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**ARTICLE** *in* JOURNAL OF POLYMER SCIENCE PART C POLYMER LETTERS · JUNE 1986

DOI: 10.1002/pol.1986.140240607

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# Dynamics of Polystyrene Sulfonate Ionomers in Solution. A Neutron Spin-Echo Study

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## INTRODUCTION

In recent years, considerable attention has been focused on hydrodynamic properties and dynamics of linear polyelectrolytes such as sodium poly(styrenesulfonate) (NaPSS) in aqueous solution. Transport and dynamical properties of dilute and semidilute solutions of NaPSS have been studied by various experimental techniques such as viscometry,<sup>1</sup> sedimentation velocity,<sup>2</sup> dynamic light scattering,<sup>3-6</sup> and neutron spin-echo (NSE).<sup>7,8</sup> These investigations revealed spectacular features, especially in solutions without added salt, where the polyelectrolyte chains are extended and have a rather stiff local conformation. When salt is added, the chains contract progressively and gradually assume a random coil conformation. In this latter situation, where the Coulomb interactions, to a more or less extent are screened, the dynamical characteristics are reminiscent of those usually observed from solutions of neutral flexible polymers.

Ionomers<sup>9-12</sup> are another class of important ionic polymers, containing relatively few ionic groups on a polymer chain. These polymers are expected,<sup>13,14</sup> under certain solvent conditions, to exhibit similar conformational and dynamical features as "ordinary" linear polyelectrolytes. Ionomers are copolymers<sup>9</sup> where one constituent is an organic monomer such as styrene and the other constituent is the same organic molecule carrying a metallic group (usually a sodium sulfonate group). Although ionomers have been available commercially for a number of years, there has been relatively little work published on their solution behavior. One reason for this lack may be that most of the commercially available ionomers show very limited solubility in conventional solvents at ordinary temperatures. In ionomer solutions the dominating forces involve hydrogen bonding, dipolar forces, hydrophobic interactions, and to a lesser extent Van der Waals forces.

Ionomers (e.g., metal sulfonate ionomers as in the present study) in solution display different conformational and interaction behavior depending on the polarity of the solvent. In polar media, as defined by a high dielectric constant, such as dimethyl sulfoxide (DMSO) (highly polar) and dimethyl formamide (DMF) (moderately polar), a sufficient number of the metal counterions of the sulfonate groups are dissociated causing extension of the polymer chain via Coulomb repulsion of similar charges. This type of solvents induce classical polyelectrolyte behavior of

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sulfonate ionomers (stiff and rodlike conformation of the chains as in salt-free solutions of "ordinary" polyelectrolytes) even at quite low<sup>14</sup> (ca. 2 mol%) sulfonate levels. In weakly polar or non-polar solvents [e.g., tetrahydrofuran (THF)], the interaction situation is controlled by aggregation of ion pairs.<sup>11,12</sup> In this case, the solvent does not possess sufficient polarity to cause ion pair dissociation. This situation resembles in certain aspects that of linear polyelectrolytes in the presence of salt.

In the present investigation, dynamics on the scale of segmental diffusion, of sulfonated polystyrene (SPS) ionomers of different sulfonate levels and polystyrene (PS) in diluents of low polarity (THF) and high polarity (DMSO and DMF), are studied by means of quasi-elastic neutron scattering (NSE). The neutron spin-echo technique<sup>15</sup> has made it possible to examine dynamical processes of polymers<sup>16</sup> simultaneously in space and time on a semilocal scale. This technique is a neutron equivalent of photon correlation spectroscopy (PCS), measuring the same physical quantity, but at larger momentum transfer and shorter time (in the range of nanoseconds) than the optical technique. In addition, a comparison of transport properties of SPS in polar and non-polar solvents is made by means of viscosity measurements. The principal aim of the present study of ionomers at various environmental conditions is to gain an insight into the interactions governing their dynamics.

