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Small-Angle Neutron Scattering Studies of Low-Polarity Telechelic Ionomer Solutions. 3. Temperature Dependence of the Ionic Association

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ABSTRACT: The effect of temperature on the structure and single chain conformation of associating solutions of carboxy−telechelic polystyrene ionomers has been investigated in the dilute to semidilute concentration regime using the technique of small-angle neutron scattering. By applying different labeling methods, the temperature dependence of both the total scattering and single chain scattering functions was obtained independently. It was observed that temperature has a significant impact on the structure of the ionomer aggregates. Increasing temperature results in dissociation of the aggregated particles and the formation of smaller size multimers. Interestingly, the extent to which the multimers dissociate at a specific temperature compared to their initial state at room temperature is independent of concentration or ionic level, which indicates that it is independent of the degree of aggregation of particles. This leads to the conclusion that the apparent degree of aggregation can be controlled independently by concentration and temperature. For all systems studied the multimers formed through the ionic association keep an extended configuration over all the temperatures investigated. The Flory−Huggins polymer−solvent interaction parameter of the ionomer solutions showed only a slight decrease with increasing temperature. Despite the significant effect of temperature on the multimer structure, temperature was not observed to influence the single chain dimensions of the ionomer solutions. It was observed that the single chain dimensions remained unchanged over the range of variables studied. On the basis of these results, it is proposed that dissociation of the multimers takes place by disruption of the configuration of only a small number of bridging chains which connect different ionic clusters without influencing the main architecture of the associating structure.

I. Introduction

Since the observation that the presence of a small number of ionic groups in ionomers leads to a uniquely different behavior of these systems, a number of studies have been devoted to the investigation of this behavior and the factors that are responsible for it. In particular, the ionic aggregation observed in the bulk, as well as the association behavior displayed by low-polarity ionomer solutions, is generally accepted to originate from the formation of "cross-links" between the ionic pairs on the same or different chains via dipolar interactions.[1] Due to the physical rather than chemical nature of this phenomenon, the ionic cross-links are reversible, and therefore the extent of ionic aggregation depends primarily on the strength of the dipolar attraction forces. In addition to factors such as the nature of the cation/anion or ionic content, the ionic interactions are expected to be strongly influenced by temperature. The temperature dependence of the ionic aggregation has long been important in the exploration of the solid-state behavior of ionomers, as the potential of weakening the ionic interactions by elevating the temperature can result in a variety of potential applications as both the melt processability of a thermoplastic material and the mechanical properties of an elastomer can be achieved with a single material system. It has been suggested that a critical temperature should exist at which sufficient energy is available to overcome the enthalpic driving force for aggregation in ionomers, leading to complete aggregate dissociation.[2] Indeed, at high enough temperatures ionomers in general exhibit flow; however, there has been no experimental evidence of the existence of an aggregate dissociation temperature as ionomers decompose before the aggregates break down. In fact, SAXS studies of ionomers at elevated temperatures have shown that the structural identity of the ionic microdomains persists even at temperatures where flow occurs.[3−5]

A significant effect of temperature has also been observed on the association behavior of ionomers in low-polarity solvents. A unique behavior displayed by ionomer solutions upon variation of the temperature was among the first observations that suggested an unusual behavior in these systems. In viscometric studies of a 0.32 mol % randomly sulfonated polystyrene ionomer (SPS) in xylene, Lundberg et al. observed a marked decrease of the ionomer solution viscosity with increasing temperature which was considerably more dramatic than the one displayed by the corresponding nonionic polymer solution.[6,7] Addition of a small amount of a polar cosolvent in the ionomer solution further led to viscosity−temperature relations that were far from conventional, as both thermal thinning and thermal thickening behavior were attained. This was suggested to be due to a favorable increase of ionic interactions with temperature through cosolvent−ion pair interactions which lead to an increase in viscosity; at higher temperatures these interactions diminish.[6,7] In solutions

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of halato–telechelic Mg-neutralized carboxylato-polybutadiene in toluene increasing temperature was also observed to result in a larger decrease of the solution viscosity compared to that of the nonionic polymer solution, as well as retardation of the gel formation that is observed in these systems.[8] This behavior was suggested to have its origin on the dissociation of the aggregated particles and the formation of smaller size particles with increasing temperature.[8–10] Interestingly, the viscosity of the telechelic ionomer solutions was observed to display excellent thermoreversibility. Viscoelastic measurements of these solutions indicated thermorheological simplicity that follows an Arrhenius type of behavior,[11] suggesting that the deformation mechanism of these solutions is controlled by the thermal dissociation of the aggregates. The activation energy, E_{act}, for such a process was observed to be significantly higher than the thermal energy and to strongly depend on cation type according to $E_{act} = 85.3n/r_i$, for a series of alkaline and alkaline earth cations, where n is the cation valency and r_i the ionic radius.[12]

Recently, the equilibrium properties of telechelic ionomer solutions in low-polarity solvents have been theoretically considered by Semenov et al.[13] In this approach the ionic pairs are considered to associate in micelles of large aggregation number. Attraction between two micelles is attributed to bridging between the micelles with chains that belong to different micelles. The energy of such an attraction was calculated to be much larger than the thermal energy (kT) if the degree of aggregation, p, defined as the number of chains per micelle, is high, and it was predicted to be $\sim p^{0.3}kT$, where k is the Boltzmann constant. A numerical molecular dynamics simulation study on solutions of semiflexible telechelic ionomers showed that the critical temperature for aggregate formation as well as the equilibrium structures of the aggregates depends strongly on the chain rigidity and system density.[14] By applying a phenomenological approach, Joanny proposed a phase diagram for random copolymer ionomer solutions[15] which predicts the existence of both a spinodal curve at temperatures below the θ-temperature and a gelation curve. The gel concentration was predicted to increase, and its dependence on the fraction f of the ionic groups per monomer was observed to change from $1/f$ to $1/f^{8/5}$ with increasing temperature. Phase separation was predicted to occur at constant concentration as temperature decreases. Disagreements, however, have been reported with this theory. For halato–telechelic polymers the demixing transition was observed to occur at increasing dilution and constant temperature,[9] while a statistical mechanical analysis based on gel formation due to dimerization argues that the gel concentration should decrease with f if the dimerization energy is less than 2 kcal/mol, while it should increase with f for dimerization energy larger than 6 kcal/mol.[16]

It is apparent that temperature plays a significant role in the behavior of ionomers. Understanding the thermodynamics that govern these systems is of utmost importance, as it can provide insight into the mechanisms and laws that underlie the ionic aggregation phenomenon. From the available information on temperature studies on ionomers it is apparent that the weakening of the ionic interactions with increasing temperature depends on both the extent of aggregation and the ionic content of the system. The fact that the degree of aggregation can be controlled in solution by the choice of concentration, while it is fixed in the bulk, makes a study of the effect of temperature on the aggregation process of ionomers in solution very attractive. Except however for rheological measurements, the number of studies that have directly probed the effect of temperature on the structure of ionomer solutions is very limited. SANS total scattering studies on dilute solutions of a 1.39 mol % Na-neutralized SPS ionomer (M_w: 1×10^5) in xylene, in the temperature regime 24–75 °C, have reported that temperature had no influence on the single chain radius of gyration at the concentrations studied.[17] However, this analysis neglected the effect of intermolecular interactions on the measured total scattering function, although SANS[18] and light scattering studies[19] on similar ionomer solutions have shown that ionic association prevails even in the very dilute concentration regime. Analysis according to the open association model, which assumes equilibria between all multimers in solution, showed a negative enthaply of aggregation and a positive entropy of aggregation which was considered to arise from increased configurational freedom of the single chains inside the aggregates. A similar study on the same system at 0.95 mol % neutralization showed a similar behavior despite the fact that at this lower ionic content the ionomer solution behaves more closely to a closed association model that assumes equilibria between isolated chains and three-chain aggregates. For this system it was shown that temperature has no significant effect on both the aggregates and single chain dimensions as well as on the extent of aggregation, while again an increase in entropy was observed with no change in enthalpy.[20] Both of these studies were focused in the low concentration regime where the extent of aggregation is relatively not large. It is of interest to mention here the results of a recent dynamic light scattering study on the effect of temperature and concentration on the acid form of sulfonated polystyrene solutions in a nonpolar solvent.[21] Although it is expected that the aggregation of acid groups is weaker than that of salt groups, these systems displayed a phase behavior similar to predictions for ionomers[15] and a gel transition at sufficiently high concentration that is dependent on temperature.[22] This study showed a difference in behavior of the hydrodynamic radius of the acid compared to its nonionic counterpart which is dependent on both concentration and temperature. The most dramatic difference was observed in the semidilute regime and at temperatures close to the cloud point of the solution. In the semidilute concentration regime intermolecular aggregates were observed to be present even at temperatures of 40 °C above the cloud point, while there was a continuous decrease of the hydrodynamic radius of the acid solution toward its value for the nonionic polymer solution with temperature in the dilute solution regime.

