimetry, Dynamic-Mechanical
Analysis, Small Angle X-ray Scattering and Water Absorption were
used to provide information on the nature of ionic interactions in
these ionomers. From these structure-property studies, the ionomeric
structure is best described as consisting largely of ionic multiplets
composed of ion pairs, quartets, etc.

Previous studies on ionomers carried out in this laboratory
and elsewhere had established that salt groups tend to aggregate
to form micro-phase separated clusters.[1] The small angle x-ray
profiles of the cesium ionomers studied in this work show little
evidence of ionic clusters. There is a suggestion of increased
intensity in the case of the highly sulfonated cesium ionomer but
it is ill-defined. Because of the low scattering intensity it is
difficult to perform rigorous quantitative analysis on the
scattering profiles. However, it may be concluded that the per-
centage of salt groups present in the form of clusters is small,

probably less than 10% in all cases.

Since little evidence of clustering is indicated by the SAXS studies, phase separation between the salt groups and the polymer matrix must not occur to any significant extent either. This fact is supported by the DSC results which show only one transition which increases linearly with sulfonation over the entire sulfonation range studied. In addition, the dynamic-mechanical analysis confirms and extends the SAXS and DSC results in that it shows the effect of ionic groups in increasing the modulus and glass transition temperature due to chain stiffening and/or ionic crosslinks.

Since ionic clusters were not found to exist to any significant extent, the nature of the ionic interactions and their importance in determining the material properties was also studied. It was found that strong ion association, possibly ion pairs in the case of cesium, exists in the dry state. Thus, water was found to initially act to disrupt these associations. The ionic interactions between the cation and anion is probably what brings about the enhanced material properties. Therefore the differences between the cesium and sodium ionomers may be a direct result of the differences between these ions' respective potential in promoting such interactions. Water, as well as any other factor which may effect this cationic-anionic interaction, will thus affect the material properties. Therefore the key to controlling ionomeric properties may lie in the ability to control the specific interactions between cation and anion.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

C H A P T E R   I

IONOMERS: Introduction and Review

A. Background

Twenty-five years have passed since the concept of neutralizing
acid side groups in carboxylated elastomers to produce "ionic cross-
links" was introduced.[2] The latter introduction of an ethylene-metal
methacrylate copolymer, Surlyn[R], by the duPont Company in 1964, marked
the official beginning of the concept of an "ionomer".[3]

The term ionomer was apparently coined by duPont to describe a
class of materials that lie between the purely organic and inorganic
regimes. In general, the term came to mean a polymer which is com-
posed of usually a hydrocarbon backbone containing pendant acid groups
which are neutralized partially or completely to form salts. Today,
the term ionomer is taken to represent polymers containing less than
fifteen mole percent of salt groups, thus excluding the area of
polyelectrolytes.

The concentration and distribution of the salt groups in an ionomer
may vary but the hydrocarbon backbone remains the major component. The
range of backbones to which anionic (i.e., carboxylates, sulfonates,
phosphonate, etc.) and cationic (i.e., ammonium, pyridinium, etc.)
groups have been attached include: polyethylene[4], polystyrene[5],
polybutadiene[2], polyoxymethylene[6], polypentenamer[7], polytetra-
fluroethylene[8], ethylene-propylene-diene terpolymers[9], and recently
polysulfone[10]. Thus, the past twenty-five years have witnessed an

1

explosive growth in the literature. Besides individual publications, patents, and review texts, the field has grown through the installation of several symposia dealing with ion-containing polymers.[11]

In order to put this study into perspective, a review of relevant investigations and theories concerning ionomers is presented. This is followed by a comprehensive survey of specific work done on similar systems as well as previous studies conducted on polysulfone and its sulfonated derivatives.

B. Ionomer Theory

The reasons for such increased interests in ionomers can be understood if one realizes that the incorporation of ions into an organic polymer can modify the properties of that material immensely. Increases in the glass transition temperature by hundreds of degrees, increases in the modulus by three orders of magnitude and increased solution viscosity of over four orders of magnitude, are among the effects reported.[12] As a result of recent extensive investigations, it has become clear that the reason for such dramatic effects is the aggregation of ionic groups in a low dielectric medium. In addition, further investigations into the structure of such aggregations has resulted in the conclusion that a separate phase containing ionic rich "domains" exists. Theoretical and experimental evidence for such a phase has been reported but the nature of such a phase remains a major point of controversy in ionomer theory and is the main subject of the section below.

In early work with carboxylated polybutadiene, it was realized that their physical and mechanical properties were influenced by neutralization of the pendant acid groups. The concept of a metallic salt crosslink was introduced to explain such behavior.[13] As more work was carried out on such ionomers, it became more apparent that this simple explanation was not adequate for describing such behavior. To explain the effects monovalent ions have of producing "crosslinks" in carboxylated butadienes, Otocka postulated the existence of dipole-dipole interactions leading to an ionic quartet.[14] This concept recognizes the possibility that the salt groups are present as contact ion pairs in a medium of low dielectric constant. Further investigations have shown both theoretically[15] and experimentally[16] that when ions are dispersed in a polymer matrix of low dielectric constant, ion pairs and higher order multiplets form.

It was further suggested by Eisenberg[15b] that such multiplets could aggregate into clusters which would incorporate both ionic and non-ionic material as well as to form a separate phase from the remainder of the hydrocarbon matrix. The factors involved in cluster formation would thus be the elasticity of the polymer chains as well as the electrical work of cluster collapse since:

   a. Upon cluster formation, work is done in stretching the polymer chain (entropy effect).

   b. Electrostatic energy is released when multiplets form clusters (enthalpy effect).

Thus, if the attractive forces between multiplets are larger than the elastic forces which prevent multiplets from randomly

approaching each other, clustering should be present.

Attempts to prove or disprove such a structure have resulted in conflicting data and various interpretations. The majority of the evidence[17], however, suggests that at least in the proper range of concentration and temperature, the salt groups aggregate to form microphase separated clusters. This conclusion, as well as models for such clusters are discussed below.

C. Ionomer Structure

  1. Cluster Theory

The only comprehensive theoretical attempt to predict the morphological microstructure of ionomers is that of Eisenberg.[15b] Here the basic structural entity is the contact ion pair from which triplets, quartets, etc., termed multiplets, can be built up where by each is only separated by a distance corresponding to their ionic radii. The development is based on two considerations: 1) Steric arguments are used to calculate the largest number of ion pairs which can group together without the presence of intervening hydrocarbon, and 2) energetic considerations are invoked to argue for the formation of larger entities which are composed of systems of ion pairs separated from each other by a hydrocarbon "skin" consisting of a portion of the backbone.

Based on the steric arguments, Eisenberg calculated a maximum value of eight ion pairs for a multiplet in the case of an ethylene-sodium methacrylate copolymer. The energetic considerations predict

the conditions for which clustering of the multiplets would occur. Electrostatic energy is released when multiplets come together to form a cluster. The work involved depends on the cluster geometry and the dielectric constant of the medium. An elastic force tending to pull apart clusters is calculated from rubber elasticity theory. Since the electrostatic forces have little temperature dependence, and the elastic forces are proportional to temperature, it is apparent that these two forces must exactly balance each other at some critical temperature and above which clusters will become unstable. Furthermore, there is a critical multiplet concentration for cluster formation since the elastic forces will be greater than the electrostatic forces for small ionic concentrations.

Eisenberg's theory represents an excellent first approximation to the problem of the structure of ionomers. Some of the assumptions built into this treatment, though, affect the results. The spherical structure required for multiplet formation severely restricts its size. Exclusion of any hydrophobic material from the multiplets also affects the calculated multiplet dimensions. Eisenberg points out that experimental and theoretical studies of low molecular weight salts in media of low dielectric constant have shown that multiplets definitely exist. Experimental studies dealing with the morphology of ionomers have not proved conclusive, though.

2. Morphological Studies

    a. Electron Microscopy

Davis, Longworth, and Vaughan studied the electron microscopy of ethylene-methacrylic acid copolymers and ionomers.[18] Using surface replication, they observed a lamellar spherulitic morphology for the acid copolymers. For the ionomers, however, no such structure was apparent and only a random grainy morphology was observed. When thin films were made by casting the acid onto dilute base, a randomly arranged lamellae structure with irregular clumps of aggregated ionic material was observed. These regions were reported to be about 150 A in diameter.

Using butadiene-methacrylic acid copolymers, Marx reports similar results.[19] Their reported value of the granular size, 25 A, is considerably smaller than that for the ethylene ionomer. Pineri and coworkers have also used electron microscopy to look at a ter-olymer of butadiene, styrene, and vinyl pyridine complexed with iron.[20] Their results show iron rich regions distributed hetero-genously throughout the polymer and varying in size from 100 to 1000 A. Similarly, Gierke and others have shown grainy micrographs from un-stained, ultramicrotomed sections of perflurosulfonated acid films coated with silver and tin.[21] They report that such micrographs reveal metallic clusters approximately spherical in shape with diameters of 30 to 100 A.

It should be pointed out, however, that the validity of such electron microscopy results has recently been questioned.[22]

Handlin and others examined the morphology of ethylene-methacrylic acid, sulfonated polypentenamer, sulfonated polystyrene, and sulfonated EPDM ionomers. They present a different explanation of the microscopy results for these ionomers based on the transfer theory of imaging which had been overlooked in previous ionomer studies.

b. Mossbauer Spectroscopy and Neutron Scattering

Recently, Pineri and coworkers, utilizing Mossbauer spectroscopy and neutron scattering, have added new methods for the elucidation of ionomer structures.[23] Studying a butadiene-styrene-vinyl pyridine copolymer complexed with iron, they found that the iron nuclei could exist in three possible environments: 1) Dimers, which account for about 20% of the iron, consisting of two asymmetric Fe(III) complexes. 2) Quasi-isolated complexes, accounting for 20% of the iron, exist due to ferromagnetic coupling in the vicinity of the clusters. 3) Ionic clusters, containing the remaining 60% of the iron, were also determined to be present with their size being usually less than 30 A and consisting of about 30 ionic groups.

Pineri complemented the Mossbauer results with neutron scattering experiments as well as small angle x-ray scattering. Their contributions reveal that more than 80% of the clusters are less than 30 A with the average value of about 10 A. These results are in good agreement with the Mossbauer results as well as to those of MacKnight, Taggart and Stein[24] used in proposing their cluster morphology model to be discussed subsequently.

c. Small Angle X-Ray Scattering

Small angle x-ray scattering has been the mainstay in the interpretation of ionomer structure. The major difference in the scattering curves of an ionomer and its parent acid polymer is the appearance of a low angle peak for the ionomer centered around $2\theta = 4^{\circ}$. This peak, which will be referred to as the ionic peak, appears to be a common feature of all ionomers which have been examined, regardless of the presence of absence of backbone crystallinity. The ionic peak possesses the following characteristics according to MacKnight, Taggart, and Stein:

1) The ionic peak occurs in all ionomers regardless of the nature of the cation.

2) The magnitude and location of the peak is dependent on cation type. For example, cesium's peak occurs at lower angles with much more intensity than a lithium ionomer due to differences in size and electron density.

3) The ionic peak is relatively insensitive to temperature.

4) The ionic peak is destroyed when the ionomer is saturated with water but the general scattering profile remains different than that of the parent acid polymer.

Interpretation of scattering data can differ from one experimentor to another since the results are dependent on the model used in the analysis. A technique which has been widely used for the structural determination of amorphous materials such as glasses and liquids is the radial distribution function (RDF). The RDF is the Fourier transform of the angular dependence of the scattered x-ray intensities. RDFs, though, are susceptible to a number of inaccuracies such as absorption corrections,

normalization and neglected contributions from very small angle x-ray scattering.

In the small angle region, the asymptotic limit of the scattering profile can be analyzed to give information on the inhomogenity, L_p, as was first described by Porod in 1951.[25] The limiting intensity of a small angle scattering profile, as the scattering angle goes to zero, has been shown by Guinier and Fornet to be related to the radius of gyration of the scattering source for a dilute two phase system of uniform spheres.[26] The application of Porod or Guinier analysis to ionomers must then be done cautiously because of deviations from the ideal models on which their theories are based. These deviations may include non-uniform particle size and density, lack of sharp phase boundaries and the presence of interference effects between particles that cause the ionic peak.

Thus, models have been presented based on these different types of analysis of the ionic peak. In the following section a brief review of proposed models will be given in light of the type of analysis used. In addition, the proposed nature of the scattering source will be discussed as well since it also leads to different interpretations.

3. Proposed Models

The morphological investigations of ionomers have shown that the major structural reorganization occurs upon neutralization of an acidic polymer and that they strongly suggest the formation

of ionic aggregates or domains. Theory also predicts clustering of salt groups in such systems. This idea was apparently first proposed by Bonotto[27] and later a model was proposed as well.[28] The quantitative aspects of this model are not given but their idea is that small clusters act as multifunctional crosslinks. It is not clear, however, whether this model assumes microphase separation of the clusters or whether their clusters are multiplets or clusters in the sense defined by Eisenberg.

a. Longworth and Vaughan Model (1968)

Longworth and Vaughan[29] presented a model which explicitly assumes microphase separation of the ionic domains from the hydro- carbon phase. This model is based largely on the analysis of the ionic x-ray scattering peak of ethylene carboxylic ionomers. They assume that the ionic peak is a maximum of Bragg diffraction. That is, the Bragg spacing of 20 A they measured represents a repeat unit within the ionic phase. The idea that the ionic peak represents a structural repeat distance is supported by the fact that lithium salts exhibit such a peak since lithium is too poor a scatterer to cause an interference maximum at the concentrations present in their ionomers. They assume that the nature of the repeat unit within the ionic domains is due to the hydrocarbon chains and not an ordered arrangement of the ions themselves.

The difficulties with this model are as follows:

11

1) It is hard to envision the presence of a potential capable of producing regular 20 A spacings between multiplets in a system where the multiplets occur randomly along the chain.

2) The model does not account for the differences in intensity due to different cations. If the cations themselves are not responsible for the scattering then it is hard to understand why the heavier metals show more scattering intensity.

3) Recognizing that for such a diffraction peak to be observed, at least five repeat units would be required, making the lower size limit of an ionic domain about 100 A. While the spherulitic morphology is definitely disrupted, such large entities should disrupt the crystallinity as well but no change in the melting point or degree of crystallinity was observed. In addition, there was also no change in the line width of the 110 and 200 crystalline diffraction peaks. Thus, these results indicate that the basic crystallite size is unaffected by the presence of ionic domains which hardly seems likely if they are of such large dimensions.

b. Marx, Caulfield and Cooper (1973)

In this work, Marx and others[30] interpret the ionic peak of carboxylated ethylene ionomers in a very different manner than Longworth and Vaughan. They assume that no phase separation occurs and the acid groups exist as aggregates homogeneously distributed in the amorphous phase. Their aggregates contain two or more carboxyl groups depending on the composition of the copolymer and

the amount of water present. In this "aggregate" model the ionic peak is assumed to arise from an electron density difference between the metal cations and the hydrocarbon matrix.

Several questions arise in view of this model. In the first place, their interpretation of the ionic peak implies a considerable degree of regularity in the distance between scattering sites which thus implies the presence of a paracrystalline lattice structure of the scattering sites. If such a regular paracrystalline lattice were really to exist, it is difficult to understand how the crystalline morphology could persist relatively unaltered in the salt form of the ionomer. Secondly, some sort of potential would be necessary to impose such a regularity and it is hard to see how the origin of this potential is in the amorphous phase of a random copolymer. Lastly, it is also difficult to rationalize the presence of an ionic peak for the lithium ionomer if it is assumed that the ionic peak arises from electron density differences between the cation and hydrocarbon matrix.

The work of Marx, Caulfield and Cooper does, however, present several important experimental findings. A characteristic ionic peak is present in a carboxylated butadiene ionomer as well as the semicrystalline ethylene ionomer. In both cases the effect of water on the ionic peak was studied in detail. They found that water tends to shift the ionic peak to smaller angles (larger spacings) while complete saturation completely destroys the peak. On the other hand, methanol and other low molecular weight compatible

diluents merely diminish the intensity and do not affect its position. They propose that water increases the average number of carboxyl groups in each multiplet since it is completely compatible with the ionic sites.

c. Binsbergen and Kroon (1973)

This model is very similar to the aggregate model of Marx, Caulfield and Cooper and so it brings up the same objections. Binsbergen and Kroon[31] thus state that the ionic peak is due to a most frequently occurring distance between nearest neighbor clusters, similar to the diffuse diffraction peaks observed with liquids. They assume the ionic domains to be located in the center of spheres which are randomly packed. The number of carboxyl groups in each cluster is similar to that derived form the aggregate model. Binsbergen and Kroon's model does differ from that of Marx and others in that the spacing is calculated directly from the Bragg spacing and not from a paracrystalline model.

d. MacKnight, Taggart and Stein (1974)

The previous models discussed were all based on analysis of the ionic peak. All of these models assume that the origin of the ionic peak lies in some structural regularity imposed by the presence of salt groups in the system. Certainly, the random packing of spheres will give rise to a maximum similar to the ionic peak if the volume of spheres is sufficiently great. In such a case,

though, the location of the peak maximum will be related to the radii of the spheres and not to the distance between them. Additional studies have been made on ionomer structure based on diffraction data and using RDF analysis mentioned in the prior section.

Working with the cesium salt of an ethylene-acrylic acid copolymer, Roe found by RDF analysis that there was no evidence of aggregates 15 A or smaller and that there was good evidence for dimer formation.[32] It was later pointed out by Kao and others that Roe omitted the ionic peak from the scattering data used to construct the RDF.[33] When the ionic peak was included in the RDF analysis, fluctuations of the order of 20 A were found present in the salt but absent in the acid copolymer. Such a result was the basis for the model of MacKnight, Taggart and Stein.[24] This model uses both RDF analysis and analysis of low angle x-ray scattering with the theories of Porod and Guinier to suggest an entirely different origin for the ionic peak than previously proposed.

MacKnight's results show a build up of electron density in the 4 to 16 A region and a negative value at distances greater than 16 A for RDF analysis. The detailed shape of the RDF cannot be reproduced by imposing a hard sphere model. Thus, the RDF results point to the presence of an average 8 to 10 A radius cluster randomly distributed in the hydrocarbon matrix. From the composition of the copolymer it follows that the clusters of this average size would contain about 50 cesium ions per cluster and the total volume fraction of such clusters in the material would be

2 to 5%. This in turn would give an average distance between

clusters of several hundred angstroms, a distance much too great

to cause the ionic peak. Thus, RDF analysis indicates that the ionic

peak does not arise from interference between scattering centers

as was assumed by the models of Marx et al. and Binsbergen.

The interpretation of the origin of the ionic peak was thus

considered in light of the RDF results. It has already been noted

that the distance between clusters is too great to cause the ionic

peak. Also, the volume fraction of clusters is too low to cause the

ionic peak to occur from interference of random close packed

spheres. It is postulated then that in the dry state a cluster of

8 to 10 A in radius is shielded from the surrounding matrix

ions, which are not part of a cluster, by a shell of hydrocarbon

chains. Since the coordinated metal ion is then the main

structural entity, a charge imbalance will exist within the cluster.

The surrounding matrix ions will thus try to approach the center of

the cluster but will not be able to come closer than the thickness

of the hydrocarbon shell. Thus, a preferred distance between

the cluster and the matrix ions will exist and give rise to an

ionic peak of a 20 A spacing. In addition, water should tend to

congregate around the clusters, raising the dielectric constant

of that region. This would lead to destruction of the preferred

distance between the cluster and the matrix ions causing a loss of

the ionic peak but leaving the cluster intact. Such a model is

similar to the "shell-core" model proposed for the structure of

16

certain phase separated metal alloys.[34] Scattering patterns of such

alloys also yield peaks which are assigned the same cause as the ionic

peaks of ionomers.

4. Recent Developments in Ionomer Morphology

Since the appearance of the MacKnight, Taggart and Stein Model,

work has continued to try to add more light to the problem of

determining ionomeric structures. One of the problems in determin-

ing such a morphology is that no direct technique has proven useful

in conclusively determining ionomeric structures. The remaining

techniques are subject to interpretation and analysis which leads

to speculation of the results. Pineri and others[16c,20] have

recently added a new dimension to the elucidation of the morphology

of ionomers by combining the techniques of electron spin resonance

(ESR), Mossbauer spectroscopy and small angle neutron scattering.

In their studies, Pineri et al. used Fe(II) complexes of

a butadiene-styrene-vinylpyridine terpolymer to obtain the most

definitive current experimental evidence for the state of

aggregation of salt groups in ionomers. By combining both neutron

and small angle x-ray scattering, which depends on the coherent

diffusion length rather than electron density, Pineri found that

the majority of clusters are less than 30 A in radius with the

average begin about 10 A. These results are in excellent agreement

with those of MacKnight, Taggart and Stein discussed previously.

Additionally, Mossbauer spectroscopy proved to complement the

scattering results. The resultant absorption spectrum gives

information about the electronic environment of the iron

nucleus. The results of Pineri reveal three types of structures:

dimers, quasi-isolated complexes, and clusters. Considering the

quasi-isolated complexes along with the clusters it becomes apparent

that together such structures are identical to the "shell-core"

model. Even the sizes of the clusters determined by this technique

are nearly identical to the MacKnight, Taggart, Stein Model. Thus,

especially in the case of transition metals, the basic structural

entity may be a coordinated complex rather than an ion pair.

D. Physical Properties of Ionomers

   1. Relaxation Behavior

It is now well established that the physical properties of

polymers can be modified profoundly through ion corporation. In

many systems, the polymer matrix is effectively "crosslinked"

through association of the ionic groups. The ionic aggregates

can relax thermally, with the temperature of the relaxation

depending on a range of molecular parameters which influence

the structure of the ionic domains. The relaxation of the ionic

aggregates therefore yields a new transition in addition to that

of the glass transition of the matrix. This new transition peak

usually appears at a higher temperature than that of the matrix.

Moreover, the glass transition of the polymer matrix is also caused

to rise as a result of the strong ionic interactions.

Many studies have been devoted to the elucidation of the structures of ionomers and their effect on various physical properties. As mentioned in the Introduction, the earliest investigations dealing with the physical properties of ionomers were based on ion-containing rubbers. Evidence from small angle x-ray scattering, neutron scattering, electron microscopy and Mossbauer spectroscopy has shown that ionic clusters exist in rubber based ionomers. In general, it has been found that the glass transition temperature, T_g, does not change upon neutralization and the fact is considered to be evidence for micro-phase separation. However, in the work of Otocka and Eirich[36], large linear increases in T_g with ion content were observed for both metal carboxylate and pyridinium iodide copolymers. This regular increase in T_g with ion content was explained as due to only ion quadrupole crosslinking. However, the same effect would result if a fraction of the ionic material remained as isolated complexes or quadrupoles and the remaining ionic groups were segregated into a separate phase. Therefore a regular increase in T_g with ion content does not by itself rule out the possibility of clustering.

The viscoelastic properties of styrene based ionomers were first investigated by Fitzgerald and Nielsen[37] as well as Erdi and Morawetz[38]. The main body of experimental investigations concerning the relaxation behavior of styrene ionomers consists of a group of articles by Eisenberg and coworkers.[39] The T_g's measured by differential scanning calorimetry (DSC) are observed

to monotonically increase as a function of salt group concentration for both low and high molecular weight styrene-sodium methacrylate copolymers. It is interesting to note that no discontinuity is observed near six mole percent which is the minimum concentration for ionic clustering on the basis of x-ray evidence.

Eisenberg et al. also showed that cesium ions yield crosslinks of lower stability than sodium but that the counter ion type does not affect the critical ion concentration (onset of clustering). The presence of un-neutralized acid groups suppress ionic clustering and decrease the effectiveness of the ionic multiplets as crosslinks. In addition, it was observed that the percent neutralization and not the cation type is the most important factor in determining the rheological properties. The higher the percent neutralization, the higher the initial modulus and the faster the rate of relaxation.

2. Dynamic-Mechanical Behavior

The modulus of a polymer is determined by the hinderance of seg-mental motion. Significant slowing of this motion occurs at the ion concentration at which the length of the moving segment becomes longer than the average interion distance. Thus, to reach a certain modulus at a certain ion concentration, a specific number of repeat units would have to be in cooperative motion. At this particular value of modulus and ion concentration, the average interion distance and the length of the moving segment will be equal. Therefore, a rearrangement of the ionic multiplets is not required

for relaxation of the segment. However, if more than one ionic group
is present in this moving segment, it will slow down the relaxation
since being incorporated into a multiplet, the segment has to be
released in order to move.

The dynamic-mechanical properties of elastomeric ionomers
show that there is very little increase in T_g with increasing degree
of neutralization.[16c,35b,36a,b] In the case of the butadiene-styrene-
vinylpyridine terpolymer the βrelaxation which is associated with
T_g, remains constant at $-56^{\circ}C$ regardless of the percent neutralization.
The αpeak at $67^{\circ}C$, which is assigned to the breaking and reforming
of isolated ion pair - ion pair associations, does not occur at
high levels of neutralization but instead a second maximum, labeled
α', occurs at $57^{\circ}C$ and is broadened and shifted to higher
temperatures at the highest levels of neutralization. The α'
relaxation is thus assigned to motion occuring within the larger
aggregates or clusters. Pineri speculates that this is evidence for
phase separation and that a small fraction of polymer also contains
hydrogen bonded groups as well.

In the work of Eisenberg and Navratil[39e], two loss peaks
were observed for styrene-methacrylic acid copolymers containing
less than six mole percent sodium methacrylate. It has shown
that the glass transition, labeled β increases in temperature with
increasing ion content, while a higher transition labeled α, remains
relatively constant. However, at concentrations above six mole
percent there is a continuous increase in the αpeak along with a

broadening of the β peak. Thus, from these results it is apparent
that there is a distribution of relaxation processes occurring
which are associated with a distribution of ionic aggregate
sizes. At low concentrations, where phase separation is not
dominant, the α relaxation above T_g is due to isolated multiplets.
At higher concentrations, where phase separation is more
efficient, the broader, higher temperature relaxation occurs
due to the motions of salt groups in large clusters which themselves
also have a distribution in size.

Work on the dynamic-mechanical properties of crystalline
ionomers has centered around the sodium salt of ethylene-
methacrylic acid copolymers.[40] In general, the response for both
the parent acid copolymer and its salts resembles that of low
density polyethylene. In the acid copolymer a relaxation
labeled β', occurs between 0 and 50°C depending on the concentration
of acid comonomer. This peak is assigned to the micro-Brownian
segmental motion accompanying the glass transition. The increased
temperature of this peak over that of branched polyethylene (-20°)
is attributed to dimerized carboxyl groups. As the acid groups are
neutralized the β' peak disappears completely and the β peak
shifts to lower temperatures. The β peak is therefore assigned
to a relaxation occurring in the amorphous branched polyethylene
phase from which most of the ionic material has been excluded.
As the percent crystallinity increases, the temperature of the β
relaxation is seen to increase. For a dry, annealed 95%

neutralized sodium ionomer, the β peak is also seen to decrease
in temperature as the amount of acid comonomer is increased. In
addition, an α relaxation occurs which moves to higher temperatures
with ion content and which is assigned to motions within the
ionic phase. Thus, the similarities between low density poly-
ethylene and the ethylene ionomers is due to phase separation of
the ionic material from the amorphous polyethylene phase. This then
allows the relaxations of each phase to occur somewhat independently
of each other.

