Salt-Free Polyelectrolyte Behavior of Polystyrene-Based Telechelic Ionomers in a Polar Solvent. 1. Viscosity and Low-Angle Light Scattering Studies

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ABSTRACT: Some characteristic behavior, typically observed for salt-free polyelectrolytes in water, was observed for the first time for polystyrene (PS)-based telechelic ionomers, which have ionic groups located only at the chain ends, when dissolved in a polar solvent, dimethylformamide (DMF). The characteristic behavior observed by both viscosity and low-angle light scattering measurements for the telechelic ionomers, especially that of the monofunctional ionomer, demonstrates an important role of *intermolecular* electrostatic interactions in causing the characteristic behavior of telechelic ionomers. The behavior observed in our experiments can best be described by the following picture: each ionomer molecule with a coil conformation, very close to that of polystyrene of the same molecular weight, is separated from yet strongly interacts with other ionomer molecules; and these strong *intermolecular* electrostatic interactions cause a marked upturn in reduced viscosity and a reduction in scattered intensity.

Introduction

Ion-containing polymers that contain a relatively small number of ionic groups (up to 10–15 mol %) in nonionic backbone chains are referred to as ionomers. Because of significant changes in physical properties caused by incorporation of ionic groups into polymer chains, much work has been devoted to elucidating the structure–property relationship of ionomers in the solid state.[1-10] Compared with the work conducted on solid state behavior, relatively little has been done to study the structure–property relationship of ionomer solutions. This is in marked contrast to the situation of another class of ion-containing polymers, polyelectrolytes, where major interest has been concentrated on (aqueous) solution properties.[11-15] Recently, however, ionomer solutions have begun to be actively studied because of the realization of their unique behavior, and interesting results have been reported.[16-42] Since a definite distinction between polyelectrolytes and ionomers has not been established,[43] we follow the common practice of terminology that is based on material: ion-containing polymers are referred to as ionomers when the concentration of ionic groups is too low for water solubility, while they are called polyelectrolytes when they have a sufficient number of ionic groups to be water soluble.

So far, two types of ionomers in terms of the molecular architecture have been widely used for studying the structure–property relationship of ionomer solutions: *random ionomers* and *telechelic ionomers*. In random ionomers, such as partially sulfonated polystyrene (sodium salt), ionic groups are randomly distributed along backbone chains. However, some basic parameters, such as the contour length between ionic groups and the number of ionic groups per polymer chain, are not well defined. In addition, there is a distribution of the number of ionic groups per chain for typical random ionomers. On the other hand, in telechelic ionomers, ionic groups are located only at the chain end(s): monofunctional telechelic ionomers have only one ionic group at the chain end of a linear chain, difunctional telechelic ionomers have two ionic groups at the chain ends of a linear chain, and trifunctional telechelic ionomers have ionic groups at the chain ends of three-arm star polymers, etc. Therefore, the distance between ionic groups, as well as the number and the location of ionic group(s), is well defined for telechelic ionomers, and thus they are considered to be a simple model system for more complex random ionomers.[19-21,23] Recently, ionic block copolymers in which one block is partially or entirely ionic have been prepared and their solution behavior has been reported.[42,44] Although these ionomers show interesting solution behavior, they are not directly relevant to our present work.

It is now well established that random ionomers show two types of behavior depending mainly on the polarity of the solvent:[18] (1) *aggregation behavior* arising from dipolar attractions of ion pairs in a nonpolar or low-polarity solvent, such as toluene (ϵ = 2.4) or tetrahydrofuran (ϵ = 7.6); (2) *polyelectrolyte behavior* arising from electrostatic interactions among ions (fixed ions and counterions) in a polar solvent, such as DMF (ϵ = 37). Here, ϵ is the dielectric constant of the solvent. In this paper, we entirely focus on the *polyelectrolyte behavior* of ionomers in a polar solvent. Naturally, the investigation of the polyelectrolyte behavior of ionomer solutions is concentrated on an organic solvent system, and this gives various advantages compared with the aqueous solution system. For example, problems associated with aqueous solutions, such as autodissociation of solvent (water), complex water structure, and difficulties of removing foreign particles from the solution, etc., can be reduced for an organic solvent system.[45] In addition, the scattered intensity of light from the ionomer/organic solvent system is much stronger than that from the polyelectrolyte/water system, since the number of charges of ionomer molecules is much smaller than that of polyelectrolyte molecules. Thus, the reduction in scattered