### BASIC CONCEPTS

In dynamic scattering experiments on macromolecular chains, the type of motion observed is defined by the correlation range which is of order  $q^{-1}$ . The momentum transfer,  $q$ , governs the spatial scale of observable motion and is defined by  $q = (4\pi/\lambda) \sin(\theta/2)$ , where  $\theta$  is the scattering angle and  $\lambda$  is the wavelength of radiation. The neutron spin-echo technique, in the same way as dynamic light scattering experiments, directly yields the normalized coherent dynamic structure factor  $S_N(q,t) \equiv S(q,t)/S(q,0)$ , where  $S(q,0)$  is the coherent static structure factor. The neutron spin-echo technique is generally employed to probe dynamics of polymer chains in the intermediate  $q$  region, where internal motions of polymer chains may play an important role. Dynamic scattering experiments are often analyzed by introducing a characteristic relaxation frequency  $\Omega$  taken from the initial slope of the logarithm of the normalized coherent intermediate scattering function  $S_N(q,t)$ <sup>17</sup>

$$Q \equiv - \lim_{t \rightarrow 0} \frac{\partial \ln S_N(q,t)}{\partial t} \quad (1)$$

Hence  $Q$  can be determined from the short-time behavior of the measured  $S_N(q,t)$ .

Since solutions of ionomers in many respects exhibit features which are similar to those observed for linear synthetic polyelectrolytes, the present results will be discussed in the framework of the models and terminology developed for describing static and dynamic properties of polyelectrolytes. Let us first recapitulate the basic notations for describing polyelectrolyte systems.

In the theory of Odijk,<sup>18</sup> for polyelectrolyte solutions the polyion can be visualized as a wormlike chain of contour length  $l$  and bare persistence length  $L_p$ , bearing elementary charges which interact via a Debye-Hückel potential with screening length  $\kappa^{-1}$ . Due to the charges the chain is locally stiffened, and a measure of the electrostatic contribution to the stiffness of the polyelectrolyte chain is the electrostatic persistence length  $L_e$ . In this model it was assumed that chain flexibility is controlled entirely by counterion screening.

The scattering function or the static structure factor  $S(q)$ , which is proportional to the scattering intensity, is of fundamental importance for the interpretation of static and dynamic scattering results in interacting systems. Let us first summarize

the most characteristic features of  $S(q)$  observed from aqueous polyelectrolyte solutions without added salt. Neutron scattering data<sup>8,19</sup> on salt-free solutions of NaPSS revealed that in the limit of  $q \rightarrow 0$  the scattering function assumed a small value which was attributed to the very small osmotic compressibility of these solutions. The value in this limit is related to the osmotic compressibility by  $S(q \rightarrow 0) = T \cdot \partial c / \partial \pi$ , where  $T$  is the absolute temperature,  $c$  is the polyion concentration, and  $\pi$  is the osmotic pressure due to the polyions. At higher  $q$ ,  $S(q)$  was found to increase and gradually pass through a pronounced maximum. The resulting characteristic peak is probably associated with a repulsive interchain interaction,<sup>19</sup> giving rise to some short-range order between chains. The maximum point of the peak was observed to be located at  $q_m$  which varied with the polyion concentration as  $c^{1/2}$ .

These observations could be rationalized in terms of a "correlation hole"<sup>7</sup> of diameter  $\xi \sim a \cdot c^{-1/2}$ , where  $\xi$  represents an average distance between neighboring chains<sup>20</sup> and  $a$  is the monomer or segment size. The correlation hole has a size comparable with the overall size of one chain and is defined from a repulsive potential produced by the polyions in the region surrounding it. Each polyelectrolyte chain is surrounded by a correlation tube, from which other chains are strongly expelled. The radius of the correlation tube is approximately the Debye-Hückel screening length  $\kappa^{-1}$ .<sup>7</sup>

When salt is added to an aqueous polyelectrolyte solution the situation is quite different. In this case, the electrostatic forces are screened and the osmotic pressure is reduced. As a result, the interaction peak progressively disappears with increasing salt concentration; at sufficiently high salt concentration the static structure factor exhibits a behavior similar to that observed for solutions of neutral polymers.

