Small-Angle Neutron Scattering Studies of Low Polarity Telechelic Ionomer Solutions. 2. Single Chain Scattering

Eleni Karayianni,[‡] Robert Jérôme,[§] and Stuart L. Cooper*,[†]

Department of Chemical Engineering, University of Wisconsin—Madison, 1415 Engineering Drive, Madison, Wisconsin 53706

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ABSTRACT: A direct probe of the single chain conformation in associating low polarity model telechelic ionomer solutions has been obtained using small-angle neutron scattering. A contrast matching technique was employed utilizing a solution of hydrogenated and deuterated ionomer chains in a mixture of labeled and unlabeled solvent molecules. The scattering data at all concentrations and ionic levels examined show an excellent fit to the wormlike chain model. Single chain scattering patterns were obtained for two sodium-neutralized carboxy−telechelic polystyrene ionomers that differ by a factor of 2 in their molecular weight, in a concentration range from the dilute to the concentrated solution regime. The single chain dimensions were found to be influenced by both the ionic interactions and the extent of association. Both ionomer systems showed a contraction of the chain dimensions in the dilute solution regime which is more pronounced for the lower molecular weight telechelic ionomer. As concentration increases, the single chain dimensions increase until they reach a plateau value in the concentrated solution regime. This plateau value is very close to the chain dimensions of the ionomer in the bulk, as was found from a previous SANS study on similar ionomer systems. This plateau value chain dimension is also the same as the unperturbed dimension of the nonionic parent polymer in the bulk. The effect of concentration on the ionomer chain dimensions is attributed to the influence of ionic interactions as the nonionic form of the material shows larger chain dimensions in the concentration regime studied. These results indicate that intramolecular interactions with the formation of self loops prevail in the dilute solution regime. Intermolecular interactions with ionic groups connecting to different chains prevail in the concentrated solution regime, as evidenced by an extension of the chain dimensions.

I. Introduction

The effect of ionic association on the single chain conformation of low polarity ionomer solutions is an important aspect that needs to be understood in order to be able to provide conclusive answers on the aggregation phenomenon in ionomers. In nonionic dilute polymer solutions, the single chain conformation for a given polymer is dependent on the polymer/solvent interactions. Single chain collapse is observed in poor solvents, while single chain expansion occurs as the quality of the solvent for the polymer increases. In associating ionomer solutions, the single chain conformation is expected to further be influenced by the extent of association and the strength of ionic interactions. Experimental studies that provide direct evidence on the intramolecular correlations in ionomer solutions have only recently been applied, and these have been almost solely restricted to the random sulfonated polystyrene ionomers (SPS). Small-angle neutron scattering (SANS), which is the most direct method to probe single chain dimensions in systems that show strong intermolecular interactions, has been used in some of these studies.

By varying the labeling level of the polymers, Lantman et al. investigated the single chain dimensions in solutions of a 4.2 mol % Na-neutralized SPS ionomer (M_w: 10^5) in deuterated tetrahydrofuran, a moderate polarity solvent, in the semidilute concentration regime.[1] In this regime, SANS studies on the multimers showed that significant intermolecular association exists, the extent of which increased with increasing concentration.[1] Most surprisingly, this study showed that the *z*-average radius of gyration of the single chains was not influenced by the association as it remained constant with polymer concentration. However, only two labeling levels were tested in this study, so there was no statistical averaging in the application of the isotope labeling technique. Gabrys et al. applied the contrast matching technique that provides direct information on the single chain scattering function in similar solutions, with varying ionic level (1, 3.4, and 4 mol %) and cation type (Na and Zn).[2] In agreement with the experimental findings by Lantman et al.,[1] this study showed that the single chain radius of gyration of the ionomer does not significantly change with concentration over the concentration regime studied. In fact, the single chain dimensions of the ionomer were observed to be the same as those of the nonionic polymer solution at the same concentration. Moreover, the single chain dimensions were shown to remain unaffected by both the ionic content and cation valency, despite the fact that the ionomer solution properties are strongly influenced by these factors. The application of the contrast matching technique, however, was not successful for the Zn-neutralized solutions, as scattering from the aggregates was present in the scattering patterns, which makes analysis of these results difficult. The findings of these studies that neither single chain collapse nor single chain expansion occurs during association, especially at the lower concentrations studied, were initially considered to be rather unexpected in view of the viscometric measurements, that showed a reduction in the ionomer viscosity compared to its nonionic counterpart at concentrations below a crossover concentration,

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* Author to whom correspondence should be sent.

[†] Current address: College of Engineering, University of Delaware, 135 Dupont Hall, Newark, DE 19716.

[‡] Current address: Du Pont de Nemours International S.A., 2 chemin du Pavillon, P.O. Box 50, CH-1218 Le Grand-Saconnex, Geneva, Switzerland.

[§] Present address: University of Liège, Center for Education and Research on Macromolecules (CERM), Sart-Tilman, B6, 4000 Liège, Belgium.

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c^*.[3] The original interpretation of this behavior was attributed to be due to the domination of intramolecular association that leads to the collapse of the ionomer chains in solution below c^*. The evidence, however, from the single chain SANS studies, along with the observation from both SANS[1] and light scattering experiments[4] that intermolecular association exists even in the dilute concentration regime, led to reconsideration of the interpretation of the viscometric experiments. The results of scattering studies on the random sulfonated polystyrene ionomer solutions have led to the suggestion that the decrease of the ionomer solution viscosity in the dilute concentration regime should not be viewed in terms of the conformation of the isolated chains alone but rather in terms of the fraction of isolated coils vs multichain aggregates as well as the relative density packing inside each aggregate.

An extended number of light and SANS scattering studies that probe the multimers in solution have been conducted in the dilute concentration regime for the Na-neutralized SPS ionomer in xylene, a lower polarity solvent.[5−7] Due to the low concentration regime, the results of these studies were analyzed according to models that assume equilibria between isolated coils and small aggregates which provide information on the fraction, as well as the dimensions of the various aggregates in solution. These analyses showed that the radius of gyration of the isolated coils is reduced compared to the nonionic polymer solution and it further decreases with increasing sulfonation level, indicating single chain collapse. Above an ionic level of 1.4 mol % the dimensions of the isolated single chains in solution are even smaller than those expected by the nonionic polymer in a poor solvent. At increasing ionic level the aggregates became less compact, which was suggested to be due to the occurrence of chain expansion during aggregation. Such a single chain expansion has been reported in contrast-matching SANS studies on a 1.25 mol % solution in the semidilute regime.[8] However, only two concentrations were investigated in this study, and furthermore, these solutions have been shown to be time and sample preparation dependent, which would require further investigation before conclusive arguments can be drawn. It should be noted that these results on the conformation of the isolated ionomer chains have been obtained from model analyses of the multimer structure, and they are not direct evidence of the single chain conformation. These model analyses are based on a number of assumptions regarding the equilibrium mechanism, the concentration dependence of the molecular parameters associated with each type of aggregate taken into account in the analysis, and the intermolecular interactions of the solution. Analysis of the distribution of the decay rates from dynamic light scattering measurements, on a 1.3 mol % Zn-neutralized SPS ionomer in xylene, provided evidence of a transition from a single-mode distribution at concentrations below a concentration, c^+, that is lower than the crossover concentration, c^*, to a two-mode distribution above c^+.[9] The single mode was assigned to the diffusion of isolated chains, while the second mode was assigned to the diffusion of multimers, which become dominant as concentration increases. The hydrodynamic radius of the isolated chains in solution was observed to be similar to that of the nonionic polymer in the concentration regime below c^+, while above c^+ the hydrodynamic radius of the isolated chains shows a slight but monotonous increase.