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intensity due to the destructive interference of light is less significant for ionomer solutions; for example, the excess scattered intensity, R_θ, from the ionomer/organic solvent system (e.g., partially sulfonated polystyrene ionomer in DMF) is (1–20) × 10^{-6} (cm^{-1}),[30,33] while that from polyelectrolyte/water (e.g., poly(sodium methacrylate)) is (0.1–1) × 10^{-6} (cm^{-1}).[46] It is important to note, however, that the characteristic polyelectrolyte behavior, typically observed for polyelectrolytes in water, has been found to be retained for ionomer solutions.[45]

In this paper, we report the "polyelectrolyte" behavior observed by viscosity and low-angle light scattering measurements for polystyrene-based telechelic ionomers in a polar solvent, DMF. Although some experimental results showing aggregation behavior of telechelic ionomers have been reported in nonpolar solvents,[19–21,23] no polyelectrolyte behavior has been reported until recently for this type of ionomer in polar solvents.[35,36] To the best of our knowledge, this is the first case in which some polyelectrolyte behavior is observed for telechelic ionomers. The motivation of studying polyelectrolyte behavior of telechelic ionomers came from the observation that random ionomers (partially sulfonated PS ionomers) in a polar solvent (DMF) always show polyelectrolyte behavior (observed by viscosity and low-angle light scattering measurements), whatever the (average) number of ionic groups per chain is;[33] even in an extreme case, where the number of charges per chain is less than 1 on average, characteristic behavior is still observed. These results suggest the important role of *intermolecular* electrostatic interactions in causing characteristic behavior. However, there still is a possibility that, in random ionomers with a very small number of ionic groups per chain, some chains have a larger number of ionic groups than the other chains due to random distribution of the ionic groups; therefore, the effect due to *intramolecular* electrostatic interactions cannot be separated from that due to *intermolecular* electrostatic interactions. To overcome this problem, in this work we use telechelic ionomers that have only one or two ionic groups per chain located only at the chain end(s). Especially important are the results obtained on the monofunctional telechelic ionomer; since no *intramolecular* electrostatic interactions are available for this type of ionomer, only the effect of *intermolecular* electrostatic interactions should be observed. Therefore, we can focus on the effect of intermolecular electrostatic interactions on characteristic behavior.

It is well-known that polymer solution behavior is controlled by the balance between intramolecular interactions and intermolecular interactions.[47,48] This has been one of the most important problems in the investigation of the aggregation behavior of random ionomers in nonpolar solvents,[18] where the competition between intra- and intermolecular dipolar (attractive) interactions determines the overall solution behavior. However, it is even more important to distinguish these interactions in the polyelectrolyte solution. For example, there has been a controversy with respect to the origin of an upturn in reduced viscosity with decreasing polyelectrolyte concentration: is it intramolecular interactions, which can cause chain expansion, or intermolecular interactions that cause a marked increase in viscosity upon dilution?[49–52] Our results may shed some light on this problem.

Experimental Section

Materials. Both mono- and difunctional telechelic ionomers were prepared by living anionic polymerization. First, polystyrene-based telechelic polymers (α,ω-dimethylamino PS and ω-dimethylamino PS) were synthesized in THF at −78 °C. The difunctional initiator was naphthalene–lithium and the monofunctional initiator was *sec*-butyllithium. After the purification by precipitation into methanol, these polymers were converted to ionomers by quaternizing the tertiary amino groups with quaternizing agent, bromoethane (C_2H_5Br), in THF. The reaction was quantitative after several weeks. After quaternization, the resulting ionomers were precipitated into a large excess of heptane several times to remove the excess quaternizing agent and then dried under vacuum. The details concerning the preparation of polymers are described elsewhere.[53] The basic structures of the mono- and difunctional telechelic ionomers are shown in Figure 1. In addition, the basic molecular parameters of the telechelic polymers, such as molecular weight, polydispersity, and functionality of the polymers, are summarized in Table 1. Polymer solutions were prepared by dissolving the dried polymers in DMF under stirring for 1 day at room temperature; the polymers were easily dissolved.