The dynamics observed from neutron spin-echo measurements on polyelectrolyte or ionomer solutions are characterized, for high enough  $q$  values, by a normalized intermediate scattering function  $S_N(q, t)$ , which may be related to an effective,  $q$ -dependent, diffusion coefficient  $D(q)$

$$S_N(q, t) = \exp \{ - \Omega \cdot t \} \quad (2)$$

$$\Omega = D(q) \cdot q^2 \quad (3)$$

The  $q$ -dependent diffusion coefficient may be expressed in the following general form<sup>7</sup>

$$D(q) \equiv \frac{\Omega}{q^2} = k_B \cdot T \frac{\mu(q)}{S(q)} \quad (4)$$

where  $k_B$  is the Boltzmann constant,  $k_B T S^{-1}(q)$  measures the strength of the restoring forces for a wavevector fluctuation, and  $\mu(q)$  is a wavevector dependent mobility, introduced to account for the internal structure and for the small-scale rigidity of a polyelectrolyte or an ionomer chain. It should be noted that eq. (4) is very general and not restricted to polyelectrolyte systems. The theoretical prediction<sup>7</sup> for the mobility as a function of  $q$  is:  $\mu(q) = \mu(L_p^{-1}) (q L_p)^{-1}$  for  $q > L_p^{-1}$ . In the range  $L_p^{-1} < q < q_m$  (rodlike behavior with important interchain effects). The conjecture is that the static structure factor increases as  $S(q) \sim q$ , whereas in the domain  $q > q_m$  (pure rodlike behavior without interference between chains)  $S(q)$  varies as  $q^{-1}$ . The theory<sup>7</sup> predicts distinction between two types of diffusion modes depending on the spatial scale probed. In the domain  $L_p^{-1} < q < q_m$  the diffusion coefficient is expected to decrease rapidly with  $q$  [cf. eq. (4)]

$$D(q) \sim q^{-2} \quad (5)$$

In the regime  $q > q_m$  the conjecture is that the diffusion coefficient is independent of  $q$  but dependent only on polyon concentration

$$D(q) = \text{Const} \cdot c \quad (6)$$

In summary, the theory for describing dynamics of interacting systems of this type essentially consists of three basic notations: (a) locally rigid chains of the type described by Odijk, (b) a correlation hole picture, and (c) modified Kawasaki-Ferrell dynamics for rigid rods.

### EXPERIMENTAL

The starting polymer employed in this study was a narrow molecular weight fraction of polystyrene with  $M_w = 115,000$  and  $M_w/M_n \leq 1.06$  purchased from Pressure Chemical Co., Pittsburgh, Pennsylvania. The polystyrene fraction was sulfonated according to procedures described elsewhere.<sup>21,22</sup> In general, these polymers were prepared by solution sulfonation employing acetyl sulfate as the sulfonating agent. The sulfonation of polystyrene was carried out at 50°C in ethylene dichloride. The polymers were neutralized and recovered by coagulation with methanol. The sulfonate content of the recovered polymer was determined by sulfur analysis of the salt as well as by titration of the sulfonic acid precursor. For this study sulfonated polystyrenes (SPS) containing 1.1, 3.6, and 9.2 mol% sulfonate groups, respectively, were prepared. Characterization of these sulfonated polymers in terms of molecular weights and molecular weight distributions indicated that the sulfonated adducts were identical<sup>21</sup> to those of the starting polystyrene.

The deuterated solvents dimethylsulfoxide (DMSO), dimethylformamide (DMF), and tetrahydrofuran (THF) from Aldrich Chemical Co. were used without further purification. The viscosities ( $\eta$ ) of these solvents as measured using a standard Ubbelohde viscometer are DMSO,  $\eta = 2.13 \cdot 10^{-3}$  Pas, DMF,  $\eta = 0.92 \cdot 10^{-3}$  Pas, and THF,  $\eta = 0.50 \cdot 10^{-3}$  Pas.