In this study we have undertaken SANS experiments in order to explore the effect of temperature on the association phenomenon and structure of low-polarity ionomer solutions. By applying appropriate labeling techniques, the influence of temperature on both the aggregates and the single chains that comprise the aggregates was determined in an independent way. This study is an extension of work presented previously in which the technique of SANS was applied to investigate the effect of concentration and ionic content on the association behavior of Na-neutralized carboxy–telechelic polystyrene ionomer solutions.[23-25] Temperature-dependent SANS studies have been conducted on the same ionomer systems. The temperature was varied from 25 to 80 °C at concentrations covering the dilute through the semidilute regime.

II. Experimental Section

A. Materials. The materials used for this study were halato carboxy-telechelic polystyrene ionomers neutralized with Na^+. Both hydrogenous and deuterated polymer chains have been synthesized to allow for labeling of the polymer solutions that is required for the neutron scattering experiments. The synthesis and molecular characterization of these systems have been described in detail previously.[23,25] In accordance with the previous studies, the materials are described as i-*x* where *x* is the targeted polymer molecular weight in thousands. The weight-average molecular weights of the materials are i-17 (h: $M_w = 21\,880$; d: $M_w = 16\,120$), i-6 (h: $M_w = 9524$; d: $M_w = 7180$), and i-8 (h: $M_w = 10\,360$; d: $M_w = 9943$), where h and d denote the hydrogenous and deuterated forms of the ionomer, respectively. The polydispersity was less than 1.10, and the functionality of the ionomers was greater than 1.95.

B. SANS Sample Preparation and Data Acquisition. Small-angle neutron scattering experiments have been performed at the Cold Neutron Research Facility (CNRF) at the National Institute of Standards and Technology (NIST) in Gaithersburg, MD, using the 30 m SANS instrument of the ILL type. The solutions were held in a seven-position multisample holder, and their temperature was controlled electronically to ±0.1 °C. The solutions were kept at the desired temperature for a minimum of 2 h to ensure thermal equilibrium. Data were acquired in time slices of 10 min with an average of 7×10^5 counts accumulated for good statistics. The scattering from the solution at a specific temperature was corrected for the scattering from the empty cell, background (^{6}Li blocked beam), solvent, and detector response measured at the same temperature. The transmission of the solutions, cell, and solvent were also measured at each temperature. The corrected scattering data were radially averaged and placed on absolute scale by comparing with the scattering of appropriate scattering standards to allow representation in the form of absolute cross section, $(d\Sigma/d\Omega)_{abs}$, versus scattering momentum vector, *q*, according to procedures developed at NIST.

1. Total Scattering. For the total scattering measurements two system configurations were used to allow for a broad *q* range to be explored due to the wide range of multimer sizes expected in these solutions. In the first configuration the sample-to-detector distance was set at 13 m and neutron wavelength 8 Å which allowed access to the *q* range 0.0035–0.0271 $Å^{-1}$. The scattering data were placed on an absolute scale by comparison with the scattering from both a C1 polystyrene standard of thickness 0.153 cm that has zero cross section $(d\Sigma/d\Omega)\,(0) = 594$ cm^{-1} ± 5% and a silica gel standard of thickness 0.1 cm and $(d\Sigma/d\Omega)\,(0) = 32$ cm^{-1} ± 1%. In the second system configuration, the sample-to-detector distance was set at 9 m, with detector center offset −22 cm and neutron wavelength 6 Å, which provided access to the *q* range 0.0067–0.0722 $Å^{-1}$. The silica gel standard was used for absolute scaling of the data in this configuration. For all temperatures studied the solutions were measured in quartz cells of 5 mm path length, which provided transmissions between 0.5 and 0.7.

The total scattering function of the telechelic ionomer solutions was probed in solutions of totally hydrogenous ionomers in deuterated toluene. The coherent cross section, $(d\Sigma/d\Omega)_{coh}$, in this case is[26]

$$\left(\frac{d\Sigma}{d\Omega}\right)_{coh} = (b_1^* - b_0^*)^2 S_{11}(q) = K_1^{*2} S_{11}(q) \qquad (1)$$

where b_1^* and b_0^* are the total coherent scattering length densities of the monomer and solvent molecules, respectively, $K_1^* \equiv (b_1^* - b_0^*)$ is the contrast factor of the experiment, and $S_{11}(q)$ is the polymer–polymer scattering function that is related to the total scattering function, $S_t(q)$, which contains the contributions of both intrachain, $S_S(q)$, and interchain scattering, $S_P(q)$, functions as

$$S_{11}(q) \equiv N_1 {Z_1}^2 S_t(q) = N_1 {Z_1}^2 (S_S(q) + S_P(q)) \qquad (2)$$

where N_1 is the number density of the polymer chains and Z_1 is the degree of polymerization.

2. Single Chain Scattering. For the single chain scattering measurements the system configuration was set to a sample-to-detector distance of 3 m, detector center offset of −15 cm, and neutron wavelength 6 Å, which provided access to the *q* range 0.0153–0.1909 $Å^{-1}$. The solutions were placed in quartz cells of 2 mm thickness, which provided transmissions in the range 0.5–0.7. The absolute scaling of the scattering data was made through comparison with the scattering from a water standard of thickness 0.1 cm and average scattering cross section at 6 Å, $(d\Sigma/d\Omega)(q) = 0.816$ cm^{-1} and from a 1 mm thickness silica gel standard. The scattering of water, which is mainly isotropic, was obtained from measurements performed at NIST 2 days prior to our experiments.

The single chain scattering function of the telechelic ionomer solutions was measured directly by preparing contrast matched ionomer solutions. This was achieved by selecting the fraction of labeled solvent molecules so that the average coherent scattering length of the solvent, b_s, matches that of the polymer, b_p:

$$b_p = x b_D + (1 - x) b_H \equiv b_s = x_s b_{sD} + (1 - x_s) b_{sH} \qquad (3)$$

where *x* and x_s are the mole fractions of the labeled polymer chains and solvent molecules, respectively, and b_D (b_H) and b_{sD} (b_{sH}) are the coherent scattering lengths of the deuterated (hydrogenous) polymer repeat units or solvent molecules, respectively. The mole ratio of labeled polymer chains was chosen to be 0.50, which corresponds to a mole ratio of the labeled solvent molecules required to satisfy eq 3 of 0.655.[23] The coherent scattering cross section from contrast-matched polymer solutions is described as[26-28]

$$\left(\frac{d\Sigma}{d\Omega}\right)_{coh} = \frac{M_{1,w} c N_A}{{m_0}^2} [x(1 - x)(b_H - b_D)^2 S_S(q)] = K S_S(q) \qquad (4)$$

where $M_{1,w}$ is the weight-average molecular weight of the polymer chains, *c* is the polymer concentration, N_A is Avogadro's constant, and m_0 is the polymer repeat unit molecular weight. In this case, the experiment directly yields the single chain scattering without having to take into consideration the intermolecular interactions.