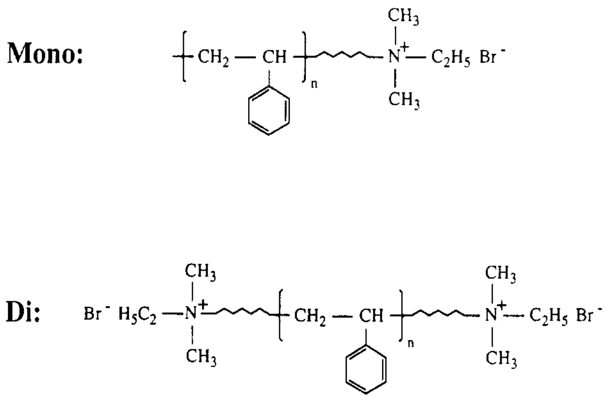

Figure 1. Chemical structures of mono- and difunctional telechelic ionomers.

Table 1. Molecular Characteristics of Telechelic Polymers

polymer	M_n[a]	M_w/M_n[a]	functionality[b]
mono	14 500	1.09	0.98
di	11 900	1.10	1.94

[a] From GPC measurements. [b] From titration.

Measurements. The reduced viscosity was measured with a modified Ubbelohde viscometer at 25 ± 0.05 °C in a thermostated bath. The viscometer had a sintered-glass filter to remove dust particles and had caps to prevent solvent evaporation and exposure to air. The measurement at each concentration was conducted until the relative error of three successive measurements became less than 0.5%. The details concerning viscosity measurements are described elsewhere.[33]

Low-angle laser light scattering (LALLS) experiments were conducted with a KMX-6 low-angle laser scattering photometer (Chromatix) at a wavelength of 632.8 nm at 25 ± 0.5 °C. The instrument was designed only for low-angle (2–7°) measurements but with high precision.[54] The usual calibration by standard materials (e.g., benzene) was unnecessary for this instrument, since absolute scattered intensity was directly calculated from geometric parameters and the ratio of radiant power.[54,55] Moreover, the effect of foreign particles was minimized due to the very small scattering volume (0.1 μL), and the dust effect was easily eliminated by using a flow system. The optical clarification of the solution was carried out by passing the solution using a syringe pump through two membranes (Fluoropore Filter: Millipore), whose pore sizes were 0.5 and 0.2 μm, in succession. The measurements were conducted at three different points of the cell window to make sure that the effect of the roughness of the cell window on scattering was negligible. The specific refractive index increment, d*n*/d*c*, was measured at 25 ± 0.1 °C by using a KMX-16 differential refractometer (Chromatix) with 632.8-nm wavelength. The d*n*/d*c* values for telechelic polymers in DMF are listed in Table 2. Details concerning low-angle light scattering experiments are described elsewhere.[32]

Data Analysis. To analyze low-angle light scattering data, the reciprocal reduced scattered intensity, Kc/R_θ, is plotted as a function of c, where R_θ is the excess reduced scattered intensity

Table 2. Specific Refractive Index Increment, d*n*/d*c*, of Telechelic Polymers in DMF

polymer	d*n*/d*c*
mono	
(unquaternized)	0.159
(quaternized)	0.153
di	
(unquaternized)	0.163
(quaternized)	0.146

at scattering angle θ and c is the polymer concentration (g/cm^3). Since the scattering angle used in this work is very small (6–7°), we can safely assume that the R_θ value obtained is equal to the extrapolated value to zero angle, i.e., R_0. The reciprocal reduced scattered intensity at zero angle can be expressed[48,56,57] as

$$\frac{Kc}{R_0} = \frac{1}{RT}(\partial\pi/\partial c) \qquad (1)$$

where $\partial\pi/\partial c$ is the inverse osmotic compressibility, R is the gas constant, and T is the absolute temperature. K is the optical constant for vertically polarized incident light, defined by