3. Recent Advances in the Structure-Properties of Ionomers

Today ionomers are finding their way into packaging materials,
electronic components, electrochemical separators, membrane
technology and even the human body. But in order to optimize
their performance, one must come to understand how to control their
behavior by understanding the nature of the ionic interactions.
Thus, much of the recent work in ionomers has been directed toward
such an undertaking. With a better understanding of the effects
of ionic groups on polymer properties, recent work on ionomers has
included a great deal of application of ionomer theory in order to
help modify existing polymer systems so as to improve their
performance as well as increase their range of application. A
review of such recent studies has recently been given by MacKnight
and Earnest.[1]

Several new ionomer systems were developed by MacKnight and coworkers as a result of post polymerization reactions carried out on polypentenamer.[41] The aim of these studies has been the preparation of derivatives containing side groups of different chemical nature and concentration but with identical chain backbones.

The most complete study of the properties of substituted polypentenamers and the most relevant to this thesis is that of the sulfonated derivatives by Rahrig.[42] Of greatest interest here is the small relaxation, labeled α, located near -13°C. This relaxation increases in magnitude as the degree of sulfonation increases thereby indicating that it is due to the ionic groups. By saturating the sample with water the α relaxation is destroyed leaving only the β relaxation unaffected.

For polypentenamers sulfonated above 10 mole percent, the T_g measured by DSC is observed to increase sharply with ion concentration. This large increase in T_g may be due to the reinforcing and constraining effects imposed by clustered salt groups. Therefore, the ionic aggregates have not only phase separated from the amorphous regions but also are continuing to oppose segmental motion as well. This is born out by the fact that such a rapid increase in T_g cannot be explained by the copolymer effect.

The best evidence for a separate ionic phase comes from studies of water saturated materials. The hydrogenated sulfonated polypentenamers absorb about eleven molecules of water per sulfonate group and the effect of this on the dynamic-mechanical response is

drastic. As was the case in the unsaturated sulfonate salts, the α relaxation is lowered over 150°C by the influence of this water.

Studying the effects of the type of pendant acid group in polypentenamer, Rahrig found that the strength of the ionic interactions were roughly of the order: phosphonate >sulfonate > carboxylate =thioglycolate. Similarly, in comparison of the physical properties of polystyrene containing identical amounts of either carboxylate of sulfonate salts, Lundberg and Makowski found comparable results.[43]

Using ionomers prepared by attaching the respective salt group directly to the phenyl ring with a post polymerization reaction which presumably does not alter the molecular weight, Lundberg and Makowski showed that the increased ionic association of the sulfonated salts was responsible for their higher T_g's and melt viscosities. It was also found that the effects of the sulfonate salts could be greatly reduced using polar plasticizers.[44] The reduction in melt viscosity is much greater in the case of glycerol which supposedly migrates to the ionic phase than for dioctyl phthalate (DOP) which plasticizes the hydrocarbon polystyrene backbone. Since this effect cannot be entirely due to the depression of T_g, it is concluded that the ionic associations can be pre-ferentially plasticized with polar substances while the backbone may be independently plasticized by a less polar substance.

An example of a direct application of ionomer theory to produce a workable material is a class of ionomers based on

lightly sulfonated ethylene-propylene-diene (EPDM) terpolymer.[45] Residual unsaturation is incorporated in this system through the use of a diene termonomer such as 5-ethylidene-2-norbornene (ENB). Sulfonation of the ENB portions is done by the reaction of acetyl sulfates. The salt forms of sulfonated EPDM's are somewhat thermoplastic in nature but because of the temperature dependence of the ionic associations their processing behavior is best controlled through the use of preferential plasticizers. Agarwal and others[46] have shown that certain metal derivatives of fatty acids, notably zinc stearate, could markedly improve processability as well as mechanical properties of sulfonated EPDM's. Plasticization of the ionic phase with stearic acid derivatives causes a reduction in melt viscosity. Depending on the stearic acid salt used, the stress-strain properties may also be affected. Although quantitative reasons for this behavior are not known, it is evident that the melt properties and possibly the structure of these ionomers are significantly dependent on the neutralizing species and not simply on whether the cation is monovalent or divalent. This is borne out by the fact that the amount of water absorbed by these materials is dependent on cation type as is also the dynamic-mechanical behavior.

Today, several ionomer systems are under extensive investigation. One of these which has recently become increasingly important in electrochemical applications is the Nafion[R] ionomer system. These materials were developed by the duPont Company as electrochemical

separators about ten years ago.[47] They consist of hydrophobic fluorocarbon backbone chains with hydrophillic perfluorinated ether side chains which are terminated by alkali sulfonate salt groups. The Nafions posess many exceptional properties which are not encountered in other ionomers such as high water permeability[48], permselectivity to ions[49], and durability in harsh environments[50].

An interesting and important aspect of Nafion membranes is their ability to absorb relatively large amounts of water. The effects of this water on their behavior have been studied extensively.[51] The polymers typically absorb 10 to 50% of their dry weight in water, depending on polymer equivalent weight, counterion, temperature and prior thermal history. Counterions with large hydration energies increase water uptake as does lowering the equivalent weight. In addition, it is interesting to note that up to 50% more water is taken up if the materials are boiled in water compared to room temperature equilibration. This increase of water is permanently retained after cooling suggesting a swelling of the ionic domain regions.[52]

Using heats of dilution, sorption-desorption curves and Mossbauer spectroscopy, Rodmaqc and others, have found that in sodium Nafions, three to four water molecules are present for each ionic group at equilibrium.[51d] Similar work with iron salts gave a value of four to five. In addition it was found that water is located very close to the iron cations in various complexed structures depending on the amount of water present. These results

are supported by a sodium-23 NMR study.[53] In this study, Mauritz

and Komorski found that decreasing the water content or increasing

the temperature results in an increased interaction between the

sodium cation and the polymer matrix. An equilibrium is established

between bound and unbound sodium cations when the proportion of

water molecules to ionic groups is four, the limit in the first

hydration shell of sodium. If less water than this is present,

contact ion pairs form. Similar studies on crosslinked polystyrene

sulfonate resin gave a value of three to four water molecules per

ionic site.

The first interpretation of the effects of water on the

dynamic-mechanical properties of Nafion is that of Yeo and

Eisenberg.[50b] In their studies, they found the rate of diffusion

of water in sodium Nafion membranes to be relatively close to the

self diffusion coefficient of water. The usual diffusion coefficient

of water in a polymer such as polyethylene or polytetrafluroethylene

is three to four orders of magnitude slower. The introduction of

ionic groups into the polymer does not necessarily have to

increase this rate of diffusion, though. In the case of polystyrene,

it is reduced by a factor of 300.[54] Thus, the transport of water

in Nafion membranes may be directly related to their particular ionic

cluster morphology.

Since Nafions exhibit ionic clustering they are capable of

absorbing large concentrations of water due to the high con-

centration of ions present in each cluster. It also has been

shown that this water breaks down the time-temperature superposition in these ionomers possibly because it increases the degree of clustering.[55] This behavior, though opposite that exhibited by ethylene-methacrylic acid ionomers which show a decrease in clustering with water[30], is supported by the fact that water does not affect the glass transition temperature of Nafions since it would localize in the phase separated ionic regions.[50b]

The recent observations of water sensitivity of the primary relaxations of Nafions has led to conflicting ideas regarding the assignment of the relaxation mechanisms for the α and β peaks. Thus a summary of the evidence to date seems appropriate in order to understand the phenomena that make these assignments difficult.

Yeo and Eisenberg compared the DSC glass transition temperatures of different Nafions and of polytetrafluroethylene.[50b] They found that the incorporation of ions into the polymer extends the glassy state to higher temperatures. Except for lithium, this increase in T_g was found to be inversely proportional to the ionic size and unaffected by low levels of water. These results were supported by the dynamic-mechanical relaxations as well. In the salts, the position of the αpeak for Na^+, K^+, and Cs^+ salts was in good agreement with the q/a effects which has been found operative in many ion-containing systems.[56] This effect suggests that the glass transition should be proportional to the ratio of the charge, q, to the distance between the charges, a.

The effect of water on the dynamic-mechanical β peak in acid (23°C, dry) was found to move to lower temperatures with increasing water content. Similar behavior was seen with the salts' β peak (150°C, dry), again moving to lower temperatures with increasing water content, although now much smaller. The downward motion of the peak with increasing moisture parallels the behavior found in other polymers, such as polyacrylamide[57], nylon[58], and polyvinyl alcohol[59]. This type of behavior is most probably due to a change in the nature of the group responsible for the relaxation and/or a change in the barrier of rotation for that group. Yeo and Eisenberg conclude, though, that it is possible that this relaxation involves the glass transition of the ionic clusters as evidenced by the decrease in peak temperature with water content. In addition, they point out that the loss modulus decreases with water content and is unusually low just before the α relaxation. They suggest that since the density of the salts are much lower than the Nafion precursor, some form of unusual packing is to be expected which would correlate with the high degree of water transport observed.

Phase separation of the ionic regions from the backbone in Nafions is probably ill-defined especially at low levels of water. Recently, Roche and others have used small angle neutron scattering (SANS) to study the phase separation in these systems.[51d] They found that at high water content Nafion membranes are essentially two phases with the water molecules clustered in one phase and the perfluroethylene backbone in another. The transition zone between

the two phases was found to be small. At lower levels of water content the two phases become ill-defined and deviate from two phase behavior. Thus, whatever happens in one phase would be expected to have some effect on the other phase. Another fact is that since the matrix and the ionic regions are in such proximity, the water molecules may also interact with the matrix. Thus, plasticization by water may affect not only the molecular motion within the ionic domains but also the fluorocarbon as well.

In the DSC studies of Yeo and Eisenberg, the primary relaxation moved to higher temperatures upon drying as well as upon increased ion content. This indicates that the α relaxation is associated with the ionic regions. The best evidence for this may be the qualitative comparison of the tanδ behavior with other ionomers.[60]

In hydrocarbon ionomers, two tanδ peaks are usually observed. The one occurring at low temperatures exhibits a similar gradual movement to higher temperature with increasing ion content and has been identified with the matrix glass transition. The higher temperature peak, which is found about 50 to 150°C above the T_g of the pure matrix, shows a marked counterion sensitivity and shifts dramatically to higher temperatures with increasing ion content. These features are also observed in Nafions.

Hence, it seems reasonable to reverse the original assignments of the α and β peaks. Such a reversal has been proposed recently by Eisenberg at a symposium on perfluorinated ionomer membranes.[61] By switching these assignments it helps clear up some long standing

questions. The problem of low modulus at the α temperature is no longer a problem if one assigns the β peak to the glass transition of the matrix. Thus, observation of an ionic relaxation above the matrix T_g would be consistent with other ionomer relaxation behavior. In addition, if time-temperature superpositioning is now done with the β peak temperature as the reference, the relative positions of the master curves for the precursor, acid form, and various salt form become more understandable.

4. Interactions of Sulfonates with Water

In this last section of review a comparison of ionic sulfonates will be given especially in relation to the effects of water on their ionic selectivity and resultant properties. The general properties of sulfonate ion exchange materials have been well characterized, therefore, comparison of their properties with Nafions' as well as other ionomers' should prove useful.

Although Nafions may first be expected to demonstrate ion selectivity behavior similar to other sulfonate resins, there are several notable differences between the two types of polymers. Since Nafions are presumably not crosslinked, solvent swelling will be far more dependent on counterion type and thermal history than in the case of sulfonated poly (styrene sulfonate) resins. Secondly, the phenomena of ionic clustering in Nafions would be expected to affect their selectivity properties since such clusters will exist as microphase separated regions, something not possible

for crosslinked polymers.

Divinylbenzene crosslinked poly (styrene sulfonate) exhibits cation selectivity sequences which are theoretically predictable by Eisenman's theory of ion exchange.[62] In this approach the electrostatic field strength of the anionic exchange site is found to be the principal factor in cation selectivity. Because sulfonate anions have relatively low charge density, the order of cation affinity is also determined by the respective free energies of hydration. Cations with smaller hydration energies gain more energy by interacting with the anionic exchange site and therefore are the more preferred.

Thus, the order of selectivity for alkali metal ions in a sulfonated environment is usually $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+ > H^+$. It should be pointed out that the amount of absorbed water present will affect the magnitudes of the selectivity but not the sequence. At high water content, the differences in relative selectivity between the cations will be greatly reduced. In the case of crosslinked poly (styrene sulfonate), the selectivity has also been shown to be affected by the amount of crosslinking.[63] Thus, the overall selectivity properties of a resin are determined by a combination of interrelated effects such as ion-exchange capacity, crosslinking and water absorption.

Even though Nafions possess notable differences in behavior from other sulfonated resins, it is still useful to compare their properties to those of poly (styrene sulfonate). Boyd discusses

hydrogen ion to metal exchange for poly (styrene sulfonates) in terms of enthalpy, entropy, and volume changes of reaction.[64] Enthalpy and entropy changes are small and negative for alkali metal exchange in low crosslinked poly (styrene sulfonate). No evidence for ion pairing was found and so the thermodynamic behavior was believed due to differences in ionic hydration between the two exchanging ions. Ion pairs may form for higher crosslinked resins at low water content due to increased electrostatic interactions. In contrast, positive entropies appear to be involved in divalent to univalent cation exchange. This is most likely due to a gain in entropy of solution when a divalent cation is replaced by two univalent ions which have much smaller hydration energies. As divalent ions are removed, larger amounts of water are released as well.[65] This release of water will cause a positive entropy change in the system and because of the energy required to dehydrate a divalent cation, the enthalpy of exchange will also tend to be positive.

A major factor in ion selectivity of Nafions thus appears to be the positive entropy changes associated with replacement of hydrogen by a metal cation. In all cases this exchange is accompanied by water release and polymer contraction which are both entropy producing processes.[66] Thus it would appear that the entropy increase upon desorption of water is responsible for the ion selectivity in Nafions.

From this review of ionomer theory and comparison of ionomer
behavior it should be apparent that regardless of the starting
polymer, incorporation of ions into a polymer leads to a material
which is often quite different. In addition, the properties of
ionomers seem to be common to many ionomer systems regardless of
the nature of the backbone. Therefore, the basis for the explanation
of the behavior of sulfonated polysulfone ionomers will come not
only from ionomer theory but also from the behavior of other sul-
fonated materials such as polypentenamer, EPDM, polystyrene and
polytetrafluroethylene.

C H A P T E R II

POLYSULFONE: Properties and Modification

A. Background

Polysulfone, a high performance, tough, temperature resistant
thermoplastic, was introduced by the Union Carbide Company in 1967.[67]
Because of its thermoplastic nature and retention of properties under
relatively harsh conditions for polymers, polysulfones have found
application in such areas as the production of electronic and elec-
trical equipment, home appliances, and microwave cookware.

The polysulfone evaluated in this study is the bisphenol A
based poly(aryl ether) sulfone manufactured by Union Carbide as
Polysulfone P-1700. It is prepared by a nucleophillic displace-
ment reaction involving the sodium bisphenolate with an activated
diphenyl sulfonyl halide.

Many aromatic polyethers, like polysulfone, have been prepared
by the solution condensation of a dialkali metal salt of a
dihydric phenol with an activated or negatively substituted aromatic
dihalide in an anhydrous dipolar aprotic solvent at elevated temper-
atures. In general, the reaction is rapid, free of side reactions,
and yields polymers of good color and texture. Bakelite poly-
sulfone (Union Carbide's P-1700) is thus prepared in this manner
by reacting the disodium salt of bisphenol A with 4,4' dichloro
diphenyl sulfone in dimethyl sulfoxide. Only aprotic, dipolar
solvents are useful in this polymerization. Water or other competing

35

nucleophilles must be absent if high molecular weights are to be
obtained. Besides providing a good solvent system, the highly polar
solvent is believed to be essential in providing the rapid polymer-
ization rates observed. The rates of polymerization are also found
to depend on the basicity of the bisphenol salt and upon the electron
withdrawing power of the activated group in the dihalide. The
resulting polyethers are amorphous, rigid, tough thermoplastics with
high glass transitions. In addition they possess noteworthy thermal
stability and electrical properties. A summary of basic mechanical
and physical properties is given in Table 2-1.

Polyethers, in general, are not soluble in or affected by
aqueous inorganic bases or acids. They are generally soluble in
polar organic solvents such as polar aromatics, chlorinated hydro-
carbons, dimethyl formamide and N-methyl pyrrolidone. Polysulfone
possesses excellent thermal stability up to 400°C in absence of
oxidizers in spite of the presence of methyl groups along the chain.
From thermal analysis work, the bond dissociation energies for
polysulfone were determined and are contained in Table 2-2.

Two major schemes have been proposed for the degradation of
polysulfone based on the identification of sulfur dioxide and
methane by mass spectrometer-pyrolysis studies.[67] The first is
based on rupture of the sulfone link producing a phenyl and
sulfonyl radical. These in turn will produce a diphenyl link
with the expulsion of sulfur dioxide in the case of the sulfonyl
radical. The second scheme involves the loss of a methyl group

producing methane as well as various by-products from the remaining bisphenolate radical.[67] Additionally, at very high temperatures (>500°C), phenol and other aromatic ether degradation products were also identified. Thus, the weakest links in the polysulfone repeat unit are the carbon to sulfur bond between aromatic rings and the carbon to carbon bond between the methyl group and the center carbon of the isopropylidene moiety.

The properties of polysulfone have been evaluated by many researchers. The most important of these, in relation to this thesis are those involving the dynamic-mechanical spectra and the effects of the presence of low molecular weight diluents on these properties. Since polysulfone is a high performance thermoplastic, its low temperature mechanical behavior should exhibit relaxations which bear this out. Johnson[67], among others, showed the existence of a relaxation at -100°C as evidence for the material's toughness and high impact strength. Unfortunately though, results on the full dynamic - mechanical spectra of polysulfone differ from one researcher to another.

In general, most researchers report a γ relaxation in the region of -120 to -100°C that is effected by the presence of water. In addition, some researchers report a β relaxation in the range of -50 to -40 C which is only present in samples containing water. The α relaxation, taken to be the glass transition, is reported to be between 185 and 195°C depending on the type of measurement used. The proposed mechanisms for these relaxations are even more diverse than

the identification of the relaxations themselves.

The dynamic-mechanical properties of poly(aryl ethers) such as polysulfone have been investigated by several researchers. Heijboer[68] observed a secondary relaxation at approximately $-100^{\circ}C$ and noted its position and magnitude were affected by annealing. Baccareda[69] detected another transition at $-45^{\circ}C$ and showed the size of the loss peak was significantly increased by water absorption. Robeson and Faucher[70] noted a transition at $-100^{\circ}C$ and showed it could be almost completely eliminated using low molecular weight diluents as antiplasticizers. Kurz and others[71] studied polysulfone along with other related poly(aryl ethers), namely poly (4,4'-oxydiphenylene sulfonyl) (PODPS) and poly (4,4'-methylene diphenylene sulfonyl) (PMDPS). All three polymers contained a diphenyl sulfone link and all possessed a relaxation at $-110^{\circ}C$. For PODPS and PMDPS, transitions at 0° and $15^{\circ}C$, respectively, were observed as well. They concluded that the low temperature relaxation is due to a molecular process directly involving the sulfone group, since it is the logical portion of the molecule to be affected by water absorption. Similarly, Allen and coworkers[72] reported the affect of water on the low temperature relaxation is related to the polarity of the molecule. They concluded, however, that the low temperature relaxation could be due to paraphenylene linkages which are affected by water absorption. Their conclusion is based partly on the fact that the low temperature relaxations of other systems such as polyphenyleneoxide $(-60^{\circ}C)$[72] and polyethyleneterephthalate $(-40^{\circ}C)$[73] also exhibit similar behavior.

In order to try to elucidate the relaxation mechanisms in polysulfone, Robeson, Farnham and McGrath studied the effects of substitution in the polysulfone system.[74] The effect of substituents on the phenylene units of polyesters and polycarbonates has shown to have dramatic effects on the secondary loss behavior.[75] In polycarbonates, dimethyl substitution on the bisphenol A portion showed no effect on the -100°C transition whereas tetrachloro substitution results in shifting the transition up to 80°C. In the particular case of polyethyleneterephthalate though, dimethyl substitution does cause the secondary loss transition to shift from -80°C to 60°C. In Robeson's work, dimethyl substitution in polysulfone shifts the peak from -100°C to 45°C, while tetramethyl substitution gives a very complexed spectra.

Robeson's results with dimethyl substituted polysulfone show no prominent transition at -100°C when dry but a definite resolvable transition when wet. This fact along with other results on non-sulfone containing poly(aryl ethers) leads them to suggest that when dry the small transition at -100°C in polysulfone is due to the aryl ether groups. Upon water absorption another transition, involving a sulfone-water complex, appears which overlaps the aryl ether relaxation. Thus, it is necessary to conclude that these results do not agree with those of Kurz or Baccareda. Robeson and the others point out that sulfonation of the polysulfone molecule does not affect the large transition at -100°C when the sulfonation level is high (both acidic and salt forms) and water is present.

B. Sulfonated Polysulfone

    1. Sulfonation

Sulfonation is a powerful and versatile polymer modification tool. Many homopolymers, random copolymers, and graft copolymers containing aromatic rings or double bonds have been sulfonated.[76] Polysulfone, being a high performance thermoplastic resin, is thus an excellent candidate for chemical modification by sulfonation. Sulfonated polysulfone membranes have been reported to be useful in desalination applications.[77]

Polysulfone P-1700 can be sulfonated at room temperature in 1,2 dichloroethane using a 2/1 sulfur trioxide to triethyl phosphate (SO_3/TEP) complex as the sulfonating agent. The resultant polysulfone sulfonic acid is neutralized with sodium methoxide to produce the sodium salt or with cesium acetate to produce the cesium salt. Compositions ranging from 0.1 -SO_3Na groups per polysulfone repeat unit to 1.0 -SO_3Na can easily be synthesized by varying the SO_3 to polysulfone ratio.

SO_3/TEP was used as the sulfonating complex since the high reactivity of the SO_3 can be conveniently controlled by varying the SO_3/TEP ratio and since this complex minimizes crosslinking due to sulfone forming side reactions.[78] Sulfonation is very facile at room temperature using such a 2/1 complex due to the weak bonding of the second molecule of SO_3 with one of the TEP ester oxygens. Lower ratios do not give sufficient sulfonation and higher ratios

are unnecessary. In addition to thorough and uniform sulfonation, polysulfone can first be molded or processed into films or fibers and surface sulfonation performed as well. In order to ensure proper surface sulfonation, the SO_3/TEP complex is added while in a cyclo-hexane or tetrachloroethylene solution.

The free acid form is soluble in several organic solvent systems but the salt forms are soluble only in polar solvents such as DMF, DMSO, methyl pyrrolidone and diethylene glycol monoethyl ether. Even this solubility, though, is dependent on the degree of sulfon-ation and counterion type. DMF is a good solvent for the preparation of solution cast films but it does have the drawback of difficulty of solvent removal.

Nuclear magnetic resonance (NMR) of the sulfonated material indicates that the sulfonation occurs predominantly (>80%) ortho to the ether bond in the bisphenol A portion.[79] This conclusion is supported by the fact that bisphenol S polyether, $\{-O-\emptyset-SO_2-\emptyset-\}$, does not undergo sulfonation under the same reaction conditions most likely because the phenyl groups of the sulfone portion are electron-ically deactivated.

2. Properties Measured to Date

The introduction of ionic groups into polysulfone dramatically increases the glass transition temperature, T_g, by as much as $130^\circ C$. This is probably due to increased intermolecular association as well as to increased molecular bulkiness. Noshay and Robeson have shown

that this increase in T_g is linear with the degree of sulfonation.[80] Their mechanical loss data indicates that compositions containing 0.5 and 1.0 $-SO_3Na/PSF$ have T_g values of 240°C and 300°C respectively, compared to 180°C for the unmodified polysulfone. Not surprisingly, the value for the free acid form at 1.0 $-SO_3H/PSF$ is 230°C, significantly lower than for the sodium ion form. This demonstrates the importance of ionic interactions in increasing the glass transition.

The effect of sulfonation and subsequent neutralization on the reduced viscosity of polysulfone sulfonated to the extent of 0.3 $-SO_3Na/PSF$ reported by Noshay and Robeson are quite puzzling. The reduced viscosity was essentially the same for polysulfone, the sulfonic acid, and the sodium salt. There is no guarantee, of course, that there is no molecular weight changes during the sulfonation. Also at a particular concentration the degree of chain expansion due to intramolecular ionic interactions and the effects of intermolecular repulsive forces as well as chain extension in solution, may all balance out so that solution viscosities would not be good indicators of increased interaction in these ionomers. Robeson and Noshay suggest, though, that such results indicate that no drastic degradation or crosslinking occurred upon sulfonation, at least at this composition.

Noshay and Robeson also reported findings of a low temperature transition similar to that of polysulfone. While polysulfone's transition at -100°C is enhanced by water, sulfonated polysulfone's

43

behavior is somewhat different. The -100°C transition is in-
fluenced significantly by sulfonation. The free acid form displays
a -100°C transition which is enhanced by water absorption to a much
greater extent than is unmodified polysulfone. However, Noshay and
Robeson report that the sodium ionomers display different behavior.
When dry, the -100°C transition is significantly reduced in magnitude
and located at higher temperatures, especially at higher sulfonation
levels. Upon exposure to water the -100°C transition is restored
and enhanced in magnitude. They go on to explain this behavior in
terms of the 'ionomer concept". They claim that the transitional
shift to higher temperatures when dry is due to intermolecular
clustering of the ionic groups which thus increases the energy
barrier of relaxation. Restoration of the -100°C transition in the
presence of water is thus due to dissociation of the clusters.

It should be pointed out that Noshay and Robeson's results were
obtained with compression molded samples which have been shown by
them to give different results than solution cast films. Their
results were not repeatable using solution cast films and the
results were quite different. A major reason in the difference may
be the high melt viscosity of the sulfonated ionomers which prevents
uniform films from being produced without some degradation.
Presentation of results on solution cast films as well as reasons
for the difference between them and compression molded films are
presented in the next chapter of this thesis. In addition, the
samples studied by Noshay and Robeson also displayed a transition

between the one at -100°C and the glass transition but they gave
no explanation of its cause. The next chapter will thus present a
full discussion of the transitions in polysulfone and its sul-
fonated derivatives.

The only other reports in the literature on sulfonated poly-
sulfones are two concerning desalination membrane feasibility
studies.[81] These report good results from moderately sulfonated
membranes because they have a good water permeability to salt
permeability ratio. In addition, because of the material's stiffness,
chemical resistance and thermal stability, they are excellent
candidates for electro-chemical separation processes involving harsh
conditions. Thus, they can be made into thinner films with longer
lifetimes than standard cellulose acetate films. One particular
result from these studies in relation to this thesis is the amount
of water absorbed by the sulfonated polysulfone material. Brousse
and others [81a] found that a a 0.25 sulfonation level, 2.5 water
molecules per ionic site were absorbed; while at a 0.40 sulfon-
ation level 3.5 water molecules per ionic site are present.