The experiments were carried out using the neutron spin-echo spectrometer IN 11 at the Institute Laue-Langevin (ILL), Grenoble.<sup>23</sup> In these experiments the incident wavelength was 8.42 Å and small angles of scatter were used in order to yield values of momentum transfer ranging from 0.026 Å<sup>-1</sup> to 0.130 Å<sup>-1</sup>. The time domain ranged from 0.5 ns to 13 ns.

The neutron spin-echo technique as well as the theoretical principles have been described in detail previously.<sup>15</sup> The neutron spin-echo spectrometer allows measurement of changes in the energy of neutrons scattered by a sample by changing and keeping track of the neutron beam polarization nonparallel to the magnetic guide field. The resultant neutron beam polarization is standardized against a purely elastic scatter (In the present study data were standardized against elastic scattering from a 10% solid solution of polystyrene in deuterated polystyrene.) in order to correct for residual field inhomogeneities. The final NSE data are obtained in the form of standardized true spin-echo polarization  $P_N$  at varying currents  $B$  (ranging from 10 A to 240 A); in the present investigation 1 A =  $5.56 \cdot 10^{-11}$  S. The variable  $P_N$  is identical to the normalized coherent dynamic structure factor  $S_N(q, t)$ . In this study the correlation function data could adequately be fitted by a single decaying exponential of the form  $S_N(q, t) \sim (-\Omega t)$ , such that  $\Omega$ , defined by eq. (1), could be obtained from the slope in a plot of  $\ln P_N$  versus  $t$ .

All solutions used in these measurements had a concentration of 3%. All experiments were performed at 26°C using standard quartz spectrometer cells. Background subtraction was made by measuring against a quartz cell containing pure solvent.

The reduced viscosities of SPS solutions in THF and DMF were measured with a standard Ubbelohde viscometer. The experimental details have been described previously.<sup>14</sup>

### RESULTS AND DISCUSSION

In order to elucidate, in terms of a well-known characterization parameter, differences in solution behavior between SPS-ionomers dissolved in polar and non-polar solvents, viscosity measurements were carried out with the aim of determining the reduced viscosity. Figures 1a and b shows the reduced viscosity as a function of concentration for SPS samples of different levels of sulfonation in THF and DMF, respectively. It is evident that in a low polarity solvent, such as THF, the reduced viscosity parameter at low polymer concentration (ca.  $5 \text{ kg m}^{-3}$ ) progressively decreases with increasing sulfonate content. This behavior is attributed<sup>14</sup> to enhanced intramolecular associations at higher levels of sulfonation. We also note that the reduced viscosity for the PS precursor is practically independent of polymer concentration, whereas for the sulfonated ionomers the reduced viscosity increases significantly at higher concentrations. This trend is readily rationalized<sup>14</sup> as being a consequence of intermolecular associations at higher polymer concentrations.

For a polar solvent, such as DMF, the reduced viscosity is observed to be almost independent of concentration for both the PS precursor and the SPS sample of lowest sulfonate content. For the SPS samples of higher sulfonate levels there is a marked upsweep in reduced viscosity at low polymer concentration, which probably is a manifestation of classic polyelectrolyte behavior.