$$K = 4\pi^2 n_0^2 (\mathrm{d}n/\mathrm{d}c)^2/N_0\lambda_0^4 \qquad (2)$$

where n_0 is the refractive index of the solvent, λ_0 is the wavelength of the light in vacuo (632.8 nm), and N_0 is Avogadro's number.[59] The dn/dc value is usually obtained by extrapolating $\Delta n/c$ values to zero concentration, where Δn represents the increment of refractive index of the solution from that of the solvent. When the interaction is relatively weak, as is the case for neutral polymer solutions at low concentrations, $\partial\pi/\partial c$ in eq 1 is expressed by virial expansion[48]

$$\frac{\partial\pi}{\partial c} = \left(\frac{RT}{M}\right)(1 + 2A_2Mc + ...) \qquad (3)$$

where M is the weight-average molecular weight of the polymer and A_2 is the (osmotic) second virial coefficient.

Therefore, we obtain the following usual equation from eqs 1 and 3,

$$\frac{Kc}{R_0} = \frac{1}{M} + 2A_2c + ... \qquad (4)$$

The light scattering data from the unquaternized telechelic polymers in DMF may be analyzed by this equation. When the interaction is very strong, as is the case of macroions in water, virial expression may not suffice to describe the strong intermolecular interactions. We must then use the original equation (eq 1) and the concentration dependence is reflected in a $\partial\pi/\partial c$ term.[60] The light scattering behavior of the telechelic ionomers in DMF may be explained by this equation.

To analyze viscosity data, the reduced viscosity, n_{sp}/c, is plotted as a function of c (g/dL). Here, $\eta_{sp} = (\eta - \eta_0)/\eta_0$, where η and η_0 represent the viscosity of the solution and the solvent, respectively.[48]

Results

The refractive index increment, dn/dc, was obtained for both the unquaternized and the quaternized samples, of both the mono- and the difunctional polymers (see Table 2). The $\Delta n/c$ values are fairly constant over the polymer concentration range studied. This constancy of $\Delta n/c$ is in contrast to the situation of the same telechelic ionomers dissolved in a nonpolar solvent, toluene, in which $\Delta n/c$ values increase with polymer concentration.[61] This increase may be related to an increasing aggregation of ionomers with polymer concentration in a nonpolar solvent, while aggregation is not expected for the dilute ionomer solution in a polar solvent.

Figure 2 shows the reduced viscosity as a function of polymer concentration for the difunctional telechelic ionomer (quaternized polymer) in DMF, as well as for the ionomer precursor (unquaternized polymer). The unquaternized polymer behaves as a neutral polymer: the reduced viscosity increases linearly with polymer concentration, which may be expressed by the Huggins equation,[62]

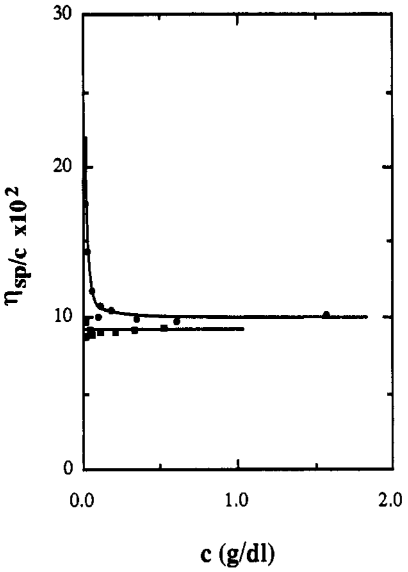

Figure 2. Reduced viscosity, η_{sp}/c, against polymer concentration for the difunctional telechelic ionomer in DMF (top curve) as well as for the unquaternized polymer.