The random placement of the ionic groups along the chain on a random copolymer ionomer system does not allow for a detailed analysis of the effect of ionic interactions on the single chain conformation. This is because single chain studies in these systems probe the overall chain conformation, which does not allow determination of the mechanisms with which the ionic interactions act and the effect on the intrachain segment conformation between the ionic groups. Furthermore, direct single chain studies in these systems have been restricted to only a small concentration regime. In this study we have chosen to investigate the effect of the ionic interactions on the single chain conformation on a model telechelic ionomer system. In this system the polymer chain is constrained exclusively between the ionic groups so this study will reveal the intrachain correlations of a true chain segment that is located between the ionic groups. No direct evidence has been provided so far on the effect of ionic interaction on the single chain dimensions of telechelic ionomers. In analogy to the random copolymer ionomer systems, the solution viscosity of the telechelic ionomers compared to the nonionic polymer has been used to extract information on the intramolecular vs intermolecular interactions. The viscosity of metal telechelic ionomers has been observed to be similar to that of the nonionic polymer in the dilute concentration regime, while at higher concentrations the ionomer viscosity shows a dramatic increase.[10] Highly dilute solutions of quaternary ammonium−telechelic polystyrene ionomers showed a decrease in viscosity of the ionomer compared to the nonionic polymer, analogous to the viscometric measurements of random copolymer ionomer solutions.[11] This was interpreted to be due to a transition from intramolecular association in the dilute concentration regime to intermolecular association as polymer concentration increases.[10−12] Evidence for the existence of a transition from intra- to intermolecular association was provided from fluorescence measurements of an intrachain excimer on solutions of quaternized α,ω-bis(dimethylamino) polystyrene in toluene.[13] This study indicated that intramolecular association prevails in the very dilute concentration regime as evidenced from the strong increase in the emission intensity that was observed at concentrations below 0.17 g/dL. It was proposed that the equilibrium conformational state of the ionomer chain in the dilute solution regime is shifted to a more cyclic conformation.

In the first part of this series the technique of small-angle neutron scattering was applied to obtain the total scattering function of the telechelic ionomer solutions.[14] The results provided information on the structure and thermodynamics of the aggregates in solution. In this study, the small-angle neutron scattering technique has been applied to investigate the single chain conformation of the telechelic ionomer solutions. By application of different labeling techniques, the contribution of the intermolecular scattering that is strong in these systems was completely eliminated so that the single chain scattering function was probed directly. The influence of the ionic interactions on the single chain conformation of the ionomers compared to that expected from the nonionic system is monitored as a function of ionic level and concentration over a wide concentration regime that spans the range from the dilute to the concentrated solution regime. This analysis allows for quantitative description of the influence of the ionic interactions on the single chain conformation and their response to

Table 1. Molecular Characterization of the Hydrogenated and Deuterated Carboxy-Telechelic Methyl Esters in Toluene at 25 °C

form	material	[η], dL/g	M_v[a]	M_w[b]	dn/dc, mL/g
hydrogenous	h-e 6	0.0872	7118	9524	0.108
	h-e 8	0.0928	8065	10360	0.103
	h-e 17	0.1479	20224	21880	0.104
deuterated	d-e 6	0.0686	4413	7180[c]	
	d-e 8	0.0853	6822	9943	0.094
	d-e 17	0.1223	14012	16120	0.097

[a] From intrinsic viscometry measurements. [b] From light scattering measurements. [c] From ref 44.

changes in the extent of association without any assumptions on the intermolecular interactions that take place in solution.

II. Experimental Section

A. Materials. This study focuses on the behavior of halato carboxy−telechelic polystyrene ionomers neutralized with sodium. The telechelic ionomers have been synthesized according to the synthetic procedures described in the first part of this series.[14] The polymers based on either hydrogenous styrene (99%, Aldrich, USA) or styrene-d_8 monomer (98+atom% D, Aldrich, Belgium) were synthesized via anionic polymerization to produce a narrow molecular weight distribution. Carbon dioxide was used as the deactivating agent to end-cap polystyrene chains with a carboxylic acid group, which was either quantitatively neutralized with sodium methoxide with formation of the ionomer or quantitatively esterified to produce the nonionic analog in the ester form. The nomenclature that will be used in this study is symbolized as n-m*x*, where n denotes whether the polymer is hydrogenous (h) or deuterated (d), m denotes the form of the material which is (e) for the ester and (i) for the ionomer and *x* denotes the targeted prepolymer molecular weight in thousands. In the cases where the index n is omitted, this indicates that the system examined is a mixture of hydrogenous and deuterated polymer chains as discussed below.

The molecular weight characterization of the hydrogenous materials has been described in detail in the first part of this series.[14] Intrinsic viscometry and static light scattering techniques have also been employed to characterize the deuterated material forms. The procedures used are exactly the same as those described previously. Intrinsic viscosity measurements were performed on an AVS 300 Schott-Geräte semiautomated viscometer measuring station using KPG-Ubbelhode capillary viscometers. The intrinsic viscosity was evaluated from extrapolation of the reduced viscosity in anhydrous toluene (99%, Aldrich) to zero concentration in the concentration regime 0.3−2.0 g/dL. The theory developed by Han[15] was used to obtain the viscosity-average molecular weight of the esters, M_v, which is applicable in the low M_w regime studied here. Light scattering experiments were performed using a Malvern 4700C light scattering system operating with a 2 W Ar$^+$ laser at 488 nm. The sample cell was a quartz cylindrical cell immersed in a refractive matching fluid, decahydronaphthalene. The solutions, prepared in spectrophotometric grade toluene (Aldrich), were filtered through a 0.2 μm Millipore filter unit. Light scattering measurements were carried out in a range of concentrations from dilute to semidilute to obtain good signal-to-noise ratio and the data were analyzed according to Zimm and Bawn plots considering the third virial coefficient of the solutions. Due to the low molecular weight of the telechelics, the scattering angle dependence of the reduced intensity was very small, so it was not possible to determine the radius of gyration of the polymer chains from this experiment. The refractive index increments of the solutions for absolute molecular weight determination were measured with a Chromatix KMX-16 laser differential refractometer at 633 nm using at least four concentrations in the regime 0-1 g/dL.

The molecular weights of the telechelics determined using these techniques are included in Table 1. From GPC measurements the polydispersity is less than 1.10 for all materials studied. It should be noted that the evaluation of the molecular weight of the deuterated telechelic esters from intrinsic viscosity measurements relies on the calibration of the viscometric curve based on hydrogenous polystyrene standards. However, this may not be exact,[16] and for its determination an absolute method for molecular weight characterization is required. For this reason, the results from the light scattering experiments are more appropriate and the polymer molecular weights that are involved in the calculations are those determined from the light scattering experiments. Table 1 also includes the intrinsic viscosity and refractive index increments of the telechelic ester solutions. To take into account the wavelength dependence of the refractive index increment, the literature data reported for similar molecular weight polystyrene solutions under similar experimental conditions at 488 nm were used for the hydrogenous telechelics,[17,18] as the measured values were in agreement with reported measurements on similar polystyrene solutions at 633 nm. It should be noted that (d*n*/d*c*) is lower for the deuterated analogs, in accordance to reported observations.[16] Due to the lack however of experimental measurements in the literature for similar solutions of deuterated polystyrene, (d*n*/d*c*) of the deuterated telechelics at 488 nm was calculated by considering the measured values and assuming that the wavelength dependence of the refractive index increment is the same for both hydrogenous and deuterated forms.