Since, uncertainity in the low temperature mechanical spectra
of polysulfone exists and due to an absence of any information on
the sulfonated systems, a major portion of this thesis will be
devoted to the study of the dynamic-mechanical properties of poly-
sulfone, the effects of sulfonation on the dynamic-mechanical
spectra, and the effects of low molecular weight diluents on this
spectra. In order to fully understand the role of low molecular

weight diluents on mechanical properties, other studies to determine

the micro and macroscopic structure of these polymers as well as the

mechanism behind the diluent's diffusion will also be discussed.

Thus, this dissertation extends the study of the dynamic-

mechanical properties of sulfonated polysulfone, helps clarify the

mechanisms for the transitional behavior in these systems and most

importantly, devotes attention to the ionic interactions and their

importance in determining material properties of ionomers. In

addition, this thesis hopes to shed some light on the behavior of

such ion-containing systems in order to be able to better control

their behavior and thus increase their range of application.

C H A P T E R III

SULFONATED POLYSULFONE: Structure-Property Relationships

A. Introduction

Many ionomers are produced by copolymerization reactions and
thus it is not always possible to alter the nature and/or concen-
tration of salt groups without affecting the other molecular para-
meters such as molecular weight and ionic group sequencing. This
factor presents a serious obstacle to a meaningful study of the
effects of the nature and concentration of salt groups on the
ionomeric properties. One method of avoiding this drawback is the
preparation of materials by post polymerization reactions on a
common precursor. It is this concept that has led to continuing
investigations especially in the area of sulfonated ionomers.

The objective of post polymerization, therefore, is to prepare
a range of ionic group concentrations while keeping all the other
parameters relatively constant. It is thus necessary to carry out
the reactions under conditions which preclude backbone modification
by chain scission of crosslinking. Recently, polysulfone has been
successfully sulfonated using a 2/1 complex of sulfur trioxide and
triethyl phosphate and isolated in both the acid and salt forms.

While the preparation of sulfonated polymers is an area where
much effort has been directed[32], the preparation of a stable, highly
sulfonated system free of covalent crosslinks had not been prepared.
Even for polymers with fully saturated backbones, sulfonation reactions

generally lead to the formation of some covalent crosslinks, quite often in the form of sulfone links.[83] In the case of sulfonation with SO_3, the reactivity of the SO_3 can be regulated by the nature of the reagent.[84] Recently, using SO_3 to trialkyl phosphate ratios of 2/1 to 4/1, the preparation of sulfonated polymers free from covalent crosslinks have been reported.[78,80] These cases generally involve the sulfonation of aromatic rings although Cantor has successfully sulfonated butyl rubbers.[83] Turbak has demonstrated that 2/1 complexes of SO_3 with trialkyl phosphates, under the proper conditions, will yield exclusively alkene sulfonates while other complexes may give a mixture of products.[78,84] Thus these factors suggested that a 2/1 SO_3 triethyl phosphate complex would be a good reagent for the sulfonation of polysulfone.

The battery of techniques used in this investigation, including Fourier transform infrared (FTIR), x-ray scattering, thermal analysis, and dynamic-mechanical relaxation, and generally useful for establishing the structure-property relationships in a polymer. Specifically, these tests will be used jointly in order to determine not only the basic structure-property relationships but also in order to determine the nature of the ionic associations (i.e., multiplets and/or clusters) present.

Overall, this thesis accomplishes four major goals. First, it determines to what extent ionic clustering occurs in sulfonated polysulfone ionomers. Second, using the results of differential scanning calorimetry, dynamic-mechanical measurements and small

48

angle x-ray scattering, it determines the extent and importance of
ionic interactions, the mechanism by which they work and their
influence on the properties of polysulfone. Third, again using
dynamic-mechanical measurements as well as diffusion data, it inter-
prets the effects of water on the properties of these ionomers,
especially in relation to Nafions and other sulfonated ionomers.
Lastly, from a study of the effects of low molecular weight diluents
on the material properties, it provides insight into the use of
sulfonated polysulfone ionomers through an understanding of the
effectiveness in controlling their behavior.

B. Experimental

Materials

Polysulfone (PSF). The starting precursor polymer in this
work was that which is commercially available from Union Carbide
under the tradenames of either Union Carbide Bakelite Polysulfone
or Union Carbide Polysulfone P-1700. Its number average molecular
weight is about 60,000.

Sulfonated Polysulfone (SPSF). The polysulfone mentioned
above was sulfonated using a 2/1 sulfur trioxide (SO_3) to triethyl
phosphate (TEP) complex in 1,2 dichloroethane at room temperature.
The resultant sulfonic acid was neutralized with either sodium
methoxide or cesium acetate depending on the salt form desired.
Compositions ranging from 0.25 ionic groups per polysulfone repeat
unit ($-SO_3^-X^+$/PSF) to 1.0 ($-SO_3^-X^+$/PSF) were prepared by varying the

49

initial SO_3 to PSF ratio. This synthetic procedure was performed by the Hybrid Cell Project Group of the Occidental Petroleum Company and the resulting samples kindly provided by them.

Characterization

Elemental Analysis. Elemental analysis, performed by the Occidental Corporation, was used to determine the degree of sulfonation by comparing the sulfur to carbon ratios of polysulfone and of the sulfonated material. Using sodium or cesium to sulfur ratio comparison, the degree of neutralization was also determined.

Nuclear Magnetic Resonance. NMR measurements were carried out on dimethyl sulfoxide-d$_6$ solutions of the precursor, the sulfonic acid and the salt forms using HMDS as the external standard. Proton NMR was used to determine if any crosslinking had occurred as well as for the determination of the sulfonate group's location on the polymer chain. Carbon-13 NMR was used to determine the degree of sulfonation in conjunction with the elemental analysis. All NMR measurements were performed by Occidental as well.

Infrared Measurements (FTIR). Solvent cast films were prepared from dimethyl formamide (DMF) solutions. FTIR spectra were obtained with a Nicolet Series 7199 FTIR Spectra System between 4000 and 400 wavenumbers (cm^{-1}) at a resolution of 2 cm^{-1}. The determination of the sulfonation level by FTIR was based on the ratio of the absorption at 1025 cm^{-1} (SO_3^- symmetric stretch) to the absorption at 1150 cm^{-1} (SO_2 symmetric stretch) or to the absorption

at 1015 cm^{-1} (aryl ether vibration). In addition, the infrared
spectra were also used to give a qualitative estimate of the water
content by examination of the 3200 to 3700 cm^{-1} region as well as
any other significant differences between the polysulfone resin and
its sulfonated forms.

Differential Scanning Calorimetry (DSC). DSC measurements
were performed using a Perkin-Elmer Model 2-B DSC with a computer
assisted baseline. The temperature range studied varied from one
experiment to another but the range of -35° to 365°C was covered
for a representative group of samples at a heating rate of 20°C per
minute. The effect of the heating rate was studied as well but
20°C per minute gave very consistent results. Indium, tin and
distilled water were used as calibration standards. The glass tran-
sition temperature was taken to be the midpoint of the change in heat
capacity. In addition to basic characterization, DSC measurements
were used to help determine the extent of phase separation, if any,
that occurs between the polymer matrix and the ionic regions, the
effects of sulfonation on the glass transition and the effects of
water on such behavior.

Experimental Techniques

X-Ray Scattering. Absorption and transmission coefficients
were obtained by use of a Siemens D-500 Wide Angle X-Ray Diffrac-
tometer. These coefficients were then used to determine the optimum
thickness for samples to be used in the small angle x-ray scattering
(SAXS) experiments. In addition, wide angle x-ray scattering was

used to determine if any crystallinity was present in the samples.
The SAXS measurements were done with a Kratky Small Angle X-Ray
Camera and a position sensitive detector using nickel filtered
copper radiation.

Dynamic-Mechanical Measurements. The dynamic-mechanical
measurements were carried out on a Vibron Dynamic Viscoelastometer
(Rheovibron), Model DDV-II (Toyo Measuring Instruments Company).
The temperature range of -160° to 320^oC (with temperature probe
modification) at a rate of about 2^oC per minute was examined.

The samples were run under a dry nitrogen environment at a frequency
of 11 Hz although other frequencies (1 and 110 Hz) were also tried.

Water Absorption and Diffusion Measurements. The quantity
and rate of water absorption was determined from timed experiments
of water uptake. The amount of water uptake was determined by changes
in weight as measured by a Mettler Microbalance with 0.01 milligram
accuracy. The samples were immersed in water, removed at the
appropriate times, blotted dry with filter paper and weighed before
being returned to the water. The time out of water was kept to a
minimum and averaged about 30 seconds. In addition to studies of
immersion in water at 25^oC, immersion at 50°, 75°, and 100^oC, being
exposed to pure water vapor in a 100% humidity environment and being
exposed to the relative room humidity under ambient conditions were
also studied. The diffusional information was obtained from equations
developed by Crank and Park.[85]

C. Results

Sample Characterization

The materials used in this study were characterized by the Occidental Petroleum Company. The polymers were analyzed in the form of thin films. The films were prepared by solution casting from dimethyl formamide, annealed at 150°C for 15 hours in vacuum, washed, and stored in an appropriate slightly basic solution until tested. The following designation will be used to describe the samples in this study:

- a. The ionic content will be described in terms of the number of ionic groups per polysulfone repeat unit.

- b. The counter ion type will be represented by the accepted IUPAC abbreviation for that element.

- c. The conditioning of the sample will also be noted by one of three terms:

    1. Wet - Referring to samples that were dried at 110°C in vacuum for 24 hours and then immersed in water at 25°C until no further weight gain occurred.

    2. R.H. - Referring to samples that were dried at 110°C in vacuum for 24 hours and then kept at ambient conditions to absorb moisture from the air. The samples were conditioned for two months without an equilibrium weight being achieved.

    3. Dry - Referring to samples that were dried at 110°C in vacuum for 24 hours and then stored in a vacuum desiccator until use.

- d. Any other characteristic information will be noted, especially if it differs from the above description.

Thus, 0.35Cs-Wet refers to a cesium sample containing 35 ionic groups per 100 repeat units and which is saturated with water. A listing

of the samples used is in Table 3-1 along with characteristic
information such as sample thickness and ion-exchange capacity.

The Fourier Transform Infrared (FTIR) spectra show four major
differences between the polysulfone resin and the sulfonated poly-
sulfone ionomers. The peak assignments for various absorbances
are in Table 3-2 with the major differences noted. Besides showing
the differences between the ionomers and the base resin, FTIR was
also used to determine the degree of sulfonation as well as to
give a qualitative indication of the amount of water present in
the samples. By taking ratios of peak areas such as the symmetric
sulfonate stretch (1025 cm^{-1}) to the aryl ether vibration (1015 cm^{-1}),
to the symmetric sulfone stretch (1150 cm^{-1}) or to the symmetric
C-H stretch of CH_3 (1364 and 1393 cm^{-1}) and by comparing these
ratios to those of known sulfonation levels, the degree of sul-
fonation can be determined. Typical FTIR spectra are shown in Figures
1 through 9.

Differential Scanning Calorimetry

The differential scanning calorimetry results are collected
in Table 3-3. It can be seen that the incorporation of ionic
groups into polysulfone can raise its glass transition by as much
as $130^{\circ}C$. The DSC scans exhibit no other transitions within the
temperature range of $25^{\circ}C$ to $325^{\circ}C$. Once over $300^{\circ}C$, depending on
the sample, reactions such as degradation begin to take place even
under a dry nitrogen environment. The glass transitions detected
by DSC for these materials become broad and increase linearly in

temperature as the degree of sulfonation increases. This trend is
shown in Figure 10 where the glass transitions are plotted against
the degree of sulfonation. The slope of the line, dT_g/dC, is about
$1.5^{\circ}C$ per mole percent sulfonate. Another important feature is that
this slope is constant throughout the entire sulfonation range studied.

X-Ray Scattering

Wide angle x-ray scattering was carried out in order to determine
the absorption coefficients for the materials so that an optimum
thickness could be determined for small angle x-ray studies. The
optimum thickness for polysulfone was calculated to be 0.190 cm.; for
0.30Cs-Dry, 0.045 cm.; and for 0.50 Cs-Dry, 0.020 cm. These diff-
erences arise mainly from the electron density differences between
the mostly hydrocarbon polysulfone and the metallic ionic groups.
Besides determining the optimum thicknesses, wide angle scans also
were used to show that no crystallinity is present in the samples.

Small angle x-ray scattering was studied to investigate the
clustering phenomena in these ionomers. Plots of scattered intensity
versus scattering angle for the ionomers generally exhibit a peak
in the region of $2\theta = 2-5^{\circ}$ as is shown in Figure 19. The scattering
profiles shown in Figures 20 and 21 are for both the wet and dry
states of 0.30 Cs and 0.50Cs. Some scattering is present in all
cases in the angular region mentioned above but the intensity is
several orders of magnitude smaller than that observed in other
ionomers where clustering is known to exist. There is a suggestion
of a peak in the case of 0.50Cs-Dry but it is ill-defined. Because

of the low scattering intensity, especially in the case of wet

samples, these scans have not been subjected to further quantitative

analysis. However, from these results, it is concluded that the

percentage of salt groups present in the form of clusters is small,

probably less than 10%. Thus, most of the ionic groups are present

in the form of multiplets and are not phase separated from the

hydrocarbon portion of the polymer.

Dynamic-Mechanical Measurements

Figures 11 through 14 display the temperature dependencies

of the tensile storage and loss moduli (E' and E") at 11 Hz for a

representative group of dry samples. Figures 15 through 18 show

the effects of water and other low molecular weight diluents on

these properties. A summary of these effects is collected in Table

3-4.

These samples display three relaxation regions labeled α,β

and γ in order of decreasing temperature. Comparing Figures 11

through 14, one can see the the αrelaxation of the ionomers is

considerably higher in temperature than for polysulfone, with that

of the sodium ionomer slightly higher than cesium. In addition, the

α relaxation shows the same linear increase with sulfonation as

does T_g measured by DSC. The β relaxation is only present in the

ionomers and appears to move slightly to higher temperatures with

sulfonation but is not affected by cation type. The incorporation

of ionic groups onto the polysulfone backbone causes the γ relax-

ation to occur 20° to $40^o C$ higher and usually with increased

intensity. Thus, the overall behavior of polysulfone ionomers shows a high temperature α relaxation (200° to 300°C), a β relaxation (-25° to -15°C) and a γ relaxation (-80° to -60°C).

Comparison of E' values at various temperatures for the samples in Figures 11 through 14 shows that in the dry state, sulfonation increases the modulus of the material. It should be noted in Table 3-4 that the modulus values remain fairly constant over a 350°C range but that they do depend on the amount of water present and prior thermal history.

In Figures 15 and 16 the effects of water on the dynamic-mechanical properties are shown. Water causes a slight increase in the modulus of the sodium ionomers but has only a very small effect in cesium ionomers. It should be noted, however, that the way in which the water is incorporated into the sample greatly affects the modulus. There appears to be a large difference between just soaking a sample in water compared with first drying the sample and then immediately placing it in water. There also appears to be a difference of this water effect depending on how the wet sample is cooled for testing. These differences are summarized in Table 3-4.

The best indication of the effects of water on the material properties is given by the tensile loss modulus, E". In the case of polysulfone, enhancement of the γ relaxation with water was not observed although it has been reported.[67] In the case of sodium ionomers, water causes the γ relaxation to diminish in magnitude

and move to lower temperatures. This, along with the effects of water on the storage modulus in sodium ionomers, is evidence for antiplasticization behavior. In the case of cesium ionomers, water tends to complicate the dynamic-mechanical spectra but does not always diminish the γ relaxation. The β relaxation, which occurs only in the ionomers, seems to be slightly more apparent in the wet samples. In addition, the higher water content tends to shift the β relaxation a few degrees to lower temperatures. Again the presence and nature of the β relaxation is dependent on the thermal history of the sample and also by the way in which water is incorporated as is shown in Table 3-4. The α relaxation, taken as the glass transition, seems to be nearly unaffected by water in the case of sodium ionomers but causes a slight increase in cesium ionomers. The amount of water present at these high temperatures is relatively low. Infrared analysis of samples after testing shows that 90% of the water initially present is lost. This is in accordance with the fact that drying samples in vacuum at 175°C does not remove the last traces of water. The exact state of the water in these materials will be discussed later.

Besides water, other low molecular weight diluents were examined. In the case of alcohols, methanol tends to show effects similar to water except that the γ and β relaxations are much closer together. The modulus is only slightly lower in the case of methanol than for dodecanol. Dodecanol tends to enhance the γ relaxation and diminish the β relaxation slightly but shifts it

almost 30°C to higher temperatures. In the case of esters the behavior is quite different. Dioctyl phthalate (DOP), a conventional plasticizer for polysulfone, causes the γ relaxation to move to slightly higher temperatures but more importantly it transforms it into a much larger and sharper dispersion. The β relaxation is not present in the case of DOP. Ethyl salicylate, which contains a hydroxyl group, seems to have an effect on the dynamic-mechanical behavior similar to that of water. In both cases, the esters tend to reduce the modulus slightly but much less than they do in the polysulfone resin. Overall, the greatest effect on the ionomeric properties comes from dodecanol which brings about the greatest decline in the glass transition. The dynamic-mechanical relaxation behavior of a cesium ionomer containing these low molecular weight diluents is shown in Figures 17 and 18.

Absorption and Diffusion Measurements

In order to better understand the role of water in determining the mechanical properties, quantitative water absorption measurements were carried out. A typical absorption curve is shown in Figure 22. In general it was found that these materials reach equilibrium fairly quickly, on the order of 24 hours in most cases.

The absorption of water in these materials was found to be proportional to the sulfonation level with the ionomers absorbing ten times more than the unsulfonated polysulfone resin. Specifically, the sodium ionomers tend to absorb on the average 1.7 times more water than the cesium ionomers at the same sulfonation level.

The amount of water absorbed at room temperature did not differ if the samples were submerged or if they were exposed to water vapor, although there was a slight difference in the rates of absorption. The sodium ionomers were found to absorb 3.5 to 4.0 water molecules per ionic site while the cesium ionomers showed a slightly broader range of 1.7 to 3.0 water molecules per ionic site. There was, however, a difference in the amounts of water absorbed when dry samples were subjected to the moisture of the air under ambient conditions. Although equilibrium is reached within 24 hours for samples subjected to 100% humidity, the absorption of water from the air at relative humidity is much slower and did not reach the same levels even after two months. After two weeks at room temperature and humidity the sodium ionomers had absorbed 1.5 to 2.0 water molecules per ionic site while the cesium samples only 0.7 to 0.8.

Varying the temperature of the water had almost no effect on the total amount absorbed and only a small effect on the rate of absorption. In general, the amount of water absorbed at $100^{\circ}C$ was almost twice that at $25^{\circ}C$ but upon cooling back down to room temperature this extra water was lost and the sample equilibrated to the $25^{\circ}C$ value. The change in temperature from 25° to $100^{\circ}C$ increased the rate of absorption of the sodium ionomers by an order of magnitude but had little effect on the cesium forms.

Applying the following equation:

$$\frac{M_t}{M_\infty} = 4\left(\frac{Dt}{1^2}\right)^{\frac{1}{2}}\left(\frac{1}{\pi^{\frac{1}{2}}} + 2 \sum_{n=0}^{\infty} (-1)^n \text{ ierf c } \frac{n1}{2(Dt)^{\frac{1}{2}}}\right)$$

at short times so that the error function is neglible, the diffusion coefficient of the water in these materials was calculated from the initial slope, $4D^{\frac{1}{2}}/\pi^{\frac{1}{2}}$, of a plot of $M_t/M\infty$ versus $(t/1^2)^{\frac{1}{2}}$. The results are in Table 3-5 along with values for some other polymers taken from the literature.
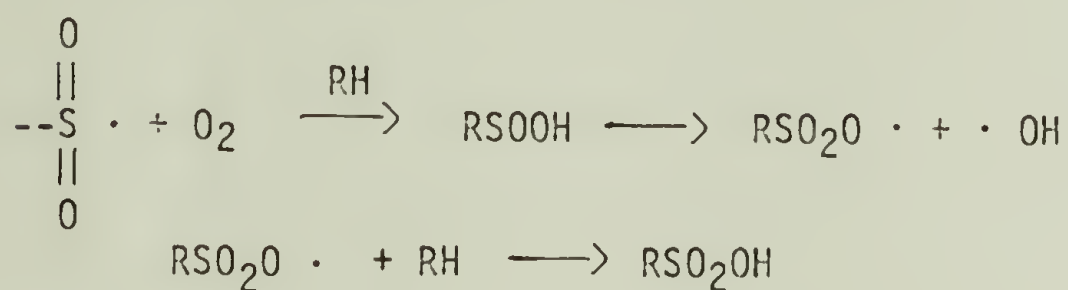
From the shape of the absorption curves and from log-log plots of the change in weight versus time, which produces a power law coefficient of 0.6, the diffusion is considered to be pseudo-Fickian as described by Frisch.[86] This conclusion is different from that reached by Noshay and Robeson[80]. Overall, though, the water absorption and diffusion results are in good agreement with those of Noshay and Robeson as well as with ionomers.

Discussion

It should be pointed out at this time that the test results for some samples, even though they are ostensibly similar in structure, differ significantly. It has been the experience of this researcher as well as others that some of the properties of ionomers may change with time. It appears that an equilibrium state may be reached only after long times. The reason for this behavior may be the presence of small amounts of un-neutralized acid groups. The acid forms of most ionomers are not stable and only a few can actually be isolated.

In most cases these acid functional groups lead to discoloration, brittleness and reduced solubility, possibly because of crosslinking.

In the case of polysulfone ionomers, thermal aging, even at moderate temperatures in nitrogen (110°C for 5 days), produced a yellowed and brittle material. Two types of acid groups could be present in these aged systems. One would be sulfonic acid groups arising from incomplete neutralization and secondly, sulfonic acid groups arising from an oxidation reaction of sulfone radicals produced by chain scission reactions. For example:

$$\underset{\overset{\displaystyle \|}{\underset{\displaystyle \|}{O}}}{\overset{\displaystyle O}{--S}} \cdot \div O_2 \xrightarrow{RH} RSOOH \longrightarrow RSO_2O \cdot + \cdot OH$$

$$RSO_2O \cdot + RH \longrightarrow RSO_2OH$$

and

$$ROOH + \text{----}SO_2\text{----} \longrightarrow \text{--}SO_2OH + RO\text{---}$$

Fourier Transform Infrared Analysis of samples before and after thermal aging did not show any notable differences other than those associated with the loss of water. In addition, further heat treatment to as high as 225°C for short times did not produce any changes in the spectra.

High temperature aging of these materials did produce some changes in the physical properties, however. Besides the changes in physical appearance mentioned above, high temperature aging causes a reduction of the glass transition temperature of the materials studied. This reduction was usually of the order of 10° to 20°C.

Eisenberg[87] has shown that the presence of any un-neutralized acid

groups will decrease the effectiveness of the ionic groups to act

as crosslinks and thus disrupt the associations (multiplets and

clusters) that give the materials their properties. Eisenberg

concludes that the acid groups allow for ion hopping which causes

a breakdown of the electrostatic interactions.

DSC results show that the cesium ionomers have lower glass

transition temperatures than sodium ionomers at the same degree

of sulfonation. This result can be explained by considering the

effective ionic radii of the counterions. The closest approach

ionic radii for sodium and cesium are 0.95 and 1.69 A respectively.

It has been shown previously that cesium ions tend to yield cross-

links of lower stability than sodium.[87] It was also shown that the

counterion type does not affect the critical ion concentration (onset

of clustering) but only the stability of the clusters once formed.

From these results, Eisenberg has proposed that the strength of the

ionic associations are proportional to the ratio of the charge to

ionic size of the cation. Therefore the type of counterion will

affect only the ionic properties which are based on the stability

of the ionic interactions. Thus, any factor affecting the nature

of the cation, such as hydration, will affect the material properties.

Analysis of ionomeric properties by cation type may lead to incon-

sistent results for this reason. Instead, analysis by the nature

of the cation, especially in the case of multivalent cations, should

be much more fruitful.

The reason for the importance of the nature of the cation type may arise from the type of association present between the cation and anion such as contact ion pairs, hydrated ion pairs, and solvated ions. In the case of alkali metal univalent cations, ionic association is minimal although cesium does show ion pairing with chloride and oxy-acid anions. Group II metals, partly because of their increased charge, will form ion pairs more readily but it will depend on the dielectric constant of the medium.

In the case of solid electrolytes, ion pairing should be enhanced for several reasons. First, within the interior of a polymer, a large concentration of ionic groups will be present with a reduced number of water molecules present for hydration. Secondly, the low dielectric constant of the polymer matrix should increase the cation to anion coulombic attraction. Lastly, the cations and anions should be in close proximity due to the surrounding hydrophobic regions. Thus, ion binding onto a macroion will be a function of the coulombic attraction between ions which causes the cations to congregate in the vicinity of the macromolecule. This causes a loss of entropy and a decrease in the energy of dilution, ΔH_D, when the counterion approaches close to the macroion in a hydrated environment. As a result, the properties of an ionomer will differ from its non-ionic precursor due to interactions between the charges on the polymer which influence the configurational properties as well as the polymer's end to end distance. These interactions between charged groups are large enough for counterion binding, thus making the

ionization potential of each group interdependent of the others.

Another major result of the DSC studies is that there is no evidence of phase separation in the ionomers. It appears that incorporation of ionic groups has not caused phase separation of the ionic regions but that instead has increased the glass transition through a stiffening and/or ionic crosslinking effect. Taking the glass transition value for 1.0Na-Dry (330°C) to be the glass transition temperature of the ionic portions, applying the co-polymerization equation yields values close to those measured by DSC for samples of low sulfonation. Plotting the increase in T_g as a function of the sulfonation level it was found that the increase is linear at about 1.5°C per mole percent sulfonate. This value of 1.5 is lower than those reported for other ionomers. Eisenberg has published a table of such values.[88] Comparatively, sulfonated polysulfone's value of 1.5 is close to that for the initial slope of polypentenamers (2) and for the initial slope of styrene-sodium methacrylate copolymer (3). In both of these other systems, though, the curves deviate from linearity at some point which has been shown to be the critical ion concentration for the onset of clustering. In the case of clustered systems the dT_g/dC values are higher such as 6 for ethylene-sodium methacrylate and 10 for ethylene-magnesium methacrylate copolymers. Thus, the results of these DSC studies, although not conclusive indicate that clustering is not present in this system.

The main task of this research is thus to prove that little
or no clustering exists in this system which would make this a
unique ionomer. The major experimental technique for investigating
clustering phenomena is small angle x-ray scattering (SAXS). As
pointed out in the results section, little evidence was found for
the existence of clusters using this technique. However, it is
not necessary to have an "ionic" peak in order to have a multiphase
system. In fact, a peak may complicate the interpretation of the
scattering profile. Instead, the presence of significant scattering
intensity in the angular region of $2\theta = 1 - 6^0$ is good evidence
for ionic regions of 25 to 50 A. Scattering intensity will be low
if the electron density difference between the phases is small. For
this reason, the cesium ionomers were analyzed since they should
exhibit a high degree of contrast.