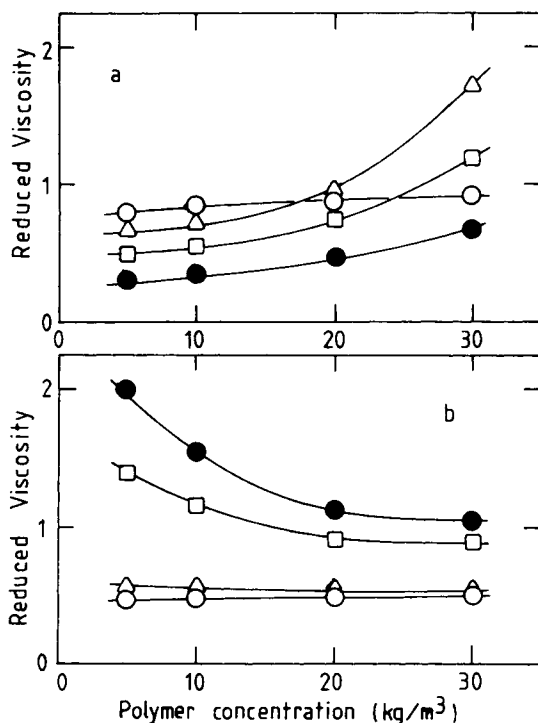


Fig. 1. The reduced viscosity as a function of polymer concentration for (a) THF solutions and (b) DMF solutions. The symbols denote: (○) PS; (△) SPS (1.1 mol%); (□) SPS (3.6 mol%); (●) SPS (9.2 mol%).

In Figure 2 the solvent viscosity reduced quantity  $\eta \cdot \ln S_N(q, t)$  is plotted versus time for SPS (3.6 mol% sulfonation level) in solvents of different polarity and at various momentum transfers. Since the solvents possess quite different viscosity we expect that this plotting procedure will normalize the data with respect to viscosity effects. The characteristic feature in Figure 2 is that the normalized dynamic structure factor exhibits a faster decay for the polar solvents than for the solvent of low polarity. At  $q = 0.026 \text{ \AA}^{-1}$  the trend is striking, while at  $q = 0.065 \text{ \AA}^{-1}$  the effect is less conspicuous. At higher  $q$  values the difference in behavior between SPS in polar and non-polar solvents seems to fade away. These results indicate that at low momentum transfers the rate of motion increases as the polarity of the solvent increases. These observations seem to rationalize within the framework of the theoretical models described above for analyzing dynamic features of aqueous polyelectrolyte solutions. In analogy with the picture for polyelectrolyte solutions the conjecture is that the  $q$  values  $0.026 \text{ \AA}^{-1}$  and  $0.065 \text{ \AA}^{-1}$  represent the region where  $q < q_m$ . In this region the theoretical prediction for an interacting system of polyelectrolyte character, such as SPS in a polar solvent, is that the rate of motion is very sensitive to changes in the value of  $q$ . Thus the observed trend, viz. that the viscosity reduced relaxation process decays faster for SPS in a polar solvent than in a solvent of low polarity is not unexpected. Likewise, we expect the difference

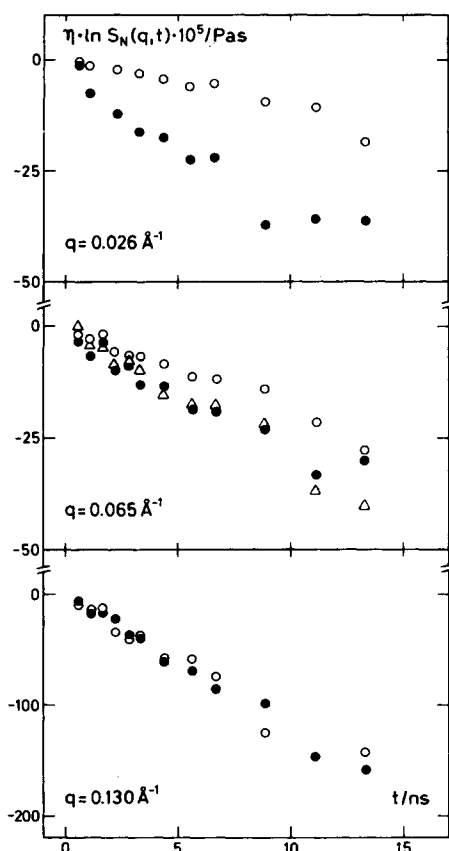


Fig. 2. Viscosity reduced correlation functions at different momentum transfers and for the following systems: (○) SPS (3.6 mol%)/THF; (●) SPS (3.6 mol%)/DMSO; (△) SPS (3.6 mol%)/DMF.