B. Small-Angle Neutron Scattering Sample Preparation and Data Acquisition. The small-angle neutron scattering (SANS) experiments were performed on the two 30 m SANS instruments at the Cold Neutron Research Facility (CNRF) at the National Institute of Standards and Technology (NIST) in Gaithersburg, MD. These data were acquired over a period of three visits to NIST in May 1992, November 1992, and November 1993. During the first visit data acquisition was performed on the SANS instrument connected to the NG-7 neutron guide that has an Oak Ridge type detector. The system configuration was set at a sample−detector distance of 5 m, neutron wavelength of 6 Å, and a detector center offset of 30 cm that covered the q range 0.0084−0.1427 Å^{-1}. The solutions were placed in quartz cells of thickness 2 mm, which was determined based on the known coherent and incoherent atomic cross sections to give sample transmissions within 0.5 to 0.8.[19,20] The scattering data from each solution and the solvent were corrected for the scattering from the empty cell and background (using a ^{6}Li blocked beam), and the corrected scattering from the solvent was subtracted from the corrected solution scattering to obtain the scattering from the polymer alone. The transmission measurements and the corrections for the detector response have been made as described previously.[14] As none of the samples exhibited anisotropy, the scattering data were radially averaged and placed on an absolute scale by measuring the scattering from a 1 mm thickness silica gel standard that has a zero cross section of $(d\Sigma/d\Omega)(0) = 32 \pm 1$ cm^{-1}. This allows representation of the two-dimensional scattering data in absolute cross section $(d\Sigma/d\Omega)_{abs}$ vs scattering momentum vector, q, which is used in further analysis. During the second visit data acquisition was performed on the 30 m SANS instrument connected to the NG-3 neutron guide that is of the ILL type. The system configuration was set at a sample−detector distance of 3 m, neutron wavelength of 6 Å, and detector center offset of 15 cm that provided access to the q range 0.0153−0.1909 Å^{-1}. The data reduction scheme was the same as for the measurements on the NG-7 instrument. The transmission measurements and corrections for the detector response are the same as described previously.[14] The data were converted to absolute scaling through comparison with the scattering from a 1 mm thick water standard that has a mean cross section of $(d\Sigma/d\Omega)(q) = 0.816$ cm^{-1} at 6 Å and a 1 mm thick silica gel. The scattering of the water was obtained from the latest measurements on this standard that had been performed at NIST 2 days prior to our visit, as it is mainly incoherent and a long counting time is required for acceptable statistics. For the absolute scaling the transmissions of the standards were also measured at the wavelength of the experiment. Experiments on the NG-3 instrument were also conducted during the third visit, in which case measurements were performed on the highest concentration solutions studied. These measurements were obtained during shearing experiments and the solutions were placed in the quartz shearing cell that is available at NIST. The system configuration at this time was set to a sample-to-detector distance of 4 m, detector offset of 15 cm and neutron wavelength of 6 Å that provided valuable data in the q regime 0.0107−0.1483 $Å^{-1}$. The data reported are those obtained under quiescent conditions. The effect of shear on the single chain dimensions of the telechelic ionomer solutions will be presented in a following paper. The time of the experiments varied from 1 h for the more concentrated solutions to 3 h for the dilute solutions so that at least 4×10^5 and up to 7×10^5 counts were collected for satisfactory statistics in the scattering data. At all times the solutions were prepared at least 1 week in advance of the experiment, especially for the concentrated solutions, to assure that aggregation equilibrium had been reached.

In order to probe single chains in polymers with strong interchain correlations with SANS, a fraction of the polymer molecules needs to be labeled, as the differentiation between intra- and interchain correlations with this technique is based on the large difference that exists in the coherent scattering length between hydrogen and deuterium. In the case of scattering from a mixture of hydrogenous and deuterated polymer chains in a solvent, the total coherent cross section, $(d\Sigma/d\Omega)_{coh}$, is[20, 21]

$$\left(\frac{d\Sigma}{d\Omega}\right)_{coh} = \frac{M_{1,w}cN_A}{{m_0}^2}[(b_H - b_D)^2 x(1-x)S_S(q) + (b_P - b_s{*}')^2 S_t(q)] \quad (1)$$

where b_H and b_D are the coherent atomic scattering lengths per repeat unit of the hydrogenous and deuterated polymer chains respectively, x is the mole fraction of the polymer chains that are deuterated, b_P is the total coherent scattering length of the polymer defined in eq 2, and $b_s{*}'$ is the coherent scattering length of the solvent normalized for the differences in partial molar volume between the polymer, V_P, and the solvent, V_s. $M_{1,w}$ is the weight-average molecular weight of the single polymer chain, m_0 is the molecular weight of the polymer repeat unit, c is the polymer concentration, and N_A is Avogadro's number. $S_S(q)$ is the single chain scattering function and $S_t(q)$ is the total scattering function, i.e., the sum of the single chain, $S_S(q)$, and intermolecular scattering, $S_P(q)$, functions ($S_t(q) = S_S(q) + S_P(q)$). The basic assumption inherent in eq 1 is that the hydrogenous and deuterated polymer molecules are identical in all their other properties except for their scattering lengths. The term identical is referred to such properties as the degree of polymerization and molecular weight distributions,[22,23] single chain and interchain scattering functions,[24,25] and molar volumes.

Two techniques are usually followed in the literature to extract the single chain scattering function of polymer solutions.[23,26] The first is the isotopic substitution method, in which the scattering data from solutions of the same polymer concentration but different isotopic substitutions are subtracted leading to the elimination of the total scattering term in eq 1. The second technique is based on the principle of contrast matching, in which scattering is measured from a solution in which the average scattering length density of the polymer matches the average scattering length density of the solvent; in this case, the last term in eq 1 due to the total scattering vanishes, and the single chain scattering function is probed directly. In this study, the contrast matching technique was considered to be more appropriate for the associating ionomer solutions, since a single only measurement is required with this technique at each concentration. This proves to be efficient not only in terms of time but also in terms of accuracy, as the association phenomenon is very sensitive to even small changes in concentration in these solutions,[14] and a small deviation in the concentration between the solutions used in an isotopic substitution technique could lead to large errors as to the single chain conformation information.

Table 2. Atomic Scattering Lengths and Partial Molar Volumes of Hydrogenated and Deuterated Polystyrene and Toluene

material	b_{coh}, 10^{-12} cm[a]	ρ, g/cm^3	σ_{inc}, 10^{-24} cm^2	V_i, cm^3/mol
h-polystyrene	2.32672	1.05[b]	637.52	99.2
d-polystyrene	10.65792	1.13	15.68	99.3
h-toluene	1.66188	0.8625[c]	637.57	106.8
d-toluene	9.99308	0.9385[c]	15.73	106.8

[a] From ref 19. [b] From ref 28. [c] From ref 29.

In order to achieve the contrast matching, the solvent used was a mixture of hydrogenous and deuterated solvent molecules, whose isotopic substitution was chosen so that

$$b_p \equiv xb_D + (1-x)b_H = b_s{*}' \equiv x_s b_{sD} + (1-x_s)b_{sH} \quad (2)$$

Under this condition eq 1 yields:

$$\left(\frac{d\Sigma}{d\Omega}\right)_{coh} = \left[\frac{M_{1,w}cN_A}{{m_0}^2}(b_H - b_D)^2 x(1-x)\right]S_S(q) = KS_S(q) \quad (3)$$

from which the single chain scattering function is obtained directly. It has been shown both in the bulk[23,27] and in solution[26] that the determination of $S_S(q)$ via polymer labeling is not restricted to small concentrations of labeled chains. Due to the low molecular weight of the telechelics and the dilute solutions studied here, the fraction of the labeled polymer chains used was 50 mol %, which yields the maximum coherent intensity. The atomic scattering lengths, partial specific volumes and densities for the materials used in this study are presented in Table 2. On the basis of these values, the mole fraction of the solvent that is required to be labeled so that the contrast matching condition is achieved is 65.5 mol %.

The scattering obtained after the data reduction includes both the coherent and incoherent scattering from the polymer. Due to the reactor source that is used at NIST, the incoherent scattering is isotropic over the whole q regime. The incoherent scattering in this study has been accounted for by considering it as a constant parameter during the modeling analysis.