The conclusions reached from the SAXS studies indicate a
virtual absence of clustering in these ionomers. This in turn has
important implications for the properties of these polymers. For
example, if no phase separation between the polymer matrix and
the ionic group occurs, it would be expected that the glass transition
temperature would be greatly enhanced due to a stiffening and/or
crosslinking effect of the salt group on the backbone. This result
has been borne out by the DSC results and the results of the dynamic-
mechanical analysis which confirm and extend the SAXS and DSC studies.

In order to present a clear view of the dynamic-mechanical

behavior of polysulfone ionomers in relation to other ionomer systems, their behavior will be discussed by treating each relaxation region individually and then summarizing their overall behavior in a final section.

α Relaxation

The α relaxation in these ionomers is taken to be the glass transition of the matrix since it correlates well with the only transition measurable by DSC. The actual temperature of this relaxation has been found to be a function of sulfonation level, counterion type, and the amount of any low molecular weight diluent present. The increase in temperature with sulfonation was found to be the same as that observed by DSC. Different counterions affected the temperature of the α relaxation in a similar manner to that observed by DSC for the glass transition. Noshay and Robeson[20] have reported a 1.0H$^+$ ionomer T_g of 230°C but when neutralized with sodium (1.0Na) it is increased to over 300°C. This then shows the importance of cation-anion interaction in determining the material properties. Comparing the results of the cesium and sodium ionomers at similar sulfonation levels, it is again concluded that the ionic radius of the counterion effects the thermal stability of the ionic interactions.

Since the ionic radius is a function of temperature, pressure, hydration, etc., changes in these factors will thus affect the material properties. The hydration effects on the ionic radius

influence the concentration dependence of the heat of dilution, ΔH_D. In the case of poly (styrene sulfonate) resin, cesium and zinc show similar behavior in that they show little increase in ΔH_D with concentration.[65a] This is due to strong ion binding which decreases the coulombic interactions. A discussion of the effects of hydration on the material properties will be given subsequently.

Water was found to affect the α relaxation of cesium ionomers differently than for sodium ionomers. In the case of sodium ionomers, water tends to diminish the α relaxation temperature slightly. In the DSC studies water had a similar but larger affect on T_g. This difference is most likely due to the fact that in the DSC experiments the starting temperature was only about $100^{\circ}C$ and at a heating rate of 20° per minute while in the dynamic-mechanical studies the samples were scanned from $-150^{\circ}C$ to beyond T_g at about 2° per minute. Thus, the amount of water present at T_g, especially at such a high temperature, is most likely different in each case. Infrared analysis of the samples after dynamic-mechanical testing shows that almost all of the water has left the sample during testing as would be expected. In the case of cesium ionomers the reverse trend was found. Only a slight increase in T_g was found in going from the dry to relative humidity state but a much larger increase occurs when the sample is first saturated with water. These results, however, are the opposite of those determined by DSC. A possible explanation for this difference may again be related to the amount of water present at T_g. As

mentioned earlier, cesium tends to form contact ion pairs more readily than sodium especially in the dry state. Thus, if a greater percentage of cations are bound there will be fewer free ions present. As small amounts of water come in contact with the ion pairs, the water tends to break them up increasing the free ion concentration and thus T_g. As additional water comes in contact with the ions, hydration occurs thus again decreasing T_g.

The effects of alcohols and esters on ionomeric properties were studied with cesium ionomers in hopes of being able to bring about conditions more conducive to clustering. In the case of methanol (saturation achieved by soaking samples for three months) the α relaxation was again increased but not to the same extent as with water. Dodecanol, a more hydrophobic material, caused an actual reduction in the relaxation compared with the dry state. It is concluded that such materials may be useful as dual plast-icizers in that they may interact with the ionic regions as well as with the hydrocarbon backbone. An intermediate size alcohol such as hexanol may have a more pronounced effect but the problem of loss due to evaporation at high temperatures is present. In an attempt to optimize the effects of alcohols, benzyl alcohol was tried but turned out to be a solvent for both the 0.30Cs and the 0.50Cs samples.

In hopes of reducing the modulus and glass transition significantly, the use of esters as conventional plasticizers was also studied. In the case of dioctyl phthalate (DOP), a

conventional plasticizer for polysulfone, little change in the glass transition occurred but with ethyl salicylate, a hydroxyl containing aromatic ester, the α relaxation temperature was actually increased. The behavior of these low molecular weight diluents cannot be readily explained using free volume theory. In conventional polymers, diluents increase the free volume, decrease the polymer segment concentration and thus decrease T_g. However, in the case of ionomers there is the additional feature of intermolecular interactions among the ionic groups. Thus, the addition of diluents at low concentrations may actually increase the density of the polymer-diluent mixture by partially disrupting some of the interactions causing a more efficient packing and thus leading to an increase in T_g. Additional diluent then may disrupt enough of the intermolecular interactions to allow for greater chain mobility and a lower T_g. Such behavior is exemplified by the water-nylon system as well as water and sulfone and mixtures. Therefore, the effects of low molecular weight diluents will depend not only on the nature of the diluent but also on the amount present as well as its ability to interact with the free volume of the polymer.

β Relaxation

The β relaxation is not present in polysulfone itself and thus arises from the sulfonation of the material. Determination of the mechanism of the β relaxation is somewhat complicated by

the differences in the results among the various ionomers. For both cesium and sodium ionomers the relaxation is dependent on thermal history as well as water content. In the case of the sodium ionomers the relaxation shifts slightly to lower temperatures with decreased magnitude upon increased sulfonation. The same effect occurs with the addition of water. For the cesium ionomers, increased sulfonation has little effect on the temperature of the relaxation but does increase its intensity. Water initially reduces the peak in temperature and increases its magnitude but then at higher concentrations brings the temperature and magnitude to intermediate values between the dry and relative humidity states. Overall, the cesium β peak is slightly more intense than that of sodium. A possibility for this difference in behavior may again be related to the differences in hydration and ionic association between cesium and sodium. Sodium has a much higher affinity for water than cesium and so for this reason the dry sodium samples may contain small amounts of water which is strongly bound. Thus, it is believed that the β relaxation arises from the hindering effect of a substituent such as SO_3^- on the phenyl ring rotation and not so much due to ionic interactions, although they most likely contribute to some extent. If this peak were due to ionic interactions alone, then water should disrupt or shift it greatly.

Water has been proposed to disrupt ion pairing in cesium ionomers and thus increase initially the coulombic interactions.

This in turn causes opposite behavior to that of sodium which may already be partially hydrated. Thus, if the β relaxation is due to the portion of the molecule containing the pendant sulfonate group, water should initially tend to facilitate the relaxation of this segment in cesium ionomers and this has been found to be the case. Robeson, Farnham and McGrath[74], who do not explain their β relaxation, postulate that relaxations of the sulfonate containing $\emptyset$-O-$\emptyset$ links in the presence of water are the same as the unsulfonated $\emptyset$-O-$\emptyset$ links in the polysulfone resin. They feel that in the presence of water polysulfone's γ relaxation is due to rotations of the $\emptyset$-O-$\emptyset$ portions coupled with the rotation of the $\emptyset$-SO_2-$\emptyset$ portions. Water should be attracted to and plasticize $\emptyset$-SO_2-$\emptyset$ rotations even though it may antiplasticize other portions. If the rotation of the $\emptyset$-O-$\emptyset$ portions are similar to those of the $\emptyset$-SO_2-$\emptyset$ in energy, the rotation of one group would thus be at the expense of the other. Sulfonation of the $\emptyset$-O-$\emptyset$ portions would thus hinder their rotation so that only $\emptyset$-SO_2-$\emptyset$ rotation would predominate in the presence of water. Thus, the β relaxation may be due to rotation of the sulfonated $\emptyset$-O-$\emptyset$ portions, while in the presence of water the γ relaxation occurs from the remaining $\emptyset$-O-$\emptyset$ portions plus those of $\emptyset$-SO_2-$\emptyset$.

Another possible explanation is that this β relaxation may be due to the actual salt groups themselves. If one views the hydrated systems as concentrated salt solutions then the melting point of the water itself would be suppressed. Theoretical calculations for such an environment predict a 20°C depression

in the melting point of water. Similarly, water under such
conditions may not freeze as it would in the unbound state. This
idea is supported by the appearance of a small transition near
-120°C for high water content samples which could be the glass
transition of the water itself.

Besides water, all of the other molecular weight diluents
studied which contained hydroxyl groups produced the β relaxation.
Only DOP did not show this relaxation. Dioctyl phthalate is a
good plasticizer for the polysulfone backbone and therefore may
be effective in plasticizing all the ϕ-O-ϕ links regardless of
whether they contain a pendant sulfonate group or not, even though
DOP may not interact with the ionic groups directly. This idea is
supported by the fact that the β relaxation for DOP containing
ionomers is much greater in magnitude than for any other system.

γ Relaxation

As just discussed, the nature of the γ relaxation which is
also present in polysulfone resin is not easily explained. If
one accepts Robeson, Farnham and McGrath's results then this
relaxation is due to motions of both the ϕ-O-ϕ and ϕ-SO$_2$-ϕ portions
depending on the water content. They report that this transition
is extremely large for wet, highly sulfonated material while it
is both lowered in magnitude and shifted to higher temperatures for
dry samples. They conclude that the reason for the higher temperature
in the dry state is due to intermolecular interactions which increase

the barrier of rotation. Water, which destroys these interactions, causes the peak to assume values similar to those of unmodified polysulfone. This explanation seems plausible for highly sulfonated material but for dry, lightly sulfonated materials it seems questionable. For example, if the polymer contained 50% sulfonated ϕ-O-ϕ links and 50% unsulfonated ϕ-O-ϕ links then in the dry state there should be two relaxations and this is not the case in the studies of Robeson, Farnham and McGrath[74], Noshay and Robeson[80] or this investigation.

In this study, by incorporating the water into these polymers after thermal treatment, it was found that slightly different results were obtained. It was found that water does shift the peak to lower temperatures but _decreases_ its magnitude contrary to Noshay and Robeson's results. This behavior is very characteristic of antiplasticization. Thus it is proposed that in the dry state the γ relaxation of the ionomers is due to both ϕ-SO$_2$-ϕ and O-O-O rotation. This conclusion is based on the results of Farnham, Robeson and McGrath and is supported by Kurz[71] who studied polysulfone as well as other poly (aryl ether) sulfones which did not contain the ϕ-O-ϕ unit. Kurz found that a transition near -100°C was present regardless of the presence or absence of ϕ-O-ϕ links. The intensity of this peak was slightly increased by water but its position was shifted to lower temperatures. The key point, though, is that the existence of the γ peak in Kurz's study was not dependent upon the presence of water. Thus, upon addition of water

in these ionomers the ϕ-O-ϕ and ϕ-SO$_2$-ϕ transitions remain coupled and are both shifted to lower temperatures. The water may cause a slight increase in the ϕ-SO$_2$-ϕ portion since it is the likely portion of the chain to attract water but it will cause an antiplasicization of the ϕ-?-ϕ regions. Therefore the "net" intensity is less for wet systems than dry. This explanation is supported by the fact that alcohols and esters have little effect on the γ relaxation other than a slight shift to lower temperatures.

Overall, the dynamic-mechanical results show the importance of ionic groups in imparting a stiffening effect in polymers. The modulus values for the samples studied support the phenomenological explanation of the relaxations in sulfonated polysulfone ionomers. In the case of sodium ionomers water increases the modulus over almost the entire temperature range studied. This fact along with the decline in magnitude and shift to lower temperature of the γ relaxation supports the proposed idea of antiplasticization. Cesium ionomers, which may exhibit ion pairing in the dry state and which have a lower affinity to water than sodium, show only a small change in the modulus upon absorption of water. As far as sulfonation level effects, sodium shows the greatest increase in modulus. This may be due to the differences in ionic association of cesium and sodium.

Thus, it may be concluded from these dynamic-mechanical results that the sulfonated polysulfone membranes tested are not clustered to any significant extent. Their structure may best be described as consisting largely of ionic multiplets composed mainly of ion

pairs, quartets, etc. These ionic associations are thus responsible for imparting the stiffening effect to the backbone which leads to the increased modulus and glass transition of these ionomers.

Absorption and Diffusion Measurements

In order to discuss the effects of water absorption and the diffusion mechanisms involved in these ionomers it seems appropriate to present them in relation with results of other sulfonated polymers. This will be done by first presenting preliminary information on hydration, ionic association and diffusion and then working this into the results of specific systems so as to obtain a possible explanation for the behavior of water in sulfonated polysulfone membranes.

Results in the literature are somewhat misleading at times due to differences in definitions of the terms coordination and hydration. In this discussion, the following definitions will be taken to distinguish between coordination and hydration:

a. Coordination is the number of water molecules in the immediate neighborhood of the ion and depends on the distance between the water molecule and the ion.

b. Hydration is based on the dynamic behavior of the water in a solution about the ion at a given temperature and involves the number of water molecules which move with the ion during transport.

Thus, the coordination number will usually be larger than the hydration number.

The importance of water on ionomeric properties arises from

the fact that hydration affects ion pairing. The tendency of sulfonated materials to associate with a hydrated cation will be hindered by the substitution of the large organic anion for the water which is displaced from the hydration shell of the cation. It is suggested that water competes with the anions for position within the critical radius of the cation. Larger cations will thus allow the larger organic anion more success in competing for the water molecules. Thus, in the case of ionomers, both the cation and anion may be hydrated.

Bockris and others[89] measured the effects of concentration and cation radius on hydration. They found values of Na^+ = 4.5 and Cs^+ = 2.5 giving a ratio of 1.8 as measured by ionic compressibility. In a different approach, Lindemann[90] calculated the mean free path (distance travelled between collisions) of the cations. He explained that the mobility of smaller ions is not hindered by bound water but instead it is based on their smaller mean free paths resulting in greater attraction between the ions and water molecules. Thus, the hydration numbers for the cations will be inversely proportional to their mean free paths. Lindemann found values for Cs^+ of 1.21×10^{-9} cm. and 0.68×10^{-9} cm. for Na^+ making the ratio of their inverses equal to 1.78.

The affects of hydration on ion pair formation has been studied in the case of ionomers as well. Bonding of a sodium ion to a site on a polymer will produce a broadened Na-23 NMR resonance spectra.

This broadening can arise from two sources:

1. The production of a substantial electric field
    gradient due to distortion of the sodium elec-
    tronic environment.

2. Decreased mobility due to the influence of the
    polymer in increasing the relaxation time.

In Nafions, by decreasing the water content, a large chemical shift

and line width broadening occurs. Similar effects are seen by

decreasing the temperature. This phenomenon is interpreted in

terms of the fast equilibria between bound and unbound sodium ions

in the hydrophilic regions of the polymer. Thus, the broadened

line width is evidence for significant interaction between the

sodium ions and the polymers fixed anionic sites. In similar studies

with poly (styrene sulfonate) ion exchange resin, the resonance

broadening is also seen to increase with crosslinking, possibly

due to the increased relaxation time of the polymer and its correlation

with ionic mobility. The line width broadening for water saturated

Nafions is an order of magnitude greater than for crosslinked

poly (styrene sulfonate) resin thus indicating that the sodium ions

are substantially restricted in the aqueous phase. Therefore the

idea of ion solvation by water may actually be inappropriate in

Nafions at times and the water may cause binding instead. This

idea is supported by the fact that with the addition of one percent

water to Nafions, more than 50% of the sodium ions are bound. The

largest change in the bound to unbound states of the sodium ions

appears at about 3.5 water molecules per ionic site. Thus, these

results suggest that the first hydration shell of sodium in Nafions is 3 to 4 water molecules.[91] The same technique found a value of 2.8 to 3.5 for sodium's hydration shell in poly (styrene sulfonate) resins.[92]

Nafions have been studied extensively by many other researchers as well. Roche and others[51], using various techniques, have found results similar to those of this study. They found that the amount of water absorbed was very dependent on the cation type. At room temperature the sodium form absorbed 3 to 3.5 water molecules per ionic site while the cesium form's value is about 1.7. Boiling the samples increases the amount of water abosrbed to values of 14 and 4 respectively. They also found that the amount of water absorbed is dependent on thermal history and that if less water than that needed for hydration is present contact ion pairs occur. Lastly, it was found that the rate of diffusion of water in Nafions is much higher than for any other ionomer or polymer. A possible reason for this may be due to the nature of ionic clustering in Nafions.

Water uptake has been shown to depend on the existence of clustering.[11a] Below the critical ion concentration for clustering in styrene-sodium methacrylate only one water molecule per ionic site is absorbed but above this critical concentration 3 to 5 water molecules per ionic site are present. This behavior is probably brought about by the dynamic nature of the clusters as seen by the large changes in water absorption due to counterion type. Thus, multiplets can only accomodate water at specific sites whereas clusters,

which have a large number of ions present in one place, can easily accomodate more water. As hydration decreases going to heavier cations, the elastic strain of the polymer matrix decreases so that additional clustering may occur. Thus, the clusters in Nafions may produce a more uniform site for water thus increasing the rate of diffusion. If this clustering is a factor in determining Nafion's diffusional properties then the diffusion coefficients will vary dramatically for small changes in swelling of the polymer matrix. This would then favor transport of water and/or counterions between clusters giving Nafion ion transport properties very different from other ion exchange resins. Such an idea has been shown experimentally by Yeager and others.[48b,49c,52]

To better understand diffusion in ionic membranes, diffusion theory must be viewed from the aspect of the effects of fixed ionic sites on the transport phenomena. In a rubber, a rapid, constant penetration rate of the penetrant usually occurs. This sorption equilibrium is achieved in times much shorter than the characteristic times involved in the diffusion of the penetrant. In glasses, however, there appears to be a contribution to the transport processes from the longer relaxations of the polymer. Motions of the glassy polymer chain are not sufficient enough to "homogenize" the penetrant's environment. Thus, diffusion in a glass is usually non-Fickian except in the case of water which shows pseudo-Fickian behavior in that the rate of diffusion is much less than the relaxations of the polymer so that equilibrium is rapidly established.[85]

Usually the water in a membrane at low water contents is strongly associated with the hydrophilic portions of the polymer and so movement of water is by an activated diffusional process so as not to depend on applied pressure. On the other hand, in highly hydrated membranes, the flow of water occurs between separated polymer segments and so the flux depends on the applied pressure. The flux, J_1, is defined as $J_1 = K_1 \, dP/dX$ where K_1 is the piezometric permeability coefficient and dP/dX is the pressure gradient. The flux, J_1, is also equal to the sum of the diffusive flux, J_D, and the contribution from viscous flow (convection), J_f. Thus, $K_1 = K_D + K_f$. At low hydration levels $K_f \sim 0$ (activated diffusion) but at high levels of hydration $K_f > K_D$. Thus, a change in the transport mechanism from activated diffusion to viscous flow (convection) is brought about by hydration and so this will have a significant effect on the membrane's reverse osmosis properties. If activated diffusion predominates (low hydration), the salt in a salt solution moves by diffusion along with the water. On the other hand, if viscous flow predominates (hydrated membrane), the water of the salt solution will move much faster than the salt which is still only moving by diffusion thus resulting in salt rejection. Therefore, salt rejection is a consequence of the difference between the solute flux and the water flux rather than just from the salt exclusion potential of the membrane. In ionic membranes the value of $K_f >> K_D$ indicating that viscous flow predominates. Thus, salt rejection is much higher in ionic membranes than non-ionic

membranes with similar K_1 values. This difference is most likely due to Donnan exclusion.

Thus the absorption and diffusion results of this study of sulfonated polysulfone are supported by previous experimental and theoretical studies of ionic materials. The dependence of water absorption on sulfonation, with the sodium ionomer absorbing 1.7 times more water than the cesium form, is in excellent agreement with the studies of Bockris and Lindeman who showed the effects of concentration and ionic radius on hydration of these cations. The total values of absorbed water for these two ionomers (3.5 to 4.0 for sodium and 1.7 to 3.0 for cesium) is also in excellent agreement with the values reported for other sulfonated systems. In addition, the diffusion coefficients for water in these ionomers are similar to other ionomers in which clustering is not present. The higher values for Nafions may thus be directly related to the nature of clustering and its effects on the polymer matrix.

In a truly dry state, counterions have been shown to be bound by electrostatic forces in the form of contact ion pairs. Thus water absorption in an initially dry ionic membrane may be viewed as an equilibrium process. Although the interaction between the organic polymer backbone and the water molecules is endothermic and influenced by the rate of swelling, the strong exothermic tendency of the counter-ions and the anionic side groups to hydrate results in having the initially arrived water strongly bound in the solvation layers causing little or no volume expansion (swelling). Further water

uptake beyond the hydration shell results in changing the cationic bound to unbound equilibrium. As water uptake proceeds, this dissociation allows for more complete ionic hydration. The difference between the water activity inside the membrane and out gives rise to an internal osmotic pressure. Eventually an equilibrium is reached where this osmotic pressure is balanced by the cohesive energy density of the polymer matrix. Therefore, if water cannot bring about swelling of the polymer matrix, water uptake beyond the hydration level of the cation will not occur and thus the rate of diffusion will be limited as well. In the case of Nafions, water tends to increase the cluster size which in turn swells the polymer by exerting strain on the polymer matrix. Therefore, the diffusion coefficient of water in Nafions is much higher than for any other sulfonated system.

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

The major conclusion of this thesis is that sulfonated polysulfone ionomers are not clustered to any significant extent. From these structure-property studies, their structure is best described as consisting largely of ionic multiplets composed of ion pairs, quartets, etc. The evidence to support this conclusion comes from three main experimental findings. Differential scanning calorimetry showed a linear increase of the glass transition with sulfonation throughout the entire concentration range studied. In addition, the DSC thermograms showed only one transition and no evidence of phase separation. The small angle x-ray scattering studies gave no evidence of an ionic peak nor did they show any region of significant scattering intensity, even though cesium ionomers were studied. Lastly, the dynamic-mechanical behavior serves to confirm and extend the SAXS and DSC results in that they show the effects of the ionic groups in increasing the modulus and glass transition temperature due to chain stiffening and/or ionic crosslinks.

Besides verifying that clustering does not occur to any significant extent in these materials, the nature of the ionic interactions, their importance in determining the mechanical properties and the effects of low molecular weight diluents on these interactions was also studied. It was found that ion pairs, especially in the case of cesium, may exist in the dry state. Thus,

83

water may initially act to disrupt these ion pairs rather than solvate the cations. It also was found that the ionic association and interaction between the cation and anion is probably what brings about the enhanced material properties. Therefore the differences between cesium and sodium ions, as far as their respective potential in ionic interactions, are the reasons for the difference in the cesium and sodium ionomers. Water, as well as any other factor which will affect the cationic and anionic interactions, will thus have an effect on the material properties. Therefore, in order to control ionomeric behavior, one must be effective in controlling the interactions between the cation and anion.

Overall, this thesis has accomplished four major goals. First, it determined the extent of clustering in sulfonated polysulfone ionomers. Second, using dynamic-mechanical measurements, differential scanning calorimetry and small angle x-ray scattering, it has determined the extent of the ionic interactions, the mechanism by which they work and their importance in determining the material properties of polysulfone ionomers. Third, again using dynamic-mechanical measurements as well as diffusion data, it has shown the importance of water in determining the properties of these ionomers, especially in relation to other sulfonated ionomers. Lastly, from a study of the effects of low molecular diluents, it provides insight into the requirements for bringing about effective control of ionomeric properties.

As so often happens, this research has brought out some
new problems as well as areas which still remain unanswered. Some
scattering was present in the case of the 0.50Cs-Dry sample and
so quantitative analysis of the scattering profile should be
performed to determine the nature of this scattering. This study
is incomplete in as much as only sodium and cesium sulfonate ionomers
were studied. It would be interesting to study the effects of
other cations, especially multivalent ones, as well as other acid
functional groups such as carboxylates, phosphonates and thioglycolates.
In addition, a better understanding of the cation's environment and
factors that affect it could give a better understanding of the
importance of ionic interactions. A technique which may prove
useful is far infrared. By using far infrared it may be possible
to look specifically at the cationic environment and especially how
it may be affected by temperature, humidity, etc. Lastly, low
temperature DSC, especially with comparison to the dynamic-mechanical
results, may give more information on the nature of the low
temperature relaxations in sulfonated polysulfone ionomers.

REFERENCES

1. T.R. Earnest and W.J. MacKnight, J. Poly. Sci.(Review), 16,
    41 (1981).

2. H.P. Brown, Rubber Chem. Tech., 30, 1347 (1957).

3. U.S. Patent 3,264,272 to E.I. duPont de Nemours and Co., Inc.,
    (1964).

4. R.W. Rees and D.J. Vaughan, ACS Polymer Preprints, 6, 287 and 296
    (1965)

5. R. Longworth and H. Morawetz, J. Poly. Sci., 29, 307 (1953).

6. K.S. Wissbrun, Makromol. Chem., 118, 211 (1968).

7. K. Sanui, R.W. Lenz and W.J. MacKnight, J. Poly. Sci. (Chem.), 12,
    1965 (1974).

8. W.G.F. Grot, Chem. Eng. Tech., 44, 1967 (1972).

9. H.S. Makowski, R.D. Lundberg, L. Westerman and J. Bock, ACS
    Polymer Preprints, 19(2), 292 (1978).

10. A. Noshay and L.M. Robeson, ACS Polymer Preprints 16(2), 81 (1975).

11. a. A. Eisenberg, ed., J. Poly. Sci. (symposium), 45 (1974).

    b. A. Eisenberg, ed., "Ions in Polymers", Adv. in Chem. Series
        #187, ACS, 1980.

    c. A. Eisenberg and H.L. Yeager, eds., "Perfluorinated
        Ionomer Membranes", ACS Symposium Series #180, 1982.

    d. Biennial Meeting of the Gordon Conference (Begun 1979).

    e. Macromolecular Secretariat Presentation Series, Philadelphia
        ACS Meeting, 1984.

12. A. Eisenberg and M. King, "Ion-Containing Polymers", Academic
    Press, New York, 1977.

13. W. Cooper, J. Poly. Sci., 28, 195 (1958).

14. a. E.P. Otocka and F.R. Eirich, J. Poly. Sci. (A2), 6, 921 (1968).

    b. E.P. Otocka and F.R. Eirich, J. Poly. Sci., (A2), 6, 933 (1968).

15. a. L.D. Pettit and S. Bruckenstein, J. Am. Chem. Soc., 88, 4783 (1960).

    b. A. Eisenberg, Macromolecules, 3(2), 147 (1970).

16. a. E.P. Otocka, M.Y. Hellman and L.L. Blyer, J. Appl. Phys., 40, 4221 (1969).

    b. A. Eisenberg and M. Navratil, Macromolecules, 6, 604 (1975).

    c. M. Pineri, C. Meyer, A.M. Levelut and M. Lambert, J. Poly. Sci. (Physics), 12, 115 (1974).