C. Modeling SANS Results. 1. Total Scattering. In the first paper of this series,[23] the deGennes model was applied to SANS total scattering data of the ionomer solutions in the whole *q* range, leading to information on the influence of ionic interactions on the Flory–Huggins interaction parameter, χ, as well as the ionomer single chain conformation. Following this methodology, the deGennes model is applied here to obtain information on the effect of temperature on the interactions and chain conformation of the telechelic ionomer solutions. In this model[29]

$$\frac{(b_1^* - b_0^*)^2}{N_A \left(\frac{d\Sigma}{d\Omega}\right)_{coh}} = \frac{K_N}{\left(\frac{d\Sigma}{d\Omega}\right)_{coh}} = \frac{1}{Z_1 \phi_1 V_1 S_S(q)} + \frac{1}{\phi_0 V_0} - \frac{2\chi_{PS}}{v_0} \qquad (5)$$

where ϕ_1 and ϕ_0 are the volume fractions of the polymer and solvent, respectively, V_1 and V_0 are the partial molar volumes of the polymer repeat unit and solvent molecules, respectively, v_0 is the lattice cell volume defined as $v_0 \equiv (V_1 V_0)^{1/2}$, and χ_{PS} is the Flory–Huggins polymer–solvent interaction parameter. The fit of the data to the deGennes model was made through the optimization procedures described in detail in ref 23 and considering as model parameters (i) the incoherent scattering, which was considered to be q-independent, (ii) the contrast factor, K^*, and (iii) the polymer chain statistical segment length, b, which enters into the single chain scattering function, $S_S(q)$. $S_S(q)$ was described by either the Debye or wormlike chain model as discussed in the next section. During this analysis the temperature dependence of the partial molar volumes of the polymer and the solvent were accounted for by using reported data from the literature. For polystyrene, it has been shown that the partial specific volume in toluene has a linear dependence with temperature with a temperature coefficient of 2.7×10^{-3}.[30,31] Therefore, the density of polystyrene at a temperature T, ρ_T, was evaluated according to the relation $\rho_T^{-1} = 1/1.087 + 2.7 \times 10^{-3}(T - 25)$ (g/cm^3), where T is in °C. For deuterated toluene, it was assumed that the temperature dependence of the density, ρ_{0T}, is the same as that for hydrogenous toluene[32] and was therefore evaluated as $\rho_{0T} = 0.9385 + 9 \times 10^{-4}(T - 25)$ (g/cm^3), where T is in °C.

Determination of the molecular parameters of the system was obtained by analysis of the data in the low q regime. In the dilute concentration regime and for $qR_g < 1$, where $R_g = \langle R_g^2 \rangle_z^{1/2}$ is the z-average radius of gyration of the scattering particles, the inverse scattering intensity can be described, independent of the structure of the scattering particles, as a linear function of q^2 according to Zimm, as

$$\frac{K_N c}{\rho_1^{\,2}(\mathrm{d}\Sigma/\mathrm{d}\Omega)_{\mathrm{coh}}(q)} = \frac{1}{(M_{\mathrm{w}})_{\mathrm{app}}}\left(1 + \frac{q^2 (R_g)^2_{\mathrm{app}}}{3}\right) \qquad (6)$$

$(M_w)_{app}$ and $(R_g)_{app}$ are the apparent molecular weight and radius of gyration of the multimers, respectively, as their structure is concentration dependent.[23] $(M_w)_{app}$ is related to the true molecular weight of the multimers, M_w, as

$$\frac{1}{(M_{\mathrm{w}})_{\mathrm{app}}(c)} \equiv \frac{K_N c}{\rho_1^{\,2}(\mathrm{d}\Sigma/\mathrm{d}\Omega)_{\mathrm{coh}}(q{=}0)} = \frac{1}{M_{\mathrm{w}}(c)} + 2A_2(c)c + 3A_3(c)c^2 + \ldots \qquad (7)$$

where A_2 and A_3 are the second and third virial coefficients of the polymer solution.

2. Single Chain Scattering. To obtain quantitative information on the single chain dimensions of the ionomer solutions, a statistical model was applied to describe the chain conformation in the whole q-regime probed. Previously, it was shown that the wormlike chain scattering function proposed by Sharp and Bloomfield[33] could fit the single chain scattering data very well.[24] According to this model

$$S_S(q) = \frac{2}{u_N^{\,2}}(\mathrm{e}^{-u_N} - 1 + u_N) + \frac{2}{5q^2L^2}[-11u_N\mathrm{e}^{-u_N} + 4u_N + 7 - 7\mathrm{e}^{-u_N}] \qquad (8)$$

where $u_N = q^2 n_K \alpha^2/6 = q^2 N b_K^2/6$. Here, n_K is the number of Kuhn statistical segments defined as $n_K = L/\alpha$. α is the statistical segment length, and L is the chain contour length that is defined as $L = lN$, where l is the length of a repeat unit, $l = 2.516$ Å,[34] and N is the degree of polymerization. b_K is the segment length based on the degree of polymerization which is defined as $b_K^2 = l\alpha$. The radius of gyration of the wormlike chain is[35]

$$\langle R_g^{\,2}\rangle = \frac{L\alpha}{6} - \frac{\alpha^2}{4} + \frac{\alpha^3}{4L}\left[1 - \frac{\alpha}{2L}(1 - \mathrm{e}^{-2L/\alpha})\right] \qquad (9)$$

The modeling analysis according to eq 4 has been described in detail previously[24] considering three model parameters: the incoherent scattering that is considered constant, the contrast factor K, and the segment length b_K. The data were also fit to the Debye function:[36]

$$S_S(q) = \frac{2}{u_N^{\,2}}(\mathrm{e}^{-u_N} - 1 + u_N) \qquad (10)$$

to take into account the effect of excluded-volume interactions of the polymer backbone of the ionomers in a good solvent. In this case, $u_N = q^2R_g^2$, and R_g can be expressed as[37]

$$\langle R_g^{\,2}\rangle = \frac{N^{2\nu}b^2}{(2\nu + 1)(2\nu + 2)} \qquad (11)$$

ν, the excluded-volume parameter, is 0.5 for Gaussian chains or 0.6 for polymer chains in a good solvent.

D. Light Scattering. Static light scattering experiments as a function of temperature were perfromed on a Malvern 4700C with a 2 W Ar$^+$ laser with Etalon at 488 nm. The solution was placed in a quartz cylindrical cell, and the refractive matching fluid was decahydronaphthalene. The temperature of the sample was kept constant through external circulation of water around the sample holder. Data were collected at scattering angles from 25° to 145° at 5° steps at temperatures of 25, 40, and 50 °C, using toluene as the standard. The apparent molecular weight was calculated similarly to eqs 6 and 7, where here the contrast factor is $K_{LS} = 4\pi^2 n_0^2(\mathrm{d}n/\mathrm{d}c)^2/(\lambda_0^4 N_A)$, where n_0 is the solvent refractive index, $(\mathrm{d}n/\mathrm{d}c)$ is the refractive index increment of the polymer solution, and λ_0 is the laser wavelength. The scattering cross section is the vertical polarized excess Rayleigh ratio ΔR_θ, which is defined as $\Delta R_{\theta,T} = R_{\theta,0,T}[I(\theta,c,T) - I(\theta,0,T)]/I(\theta,0,T)$, where the 0 index refers to the solvent and $I(\theta,c,T)$ is the scattered intensity measured at scattering angle θ, concentration c, and temperature T. The temperature dependence of the solvent $R_{\theta,0,T}$ was evaluated from reported analytical relations.[38,39] It is calculated that $R_{\theta,0}$ is 39.6×10^{-6} cm^{-1} at 25 °C, 40.6×10^{-6} cm^{-1} at 40 °C, and 41.3×10^{-6} cm^{-1} at 50 °C. The temperature dependence of the refractive index increment was calculated from the measured value at 25 °C[40] and by applying the Gladstone−Dale relationship.[41,42] The light scattering data were converted into coherent scattering cross section according to the relation[40] $(\mathrm{d}\Sigma/\mathrm{d}\Omega)(q) = K_N/(\rho_1^2 K_{LS})\Delta R_\theta(q)$.