III. Data Evaluation and Analysis

A. Modeling SANS Results. The procedure that is usually followed in the literature to extract chain conformation from this experiment is to restrict the analysis to a small q regime where the scattering function is a known function of q. More detailed information can however be achieved by utilizing the whole q regime that is available in a neutron scattering experiment. In this case, a model that describes the chain statistics needs to be considered. A model that has been extensively used for polymers in both bulk and solution is the Debye function[30]

$$S_S(q) = \frac{2}{{u_N}^2}(e^{-u_N} - 1 + u_N) \quad (4)$$

where the dimensionless variable u_N is

$$u_N = q^2 \langle {R_g}^2 \rangle_z \quad (5)$$

and $\langle R_g^2 \rangle_z^{1/2}$ is the z-average radius of gyration of the polymer chains. Although the Debye function has been primarily derived in the limit of high molecular weight and for Gaussian polymer chains, it has been successfully applied for polymer coils with excluded volume interactions, such as swollen polymer chains in a good solvent, for rather large u_N. $<R_g^2>_z$ can be more generally expressed as[31]

$$\langle R_g{}^2\rangle_z = \frac{N^{2\nu}b^2}{(2\nu+1)(2\nu+2)} \tag{6}$$

where N is the degree of polymerization of the chains, b is the segment length, and ν is a parameter that indicates the extent of excluded volume interactions. ν has been shown to assume a value of 0.5 for Gaussian chains and 0.6 for swollen polymer chains. For short polymer chains a model that takes into account the rigidity of the chains is more appropriate. SANS experiments of low molecular weight polystyrene in a Θ solvent[32] have shown that the radius of gyration of these polymers is more precisely described by the wormlike chain model proposed by Porod and Kratky.[33,34] This is of concern in the present study, as the telechelics studied are of low molecular weight. In addition, the conformation of these systems is studied in solution in a good solvent for the polymer backbone, in which case the excluded volume interactions are also expected to be significant. SANS measurements of a wide range of molecular weights of polystyrene in both good and Θ solvents, have indicated that the excluded volume exponent, ν, in a good solvent is significantly lower than 0.6 for molecular weights below 10^5. However, the radius of gyration of the polymer chain was observed to be larger in a good compared to a Θ solvent for molecular weights above 10^3.[35] This indicates that although excluded volume interactions are smaller in the low molecular weight regime, they still affect the chain dimensions.

In order to take into account the effect of chain stiffness on the conformation of the telechelic ionomer solutions, it is therefore necessary to consider a stiff-chain model. The evaluation however of the scattering function of polymer chains with imposed stiffness is a very difficult mathematical problem and it is generally considered either through approximations or numerical solutions for a specific range of parameters.[36−38] One model that has been extensively used to describe wormlike chains is the model proposed by Sharp and Bloomfield[39] for chains with no excluded volume interactions

$$S_S(q) = \frac{2}{u_{N,K}{}^2}(e^{-u_{N,K}} - 1 + u_{N,K}) + \frac{2}{5q^2L^2}[-11u_{N,K}e^{-u_{N,K}} + 4u_{N,K} + 7 - 7e^{-u_{N,K}}] \tag{7}$$

where n_K is the number of Kuhn segments of statistical segment length α, which is defined as

$$u_{N,K} = q^2\frac{n_K\alpha^2}{6} = q^2\frac{Nb_K{}^2}{6} \tag{8}$$

$$n_K = \frac{L}{\alpha} = \frac{lN}{\alpha} \tag{9}$$

where L is the chain contour length, and l is the contour length of a repeat unit. b_K is a segment length that is based on the degree of polymerization, analogous to b in eq 6. From eqs 8 and 9, $b_K{}^2 = l\alpha$. It has been shown[36] that eq 7 describes the single chain scattering function for $L \geq 10\alpha$ and $q^2 \leq 10\alpha^{-2}$. The mean-square radius of gyration of a wormlike chain with no excluded volume has been evaluated by Benoit and Doty[40] as

$$\langle R_g{}^2\rangle = \frac{L\alpha}{6} - \frac{\alpha^2}{4} + \frac{\alpha^3}{4L}\left[1 - \frac{\alpha}{2L}(1 - e^{-2L/\alpha})\right] \tag{10}$$

By comparing experimental studies on several polymer solutions, Norisuye and Fujita showed that eq 10 can describe the radius of gyration of polymer chains regardless of the system for $n_K < 50$.[41]

The scattering data have been modeled according to both the wormlike chain model and the Debye function to investigate the effects of both chain stiffness and excluded volume interactions on the ionomer single chain conformation. The model fit to the data was conducted by optimizing the sum of the squares of the residuals using the EO4HF optimization routine of the NAG Fortran library and analytical evaluation of the first and second derivatives of the optimized function to minimize computational errors. Optimization was performed by considering three model parameters: (i) the incoherent scattering, $(d\Sigma/d\Omega)_{inc}$, that was considered as a constant parameter, (ii) the contrast factor, K, and (iii) the segment length, b, for the Debye function, or b_K, respectively, for the wormlike chain function. The coherent scattering cross section, $(d\Sigma/d\Omega)_{coh}$, which is required for the modeling, is therefore obtained from subtraction of the measured scattering intensity from $(d\Sigma/d\Omega)_{inc}$ obtained from optimization. Modeling for the contrast factor takes into account any discrepancies that may be due to the absolute scaling of the data, especially since data obtained at different reactor times are compared, as well as differences in the molecular weight between the hydrogenous and deuterated species. The modeling of the third parameter is the main interest in this study. Although in employing the wormlike chain model l is usually considered as an adjustable parameter, for polystyrene it has been shown that l is similar to the length of the repeat unit[32,35,41] ($l = 2.516$ Å) and this is the value that will be assumed for this parameter in this study. Therefore from this modeling analysis the magnitude of the segment length is a direct measure of the single chain conformation. The modeling results have been based on the average molecular weight of the hydrogenous and deuterated chains. Modeling with $(Nb^2/6)$ as a modeling parameter instead of b, which does not require assignment of the chain molecular weight, as shown by eqs 7 and 8, led to exactly the same results, which further verifies that the modeling analysis adequately represents the average chain conformation of the individual chains in solution.

B. Small-Angle Neutron Scattering Data. Since its introduction, the technique of contrast matching has been successfully applied to polymers to yield direct information on the single chain conformation. One of the biggest issues in experimentally applying the contrast matching technique is whether the appropriate labeling level in both the polymer chains and the solvent has been applied, so that the term that corresponds to the total scattering function, as described in eq 1, is completely eliminated and therefore what is measured is the true single chain function. In dealing with associating polymers, as is the case of the ionomers presented in this study, an additional question arises from the randomness in the number of hydrogenous and deuterated chains that are associated into a multimer, which is required for accurate probe of single chains. This question is especially important in probing the solution regime as the associating particles can contain from a few to a large number of chains.

The absolute scattering intensity data obtained in the dilute and semidilute concentration regime for telechelic ionomers i-17 and i-8 are shown in Figures 1 and 2,

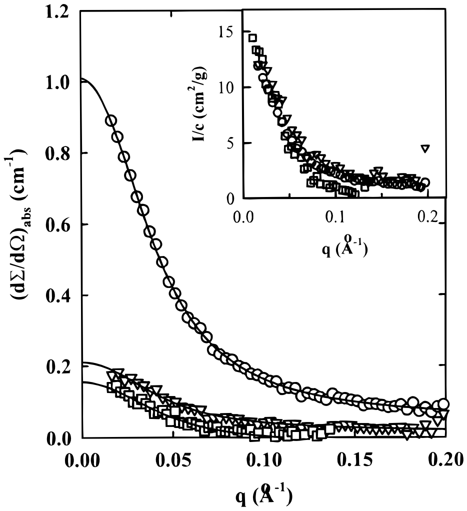

Figure 1. Absolute scattering intensity cross section of contrast matched solutions of telechelic ionomer i-17 in toluene at 25 °C at different polymer concentrations: (□) 1.03 g/dL; (▽) 1.45 g/dL; (○) 7.5 g/dL. The lines represent the fit of the data according to the wormlike chain model as described in the text. The inset is a rescaling of this figure to represent the ratio of the scattering intensity over concentration. The symbols in the inset are the same as those used in the main figure.