17. A. Eisenberg and M. King, "Ion-Containing Polymers", Academic Press, New York, 1977.

18. H.A. Davis, R. Longworth and D.J. Vaughan, ACS Polymer Preprints, 9, 515 (1968).

19. C.L. Marx, J.A. Koutsky and S.L. Cooper, Polymer Letters, 9, 167 (1971).

20. M. Pineri, C. Meyer and A. Bourret, J. Poly. Sci. (Physics), 13, 1881 (1975).

21. T.D. Gierke, G.E. Munn and F.C. Wilson, J. Poly. Sci. (Physics), 19, 1687 (1981).

22. D.L. Handlin, W.J. MacKnight, J. Williams and E.L. Thomas, Macromolecules, 14, 795 (1981).

23. C. Meyer and M. Pineri, J. Poly. Sci. (Physics), 16, 569 (1978).

24. W.J. MacKnight, W.P. Taggart and R.S. Stein, J. Poly. Sci., C-45, 113 (1974).

25. G. Porod, Colloid Zeit., 124, 83 (1951).

26. A. Guinier and G. Fornet, "Small Angle Scattering of X-Rays", Wiley, New York, 1955.

27. S. Bonotto and E.F. Bonner, Mod. Plast., 112, 1356 (1965).

28. S. Bonotto and C.L. Purcell, Macromolecules, 1, 510 (1968).

29. R. Longworth and D.J. Vaughan, ACS Polymer Preprints, 9, 525 (1968).

30. C.L. Marx, D.F. Caulfield and S.L. Cooper, Macromolecules, 6, 344 (1973).

31. F.L. Binsbergen and G.F. Kroon, Macromolecules, 6, 344 (1973).

32. R.J. Roe, J. Phys. Chem., 76, 1311 (1972).

33. J. Kao, R.S. Stein, W.J. MacKnight, W.P. Taggart and G.S. Cargill,
     Macromolecules, 7, 95 (1974).

34. A. Guinier and G. Fornet, "Small Angle Scattering of X-Rays,"
     Wiley, New York, 1955.

35. a. C.T. Meyer and M. Pineri, J. Poly. Sci. (Physics), 13,
         1057 (1975).

     b. C.T. Meyer and M. Pineri, Polymer, 17, 382 (1976).

     c. C.T. Meyer and M. Pineri, J. Poly. Sci. (Physics), 16, 569
         (1978).

36. a. E.P. Otocka and F.R. Eirich, J. Poly. Sci. (A2), 6, 921
         (1968).

     b. E.P. Otocka and F.R. Eirich, J. Poly. Sci. (A2), 6, 933
         (1968).

37. W.E. Fitzgerald and L.E. Nielsen, Proc. Roy. Soc. London Ser. A.,
     282, 137 (1967).

38. N.Z. Erdi and H. Morawetz, J. Colloid Sci., 19, 708 (1964).

39. a. A. Eisenberg and M. Navratil, J. Poly. Sci. (B), 10, 206
         (1972).

     b. A. Eisenberg and M. Navratil, Macromolecules, 6, 604 (1973).

     c. A. Eisenberg and M. Navratil, Macromolecules, 6, 734 (1973).

     d. A. Eisenberg and M. Navratil, Macromolecules, 7, 84 (1974).

     e. A. Eisenberg and M. Navratil, Macromolecules, 7, 90 (1974).

40. a. R.W. Rees and D.J. Vaughan, ACS Polymer Preprints, 6, 287
         (1965).

     b. E.P. Otocka and T.K. Kwei, Macromolecules, 1, 244 (1968).

     c. E.P. Otocka and T.K. Kwei, Macromolecules, 1, 401 (1968).

     d. E.P. Otocka and T.K. Kwei, Macromolecules, 2, 110 (1969).

e.   R. Longworth and D.J. Vaughan, ACS Polymer Preprints, $\underline{9}$, 525 (1968).

f.   W.J. MacKnight, L.W. McKenna and B.E. Read, J. Appl. Phys., $\underline{38}$, 4208 (1967).

g.   W.J. MacKnight, T. Kajiyama and L.W. McKenna, Polym. Eng. and Sci., $\underline{8}$, 267 (1968).

h.   L.W. McKenna, T. Kajiyama and W.J. MacKnight, Macromolecules, $\underline{2}$, 58 (1969).

41. a.   K. Sanui, W.J. MacKnight and R.W. Lenz, J. Poly. Sci. (Chemistry), $\underline{12}$, 1965 (1974).

b.   C. Azuma and W.J. MacKnight, J. Poly. Sci. (Chemistry), $\underline{15}$, 547 (1978).

c.   D. Rahrig and W.J. MacKnight, Adv. Chem. Series, $\underline{187}$, 77 (1978).

d.   D. Rahrig and W.J. MacKnight, Adv. Chem. Series, $\underline{187}$, 91 (1978).

e.   H. Tanaka and W.J. MacKnight, J. Poly. Sci. (Chemistry), $\underline{17}$, 2975 (1978).

42. a.   D. Rahrig, C. Azuma and W.J. MacKnight, J. Poly. Sci. (Physics), $\underline{16}$, 59 (1978).

b.   D. Rahrig, W.J. MacKnight and R.W. Lenz, Macromolecules, $\underline{12}$, 195 (1979).

c.   D. Rahrig and W.J. MacKnight, Adv. Chem. Series, $\underline{187}$, 77 (1978).

d.   D. Rahrig and W.J. MacKnight, Adv. Chem. Series, $\underline{187}$, 91 (1978).

e.   D. Rahrig, Ph.D. Thesis, Univ. of Mass., 1978.

43. R.D. Lundberg and H.S. Makowski, ACS Polymer Preprints, $\underline{19}$, 287 (1978).

44. R.D. Lundberg, H.S. Makowski and L. Westerman, ACS Polymer Preprints, $\underline{19}$, 310 (1978).

45. a.   H.S. Makowski and R.D. Lundberg, ACS Polymer Preprints, $\underline{19}$, 304 (1978).

b.   H.S. Makowski, R.D. Lundberg, L. Westerman and J. Bock, $\underline{19}$, 292, (1978).

c. R.M. Neumann, W.J. MacKnight and R.D. Lundberg, ACS Polymer
        Preprints, 19, 298 (1978).

46. P.K. Agarwal, H.S. Makowski and R.D. Lundberg, Macromolecules,
        13, 1679 (1980).

47. a. F.B. Leitz, M.A. Accomazzo and S.A. Michalek, Paper Presented
            at the 141st Meeting of the Electrochemical Society in
            Houston, Texas, May 1972.

     b. W.G.F. Grot, G.E. Munn and P.N. Walmsley, Paper Presented at
            the 141st Meeting of the Electrochemical Society in
            Houston, Texas, May 1972.

     c. W.G.F. Grot, Chem. Eng. Tech., 44, 167 (1972).

     d. J.E. Harrar and R.J. Sherry, Analt. Chem., 47, 601 (1975).

48. a. W.G.F. Grot, G.E. Munn and P.N. Walmsley, 141st Meeting of
            the Electrochemical Society in Houston, Texas, May 1972.

     b. H.L. Yeager and B. Kipling, J. Phys. Chem., 83, 1836 (1979).

49. a. S.F. Burkhardt, 152nd Meeting of the Electrochemical Society,
            Atlanta, Georgia, 1977.

     b. R.S. Yeo and J. McBreen, J. Electrochem. Soc., 126, 1682
            (1979).

     c. H.L. Yeager, B. Kipling and R.S. Dotson, J. Electrochem. Soc.,
            127, 303 (1980).

50. a. W.G.F. Grot, G.E. Munn and P.W. Walmsley, 141st Meeting of the
            Electrochemical Society, Houston, Texas, May 1972.

     b. S.C. Yeo and A. Eisenberg, J. Appl. Polym. Sci., 21, 875 (1977).

51. a. S.C. Yeo and A. Eisenberg, J. Appl. Poly. Sci., 21, 875 (1977).

     b. R. Duplessix, et al., "Water Absorption in Acid Nafion
            Membranes" in Water in Polymers, S.P. Rowland, ed.,
            ACS Symposium Series 127, 1980.

     c. R. Rodmacq, et al., "Water Absorption in Neutralized Nafion
            Membranes" in Water in Polymers, S.P. Rowland, ed., ACS
            Symposium Series 127, 1980.

     d. E. Roche, M. Pineri and R. Duplessix, J. Poly. Sci. (Physics),
            20, 107 (1982).

52. A. Steck and H.L. Yeager, Analt. Chem., 52, 1215 (1980).

53. R.A. Komorski and K.A. Mauritz, J. Amer. Chem. Soc., 100:24, 7487 (1978).

54. S.C. Yeo, Ph.D. Thesis, McGill University, Montreal, Canada, 1977.

55. T.D. Gierke, G.E. Munn and F.C. Wilson, J. Poly. Sci. (Physics), 19, 1687 (1981).

56. A. Eisenberg, Macromolecules, 4, 125 (1971).

57. J. Kolarik and K. Dusek, J. Macromolecular Sci., B10, 157 (1974).

58. Y.S. Papir, S. Kapur, C.E. Rogers and E. Baer, J. Poly. Sci. (A2), 10, 1305 (1972).

59. M. Takayanagi, Mem. Fac. Eng. Kyushu Univ., 23, 1(1963).

60. a. A. Eisenberg and M. King, "Ion-Containing Polymers", Academic Press, New York, 1977.

    b. M. Rigdhal and A. Eisenberg, J. Poly. Sci. (Physics), in press.

61. A. Eisenberg in "Perfluorinated Ionomer Membranes", ACS Symposium Series 180, 1982.

62. a. G. Eisenman, Proc. 23rd Int. Congr. of Physiol. Sci., Exerpta Medica, 87, 489, 1965.

    b. G. Eisenman in "Ion-Selective Electrodes", R.A. Durst, ed., Natl. Bur. Std. Spec. Publ., 314, Chapter 1, 1969.

63. D. Richenberg in "Ion-Exchange", J.A. Marinsky, ed., Marcel Dekker, New York, 1966.

64. G.E. Boyd in "Charged Gels and Membranes", E. Selegny, ed., D. Reidel, Holland, 1976.

65. a. O.D. Bonner and L.L. Smith, J. Phys. Chem., 61, 326 (1957).

    b. O.D. Bonner, J. Phys. Chem., 59, 719 (1955).

    c. G.E. Boyd in "Charged Gels and Membranes", E. Selegny, ed., D. Reidel, Holland, 1976.

    d. G.E. Boyd, F. Vaslow and S. Lindenbaum, J. Phys. Chem., 71, 2214 (1967).

66. a. G.E. Boyd, F. Vaslow and S. Lindenbaum, J. Phys. Chem., 71, 2214 (1967).

    b. I. Gamalinda, L.A. Schloemer, H.S. Sherry and H.F. Walton, J. Phys. Chem., 71, 1622 (1967).

67. R.W. Johnson, A.G. Farnham, R.A. Clendenning, W.F. Hale and C.W. Merriam, J. Poly. Sci., (A1), 5, 2375,2399 and 2415 (1967).

68. J. Heijboer, "Modulus and Damping of Polymers in Relation to Their Structure", Lecture presented for the Plastics and Polymer Group of the Society of the Chemical Indistry, London, October 17, 1967.

69. M. Baccaredda, E. Butta, V. Frosini and S. DePetris, J. Poly. Sci. (A2), 5, 1296 (1967).

70. L.M. Robeson and J.A. Faucher, Polymer Letters, 7, 35 (1969).

71. J.E. Kurz, J.E. Woodbrey and M. Ohta, J. Poly. Sci. (A2), 8, 1169 (1970).

72. G. Allen, J. McAinsh and G.M. Jeffs, Polymer, 12, 85 (1971).

73. I. Kawaguchi, J. Poly. Sci., 32, 417 (1958).

74. L M. Robeson, A.G. Farnham and J.E. McGrath, ACS Polymer Preprints, 16(1), 476 (1975).

75. F.P. Reding, F.A. Faucher and R.D. Whitman, J. Poly. Sci., 54, 556 (1961).

76. a. A.F. Turbak and A. Noshay, U.S. Patent 3,206,492 (1965).

    b. E.J. Geothals, Encyclopedia of Polymer Science and Technology, 13, 465 (1970).

    c. A.F. Turbak, A. Noshay and G. Karoly, U.S. Patent 3,205,285 (1965).

    d. D.W. Fox and S. Popkin, U.S. Patent 3,259,592 (1966).

    e. P.J. Chludzinski, A.D. Fickett and A.B. LaConti, ACS Polymer Preprints, 12(2), 276 (1971).

    f. W.J. Ward and R.M. Salemme, U.S. Patent 3,780,496 (1973).

g. S.G. Kimura, Ind. Eng. Chem. Prod. Res. Dev., $\underline{10}$(3), 335 (1971).

h. N.H. Canter, Ger. Offen., 1,915,236 (1969).

i. C.P. O'Farrell and G.E. Serniuk, U.S. Patent 3,836,511 (1974).

j. C. Lepatin and H.A. Newey, ACS Polymer Preprints, $\underline{12}$(2), 230 (1971).

k. W.T. O'Neill and W.V. Turner, U.S. Patent 3,642,953 (1972).

l. D.E. Winkler, U.S. Patent 3,577,357 (1971).

m. J. Ueno, M. Watanabe and Y. Tanaka, Jap. Patent 24,988(1965), (Chem. Abst., $\underline{65}$, 9110 (1965).

n. C.J. Kibler and G.R. Lappin, U.S. Patent 3,734,874 (1973).

o. R. Salle and B. Sillion, French Patent 2,212,356 (1974), (Chem. Abst., $\underline{82}$, 99140 (1975)).

77. a. J.P. Quentin, U.S. Patent 3,709,841 (1973).

    b. J. Bourganel, U.S. Patent 3,855,122 (1974).

78. A.F. Turbak, Ind. Eng. Chem. Prod. Res. Dev., $\underline{1}$(4), 275 (1962).

79. Communications from P.W. Kopf, Union Carbide Corporation.

80. A. Noshay and L.M. Robeson, J. Appl. Poly. Sci., $\underline{20}$, 1885 (1976).

81. a. C.L. Brousse, R. Chapurlat and J.P. Quentin, Desalination, $\underline{18}$, 137 (1976).

    b. N. Vinnikova and G.B. Tanny, Desalination, $\underline{24}$, 191 (1978).

82. a. E.J. Geothals, "Encyclopedia of Polymer Science and Technology", Wiley Interscience, New York, $\underline{13}$, 465 (1970).

    b. H.H. Roth, Ind. Eng. Chem., $\underline{49}$, 1820 (1957).

    c. W.P. O'Neill and W.V. Turner, U.S. Patent 3,642,953 (1972).

    d. N.H. Cantor, U.S. Patent 3,642,728 (1972).

    e. H.S. Makowski, R.D. Lundberg and G. Singhal, U.S. Patent 3,870,841 (1975).

83. a. G.D. Jones, "Chemical Reactions of Polymers", E.M. Fettes, ed., Wiley Interscience, New York, Chapter 3, 1964.

    b. T. Huff and B.H. Johnson, J. Appl. Poly. Sci., 17, 553 (1973).

84. E.E. Gilbert, "Sulfonation and Related Reactions", G.A. Olah, ed., Wiley Interscience, New York, 1965.

85. J. Crank and G.S. Park, "Diffusion in Polymers", Academic Press, London, 1968.

86. H.L. Frisch, Poly. Eng. and Sci., 20, 2 (1980).

87. A. Eisenberg, Macromolecules, 7, 84 (1974).

88. A. Eisenberg, Macromolecules, 7, 84 (1974).

89. a. J. O'mBockris, Quart. Rev., 3, 173 (1949).

    b. O.Y. Samoilov, Disc. Faraday Soc., 24 141 (1957).

90. F.A. Lindemann, Z. Phys. Chem., 110, 394 (1924).

91. R.A. Komorski and K.A. Mauritz, "Nuclear Magnetic Resonance of Ion Pairing in Perfluorosulfonate Ionomers" in Perfluorinated Ionomer Membranes, A. Eisenberg and H.L. Yeager, eds., ACS Symposium Series 180, Chapter 7, 1982.

92. R. Creekmore and J. Reilly, Analt. Chem., 42, 570 (1970).

APPENDIX

TABLE 2-1

Common Physical and Mechanical Properties of Polysulfone

Property	Value	ASTM No.
Glass Transition Temperature	195°C	---a
Softening Temperature (264 psi)	174°C	D648
Tensile Strength @ Yield	10,200 psi	D638
Tensile Modulus	2 X 10^{10} dynes/cm^2	D638
Elongation at Break	50 to 100 %	D638
Impact Strength	300 - 500 ft-lb/in^3	D1822
Density	1.24 g/cm^3	D1505

a. Measured with a torsional pendulum

TABLE 2-2

Bond Dissociation Energies of Polysulfone

Bond Type	Bond Dissociation Energy
CH_3- C	60 Kcal/mole
Ø - S	65 Kcal/mole
Ø - C	83 Kcal/mole
Ø - O	86 Kcal/mole
CH_2 - H	99 Kcal/mole
Ø - H	102 Kcal/mole
S = O	119 Kcal/mole
C∴C aromatic	148 Kcal/mole

TABLE 3-1

Sample Descriptions

Sample	Thickness	Ion-Exchange Capacity[a]
0.30 Cs	25 and 100 microns	0.635 meq/gram
0.35 Cs	50 microns	0.75 meq/gram
0.50 Cs	25, 50 and 100 microns	1.00 meq/gram
0.35 Na	50 microns	0.75 meq/gram
0.50 Na	35 and 50 microns	1.00 meq/gram
0.80 Na	35 microns	------
1.00 Na	40 microns	------

a. The ion-exchange capacity is defined as:

$$IEC = \frac{V_2 - V_1}{2P_g}$$

where V_1 equals the volume of a 0.5 N HCl solution

necessary to neutralize excess NaOH after 25 ml. of

a 0.5 N NaOH solution have been added to the acid

form of the polymer. V_2 equals the volume of the same

solution necessary to neutralize 25 ml. of 0.5 N NaOH

solution and P_g is the weight of polymer in the test solution.

TABLE 3-2

Infrared Spectra Peak Assignments

Peak Value (cm^{-1})	Peak Assignment
560	SO_2 wag
625,690 and 715	C - S stretch
835	C-H out of plane bend; p-subst. aromatic
855 and 875[a]	C-H out of plane bend; tri-subst. aromatic
1015	p-subst. aryl ether ring vibration
1025[a]	symmetric sulfonate stretch
1080, 1090 and 1110	aromatic ring vibrations
1150	symmetric sulfone stretch
1170	symmetric aryl ether stretch
1190[a]	asymmetric sulfonate stretch
1210	C - C vibration; isopropylene unit
1245	asymmetric aryl ether stretch
1295 and 1325	asymmetric sulfone stretch (doublet)
1365 and 1395	symmetric C-H bend of CH_3
1410	asymmetric C-H bend of CH_3
1490, 1505 and 1590	aromatic C·:·C stretch
2880	asymmetric C-H stretch of CH_3
2930	symmetric C-H stretch of CH_3
3040, 3080 and 3100	aromatic C-H stretch
3200 to 3700[a]	hydrogen bonding

a. These peaks are present only in the ionomers.

TABLE 3-3

Differential Scanning Calorimetry Results

Sample	T_g (Dry)[a]	T_g (Wet)[b]	Other[c]
0.35 Na	240°C	-	-
0.50 Na	270°C	-	-
0.80 Na	-	270°C	-
1.00 Na	320-335°C [d]	320°C [d]	-
0.30 Cs	245°C	208°C	None
0.50 Cs	273°C	256°C	0° - 3°C
Polysulfone	190°C	190°C	-

a. Samples dried 24 hours @ 110°C in vacuum. T_g taken as average of three runs through the range of 125° to 325°C at 20° per minute.

b. Samples dried as above then immersed in water @ 25°C for two weeks. T_g taken as average of three runs through the range of 150°C to just beyond T_g at 20° per minute.

c. Samples saturated with water as above then cooled to -35°C and run to 40°C followed by recooling to -35°C. This value is representative of the transition but the size and shape of the peak changed with each run.

d. Weak and/or broad transition.

TABLE 3-4

Dynamic-Mechanical Relaxation Summary

A. Tan Delta Behavior (@ 11 Hz)

Sample	Peak Temperature (Intensity)	βPeak Temperature (Intensity)	αPeak Temperature (Intensity)
0.35Cs-Wet	-85°C(0.020)	-21°C(0.021)	260°C(0.96)
0.35Cs-R.H.	-92°C(0.022)	-13°C(0.015)	252°C (1.12)
0.35Cs-Dry	-76°C(0.020)	-16°C(0.012)	249°C(0.93)
0.35Na-Wet	-85°C(0.022)	-17°C(0.022)	252°C(0.85)
0.35Na-R.H.	-79°C(0.026)	-17°C(0.016)	257°C(0.75)
0.35Na-Dry	-61°C(0.030)	-22°C(0.025)	261°C(0.75)
0.50Cs-Wet	-71°C(0.020)	-21°C(0.030)	287°C(0.45)
0.50Cs-R.H.	-68°C(0.027)	-19°C(0.041)	280°C(0.48)
0.50Cs-Dry	-73°C(0.022)	-16°C(0.024)	281°C(0.65)
0.50Na-Wet	-75°C(0.018)	-18°C(0.020)	282°C(0.84)
0.50Na-Dry	-64°C(0.023)	-13°C(0.013)	297°C(0.91)
0.50Cs-MeOH	-75°C(0.023)	-22°C(0.039)	288°C(0.75)
0.50Cs-120H	-76°C(0.023)	+10°C(0.019)	277°C(1.05)
0.50Cs-DOP	-82°C(0.033)	-23°C(0.019)	278°C(0.98)
0.50Cs-EtSal	-91°C(0.019)	-13°C(0.028)	287°C(0.93)
PSF-Wet	-92°C(0.016)	25-40°C(0.024)	Break at 175°C
PSF-Dry	-100°C(0.017)	---	Break at 166°C

B. Loss Modulus Behavior (@ 11 Hz)

Sample	Peak Temperature (Log E" Value)	Peak Temperature (Log E" Value)	Peak Temperature (Log E" Value)
0.35Cs-Wet	$-85^{\circ}C(8.6)$	$-21^{\circ}C(8.6)$	$250^{\circ}C(9.4)$
0.35Cs-R.H.	$-92^{\circ}C(8.8)$	$-13^{\circ}C(8.4)$	$239^{\circ}C(9.5)$
0.35Cs-Dry	$-76^{\circ}C(8.7)$	$-16^{\circ}C(8.4)$	$245^{\circ}C(9.5)$
0.35Na-Wet	$-88^{\circ}C(8.8)$	$-17^{\circ}C(8.7)$	$238^{\circ}C(9.4)$
0.35Na-R.H.	$-79^{\circ}C(8.9)$	$-17^{\circ}C(8.5)$	$246^{\circ}C(9.4)$
0.35Na-Dry	$-61^{\circ}C(9.1)$	$-22^{\circ}C(9.0)$	$244^{\circ}C(9.3)$
0.50Cs-Wet	$-73^{\circ}C(8.2)$	$-21^{\circ}C(8.5)$	$278^{\circ}C(8.9)$
0.50Cs-R.H.	$-68^{\circ}C(8.3)$	$-19^{\circ}C(8.4)$	$267^{\circ}C(8.8)$
0.50Cs-Dry	$-73^{\circ}C(8.5)$	$-16^{\circ}C(8.5)$	$263^{\circ}C(9.0)$
0.50Na-Wet	$-75^{\circ}C(8.9)$	$-18^{\circ}C(8.8)$	$277^{\circ}C(9.4)$
0.50Na-Dry	$-64^{\circ}C(9.0)$	$-13^{\circ}C(8.7)$	$284^{\circ}C(9.4)$
0.50Cs-MeOH	$-75^{\circ}C(8.5)$	$-25^{\circ}C(8.6)$	$271^{\circ}C(9.0)$
0.50Cs-120H	$-76^{\circ}C(8.6)$	$+10^{\circ}C(8.5)$	$257^{\circ}C(9.2)$
0.50Cs-DOP	$-82^{\circ}C(8.7)$	$-23^{\circ}C(8.3)$	$262^{\circ}C(9.1)$
0.50Cs-EtSal	$-99^{\circ}C(8.5)$	$-13^{\circ}C(8.5)$	$274^{\circ}C(9.0)$
PSF-Wet	$-92^{\circ}C(8.5)$	$+23^{\circ}C(8.6)$	Break at $175^{\circ}C$
PSF-Dry	$-100^{\circ}C(8.5)$	------	Break at $166^{\circ}C$

C. Storage Modulus Behavior (@ 11 Hz)

Sample	Log E' (@-150°C)	Log E' (@25°C)	Log E' (@150°C)	Log E' (@200°C)
0.035Cs-Wet	10.45	10.28	10.25	10.20
0.35Cs-R.H.	10.33	10.24	10.26	10.21
0.35Cs-Dry	10.46	10.31	10.28	10.25
0.35Na-Wet	10.64	10.33	10.36	10.32
0.35Na-R.H.	10.63	10.37	10.34	10.26
0.35Na-Dry	10.42	10.30	10.20	10.20
0.50Cs-Wet	9.961	10.13	10.02	9.972
0.50Cs-R.H.	9.981	9.960	9.850	9.798
0.50Cs-Dry	10.24	10.12	10.00	9.938
0.50Na-Wet	10.67	10.52	10.43	10.37
0.50Na-Dry	10.65	10.53	10.44	10.38
0.50Cs-MeOH	10.26	10.09	10.00	9.945
0.50Cs-120H	10.29	10.17	10.10	10.03
0.50Cs-DOP	10.25	10.06	10.04	9.970
0.50Cs-EtSal	10.25	10.12	10.01	9.960
PSF-Wet	10.38	10.24	10.02	9.35[a]
PSF-Dry	10.36	10.22	9.833	Break @ 165°C

a. Sample value at 175°C just before break.