III. Total Scattering: Data Evaluation and Discussion

The effect of temperature on the scattering patterns of telechelic ionomer solutions is shown in Figures 1, 2, and 3 at polymer concentrations of 1.45 g/dL for i-17 and 2.365 and 7.5 g/dL for the i-6 ionomer. Both SANS and viscometric measurements at 25 °C have shown that at these concentrations the extent of association is significant and shows a sharp increase with increasing concentration.[23,25] Therefore, in this concentration regime the majority of the chains in solution are intermolecularly aggregated, and the multimers consist of a large number of chains. At 25 °C, the scattering patterns of the ionomer solutions show a strong upturn at low angles that is unique to ionomers compared to their nonionic analogues.[23] As temperature increases, the scattering intensity is observed to decrease at all q. This is particularly evidenced in the low q regime, where it is observed that temperature has a strong effect on the characteristic upturn of the ionomer solutions. This marked dependence of the scattering patterns on temperature is evidence that temperature has a significant effect on the structure of the telechelic ionomer solutions.

The fit of the deGennes model to the scattering data based on the wormlike chain model is shown as lines in Figures 1−3. The deGennes model describes the scattering data very well at all temperatures studied. Although both the Debye and the wormlike chain

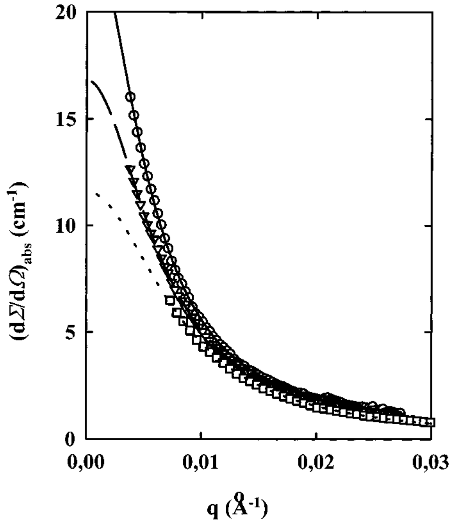

Figure 1. Absolute scattering intensity cross section of hydrogenated ionomer i-17 in deuterated toluene at concentration 1.45 g/dL as a function of temperature: (○) 25 °C, (▽) 40 °C, (□) 60 °C. Lines represent the fitting of the data according to the deGennes model by considering a wormlike single chain model as described in the text.

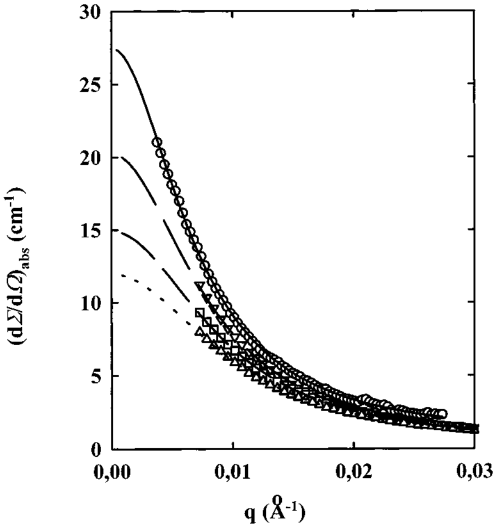

Figure 2. Absolute scattering intensity cross section of hydrogenated ionomer i-6 in deuterated toluene at concentration 2.365 g/dL as a function of temperature: (○) 25 °C, (▽) 40 °C, (□) 60 °C, (△) 80 °C. Lines represent the fitting of the data according to the deGennes model by considering a wormlike single chain model as described in the text. The continuous increase of the scattering upturn should be noted as *q* decreases, as well as the excellent fit of the data to the deGennes model in the whole *q* regime.

models provided similarly good fits to the scattering data from the dilute solutions, the wormlike chain model did not fit well the scattering patterns of the semidilute i-6 7.5 g/dL solution, whereas an excellent fit was achieved for this solution by the Debye function. This discrepancy may be due to the limitations in the range of validity of the wormlike chain function adopted as will be described in the next section. The contrast factor values obtained from the modeling analysis are shown in Table 1. These values are in good agreement with the expected theoretical value of K, 2.894 × 10^{-3} mol/cm.[4]

The Zimm plot of the ionomer solutions is shown in Figure 4 for all temperatures in the lowest *q* range explored in this study. All systems display a linear

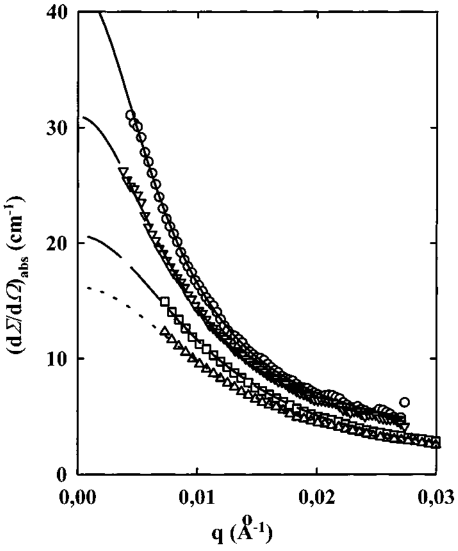

Figure 3. Absolute scattering intensity cross section of hydrogenated ionomer i-6 in deuterated toluene at concentration 7.5 g/dL as a function of temperature: (○) 25 °C, (▽) 40 °C, (□) 60 °C, (△) 80 °C. Lines represent the fitting of the data according to the deGennes model by considering the Debye chain model as described in the text.

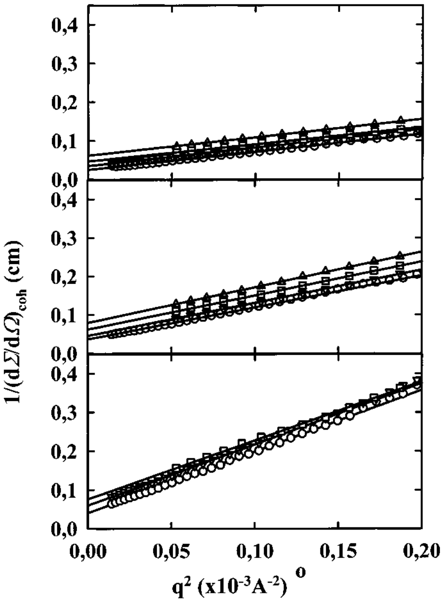

Figure 4. Zimm plot of the inverse coherent scattering intensity versus q^2 of hydrogenated ionomer solutions in deuterated toluene: (a) i-6 at 7.5 g/dL, (b) i-6 at 2.365 g/dL, (c) i-17 at 1.45 g/dL. For each system the effect of temperature on the Zimm plot is shown: (○) 25 °C, (▽) 40 °C, (□) 60 °C, (△) 80 °C. Lines represent linear regression of the data at the lowest *q* regime that was achieved experimentally.