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2c \qquad (5)$$

where $[\eta]$ is the intrinsic viscosity and k' is the Huggins constant. In contrast, the quaternized polymer (ionomer) shows a characteristic behavior: the reduced viscosity, η_{sp}/c, increases markedly with decreasing polymer concentration, reaching values much larger than that of the ionomer precursor at high dilution. Similar viscosity behavior has been reported for salt-free random ionomers in polar solvents[16,18,22,25,26,31,33] as well as for salt-free polyelectrolytes in water.[11-15]

To confirm the appearance of characteristic polyelectrolyte behavior observed by viscosity measurements, the low-angle light scattering measurements were conducted for the same polymers as those used for the viscosity measurements. Figure 3 shows low-angle light scattering results for the difunctional telechelic ionomer in DMF, as well as for the unquaternized polymer. The unquaternized polymer, as expected, shows a neutral polymer behavior: the reciprocal reduced scattered intensity, Kc/R_0, increases linearly with polymer concentration in the concentration range studied, which can be analyzed by eq 4. From the intercept, the weight-average molecular weight was found to be 12 300, which is in good agreement with the value from GPC (see Table 1). On the other hand, the quaternized polymer (ionomer) shows a characteristic behavior: Kc/R_0 rises steeply from the intercept at zero concentration, bends over, and becomes nearly horizontal at higher concentrations. Similar behavior has been reported for salt-free random ionomers in polar solvents[25,30-32] as well as for salt-free polyelectrolytes in water.[46,63,64]

The results shown above indicate that two ionic groups per polymer chain are sufficient to cause the characteristic polyelectrolyte behavior observed by viscosity and low-angle light scattering measurements. To study further the effect of the number of ionic groups, we investigated

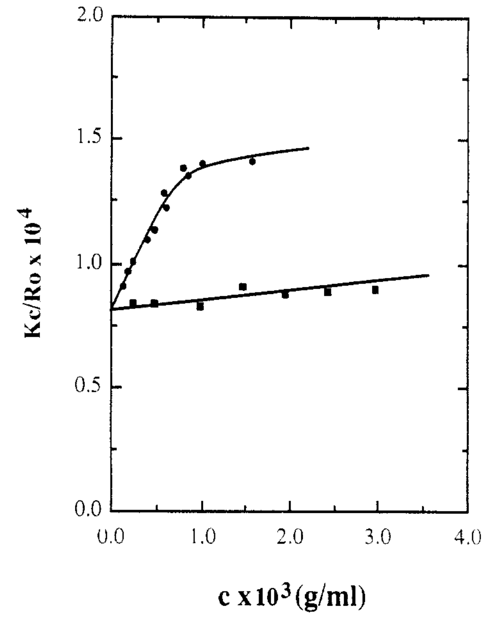

Figure 3. Reciprocal reduced scattered intensity at zero angle, Kc/R_0, against polymer concentration for the difunctional telechelic ionomer (top curve) as well as for the unquaternized polymer.

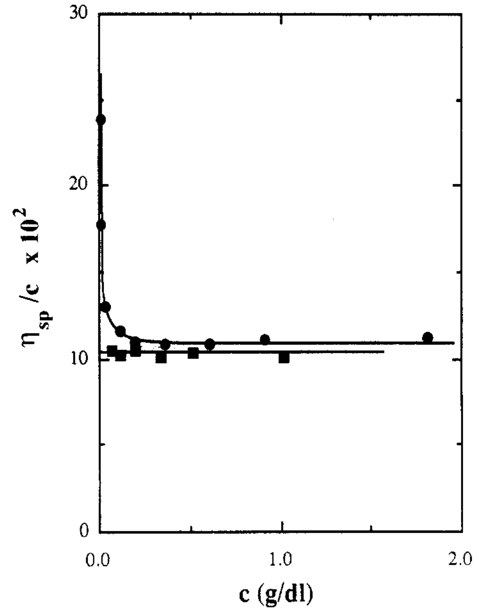

Figure 4. Reduced viscosity, η_{sp}/c, against polymer concentration for the monofunctional telechelic ionomer in DMF (top curve) as well as for the unquaternized polymer.