TABLE 3-5

Experimental and Literature Values

for Diffusion Coefficients *(water in films)*

Sample	$\bar{D}$ (25 C)	$\bar{D}$ (100 C)
Polysulfone	3.3×10^{-11} cm^2/sec	-----
0.3 Na	5×10^{-11} cm^2/sec	5×10^{-10} cm^2/sec
0.5 Na	5×10^{-10} cm^2/sec	2×10^{-9} cm^2/sec
0.3 Cs	1×10^{-9} cm^2/sec	1.5×10^{-9} cm^2/sec
0.5 Cs	1.3×10^{-9} cm^2/sec	1.5×10^{-9} cm^2/sec
Self Diffusion of Water	3×10^{-5} cm^2/sec	
Acid Nafion	2×10^{-6} cm^2/sec	
Polystyrene	3.5×10^{-7} cm^2/sec	
Polystyrene Ionomer	9.0×10^{-10} cm^2/sec	
Nylon 6	9.7×10^{-10} cm^2/sec	
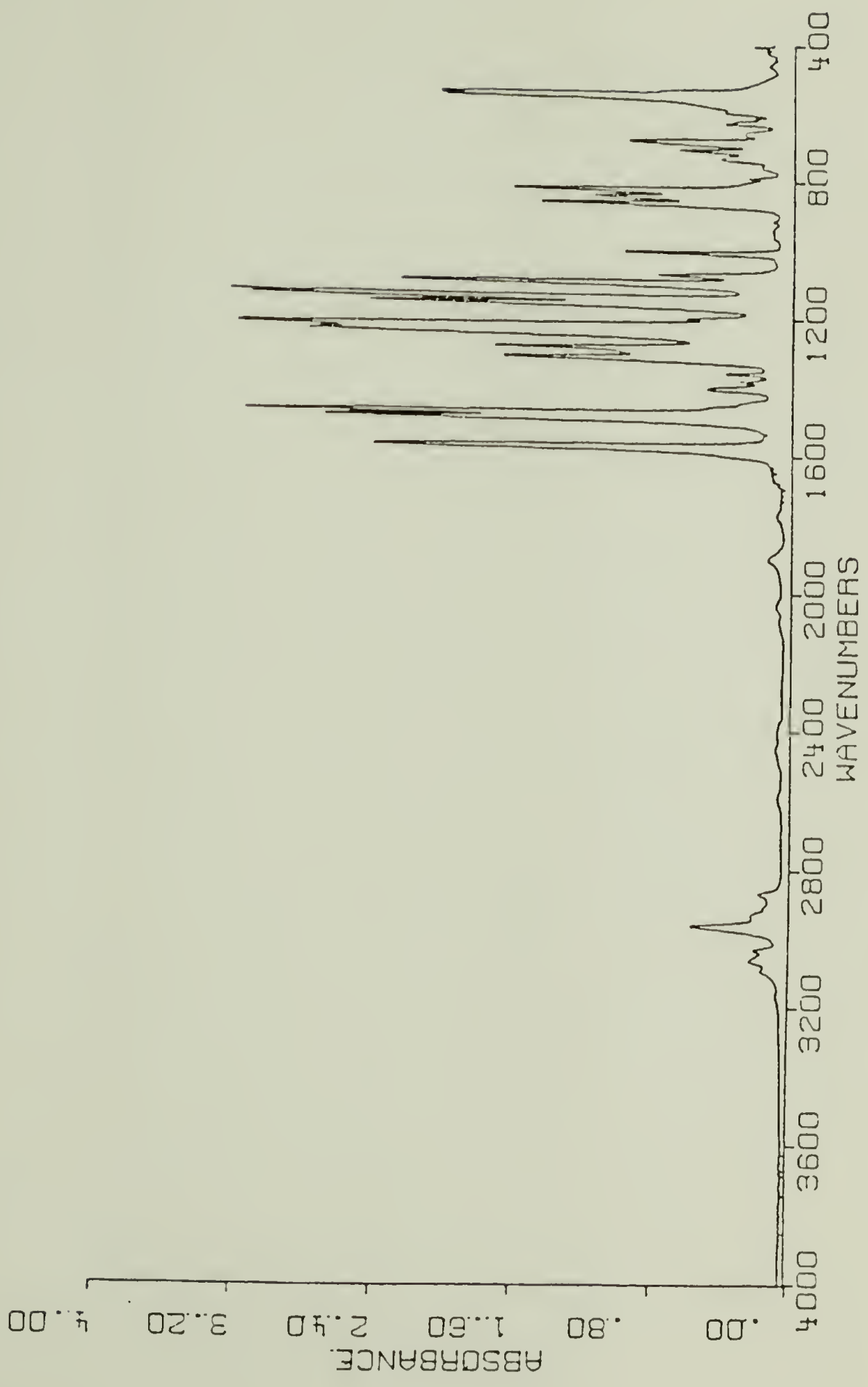
Figure 1.
Fourier Transform Infrared Spectra (4000 to 400 cm⁻¹) of Polysulfone
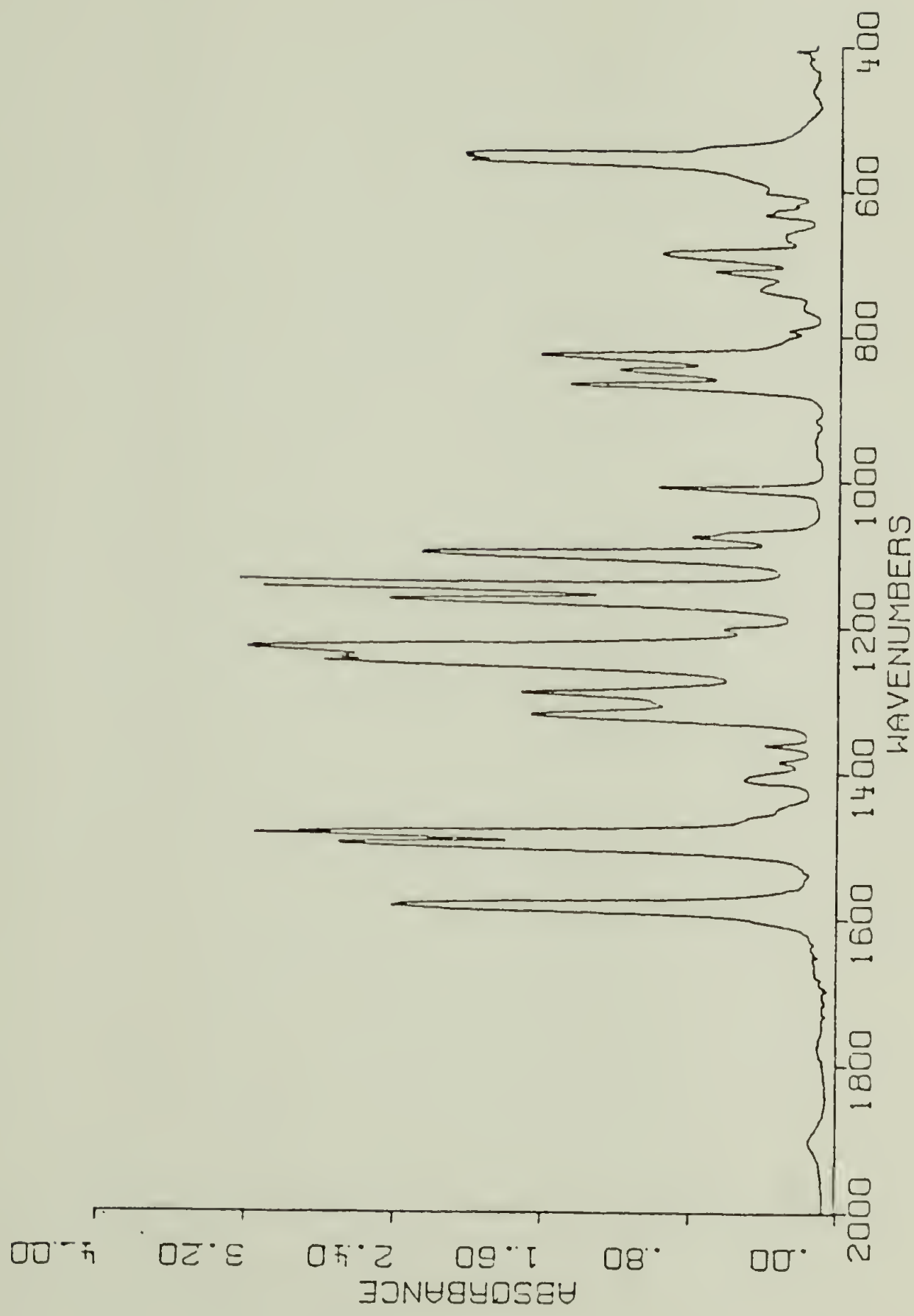
Figure 2.
Fourier Transform Infrared Spectra (2000 to 400 cm^{-1}) of Polysulfone
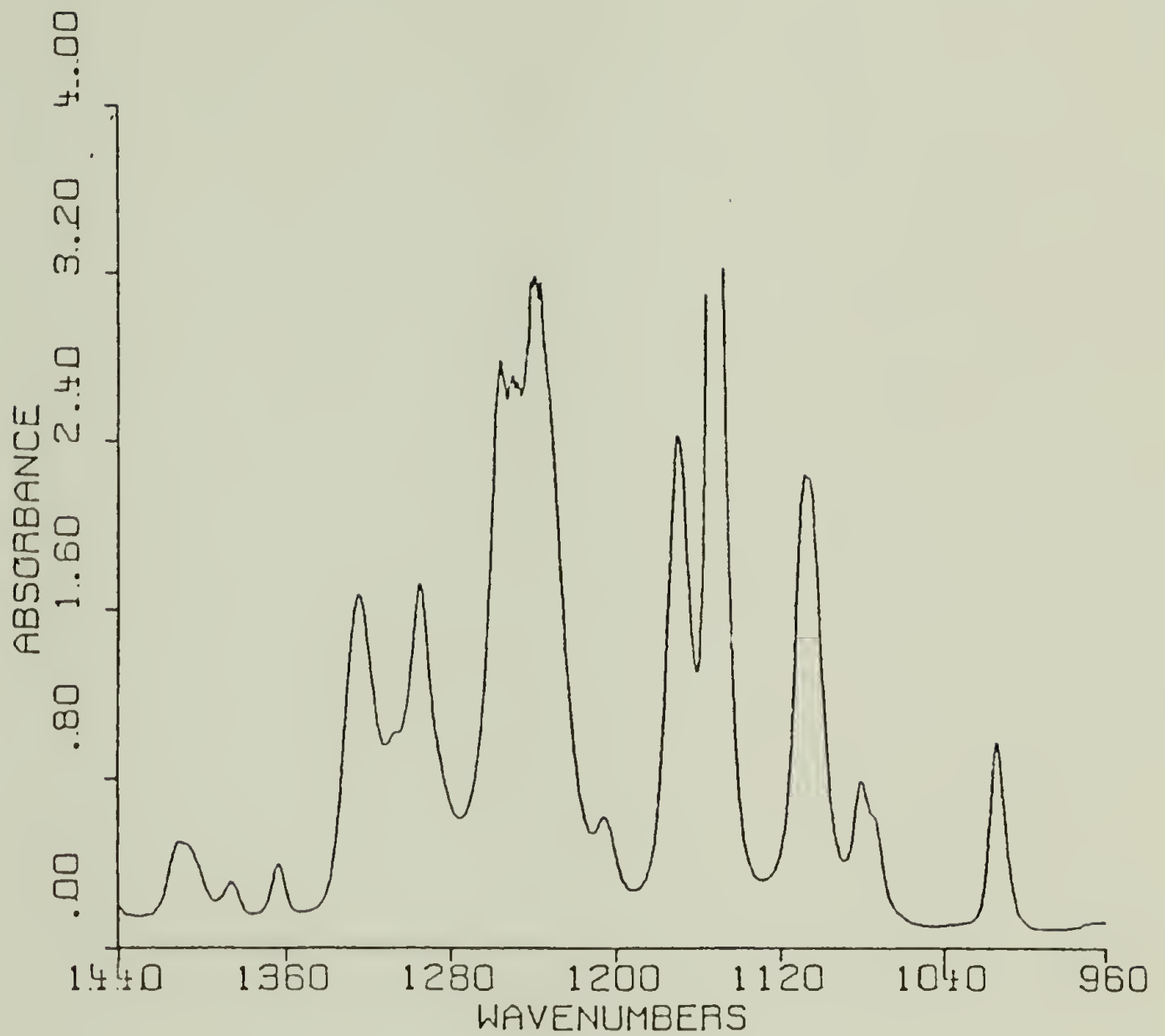
Figure 3.
Fourier Transform Infrared Spectra (1440 to 960 cm^{-1})
of Polysulfone
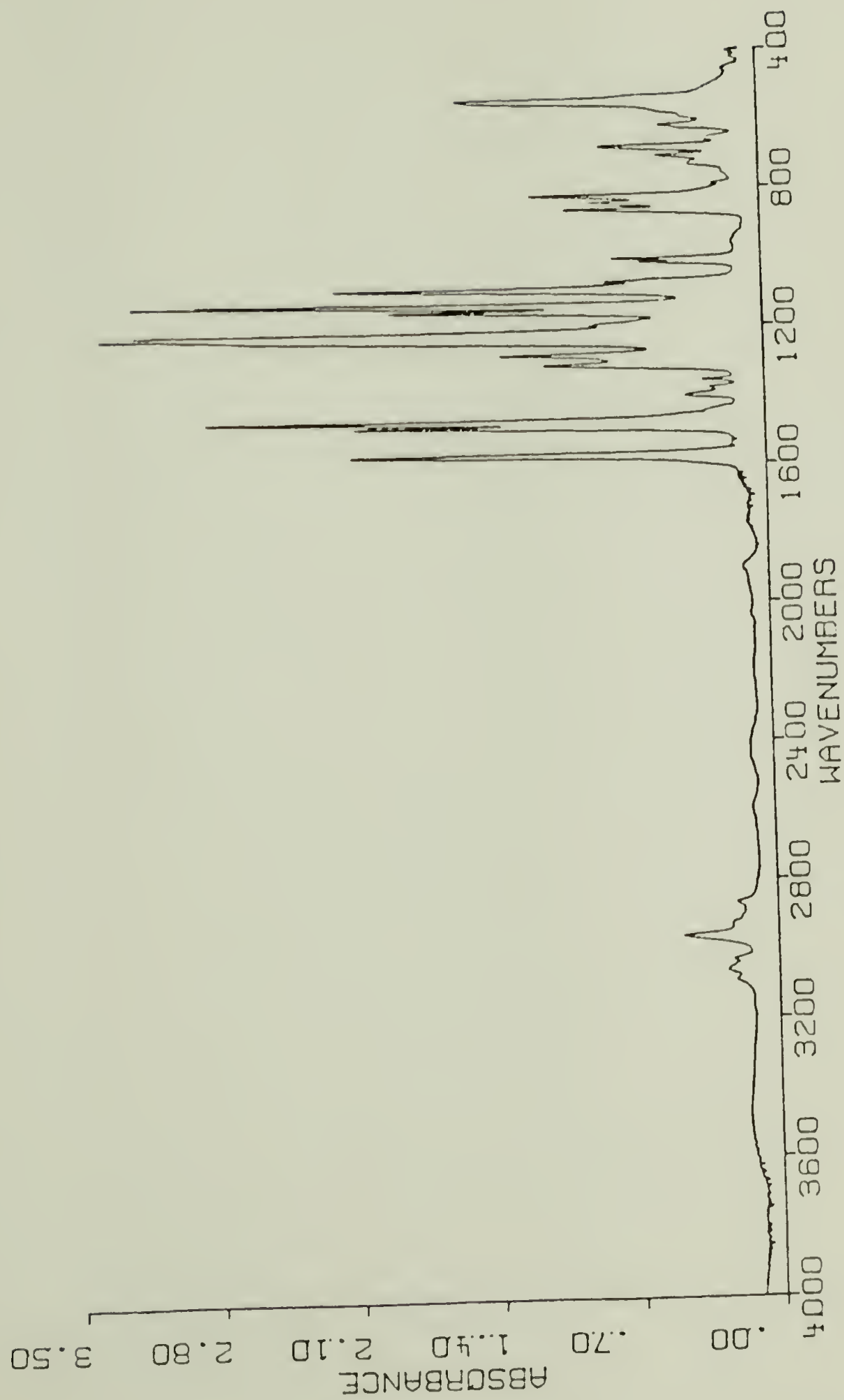
Figure 4.
Fourier Transform Infrared Spectra (4000 to 400 cm^{-1}) of 0.30 Cs -RH
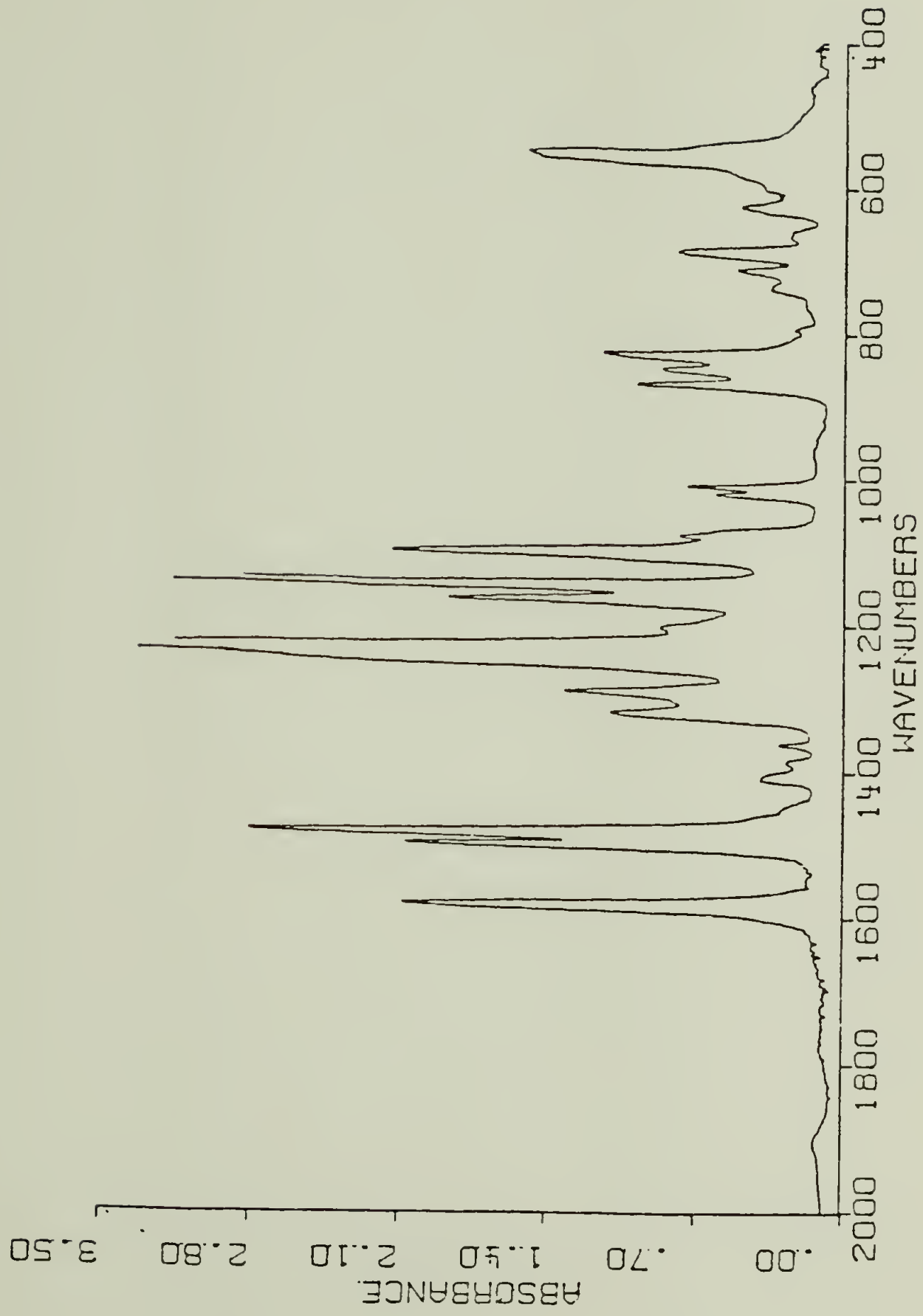
Figure 5.

Fourier Transform Infrared Spectra (2000 to 400 cm^{-1}) of 0.30 Cs - RH
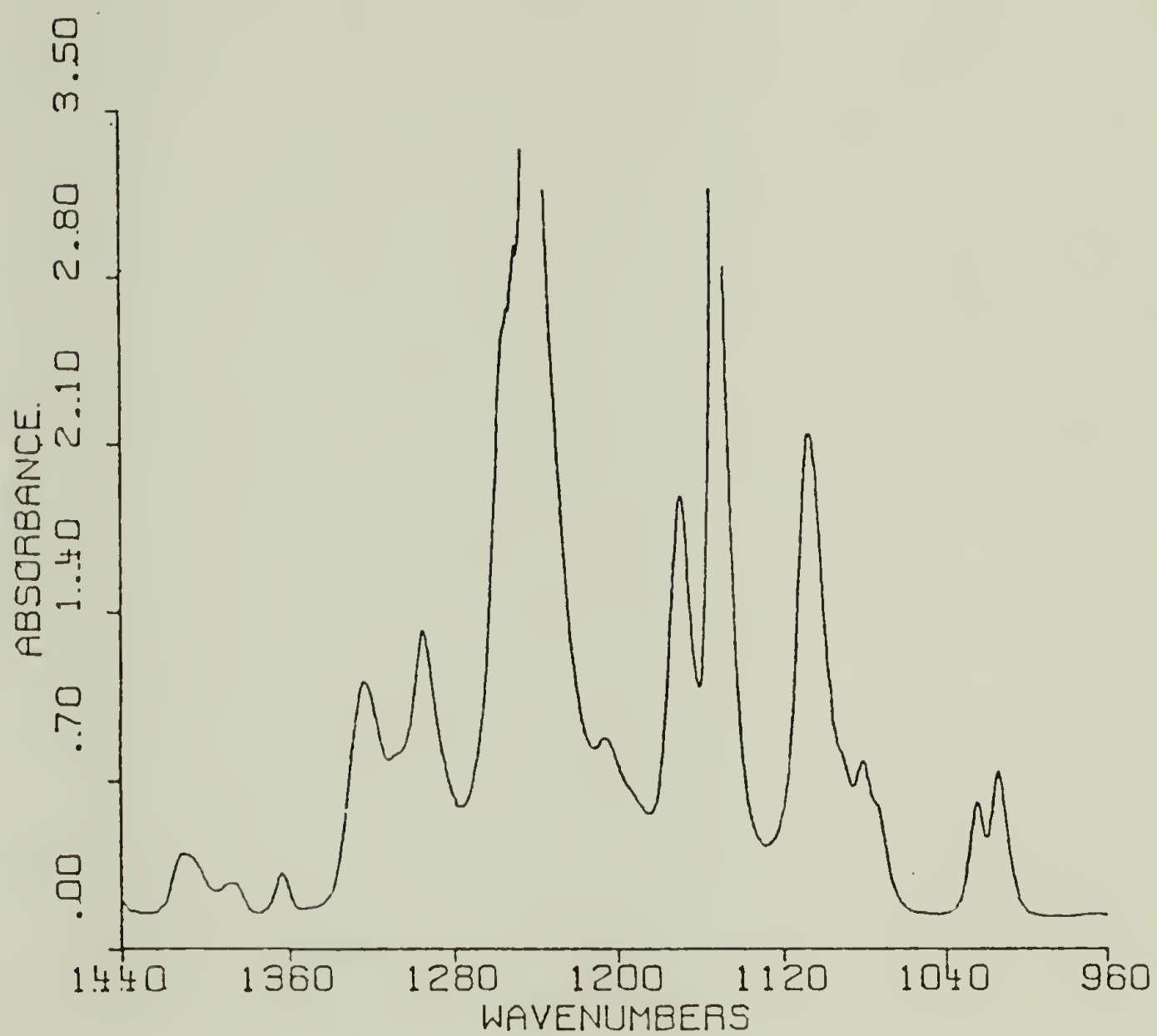
Figure 6.
Fourier Transform Infrared Spectra (1440 to 960 cm^{-1})
of 0.30 Cs - RH
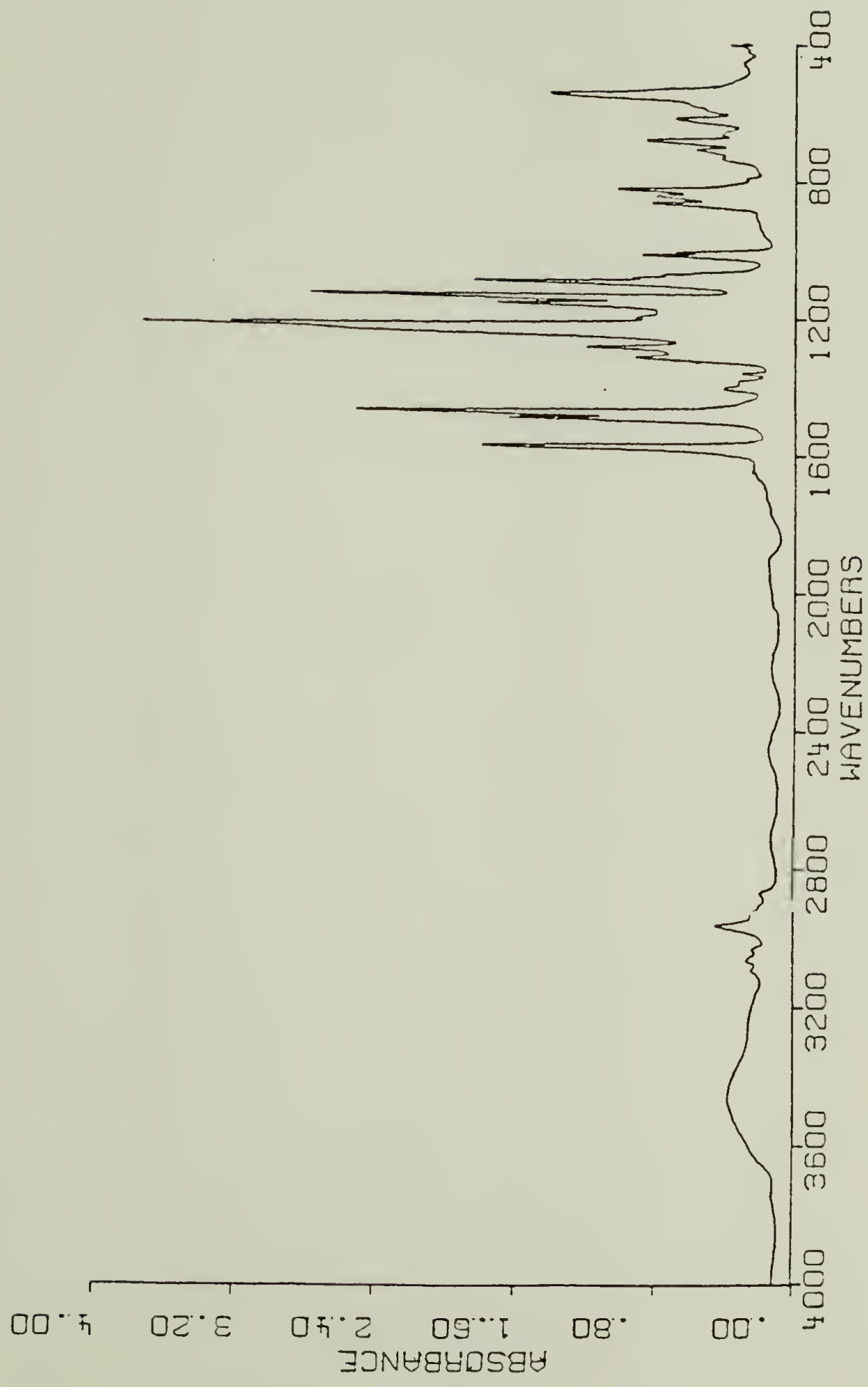
Figure 7.
Fourier Transform Infrared Spectra (4000 to 400 cm^{-1})
of 0.50 Cs - RH