Table 1. Optimized Contrast Factor from the SANS Total Scattering Data Modeling Analysis

	K (10^{-3} mol cm^{-4})		
temp (°C)	i-17, 1.45 g/dL	i-6, 2.37 g/dL	i-6, 7.5 g/dL
25	2.923	2.912	2.894
40	2.848	2.764	2.890
60	2.513	2.583	2.676
80		2.474	2.515

dependence of the inverse scattering intensity with q^2, which enables the application of eq 6. Direct observation of the Zimm plot of each solution reveals that an increase in temperature at constant concentration re-

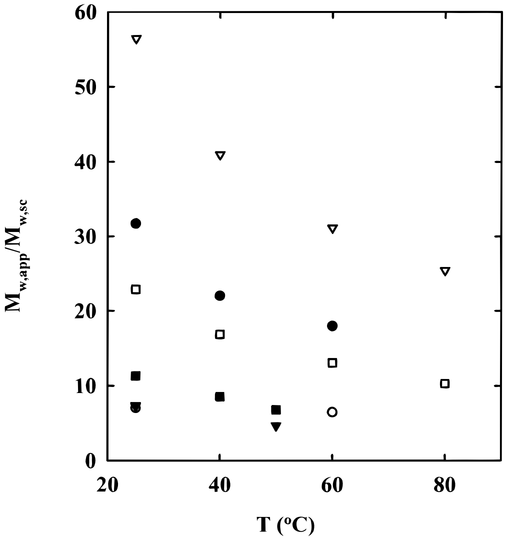

Figure 5. Effect of temperature on the apparent extent of association of the telechelic ionomer solutions: (●) i-17 at 1.45 g/dL, (■) i-17 at 0.48 g/dL, (▼) i-17 at 0.3 g/dL, (○) i-6 at 0.48 g/dL, (▽) i-6 at 2.365 g/dL, (□) i-6 at 7.5 g/dL.

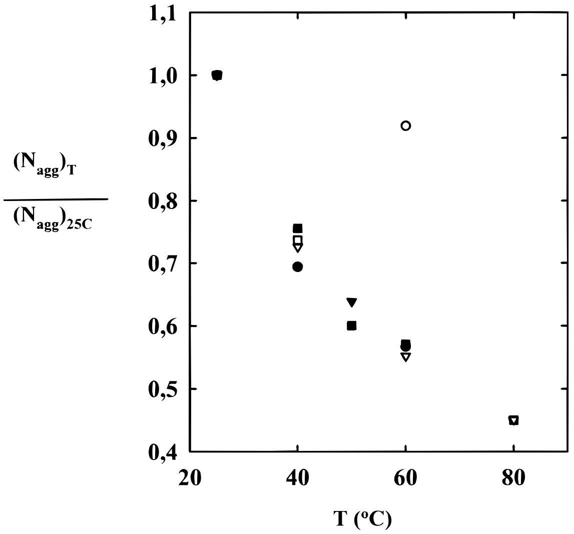

Figure 6. Effect of temperature on the extent of aggregation normalized to 25 °C. Symbols are similar to those in Figure 5.

sults in a change, and in fact a decrease, of both the intercept and the slope of the plot. These trends provide evidence that variation in temperature has a strong influence on both the molecular weight and radius of gyration of the multimers. The effect of temperature on the apparent molecular weight and radius of gyration of the ionomers obtained from this analysis is presented in Figures 5 and 7, respectively. From Figure 5 it can be seen that at a specific concentration the apparent degree of aggregation, N_{agg}, that is defined as the ratio of $(M_{\mathrm{w}})_{\mathrm{app}}$ to the single chain molecular weight, $M_{\mathrm{w,sc}}$, $N_{\mathrm{agg}} = M_{\mathrm{w,app}}/M_{\mathrm{w,sc}}$, decreases with increasing temperature. This decrease is observed to be very significant. For example, for the 2.4 g/dL i-6 ionomer solution that has a degree of aggregation of 58 at 25 °C, the extent of association is reduced 50% by 60 °C. Only for the 0.48 g/dL i-6 ionomer system the SANS data indicate that the extent of association is not affected noticeably over the same temperature range. However, static light scattering experiments undertaken to explore further the influence of temperature on low aggregation systems show that these systems do display a decrease of the degree of aggregation with temperature. Figure 5 includes the light scattering data obtained from two solutions of the i-17 ionomer at 0.3 and 0.48 g/dL concentrations. These results indicate that temperature has an effect even on low association systems.

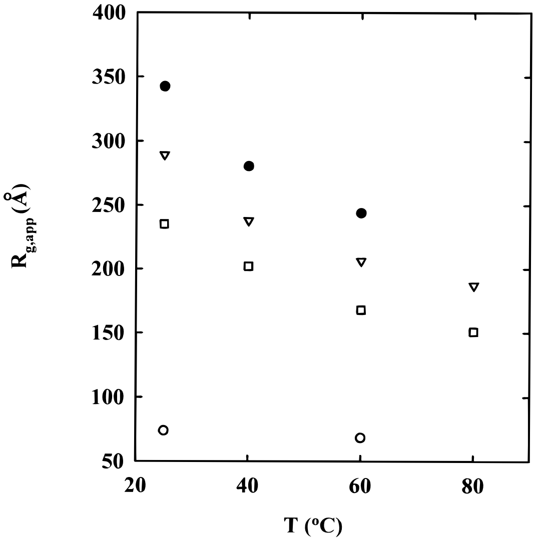

Figure 7. Effect of temperature on the apparent radius of gyration of the associating particles: (●) i-17 at 1.45 g/dL, (○) i-6 at 0.48 g/dL, (▽) i-6 at 2.365 g/dL, (□) i-6 at 7.5 g/dL.

For all ionomer solutions studied it can be observed that as temperature increases the extent of association is decreasing but in such a way that at a specific temperature the degree of aggregation is lower for the lower concentration systems, regardless of their ionic content. To better visualize how temperature influences multimers of different degrees of association or from different ionic content systems, it is more convenient to scale these data in terms of the ratio of the apparent degree of aggregation at temperature *T* to that at the initial temperature (25 °C). This plot allows direct observation of the extent to which multimers are dissociated due to temperature and is shown in Figure 6. Surprisingly, with the exception of the 0.48 g/dL i-6 system, for all systems studied temperature is observed to have the same effect on the level of dissociation independent of the starting system conditions, i.e., concentration and ionic level. This is a very intringuing observation, and certainly not expected a priori, as it indicates that no matter from which multimer one starts, for example a 60-chain versus a 20-chain multimer, providing the same thermal energy these multimers will be reduced by the same percentage of chains. This effect is also independent of the ionic level as both ionomer systems follow the same trend. In the first part of this series it was observed that at 25 °C and for the i-17 and i-6 ionomer systems the extent of association was independent of the ionic level of the ionomers over the concentration regime studied.[23] This has also been verified via light scattering experiments in a more extended concentration regime as is discussed in a forthcoming paper. The results presented in Figure 6 suggest that this observation is true not only at 25 °C but also in a more extended temperature regime (25–80 °C studied). This suggests that considerations of the effect of temperature on telechelic ionomer solutions can be viewed in terms of the apparent degree of association alone without having to take into account the ionomer system per se, in analogy to considerations made on the effect of concentration. On the basis of these observations, it can be concluded that N_{agg} is only a function of temperature and concentration and is described by the following relation:

$$N_{agg}(T,c) = f(T)\ g(c) \tag{12}$$

Equation 12 has a very important implication in determining or controlling the aggregation of an ionomer solution, as it suggests that under any experimental conditions the aggregation number depends on temperature and concentration in an independent way. By adjusting either the concentration or temperature, it is possible to achieve the same extent of association in a telechelic ionomer solution, depending on which factor is more preferential for the material's application.