the extreme case, the monofunctional telechelic ionomer, in which *only one ionic group* is attached to the polymer chain. It turned out that a characteristic behavior was observed for the monofunctional telechelic ionomer in DMF similar to that for the difunctional telechelic ionomer. Figure 4 shows the viscosity behavior for the monofunctional telechelic ionomer, as well as for its precursor in DMF. Again, the quaternized polymer (ionomer) shows a characteristic behavior, while the unquaternized polymer (ionomer precursor) behaves as a neutral polymer: a marked increase in the reduced viscosity upon dilution is clearly seen for the ionomer solution. Figure 5 shows Kc/R_0 as a function of polymer concentration for the monofunctional telechelic ionomer, as well as for its precursor in DMF. From the intercept, the weight-average molecular weight was found to be 15 600 by using eq 4, which is in good agreement with the value from GPC (see Table 1). Again, the monofunctional telechelic ionomer shows a characteristic behavior, while the ionomer precursor behaves as a neutral polymer: an "abnormal" marked increase in Kc/R_0 from the intercept, followed by a leveling off at higher concentration, is seen for the monofunctional telechelic ionomer solution.

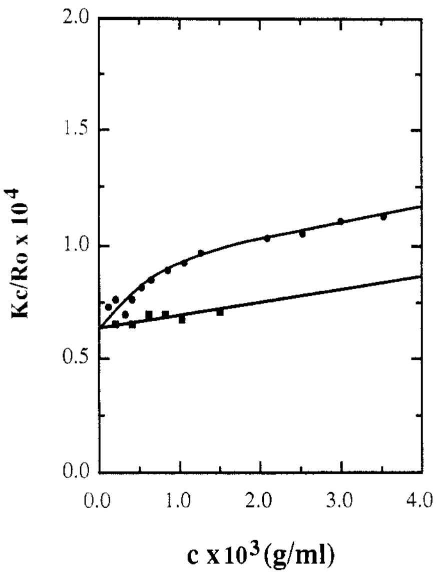

Figure 5. Reciprocal reduced scattered intensity at zero angle, Kc/R_0, against polymer concentration for the monofunctional telechelic ionomer in DMF (top curve) as well as for the unquaternized polymer.

Discussion

From these results, there seems to be little doubt that the polystyrene-based telechelic ionomers dissolved in a polar solvent (DMF) show the characteristic polyelectrolyte behavior observed by both viscosity and low-angle light scattering measurements. This type of behavior has been typically observed for salt-free random ionomers in polar solvents[45] and for salt-free polyelectrolytes in water.[11-14] Therefore, ionic polymers with various numbers of ionic groups per chain, ranging from one (monofunctional telechelic ionomers) to two (difunctional telechelic ionomers) to hundreds (random ionomers) to thousands (polyelectrolytes) all show similar behaviors; the prerequisite for causing characteristic behavior of flexible ionic polymers seems to be the existence of ionic group(s), whatever their number.

Especially important are the results obtained for the monofunctional telechelic ionomer that has only one ionic group located at the chain end. Since there is no way to interact intramolecularly, only intermolecular electrostatic interactions are available for this type of ionomer. Therefore, the characteristic behavior observed by viscosity and low-angle light scattering measurements should be associated with *intermolecular* (*electrostatic*) *interactions*. It is also important to note that this characteristic polyelectrolyte behavior is not related to a chain expansion, as is frequently inferred to explain an increase in reduced viscosity of salt-free polyelectrolytes with a decrease in polymer concentration,[11-15] since chain expansion caused by intramolecular repulsion among ionic groups on the same polymer chain is unlikely to occur for the monofunctional telechelic ionomer. The chain conformation of the monofunctional telechelic ionomer is expected to be similar to that of PS, i.e., a random coil conformation, since out of ca. 140 repeat units only one repeat unit (chain end) has an ionic group and therefore the perturbation to overall coil structure may be negligible.

The concentration regime of the monofunctional telechelic ionomer solution may be evaluated by considering the size of the polymer chain. The overlap concentration, which separates a dilute regime from a semidilute regime of the coil polymer, is usually estimated by using the following relation:[65,66]

$$c^* = M/N_0R_g^{\ 3} \tag{6}$$

where c^* is the overlap concentration and R_g is the radius of gyration of the polymer chain. The R_g of PS with molecular weight of 15 000 is ca. 40 Å in DMF;[67] therefore, c^* is estimated to be 3.9×10^{-1} (g/cm^3) for this polymer by using eq 6, which is clearly much larger than the concentration range investigated in this study (i.e., less than 2×10^{-2} g/cm^3). Therefore, the solution used in this study is in a dilute regime, and an extensive chain overlap is not expected as is typically observed for polymers in semidilute solution.[66] According to the considerations given above, we have the following picture for the monofunctional telechelic ionomer solution: coil ionomer molecules, which have a size almost identical to PS of the same molecular weight, are dispersed in DMF without significant chain overlap, and these ionomer molecules interact with each other due to strong electrostatic interactions in salt-free solution. These *intermolecular interactions* should be responsible for an "abnormal" upturn in viscosity and a reduction in scattered intensity of telechelic ionomer solutions.