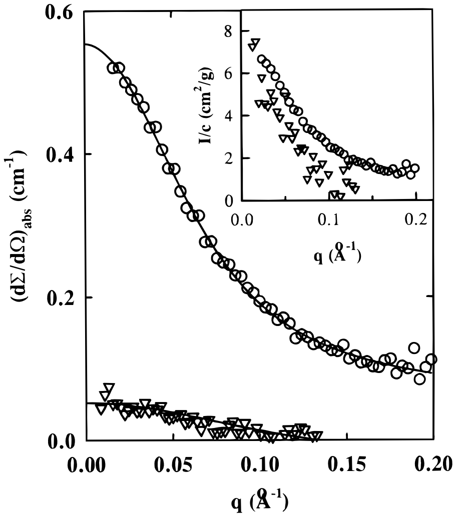

Figure 2. Absolute scattering intensity cross section of contrast matched solutions of telechelic ionomer i-8 in toluene at 25 °C at different polymer concentrations: (▽) 1.03 g/dL; (○) 7.5 g/dL. The lines represent the fit of the data according to the wormlike chain model as described in the text. The inset is a rescaling of this figure to represent the ratio of the scattering intensity over concentration. The symbols in the inset are the same as those used in the main figure.

respectively. From these figures it is observed that for each ionomer system an increase in polymer concentration results in an increase of the scattering intensity at a specific q. If the scattering functions between the two ionomer systems are compared at the same concentration, the scattering intensity is observed to be higher for the higher molecular weight backbone ionomer. Both of these dependencies are in fact in accordance with the expected behavior of the scattering profiles according to the contrast matching technique. The increase in the scattering intensity observed with an increase in concentration and molecular weight is the direct result of the fact that the contrast factor in this experiment is directly proportional to both the polymer

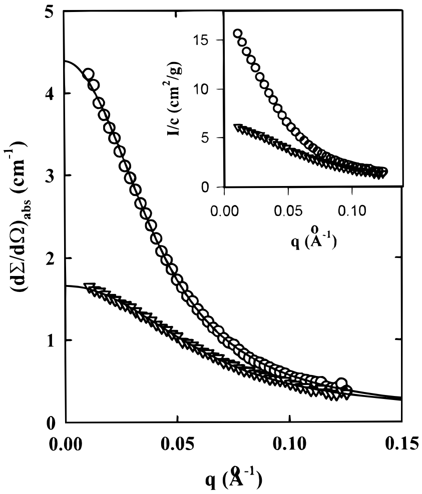

Figure 3. Absolute scattering intensity cross section of contrast matched solutions of (▽) telechelic ionomer i-8 and (○) telechelic ionomer i-17 in toluene at 25 °C at a polymer concentration of 27 g/dL. The lines represent the fit of the data according to the wormlike chain model as described in the text. The inset is a rescaling of this figure to represent the ratio of the scattering intensity over concentration. The symbols in the inset are the same as those used in the main figure.

concentration and molecular weight, as shown by eq 3. This is shown explicitly in the insets of Figures 1 and 2, where the ratio of the scattering intensity over concentration is plotted. As can be seen, when normalized over the concentration, the scattering intensities of different concentration solutions of the same ionomer collapse over the same intensity magnitude as q decreases, indicating that the aggregation effect has been removed in these solutions. Figure 3 shows the contrast-matching scattering patterns from both telechelic ionomer systems examined in this study in the concentrated solution regime. Similar to the behavior observed at the lower concentrations, the higher molecular weight ionomer shows a higher scattering intensity. Furthermore, the scattering intensity for both systems is significantly higher than the lower concentration patterns shown in Figures 1 and 2. Normalization of the scattering intensity with concentration results in the same scale as that observed for the lower concentration solutions, as can be seen from a comparison among the insets of Figures 1−3. From a comparison between the scattering patterns of Figures 1−3 with those presented in the first part of this series which probed the total scattering function of the ionomer solutions, a large difference in the magnitude as well as behavior of the scattering intensity is observed, which indicates that the molecular information probed in the two experiments is clearly different.

The modeling of the SANS scattering data by employing the wormlike chain model is shown as the solid lines in Figures 1−3. As can be seen, the wormlike chain model accurately describes the scattering patterns at all concentrations and ionomer systems examined. The modeling according to the Debye function also resulted in good fits to the data which are not shown here. The modeling fits are shown up to the limit of $q \rightarrow 0$, as at this limit any single chain scattering function, independent of chain statistics, becomes unity and the scattering data should level off at their maximum magnitude. This behavior of the scattering patterns as well as the excellent fit of the data by a single chain model provide strong evidence of the applicability of the contrast

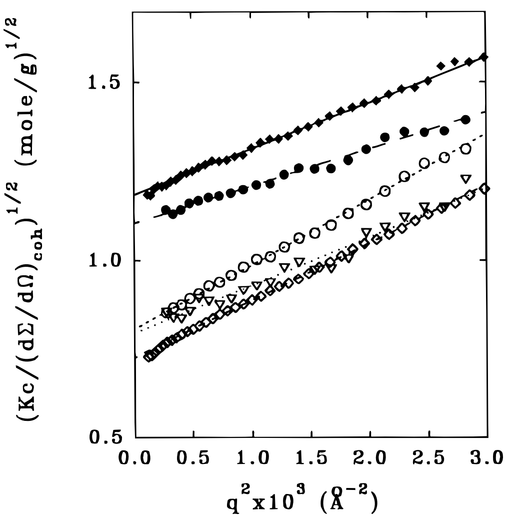

Figure 4. Berry plot of the inverse square root of the absolute coherent scattering intensity vs q^2 for contrast matched telechelic ionomer i-8 solutions in toluene at (●) 1.03 and (◆) 27 g/dL and for contrast matched telechelic ionomer i-17 solutions in toluene at (▽) 1.03, (○) 7.5, and (◇) 27 g/dL. The lines through the data indicate linear regression of the corresponding concentration solutions.

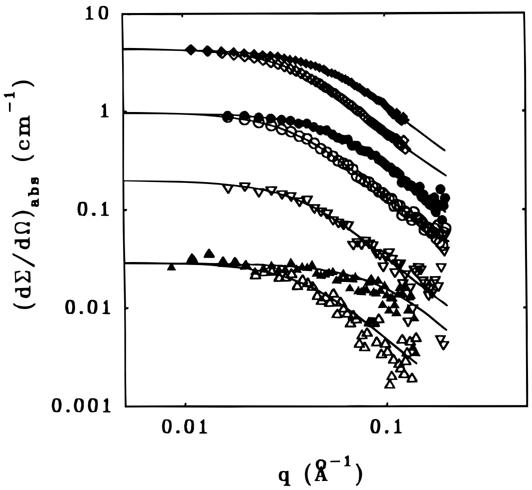

Figure 5. Double logarithmic plots of the coherent scattering intensity vs q for contrast matched solutions of i-17 in toluene as a function of concentration: (△) 1.03 g/dL; (▽) 1.45 g/dL; (○) 7.5 g/dL; (◇) 27 g/dL. The filled symbols correspond to the same concentrations for the contrast matched solutions of i-8 ionomer. The lines through the symbols are the fit of the data according to the wormlike chain model for the specific concentration. The data in this plot for the telechelic ionomer i-8 have been translated on the y-axis so that the intercept at $q = 0$ matches that of the corresponding i-17 ionomer solution.