112

Figure 8.
Fourier Transform Infrared Spectra (2000 to 400 cm^{-1})
of 0.50 Cs - RH
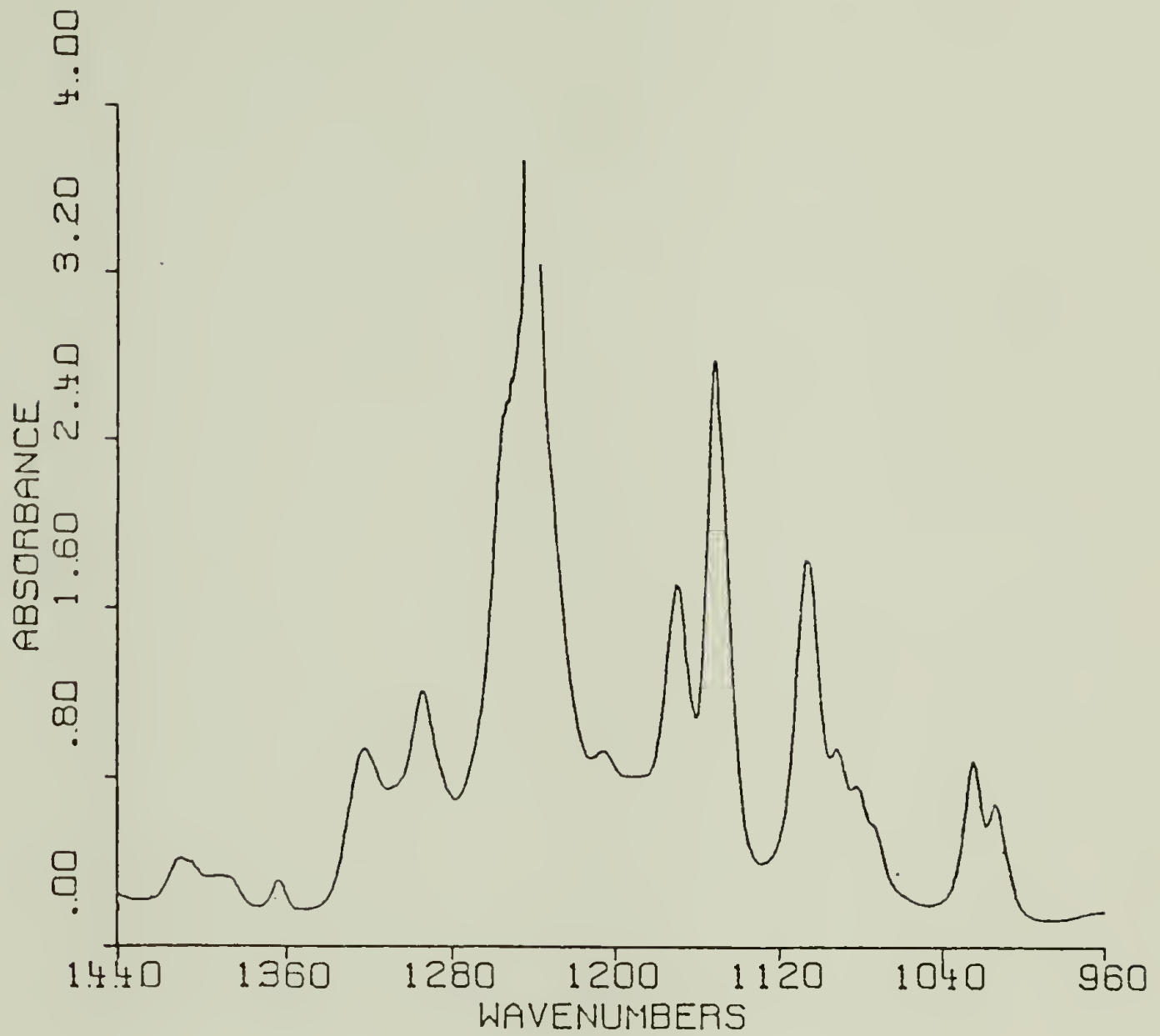
Figure 9.
Fourier Transform Infrared Spectra (1440 to 960 cm^{-1})
of 0.50 Cs - RH
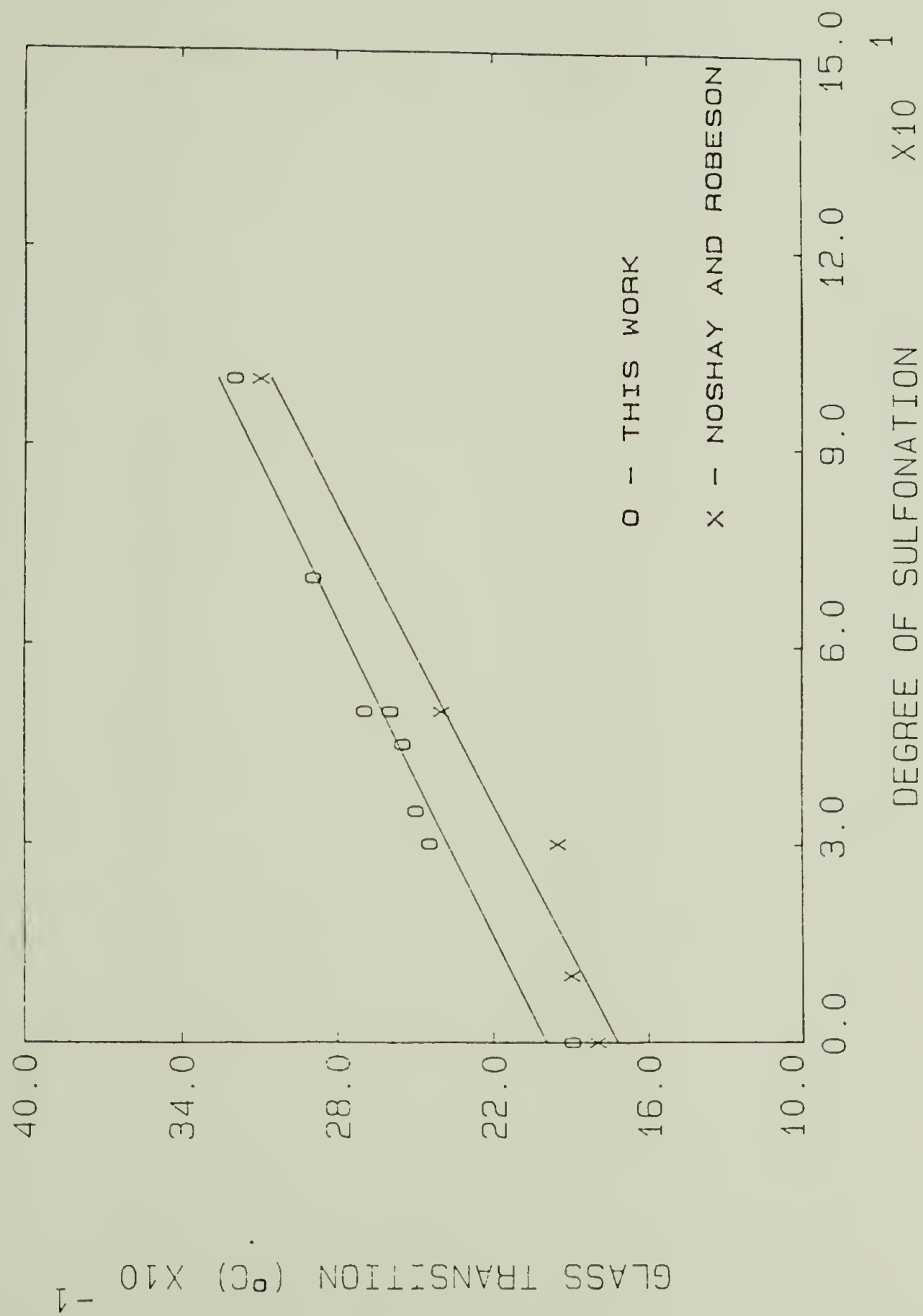
Figure 10.
Effect of the Sulfonation Level on the Glass Transition
Temperature of Sulfonated Polysulfone Ionomers
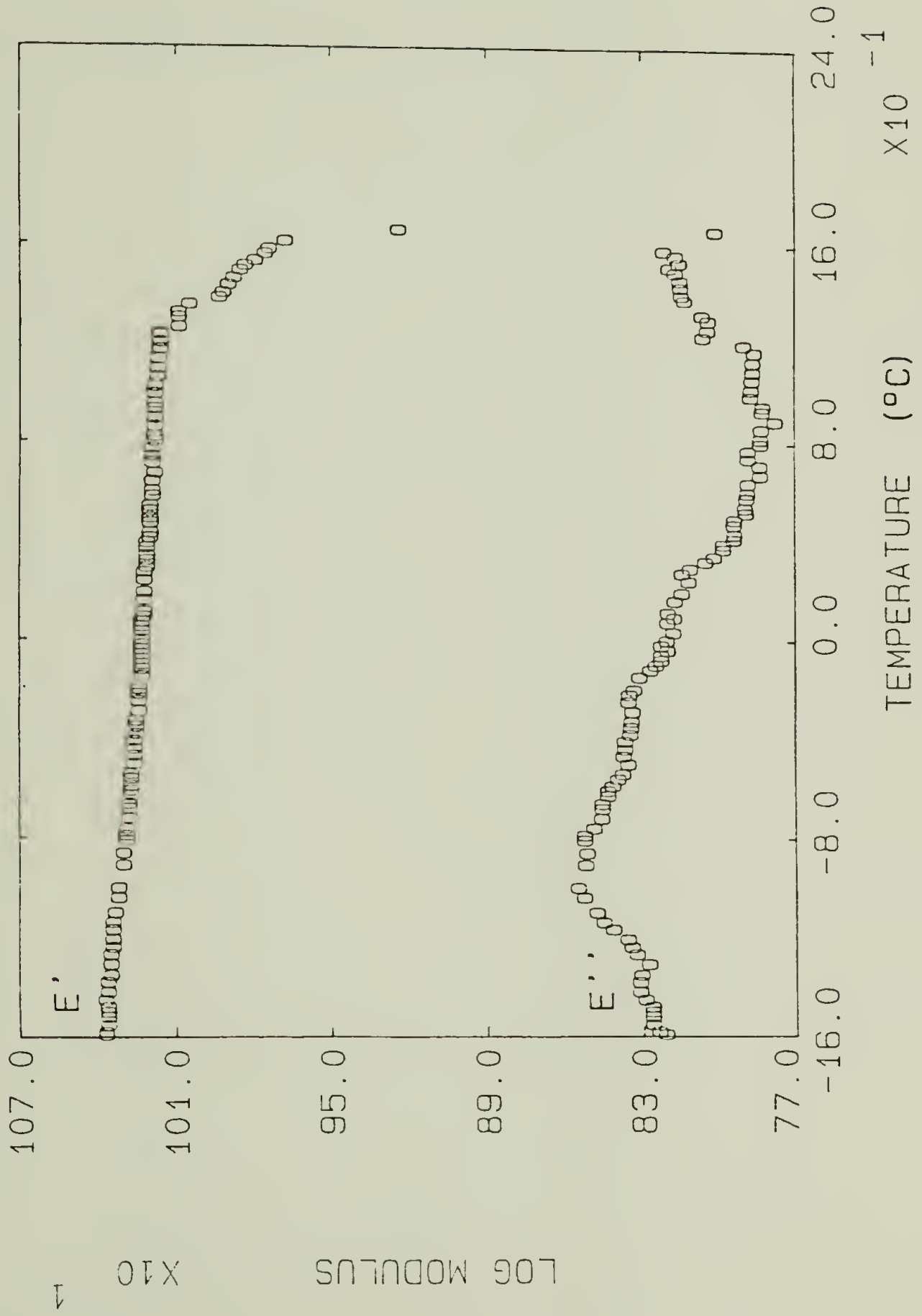
Figure 11.
Temperature Dependence of E' and E" for Polysulfone
at 11 Hz.
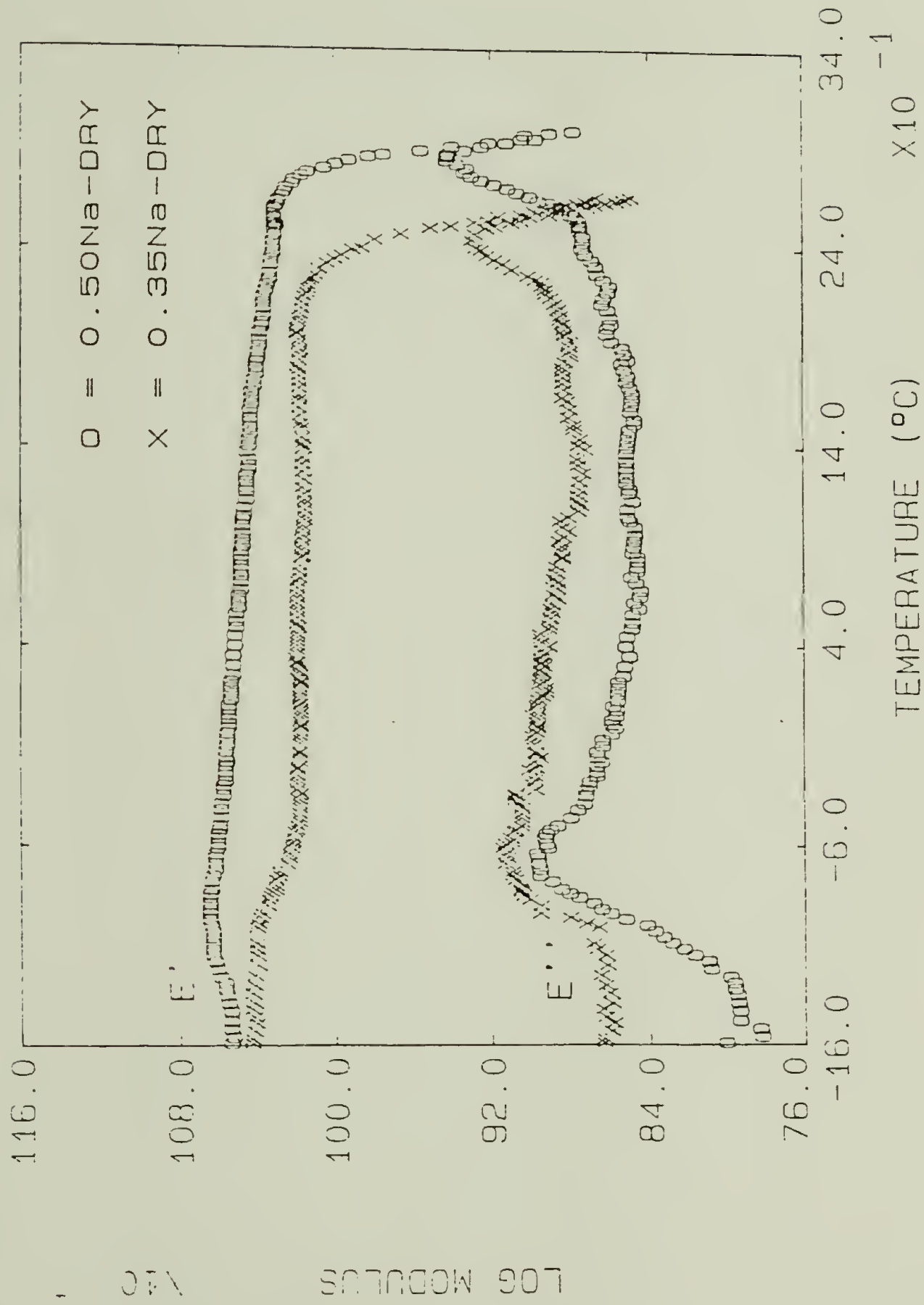
Figure 12.
Temperature Dependence of E' and E" for Sodium
Ionomers as a Function of Sulfonation at 11 Hz.

117
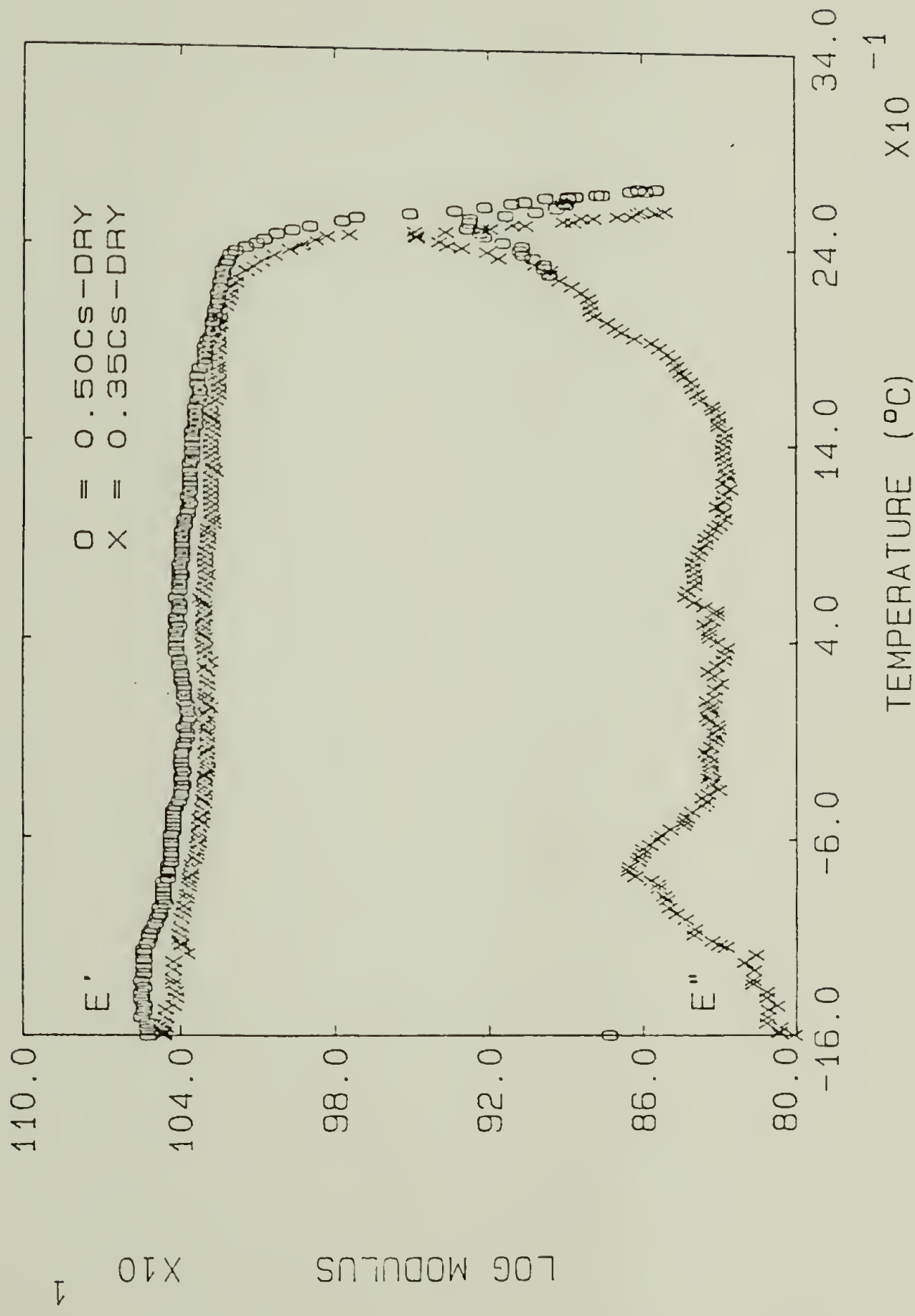
Figure 13.
Temperature Dependence of E' and E" for Cesium
Ionomers as a Function of Sulfonation at 11 Hz.
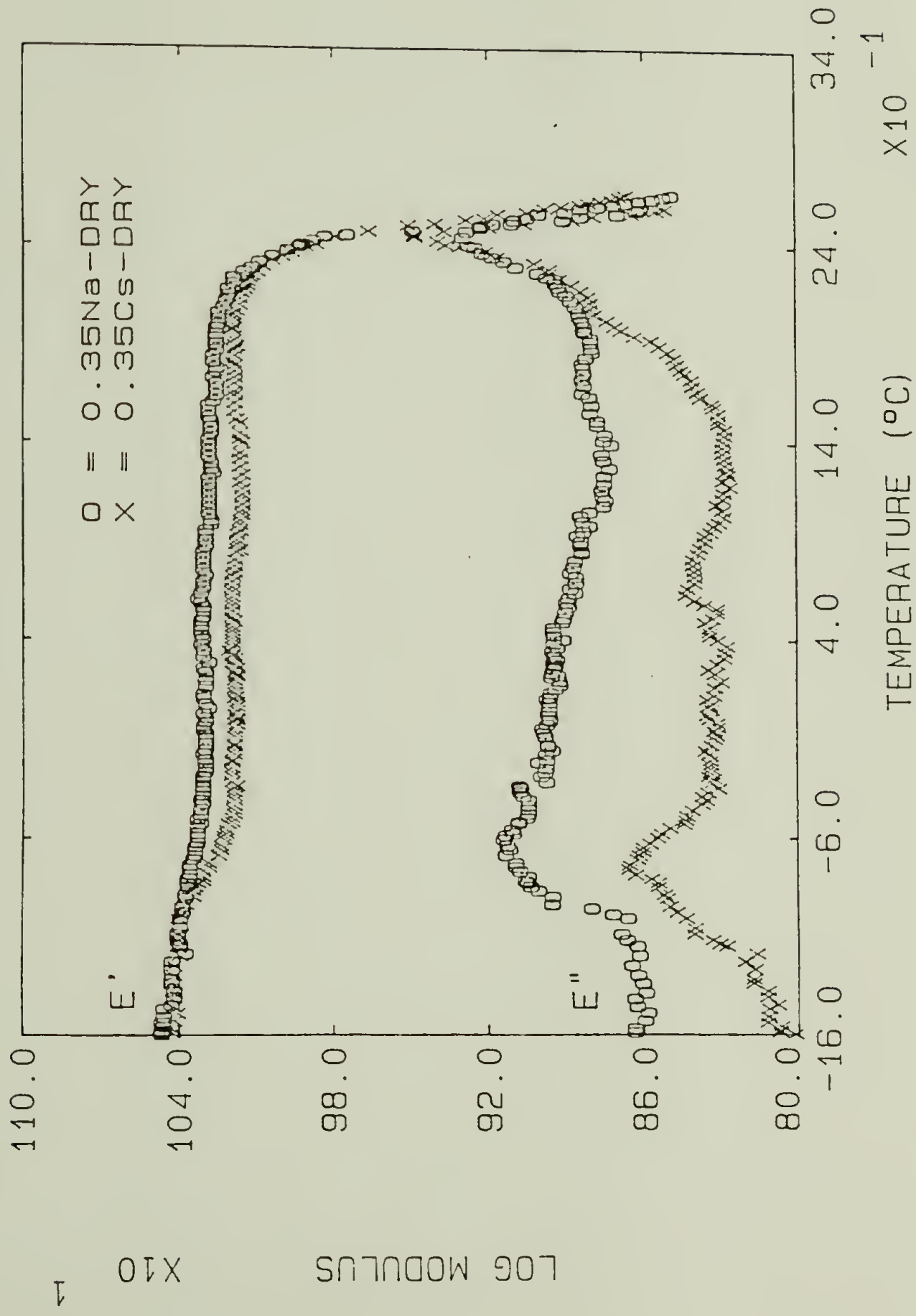
Figure 14.
Temperature Dependence of E' and E'' for Ionomers at
Constant Sulfonation as a Function of Counterion
Type at 11 Hz.
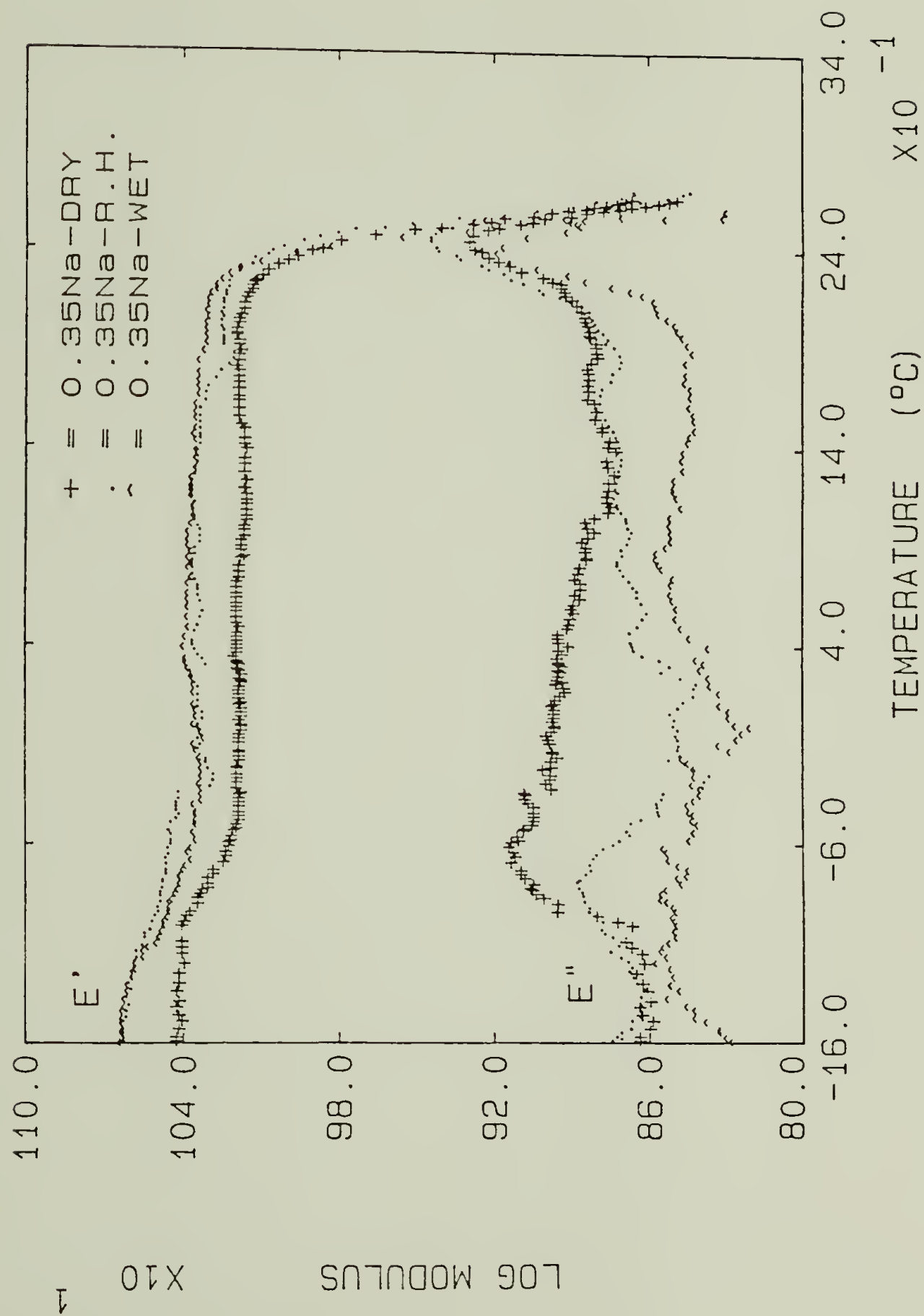
Figure 15.