Figure 7 shows the effect of temperature on the apparent radius of gyration of the multimers. It is observed that the multimer radius shows a significant decrease with increasing temperature. This is observed for all ionomer solutions studied except for the 0.48 g/dL i-6 solution where temperature is seen to have only a slight influence on the size of the multimers. This is analogous to the effect of temperature on the extent of association observed for this system. Unfortunately, the temperature light scattering experiments conducted are not able to provide precise information on the particle size due to the low molecular weight of the ionomers. In the first paper of this series it was shown that at 25 °C the radius of gyration of the multimers was larger for the ionomer with the largest polymer backbone molecular weight. This explained the earlier gelation observed with increased telechelic ionomer molecular weight.[23,25] As can be observed from Figure 7, the multimers formed by the higher molecular weight system have a larger size at all temperatures studied. It would therefore be expected that a higher molecular weight ionomer can achieve the same gelation concentration as a lower molecular weight system if the solution temperature is raised.

The analysis of the molecular parameters presented above is valid in the dilute solution regime. The solution of the i-6 ionomer at 7.5 g/dL is in the semidilute regime. In this regime the scattering particles are no longer distinct entities but for low q, the inverse of the scattering intensity is still linear with q^2 and is described as[43,44]

$$\frac{1}{(\mathrm{d}\Sigma/\mathrm{d}\Omega)(q)} = \frac{1}{(\mathrm{d}\Sigma/\mathrm{d}\Omega)(q=0)}\left(1 + \frac{q^2L^2}{3}\right) \tag{13}$$

where L is a characteristic length of the particles. Therefore, the slope of the plot in Figure 4 for i-6 at 7.5 g/dL provides information on L rather than $R_{g,app}$, while the intercept of the plot provides information on $(\mathrm{d}\Sigma/\mathrm{d}\Omega)(q=0)$ rather than $M_{w,app}$. In nonionic polymer solutions the parameter $L/\sqrt{3}$ is defined as the screening length, ξ, and describes the effect of intermolecular interactions between different chain segments to the screening of the intramolecular correlations. In the dilute solution regime $L = R_g$, while as concentration increases, L contains contributions from both the polymer size and the distance between entanglement points. From Figure 7, it is observed that L is smaller than R_g, an observation which is also valid in nonionic polymer solutions. In addition, L is also dependent on temperature decreasing with increasing temperature, in analogy to the effect of temperature on the multimer radius of gyration.

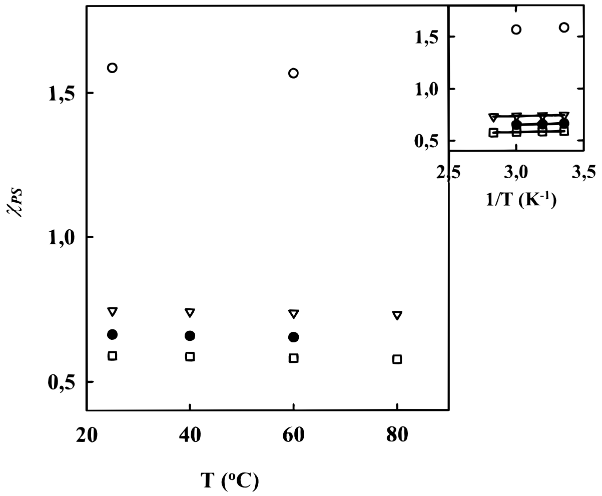

Figure 8. Temperature dependence of the Flory–Huggins interaction parameter of the telechelic ionomer solutions as predicted by the deGennes model. Symbols are the same as in Figure 7. In the inset of this figure χ is replotted as a function of the inverse absolute temperature. The lines in this inset are from linear regression of the data.

Independent of concentration, $(\mathrm{d}\Sigma/\mathrm{d}\Omega)(q=0)$ is a measure of the osmotic compressibility, $(\partial\pi/\partial c)_{T,\mu_0}$, at constant temperature and chemical potential:

$$\left(\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}\right)(q=0) = \frac{K_\pi RT}{(\partial\pi/\partial c)_{T,\mu_0}} \tag{14}$$

where $K_\pi = (b_1^* - b_0^*)^2 cN_A/\rho_1^2$, R is the ideal gas constant, and T is the absolute temperature. From Figures 1–3, it is observed that $(\mathrm{d}\Sigma/\mathrm{d}\Omega)(q=0)$ increases with increasing concentration at concentrations studied and decreases with increasing temperature. However, as shown in Figure 5, $(\mathrm{d}\Sigma/\mathrm{d}\Omega)(q=0)/c$ increases with increasing concentration in the dilute regime and shows a sharp decrease as the semidilute regime is crossed. These results indicate that the osmotic compressibility of the ionomer solutions passes through a minimum near the overlap concentration and that it increases with increasing temperature. For dilute solutions $(\partial\pi/\partial c)_{T,\mu_0}$ can be expanded in power series with concentration (eq 7). For semidilute solutions $(\partial\pi/\partial c)_{T,\mu_0}$ is a function of c/c^*,[45] where c^* is the overlap concentration. Several theories have been proposed to describe $(\partial\pi/\partial c)_{T,\mu_0}$ in the semidilute and concentrated regimes.[43,45] In our modeling analysis $(\partial\pi/\partial c)_{T,\mu_0}$ is taken into account via the Flory–Huggins interaction parameter, as is described in eq 5.

The influence of temperature on the Flory–Huggins interaction parameter as depicted from the modeling analysis is shown in Figure 8. As can be observed from this figure, the interaction parameter of the ionomer solutions shows only a slight dependence on temperature for all systems studied, and at all cases χ_{PS} is a decreasing function of temperature. In the inset of this figure χ_{PS} is plotted versus the inverse of the absolute temperature, as polymer solutions and blends usually show that χ varies linearly with T^{-1}. In fact, in the temperature regime studied χ_{PS} of the ionomer solutions also shows linear behavior with $1/T$. It is of interest to note here that for the telechelic ionomer solutions χ has shown an unusual strong dependence on concentration and ionic level, which is not observed in nonionic polymer solutions. This behavior has been observed by both SANS[23] and light scattering experiments[40] in the concentration range from 0.1 to 2.4 g/dL. From Figure 8 two additional characteristics of the ionomer solution χ parameter can be observed. First, the dependence of χ_{PS} on concentration and ionic level is preserved at all temperatures studied. Second, χ_{PS} shows a continuous decrease with increasing concentration even in the semidilute concentration regime. As defined by eq 5, χ_{PS} contains all the interactions in solution including the ionic interactions, which explains the large values observed for this parameter.[23] χ_{PS} is related to the interaction parameter χ' which describes only the intramolecular interactions within the aggregates and is therefore the common thermodynamic parameter related to the virial coefficient in nonionic polymer solutions as

$$\chi_{PS} = \chi' + \frac{v_0 M_0}{2V_1\phi_1}\left(\frac{1}{M_{w,sc}} - \frac{1}{M_w}\right) \qquad (15)$$

where $M_{w,sc}$ is the single chain molecular weight and M_w is the true molecular weight of the associating particles. For the semidilute system studied here M_w is so large that the second term in eq 15 is negligible with respect to the first. It can be calculated that for i-6 at 7.5 g/dL χ' reaches the value of 0.508. This result validates our previous analysis that had shown that, with increasing concentration, χ' increases toward its critical value 0.5, which is the value assumed by a θ-state solution.