The picture described above may also be supported by the analysis of scattered intensity. The excess scattering from the solution increases almost linearly with polymer concentration in the concentration range studied for the unquaternized polymer (ionomer precursor). On the other hand, a significant reduction in scattered intensity compared with that of the ionomer precursor is noted for the quaternized polymer (ionomer). This reduction of scattering power arises from destructive interference of light due to the nonrandom arrangement of polymer chains in solution.[48,56,59] This is consistent with our conclusion that the intermolecular interactions cause characteristic polyelectrolyte behavior, since the nonrandom arrangement of polymer chains can only be possible through interactions between the polymer molecules.

The results obtained above may be compared qualitatively with several models that are used to explain the characteristic behavior of salt-free polyelectrolyte solutions. The models that place an emphasis on *intermolecular interactions* for interpretation should be considered to explain the characteristic behavior of the telechelic ionomers. First, the scattering behavior may be explained by Doty's model that was used for analyzing light scattering data from globular protein (i.e., bovine serum albumin) solutions:[63] this model considers repulsive interactions (i.e., hard sphere type, exponential type, and screened Coulomb type) between small spherical macroions and explains the concentration dependence in terms of the reduced repulsive interactions with increasing macroion concentration due to a reduction of the size of the electrical double layer at higher overall ionic strength. The reduction in scattering power is attributed to the nonrandom arrangement of macroions arising from mutual repulsion, and the leveling off at high concentration in a Kc/R_{90} vs c plot is attributed to a reduction in the repulsive interactions at higher concentration. An application of this model to explain the low-angle light scattering results from random ionomer solutions is described elsewhere.[30,33] Second, the viscosity behavior of telechelic ionomer solutions may be explained by the recent work of Cohen et al.:[49–51] they used a mode–mode coupling approximation to the hydrodynamics of charged Brownian spheres to explain the characteristic viscosity behavior of salt-free polyelectrolyte solutions; it was pointed out that the behavior of low salt polyelectrolyte solutions is similar to that of a dense fluid of hard spheres and that the hydrodynamics of low ionic strength polyelectrolyte solutions is dominated by electrostatic repulsion between polyions. From these discussions, our system may be best explained, at least qualitatively, by the models that deal with macroions as ionic "effective" hard spheres interacting strongly with each other, such as Doty's model for light scattering and Cohen's model for viscosity.[69] More sophisticated treatment may be found in the literature.[72]

Conclusion

Some characteristic behavior is observed for polystyrene-based telechelic ionomers that contain ionic group(s) only at the chain end(s), when dissolved in a polar solvent (DMF); both viscosity and low-angle light scattering results show a characteristic behavior, which has been observed for salt-free random ionomers in polar organic solvents and for salt-free polyelectrolytes in water. The behavior exhibited by the monofunctional telechelic ionomer that has only one ionic group at the chain end demonstrates an important role of *intermolecular* electrostatic interactions and a lack of *intramolecular* electrostatic interactions (and thus chain conformational change) in causing the characteristic salt-free polyelectrolyte behavior of telechelic ionomers. Since the concentration range studied in this work is far below the overlap concentration, the models proposed for entangled polyelectrolyte chains may not be applied to our system; our results can be best explained within the framework of the models that treat macroions as interacting effective hard spheres, such as Cohen's model to explain viscosity behavior and Doty's model to explain light scattering behavior. This is a first report, which covers the overall behavior concerning the characteristic polyelectrolyte behavior of telechelic ionomers in a polar solvent. More detailed results, focused on the structures of the telechelic ionomers in a polar solvent, will be reported in the future.

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