matching technique to the telechelic ionomer solutions. In the low q regime $S_S(q)$ can be simplified to an analytical form that is independent of chain statistics and which enables evaluation of the molecular parameters. The scattering data are plotted in the low q regime in Figure 4 according to the Berry plot[42] that is linear vs q^2

$$\left(\frac{K'c}{(d\Sigma/d\Omega)_{coh}}\right)^{1/2} = \frac{1}{M_w^{\ 1/2}}\left(1 + \frac{q^2 R_g^{\ 2}}{6}\right) \qquad (11)$$

where $K' = N_A x(1 - x)(b_H - b_D)^2/m_o^2$. Therefore the intercept of the Berry plot provides the molecular weight, while from the slope of the plot the radius of gyration can be obtained. This analysis is similar to the more common analysis provided by a Zimm plot; however, it has been shown for low molecular weight polymers that the Berry plot is linear for a larger range of q compared to the Zimm plot,[36] and is therefore preferred in this study due to the absence of data in the very low q regime. From this plot it can be observed that all the solutions of the same ionomer system result in intercepts that are similar to within the experimental error, from which it is evident that the molecular weight measured in this experiment refers to the same particle. In addition the scaling of the intercept between the two ionomer systems is in the same direction as expected for the difference in backbone molecular weight. The molecular weights calculated from the Berry plot, as presented in Table 4, are similar to within experimental error to the polymer backbone molecular weights presented in Table 1, indicating that the entity probed by the neutron scattering experiment is the single chain. The radii of gyration evaluated from this plot are discussed below along with the modeling results.

Due to the dependence of the contrast factor on polymer concentration and molecular weight, simple viewing of the scattering intensity data in Figures 1−3 cannot lead to immediate understanding of the behavior of the single chain scattering function. The scattering data are replotted in Figure 5 in a double logarithmic plot of the coherent scattering intensity vs q. This representation allows for direct observation of the influence of polymer concentration and backbone molecular weight on the single chain conformation of the ionomer solutions, since as shown by eq 3, the contrast factor serves only as a scaling factor and therefore the resulting shape of the scattering curve is solely due to the single chain scattering function. In this case, knowledge of the contrast factor is not necessary to describe the data. The data in Figure 5 have therefore been obtained by translating the scattering patterns of the i-8 ionomer solutions along the ordinate, so that their scattering intensity at low q matches that of the corresponding i-17 ionomer solution at the same concentration. There are two distinct features that are of importance in this figure. First, at all concentrations studied the scattering intensity of the i-8 ionomer solutions is higher than that of the i-17 ionomer solutions. This clearly shows that the experiment distinguishes between the two different molecular weights, since the single chain scattering function is a function of the polymer molecular weight. Second, for the same ionomer system the scattering curves do not exactly match, which is an indication that some change in the chain conformation occurs with change in the polymer concentration. In order to better visualize the behavior of the scattering patterns in the telechelic ionomer solutions, simulations have been performed on the wormlike chain model that are shown in Figure 6. From eq 7, it is apparent that the single chain scattering function depends on both the molecular weight and statistical segment length. This function has been solved in the q-regime of interest and molecular weights that match those of the systems studied here for different values of the statistical segment length. As can be seen from this figure for the same segment length the scattering intensity of the lower molecular weight polymer is always larger than that of the higher molecular weight. Furthermore, an increase in the segment length is indicated by a drop of the single chain scattering function from its plateau value to a scaling behavior that occurs at lower q values for higher

Table 3. Optimized Values of the Modeling Parameters Based on the Wormlike Chain Model

material	c, g/dL	$I_{inc} \pm s$	$K \pm s$, cm^{-1}	$b \pm s$, Å
i-17	1.02	-0.0227 ± 0	0.1762 ± 0	6.688 ± 0.095
	1.45	0.01350 ± 0	$0.1965 \pm 5.3 \times 10^{-5}$	6.743 ± 0.033
	7.50	0.03419 ± 0	$0.9753 \pm 1.6 \times 10^{-5}$	7.288 ± 0.002
	27.0	$-0.0078 \pm 4 \times 10^{-5}$	$4.4000 \pm 2.6 \times 10^{-5}$	7.315 ± 0.001
i-8	1.03	$-0.03718 \pm 1 \times 10^{-5}$	0.0934 ± 0	4.670 ± 0.077
	7.50	0.04371 ± 0	$0.5100 \pm 1.6 \times 10^{-5}$	6.365 ± 0.004
	27.0	$0.05149 \pm 4 \times 10^{-5}$	$1.6080 \pm 6.2 \times 10^{-6}$	6.941 ± 0.003

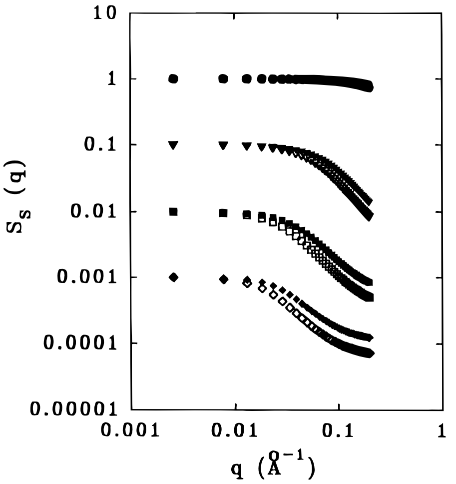

Figure 6. Double logarithmic plot of the single chain scattering function, as described by the Sharp-Bloomfield wormlike chain model vs q. The data have been obtained from simulations on the single chain scattering function expression for a system with degree of polymerization 89 (closed symbols) and 150 (open symbols). The simulated data from the top are for segment lengths, b_K: (○) 1 Å; (▽) 5 Å; (□) 10 Å; (◇) 15 Å.

Table 4. Comparison of the Evaluation of the Single Chain Radius of Gyration from Three Different Method Analyses Followed in This Study: the Wormlike Chain Model, the Debye Function and the Berry Plot[a]

		R_g, Å		Berry plot	
material	c, g/dL	wormlike chain model	Debye model	M_{1w}	R_g, Å
i-17	1.02	35.46	36.94	19440	32.91
	1.45	35.73	37.50	14635	32.83
	7.50	38.43	40.39	14374	37.34
	27.0	38.56	40.48	18300	38.80
i-8	1.03	17.97	18.20	10257	19.69
	7.50	23.94	25.27	7614	23.80
	27.0	25.86	27.23	6700	26.27

[a] The results based on the Debye function are the same for both unperturbed ($\nu = 0.5$) and swollen chain analysis ($\nu = 0.6$). The molecular weight evaluated from the Berry plot is also included in this table.

segment lengths. The behavior that was observed in the scattering patterns of the telechelics as shown in Figure 5 is consistent with the behavior expected from a wormlike chain model.

C. Single Chain Conformation of Telechelic Ionomer Solutions. The preceding discussion as well as the excellent fit of a single chain model to the data provides confidence that the contrast matching technique has been successfully applied to the telechelic ionomer solutions under all experimental conditions studied. Table 3 includes the optimized values of all the parameters fitted during the modeling analysis based on the wormlike chain model, I_{inc}, K, and b_K, along with the variances of the parameters as determined from the optimization algorithm. The results in this table indicate that the modeling analysis follows very well the dependence of K on concentration and molecular weight in accordance to its theoretical expression as defined in eq 3. As K was used in this study as a means to account for any differences in the molecular weight of the labeled chains as well as in the absolute calibration between different instrument configurations, a comparison of the model estimated values of K with the theoretically expected values from eq 3 indicates that the modeling analysis provides a nonbiased solution for the determination of the segment length. Furthermore, the variance of all model parameters, as observed in Table 3, is very good which has as a consequence that the error bars in the optimized value of the segment length, b_K, are very small if not negligible. The results of the modeling of the ionomer solutions studied according to the wormlike chain model are shown in Figure 7. Since for each ionomer system the chain contour length is the same, the effect of ionic interactions on the ionomer chain conformation can be totally attributed to changes in the statistical segment length. As shown in Figure 7, both ionomer systems show a consistent increase of the statistical segment length with increasing concentration. This increase is more pronounced for the lower molecular weight telechelic ionomer i-8 that shows a significant change of the polymer chain conformation in the dilute concentration regime. As concentration increases and reaches the semidilute concentration regime, the statistical segment length for both ionomer systems reaches a plateau.