in decay rate between the systems to be more accentuated at low  $q$ . This difference in dynamics is probably associated with a more semilocal stiffness of the ionomer chains in a polar solvent as compared with the situation in a non-polar solvent, where the chains are assumed to possess a higher flexibility. At higher  $q$  values (which should correspond to  $q > q_m$ ) where more local dynamics dominates, the present data indicate that the rate of motion is practically independent of solvent polarity.

In Figure 3 the quantity of  $\eta\Omega/k_B T q^2$ , which is directly proportional to the diffusion coefficient, is plotted versus  $q$  for various systems. This quantity is introduced, instead of an effective diffusion coefficient, in order to account for the difference in viscosity of the solvents used. The data for SPS in the highly polar solvent DMSO indicate that the diffusion coefficient decreases with increasing  $q$  at low  $q$  and becomes constant at higher  $q$ . The data for the other systems are practically independent of  $q$  over the entire considered range. In addition, the data for *all* systems coincide at higher  $q$ , indicating that the dynamics is similar for all these systems. These results seem to be consistent with the theoretical picture [cf. eqs. (5) and (6) derived for aqueous polyelectrolyte systems]. A similar trend, with a drastic increase in the diffusion coefficient at low  $q$  ( $q < q_m$ ) and a constant value at higher  $q$  ( $q > q_m$ ), has previously been reported<sup>7,8</sup> from NSE measurements on aqueous sodium poly(styrenesulfonate) solutions without added salt. When salt was added in a rather large amount,<sup>7</sup> the diffusion coefficient was found to be constant over the whole  $q$ -range studied.

In previous analysis<sup>24</sup> of neutron spin-echo data from solutions of neutral polymers the results have been rationalized in form of a plot of  $(\Omega/q^2)(\eta/k_B T)b$  against  $qb$ ,

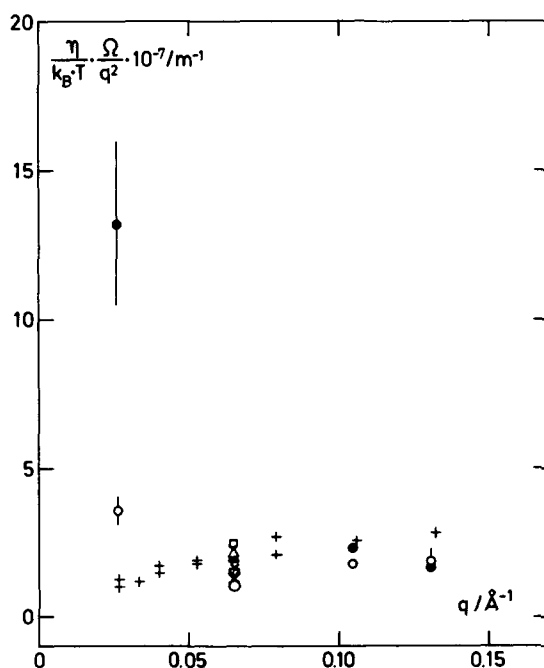


Fig. 3. Variation of the quantity  $\eta\Omega/k_B T q^2$ , proportional to the effective diffusion coefficient, with  $q$  for the following systems: ( $\Delta$ ) PS/DMF; ( $\square$ ) SPS (1.1 mol%)/DMF; ( $\times$ ) SPS (3.6 mol%)/DMF; ( $\bullet$ ) SPS (3.6 mol%)/DMSO; ( $\circ$ ) SPS (3.6 mol%)/THF; ( $\nabla$ ) SPS (9.2 mol%)/DMF; ( $\blacktriangle$ ) SPS (9.2 mol%)/DMSO; (+) PS/C<sub>6</sub>D<sub>6</sub>. The error bars represent standard errors.



where  $b$  is a segment length. By this procedure the data from various neutral polymer/solvent systems could be described by a universal curve. Included in Figure 3 are data previously<sup>24</sup> reported for PS in  $C_6D_6$ . The new data point for PS/DMF lies on the "master curve," but polar solvents show marked deviations at low  $q$ . This divergence is not surprising since the previously adopted model<sup>17</sup> is based on a Rouse-type chain with hydrodynamic interactions; this is not expected to hold for strongly interacting systems.