The results obtained from this study indicate that temperature has a significant effect on the association behavior of telechelic ionomer solutions. This observation is quite different than the one exhibited by random copolymer ionomer solutions for which temperature had no significant effect on their association structure.[17,20] This comparison is even more interesting as the random copolymer ionomer solutions studied were also neutralized with the same cation type (Na^+) and were based on the same polymer backbone (polystyrene) as that of the telechelic ionomers studied here. Furthermore, the ionic contents are similar in both systems as random copolymer ionomers studied had ionic contents 0.95 and 1.39 mol % while for the telechelic ionomers presented here the ionic content is 1.1 mol % for i-17 and 3.7 mol % for i-6. It was argued that the reason for the negligible effect of temperature on the random copolymer ionomer solutions was due to the mainly entropic character of these solutions. The results of this study indicate that with increasing temperature the aggregates formed in telechelic ionomer solutions dissociate with the formation of smaller size multimers. The differences observed in the temperature dependence of the structure of telechelic versus random copolymer ionomer solutions indicate that the aggregation mechanism is different between these two systems.

In our previous study,[20] it was observed that the telechelic ionomer solutions show characteristics of a supramolecular structure, as they could be described as fractals of dimension D. D is defined as $M_w \propto R_g^D$ and can be evaluated from the scattering intensity in the intermediate q regime, $qR_g > 1$:[46]

$$\left(\frac{d\Sigma}{d\Omega}\right)_{coh}(q) \propto q^{-D} \qquad (16)$$

At 25 °C D was found to be close to 1.76, which is an indication that the associating particles in solution exist in an extended rather than a condensed configuration and are of high polydispersity. Furthermore, this value is similar to the one expected for diffusion-limited aggregation (1.8) that is characterized by rapid aggregation and the formation of large clusters in solution.[47] Figure 9 shows double-logarithmic plots of the coherent scattering intensity versus q for three different ionomer solutions. It is striking at first sight from this figure that for the same ionomer solution there is an excellent overlap of the scattering curves at different temperatures. Changes in temperature result in change of only the low q regime, where the scattered intensity more readily reaches a plateau value. Second, it is seen that the behavior of these plots is very similar for all systems examined even for the semidilute solution. Analysis of the intermediate q regime shows that D assumes the value of 1.77 for i-17 at 1.45 g/dL and for i-6 at 7.5 g/dL and the value of 1.87 for the low concentration i-6 solution, and this value remains the same for all temperatures studied. These results indicate that temperature does not have any influence on the architecture of the associating particles, which are observed to retain an extended configuration without collapsing into more compact structures as the temperature is raised.

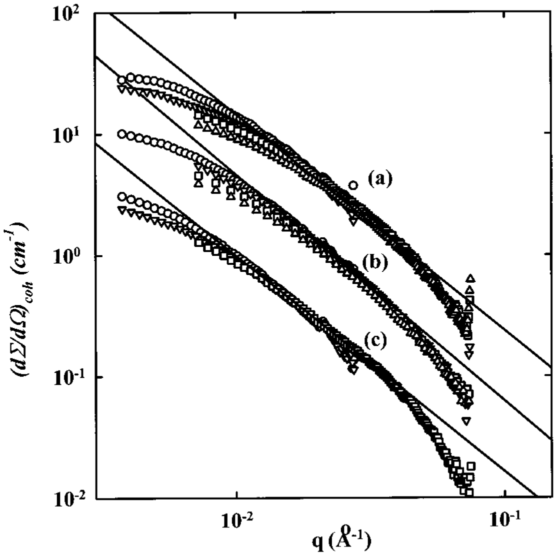

Figure 9. Double-logarithmic plots of the inverse coherent scattering intensity versus q of hydrogenated ionomer solutions in deuterated toluene: (a) i-6 at 7.5 g/dL, (b) i-6 at 2.365 g/dL, (c) i-17 at 1.45 g/dL. The curves of the systems (b) and (c) have been displaced by a factor of 2 and 5, respectively, to allow for better representation of each system. For each system the effect of temperature is shown: (○) 25 °C, (▽) 40 °C, (□) 60 °C, (△) 80 °C. Lines represent linear regression of the data at the intermediate q regime where the scattering intensity scales with q by the fractal dimension of the associating particles.

IV. Single Chain Scattering: Data Evaluation and Discussion

The effects of temperature on the scattering patterns of contrast matched ionomer solutions are shown in Figures 10 and 11 for solutions of the i-17 and i-8 ionomers, respectively, at 25 and 60 °C. From these figures it is observed that temperature has only a slight effect on the single chain scattering patterns. In all cases an increase in temperature results in a slight only decrease of the scattered intensity. This behavior is very different from the influence of temperature displayed on the multimers scattering patterns where temperature was observed to have a significant impact.

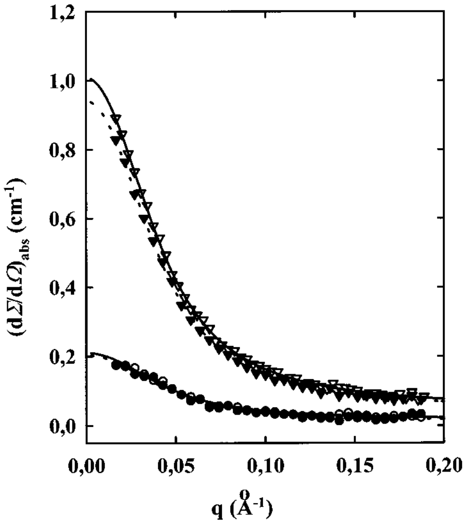

Figure 10. Absolute scattering intensity of contrast matched solutions of the i-17 ionomer system as a function of concentration and temperature: (i) 7.5 g/dL at (▽) 25 °C and (▼) 60 °C; (ii) 1.45 g/dL at (○) 25 °C and (●) 60 °C. Lines represent the fitting of the data to the Sharp–Bloomfield wormlike chain model as described in the text.

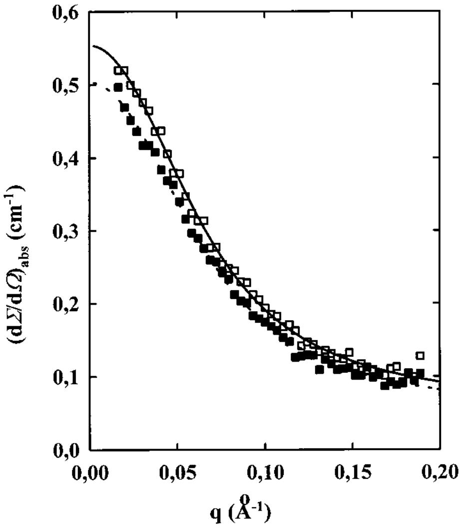

Figure 11. Absolute scattering intensity of contrast matched solutions of the i-8 ionomer system at a concentration 7.5 g/dL as a function of temperature: (□) 25 °C and (■) 60 °C. Lines represent the fitting of the data to the Sharp–Bloomfield wormlike chain model as described in the text.

The modeling of the SANS single chain scattering data according to the wormlike chain model is shown as lines in Figures 10 and 11. It can be seen that the data are fit very well to the single chain scattering function at all concentrations and temperatures studied. Modeling the data with the Debye function also provided a very good fit. The excellent description of the data according to a model that describes single chain statistics provides evidence that the contrast matching technique has succeeded in probing the characteristics of the single chains only in solution without interference from intermolecular interactions.