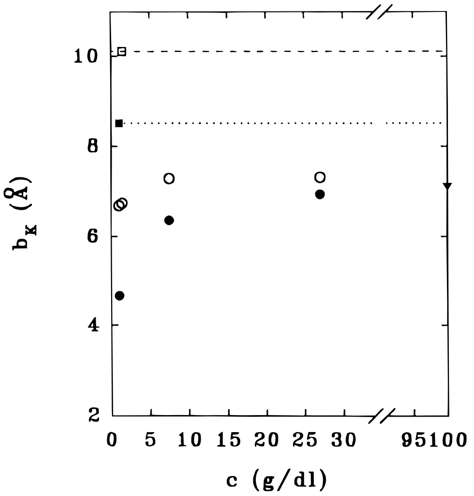

Figure 7. Effect of concentration and ionic level on the ionomer single chain dimensions for the contrast matched solutions of: (○) i-17 and (●) i-8. The data at the bulk (▼) are from SANS measurements of the single chain dimensions of i-6 in the bulk (from ref 44). The data for the esters (□) e-17 at 1.45 g/dL, and (■) e-6 at 1.04 g/dL, are from total scattering SANS measurements (from ref 14). The broken lines are only a guide for the difference in segment length between the ionomer and corresponding ester form.

These data suggest that there is a change in the single chain conformation of the telechelic ionomer solutions with varying extent of association. This change occurs at the low polymer concentration limit, where the multimers consist of only a few numbers of chains. It seems that under these conditions the ionic groups attached to the same chain find themselves closer to themselves than to the ionic groups of different chains which drives them into intramolecular interactions. This indication is further supported by the fact that intramolecular interactions are more evident in the lower molecular weight ionomer system. Taking under consideration that the energy of interaction between two dipoles is inversely proportional to their distance, the lower molecular weight ionomer would be expected to form self loops more readily compared to a higher molecular weight telechelic. In the semidilute and concentrated regime multimers consist of a large number of chains, and because of the occurrence of chain overlap in this regime a network is formed. During network formation the increase in the statistical segment length indicates that there is a transition from intramolecular to intermolecular interactions that occurs independent of the chain length, which is indicative of the preference of the chains to connect to other chains rather than to themselves. This preference is expected to occur in view of both the statistics of the chain as well as the strong intermolecular interactions that occur in that regime.

The behavior that has been observed through these SANS experiments of the single chain conformation of the telechelic ionomer solutions is unique to these solutions. Both small-angle neutron and small-angle X-ray scattering studies of polymer solutions in a good solvent, such as polystyrene in toluene, have shown that in the dilute solution regime the radius of gyration of the polymer chains in solution is expanded significantly compared to their unperturbed dimensions.[43] As polymer concentration increases, the radius of gyration decreases continuously with concentration and assumes its unperturbed dimensions in the bulk. The degree of chain expansion depends on the molecular weight of the polymer, however it has been shown that even for the low molecular weights used in this study there is a considerable chain expansion with the statistical segment length being 2−2.5 times higher than that observed in a Θ solvent.[35] From the study of Huber et al. on the chain dimensions of dilute solutions of polystyrene it can be calculated that for l = 2.516 Å the segment length b_K of polystyrene of M_w = 21 600 in toluene is approximately 9.2 Å, and that of M_w = 10 700 is 8.8 Å.[35] Both of these values are larger than the ones measured in the dilute solution regime of both telechelic ionomer solutions studied. As a comparison the results obtained from SANS experiments on two dilute solutions of the telechelic esters have been included in Figure 7. These data have been obtained from measurements of the total scattering from solutions of hydrogenated esters in deuterated solvent, and the segment length has been evaluated from the fit of the deGennes model to the data, as described in the first part of this series.[14] As can be seen, the segment length of the esters of both systems studied in the dilute solution regime is larger than the corresponding ionomer solution. These results indicate that the decrease in the single chain dimensions observed in the ionomer solutions in the dilute regime is due to the effect of the ionic interactions.

It should be noted that this contraction in the chain dimensions is even greater than that expected to occur when the polymer chain assumes its unperturbed dimensions. Data of low molecular weight polystyrene in a Θ solvent have suggested that the segment length of polystyrene is approximately 7.5 Å.[32,41] It is very interesting to note that the plateau value that is seen to be reached at the concentrated solution regime is very close to the value expected for unperturbed dimensions and this is true for both ionomer systems. Further, this value is very close to that obtained from single chain SANS studies on the i-6 telechelic ionomer system in the bulk.[44] In that study it was found that in the bulk the single chain dimensions of this telechelic ionomer system are not affected by the ionic interactions but remain the same as those exhibited by the corresponding ester. On the basis of these results it can be observed that the ionomer chains reach their unperturbed dimensions at the onset of the concentrated solution regime and they retain this conformation until the bulk. It is of interest at this point to discuss the suggestion offered by Huber et al. to explain the molecular weight dependence of the second virial coefficient of low molecular weight polymer solutions.[35] These authors suggested that chain stiffness affects the unperturbed dimensions of a solution in a good solvent resulting in values that are higher than those expected in a Θ solvent environment or in the bulk. According to this study polystyrene in toluene should reach its unperturbed dimensions at a segment length of about 8.2 Å. Unfortunately we have seen no reports on the chain conformation of low molecular weight polystyrene in a good solvent in the concentrated regime; however, it is generally believed that the solvent type can have a significant impact on the unperturbed dimensions of a polymer chain.[45,46] If this consideration is true, this indicates that the ionomer single chain dimensions remain contracted even in the concentrated solution regime, compared to the unionized parent polymer. In this study three different methods have been used for the evaluation of the single chain radius of gyration from the scattering data: the wormlike chain model, the Debye function, and the Berry plot. The value of the radius of gyration evaluated from each of these methods has been included in Table 4 for intercomparison. As can be observed from this table, the radius of gyration evaluated from the wormlike chain model according to eq 10 is in good agreement with the radius of gyration evaluated from the Berry plot, which is model independent. Both the wormlike chain model and the Debye function display the same behavior for the radius of gyration of the telechelic ionomers. It has to be noted that the Debye function has resulted in the same optimized values for the single chain radius of gyration by applying either the case for unperturbed (ν = 0.5) or swollen chains (ν = 0.6). In addition, modeling based on the Debye function for either unperturbed or swollen chains resulted in very similar values for the K parameter as those reported in Table 3 for the modeling analysis based on the wormlike chain model.