In Figure 4 the effects of sulfonation level on the characteristic relaxation frequency  $\Omega$  for SPS in DMF at  $q = 0.065 \text{ \AA}^{-1}$  are illustrated. The marked upsweep in  $\Omega$  at low levels of sulfonation is probably associated with an enhanced semilocal stiffness of the ionomer chains and/or a change of the value of the static structure factor at low contents of sulfonation. In this context we should note that the solubility<sup>14</sup> of SPS ionomers decreases drastically at low sulfonation levels.

### CONCLUSIONS

In this work we have probed the dynamics of SPS ionomers in solution by utilizing the neutron spin-echo technique. In particular, we have focused our attention on the differences in dynamic behavior at different  $q$  of SPS ionomers dissolved in solvents of various polarity. The present results may be summarized in the following way: (i) The viscosity reduced time correlation functions, at low  $q$ , decay faster for SPS in polar solvents than for SPS in solvents of low polarity. The difference in behavior is enhanced at low  $q$ . At higher  $q$  the dynamical behavior of SPS was observed to be independent of solvent polarity. (ii) The diffusion related parameter was found to exhibit a drastic increase at low  $q$  for the highly polar solvent DMSO, and to assume a practically constant value at higher  $q$  values. The observed features in (i) and (ii) could be rationalized in terms of the "correlation hole" model previously elaborated for analyzing dynamics of aqueous polyelectrolyte solutions. (iii) The characteristic relaxation frequency  $\Omega$  was found to display a marked upsweep at low sodium sulfonate contents of SPS in a polar solvent. This effect is probably due to significant changes in the interaction situation at low levels of sulfonation.

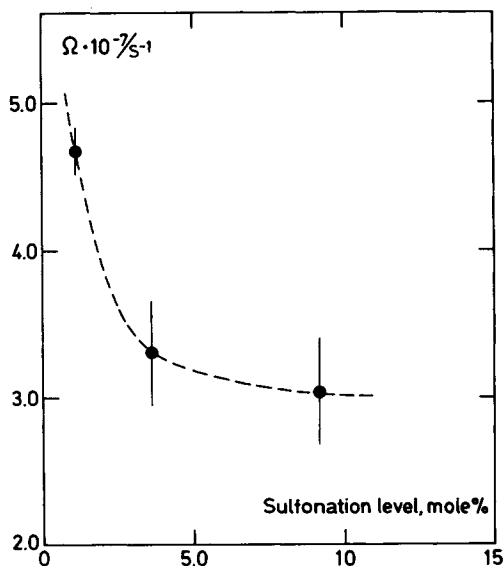


Fig. 4. The characteristic relaxation frequency as a function of sulfonation level for sulfonated polystyrene in dimethyl formamide at  $q = 0.065 \text{ \AA}^{-1}$ . The error bars represent standard errors.

The present experiments are preliminary and a more systematic study of the influence of ionomer concentrations, solvent polarity, levels of sulfonation, and  $q$  dependence of the static and the dynamic structure factor are in progress. This should lead to a more detailed picture of conformational and dynamical features of ionomer systems.

J. R. acknowledges a research grant from NTNF, Norway. The authors also thank Dr. R. Ullman, Dr. F. Ganazzoli, and Dr. S. Luzzati for fruitful discussions.

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Received August 12, 1985

Accepted January 9, 1986