Effect of Water on the Temperature Dependence of
E' and E" for Sodium Ionomers at 11 Hz.
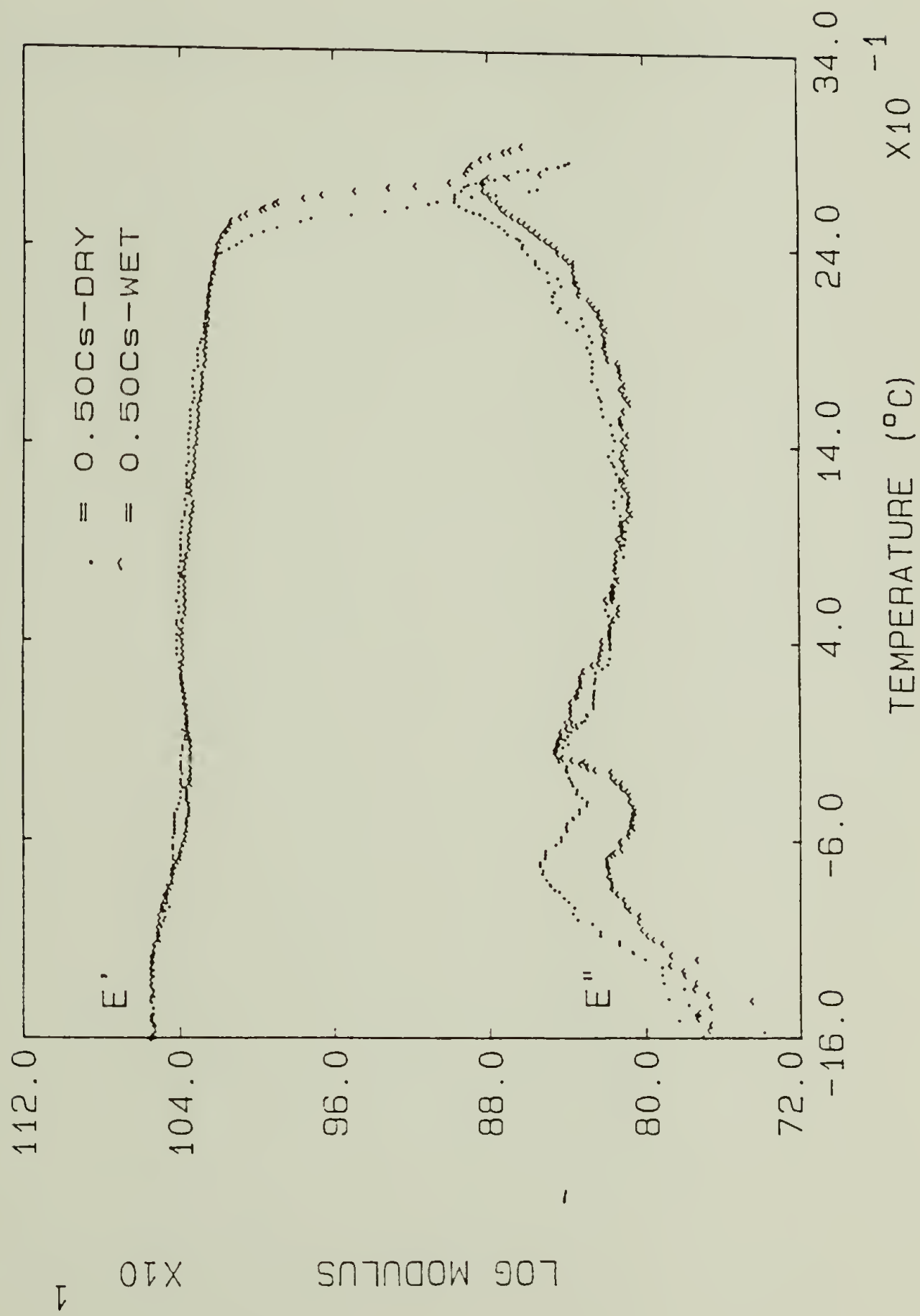
Figure 16.
Effect of Water on the Temperature Dependence of
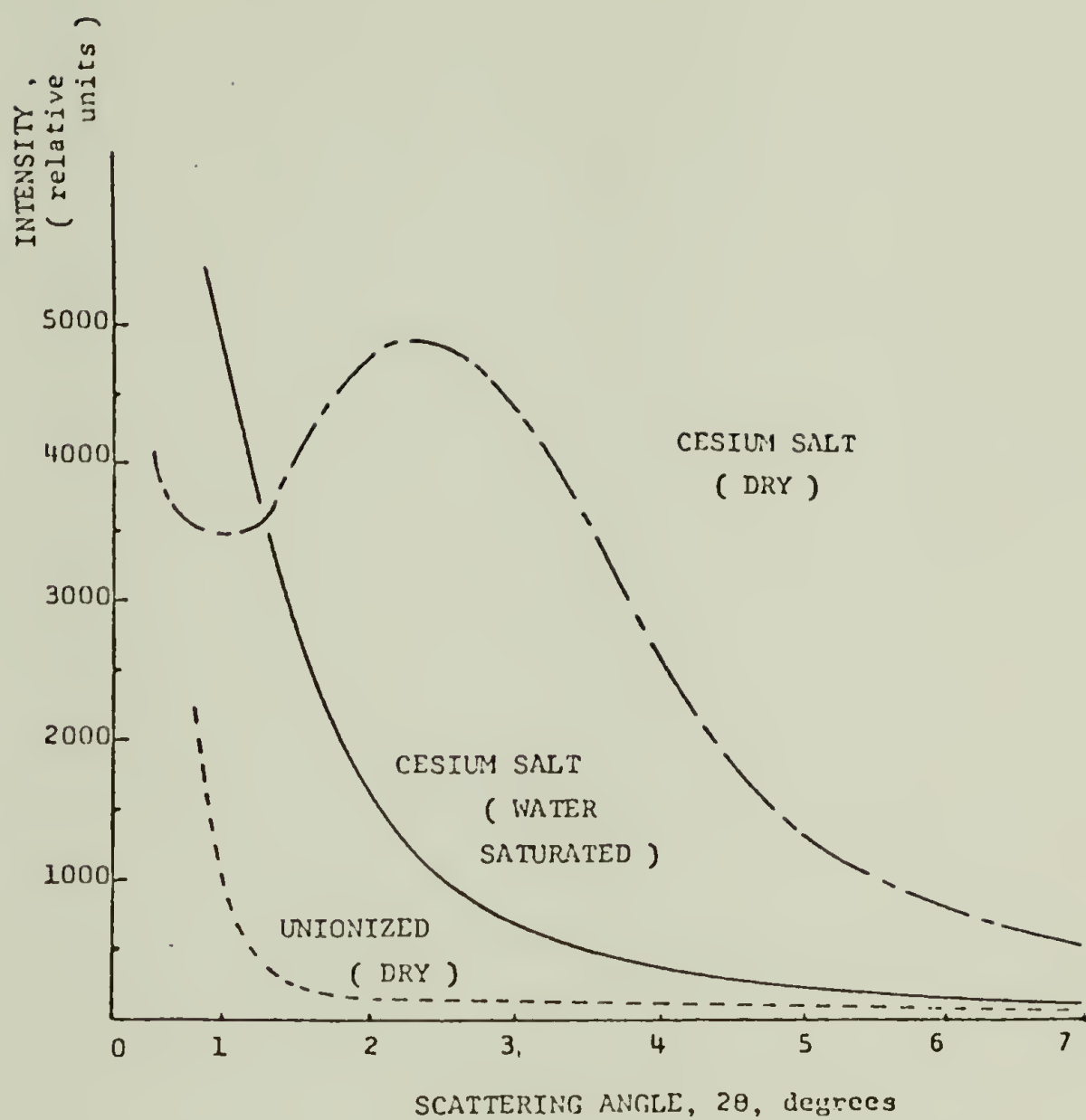E' and E" for Cesium Ionomers at 11 Hz.

121
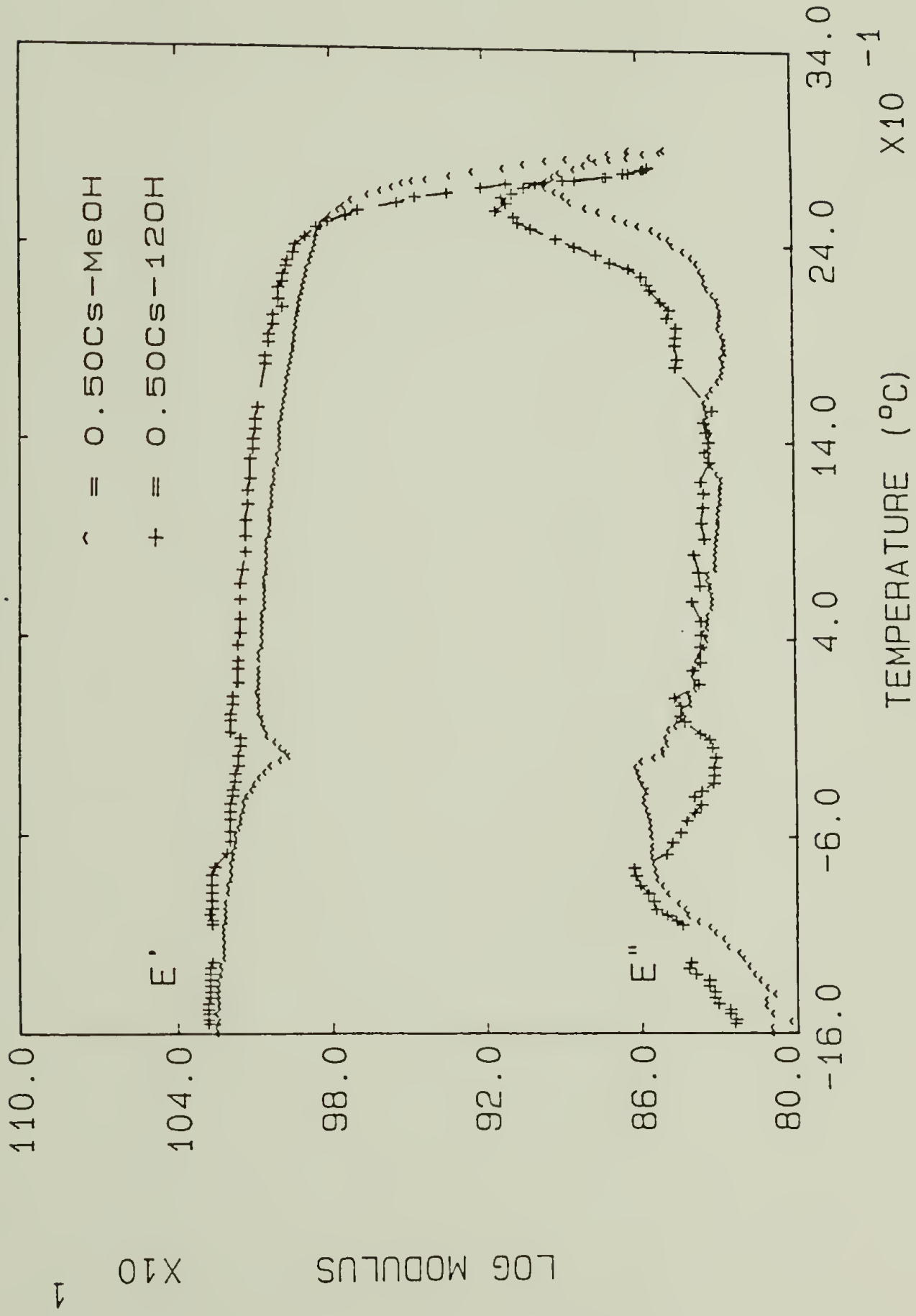
Figure 17.
Effect of Alcohols on the Temperature Dependence of
E' and E" for Cesium Ionomers at 11 Hz.
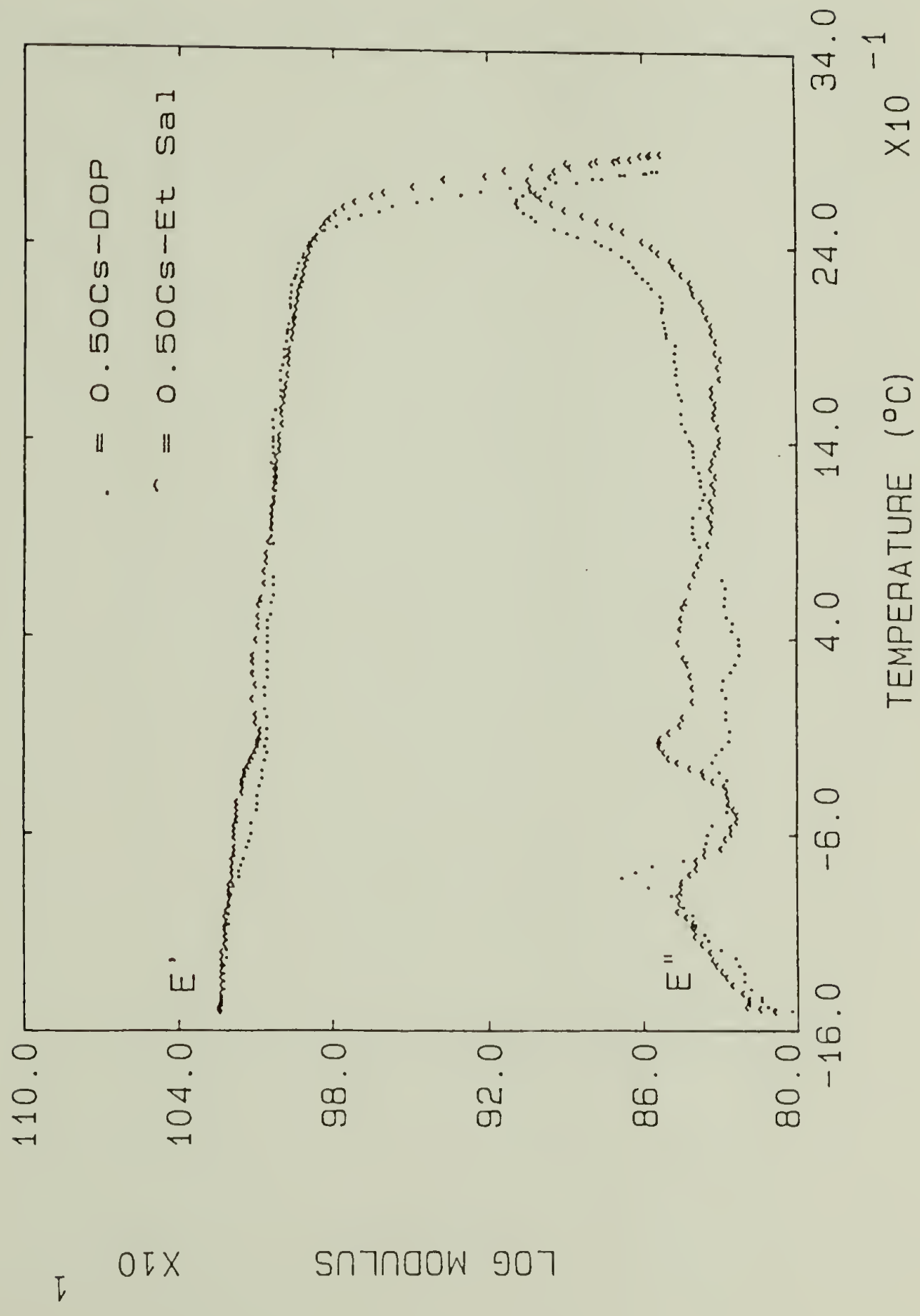
Figure 18.

Effect of Esters on the Temperature Dependence of
E' and E" for Sodium Ionomers at 11 Hz.

Figure 19.
Typical Small Angle X-Ray Scattering Profile for an Ionomer
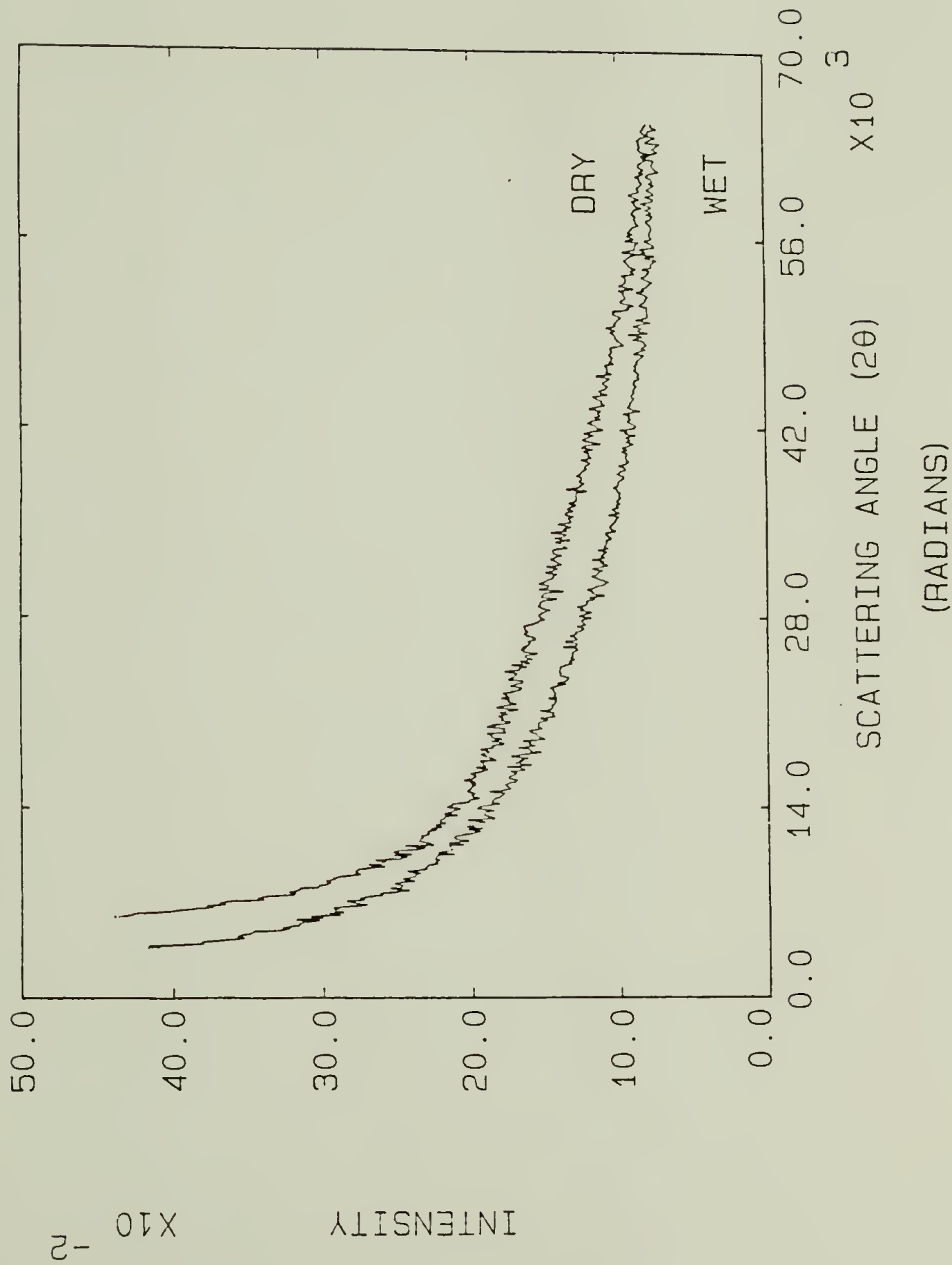
Figure 20.
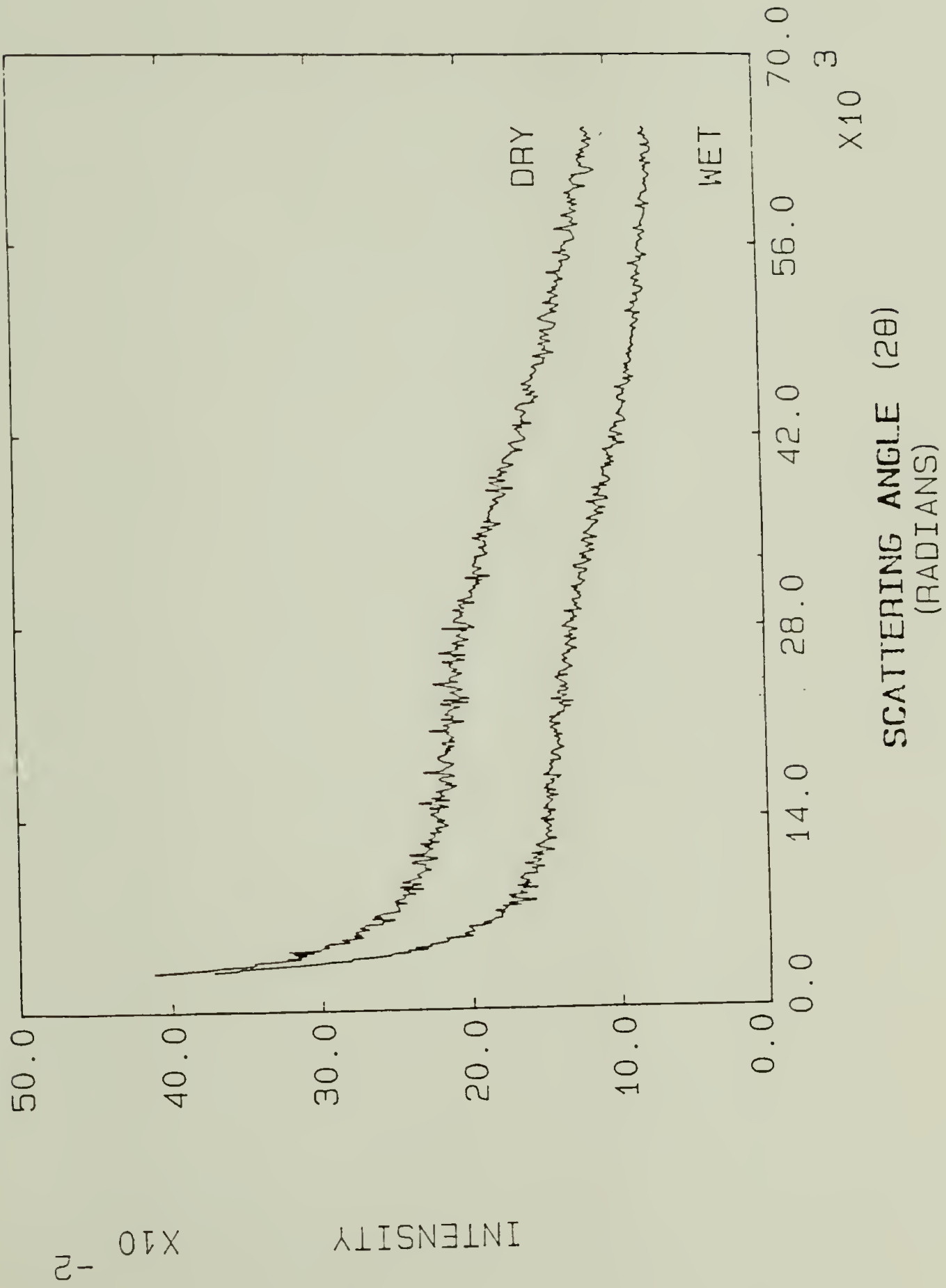Small Angle X-Ray Scattering Profile for 0.30 Cs
Wet and Dry

Figure 21.
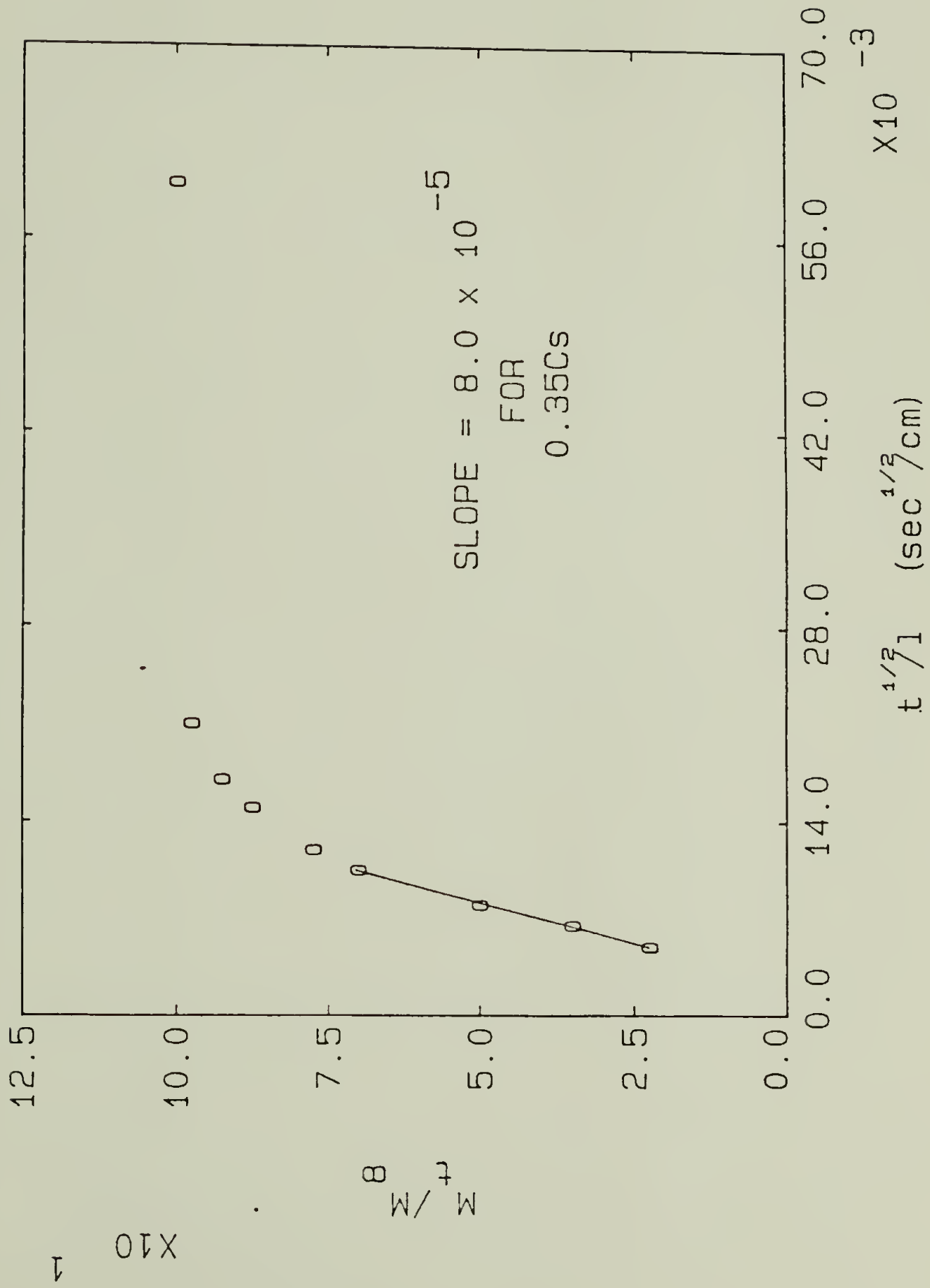Small Angle X-Ray Scattering Profile for 0.50 Cs
Wet and Dry

Figure 22.
Typical Water Absorption Curve for a Sulfonated
Polysulfone Ionomer