In the first part of this series SANS measurements on the total scattering function of the telechelic ionomer solutions had been presented.[14] This study had shown an upturn in the scattering patterns of the ionomers in the low q regime which was attributed to ionic interactions that lead to multimer formation. The scattering data of that study were analyzed by employing the deGennes model with model parameters the statistical segment length, b_K, and the Flory−Huggins interaction parameter, χ. According to this representation the system is assumed to contain single chains in solution,

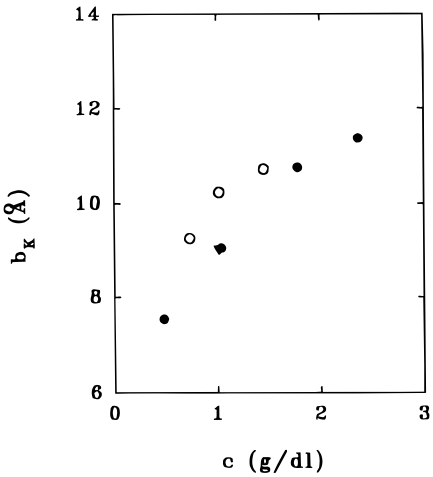

Figure 8. Effect of concentration and ionic level on the ionomer chain dimensions as obtained from the fitting of the total scattering intensity data of the telechelic ionomer solutions via the deGennes model considering wormlike chain statistics for the single chain scattering function for hydrogenated (○) i-17 and (●) i-8 solutions in deuterated toluene.[14]

while the effect of ionic interactions on the solution thermodynamics is included in the χ parameter. Any changes in the modeling results from this analysis, as reflected by changes in the single chain segment length and the interaction parameter as compared to the ester form, is evidence of the effect of ionic interactions on the structure and thermodynamics of the solution. The modeling results with respect to the segment length b_K, which had been left for this discussion, are presented in Figure 8. The striking similarity in the effect of both polymer concentration and polymer backbone molecular weight on the single chain conformation between the present and the previous study is immediately apparent. The statistical segment length that has been evaluated from the deGennes model shows that single chain contraction occurs in the dilute concentration regime, with the single chain dimensions expanding as concentration increases. The change of the segment length with concentration as observed from these data suggests that the expansion in the chain dimensions becomes less steep with increasing polymer concentration, similar to the results observed in this study. In the low concentration regime examined the segment length of the higher molecular weight polymer is again seen to be larger than the lower molecular weight telechelic, while the biggest change in the single chain dimensions is more apparent for the lower molecular weight system. The similarity in the behavior observed between the modeling from the deGennes model and the direct single chain measurements is very unexpected due to the simplicity of the deGennes model that describes the effect of the ionic interactions in the ionomer solutions in the context of a mean field theoretical approach. The similarity in these measurements helps to justify the use of the deGennes model in our previous study in analyzing the total scattering from the ionomer solutions, and it further suggests its value as a first estimation of the single chain conformation from total scattering measurements that are more easily performed experimentally compared to single chain measurements. It should be noted however that there is a difference in magnitude in the statistical segment length that is found between these two analyses. For all concentrations examined the segment length predicted from the total scattering data is higher than that obtained from the direct single chain measurements. These differences could be due to the values of the material parameters that have been taken into consideration during modeling, as well as the simplicity of the deGennes model which describes the effect of the ionic interactions through the χ parameter that is considered constant. The ability however of the model to describe the behavior of the single chain conformation is nevertheless noteworthy.

Theoretical treatments and computer simulation models of the equilibrium properties of telechelic ionomers suggest the possibility of intramolecular interactions in these systems.[47−49] However, these treatments either calculate the interactions between two polymer chains alone or do not take into account the influence of the solvent. Recently the equilibrium properties of telechelic ionomers have been analyzed based on the similarity between the ionic aggregation observed in ionomers and the microphase separation observed in block copolymers.[50,51] On the basis of this similarity, it was suggested that in the dilute concentration regime the multimers formed in solution should resemble the block copolymer micelles, forming a compact core containing the ionic groups surrounded by a corona of the chains; in this regime the chains are viewed as forming self-loops in the micelle, in which case the micelle resembles a “flower”. As concentration increases the attraction between micelles leads to their connection by bridges, that are chains that have their ends at two different micelles. This theory predicts that the number of bridges increases with increase in concentration at concentrations much larger than the overlap concentration. This picture of ionic aggregation is consistent with the results obtained from this study that support the formation of self-loops in the dilute regime with extension of chains due to bridging between different micelles as concentration increases. It should be noted that the fact that the chain dimensions measured increase with concentration and are larger than those expected from a cyclization of the polymer chains is consistent with our observations from total SANS[14] and dynamic light scattering measurements.[52] These results showed that the aggregates were in an extended rather than a contracted conformation as revealed by the rather small fractal dimension of the aggregates.

IV. Conclusions

Small-angle neutron scattering via the contrast matching technique achieved by appropriately labeling both the polymer chains and the solvent molecules has been successful in probing the single chain scattering function in associating low polarity carboxy−telechelic ionomer solutions. This was validated from the observed evolution of the measured scattering patterns with both polymer concentration and molecular weight, that showed the behavior expected from this experiment if the contrast matching was successful. In addition comparison of the scattering patterns obtained in this study to the total scattering function measured on the same telechelic ionomer solutions in the first part of this study also support the approach used here. The scattering data could be described by a single chain statistical model, which is evidence of the fact that contributions due to the aggregation of the ionomer solutions have been completely removed by the contrast matching technique.

The scattering patterns were fitted by both the Debye function that takes into account excluded volume interactions in solution and by the Sharp–Bloomfield scattering function for wormlike chains which takes into account the chain stiffness in the low molecular weight ionomer systems examined. Both models described the data very well over the whole experimental q regime, resulting in similar behavior for the single chain dimensions. Direct measurements of the single chain scattering patterns for two telechelic ionomer systems at concentrations that are in the dilute, semidilute, and concentrated regimes showed a change in the single chain conformation with polymer concentration which is opposite to that expected for the corresponding nonionic polymer solution. For the nonionic polymer the chain dimensions are extended in the dilute concentration regime and decrease toward their unperturbed dimensions at high concentrations. In contrast the single chain dimensions of the ionomer solutions showed a continuous increase with increasing polymer concentration that reach a plateau value in the concentrated solution regime. At all concentrations studied the single chain dimensions of the ionomer chains were found to be smaller than the corresponding nonionic polymer chains, which indicates that single chain contraction takes place in the ionomer solutions. The extent of contraction is larger at low concentrations and smaller separation distances for the ionic groups, as exemplified by the molecular weight of the polymer backbone in the case of telechelic ionomers. Interestingly, the plateau value achieved by both ionomer systems is similar to the unperturbed dimensions of polystyrene in a Θ solvent and is similar to the chain conformation of the ionomer chains in the bulk. These results indicate a change in the conformation of the ionomer chains that is attributed totally to the ionic interactions and which depends significantly on the extent of association. At low extents of association, where multimers of only a few chains exist, the preferred conformation of a single chain is a self-loop where the ionic groups attached to the same chain attract themselves rather than ionic groups on different chains. As concentration increases, the formation of many chain multimers occurs, and eventually a network of the multimers is formed at concentrations higher than the overlap concentration. At high concentrations the chains begin to show a preference to connect to chains that belong to different multimers, as evidenced by single chain extension. At these high concentrations chain overlap compresses the chains that cannot extend beyond their unperturbed dimensions. These conclusions are schematically shown in Figure 9, which presents a molecular picture of the effect of the extent of association and ionic content on the single chain conformation of the telechelic ionomer solutions.

Interestingly, the influence of the association formation on the single chain dimensions as probed directly through the contrast matching technique can also be described very well by the application of the deGennes model to total scattering measurements. Although this model is simplistic in nature as it does not describe specific ionic interactions but rather mean field interactions in solution, the ability of the model to describe such behavior is exceptional.

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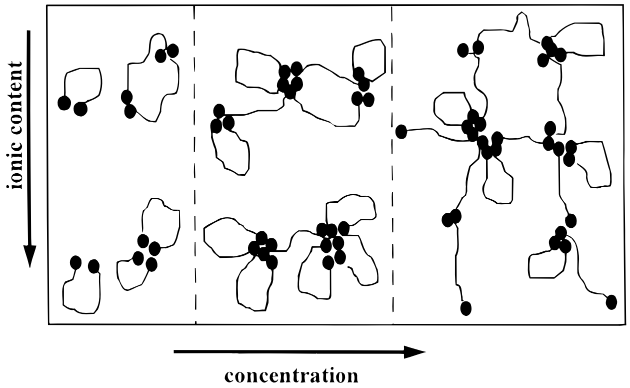

Figure 9. Schematic representation of the single chain conformation in associating telechelic ionomer solutions as a function of concentration and ionic content. The arrows are directed toward increasing concentration or ionic content respectively. The ionomer chains are indicated as solid lines, while the ionic groups, attached at the ends of the chains, are represented by the filled circles.

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