Equation 17 and Figure 12 show a Berry plot[48] of the scattering data in the low q regime:

$$\frac{K'c}{(\mathrm{d}\Sigma/\mathrm{d}\Omega)_{\mathrm{coh}}^{1/2}} = \frac{1}{M_{\mathrm{w}}^{1/2}}\left(1 + \frac{q^2 R_{\mathrm{g}}^{2}}{6}\right) \qquad (17)$$

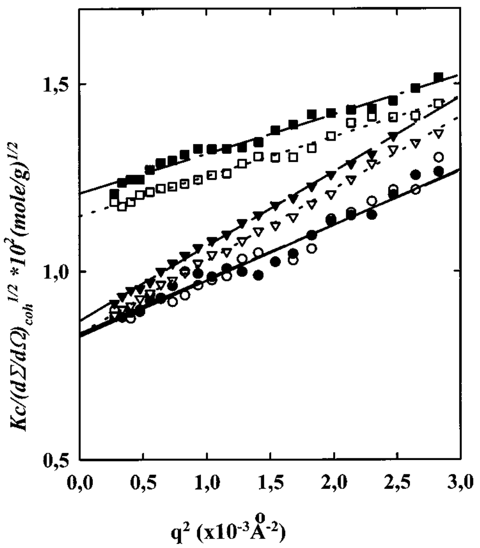

Figure 12. Berry plot of the contrast matched ionomer solutions in toluene: (i) i-8 at 7.5 g/dL at (□) 25 °C and (■) 60 °C; (ii) i-17 at 7.5 g/dL at (▽) 25 °C and (▼) 60 °C; (iii) i-17 at 1.45 g/dL at (○) 25 °C and (●) 60 °C. Lines represent linear regression of the data in the low q regime.

Table 2. Optimized Values of the Modeling Parameters of the SANS Single Chain Scattering Data Analysis

material	T (°C)	$K \pm s$ (cm^{-1})	$b \pm s$ (Å)
i-17, 1.45 g/dL	25	$0.1965 \pm 5.3 \times 10^{-5}$	6.743 ± 0.033
	60	$0.1440 \pm 4.5 \times 10^{-5}$	6.696 ± 0.028
i-17, 7.5 g/dL	25	$0.9751 \pm 1.3 \times 10^{-5}$	7.269 ± 0.002
	60	$0.9122 \pm 1.3 \times 10^{-5}$	7.398 ± 0.002
i-8, 7.5 g/dL	25	$0.5100 \pm 1.1 \times 10^{-5}$	6.365 ± 0.004
	60	$0.4660 \pm 1.2 \times 10^{-5}$	6.373 ± 0.006

Table 3. Comparison of the Evaluation of the Single Chain Radius of Gyration from Three Different Modeling Analyses: the Wormlike Chain Model, the Debye Model, and the Berry Plot

				Berry plot	
material	T (°C)	wormlike chain R_g (Å)	Debye model, R_g (Å)	M_w	R_g (Å)
i-17, 1.45 g/dL	25	35.7 ± 0.2	36.3 ± 0.1	14 635	32.83
	60	35.5 ± 0.1	36.1 ± 0.1	14 632	32.28
i-17, 7.5 g/dL	25	38.3 ± 0.0	39.1 ± 0.0	14 374	37.27
	60	39.0 ± 0.0	39.8 ± 0.0	13 267	37.11
i-8, 7.5 g/dL	25	23.9 ± 0.0	24.5 ± 0.0	7 587	23.53
	60	24.0 ± 0.0	24.5 ± 0.0	6 847	22.84

from which the molecular weight and radius of gyration of the scattering particles can be obtained. As can be seen from Figure 12, the intercept for all solutions studied of the same ionomer system is similar within experimental error, which is evidence that the experiment probes particles of similar molecular weight. The molecular weights evaluated from this plot are given in Table 3. As can be seen, these values agree well with the molecular weight of the ionomer systems determined from light scattering experiments,[24] indicating that the scattering particles probed by this experiment are indeed the single ionomer chains. The radii of gyration of the single chains evaluated from the Berry plot are also included in Table 3 and are compared to the ones obtained from the model analysis using the whole q regime, as discussed below.

The optimized values of the model parameters, K and b_K, as well as their variances as determined from the modeling analysis, are presented in Table 2. As can be observed, the optimization follows very well the theo-

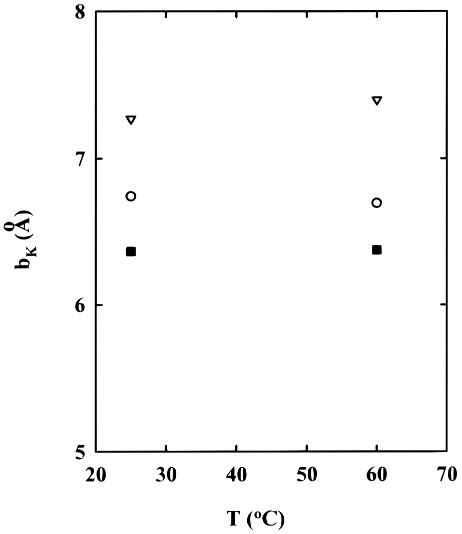

Figure 13. Effect of temperature on the segment length of contrast matched ionomer solutions: (■) i-8 at 7.5 g/dL, (○) i-17 at 1.45 g/dL, (▽) i-17 at 7.5 g/dL.

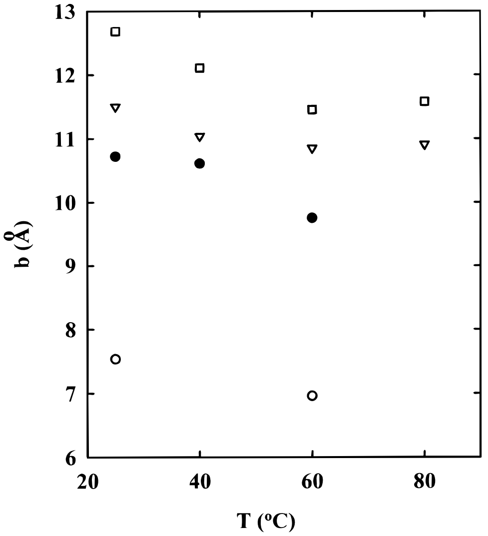

Figure 14. Effect of temperature on the segment length of the single chains of ionomer solutions as predicted by modeling of the total scattering intensity data according to the deGennes model using wormlike chain statistics: (●) i-17 at 1.45 g/dL, (○) i-6 at 0.48 g/dL, (▽) i-6 at 2.365 g/dL, (□) i-6 at 7.5 g/dL.

retically expected behavior of the contrast factor, K, with concentration and molecular weight as defined by eq 4. The variance of all model parameters is very small, indicating that the error bars in the optimized value of b_K are negligible. The results of the modeling analysis of the contrast matched telechelic ionomer solutions according to the wormlike chain model are shown in Figure 13. The results of this figure indicate that temperature has almost no influence on the single chain dimensions for the systems studied independent of the concentration regime and ionic content. The temperature dependence of the single chain ionomer dimensions is in contrast to their concentration dependence as was reported in the second part of this series.[24] In that study it was observed that at 25 °C the single ionomer chains are affected by concentration being in a somewhat collapsed state at low concentrations, extending as concentration increases, until they reach a plateau value at the onset of the semidilute concentration regime. The effect of concentration on the single chain dimensions is also seen in Figure 13, which shows that at the same temperature there is an increase in the statistical segment length with increasing concentration and polymer backbone molecular weight. The difference observed in the segment length with concentration and ionic level is noticeably larger than the difference caused by temperature. The results of the modeling analysis using the wormlike and the Debye scattering functions are shown in Table 3. These analyses show that both models provide similar values for the radius of gyration of the single chains, as previously observed.[24] Furthermore, these values are in agreement with those obtained from the Berry plot, which is independent of the statistics that govern the single chain conformation.

The influence of concentration on the telechelic ionomer single chain dimensions was shown in the second paper of this series to be described well by the deGennes model based on total scattering data.[24] The results of the modeling analysis of the temperature total scattering data based on the deGennes model with respect to b are presented in Figure 14. These results indicate that the deGennes model analysis yields a decrease of the single chain dimensions with increasing temperature. This decrease is however small, and at each temperature the concentration dependence of the segment length is kept intact.

Combination of the results of the effect of temperature on the multimers and single chains indicates that the dissociation process that is observed to take place in telechelic ionomer solutions does not alter the single chain dimensions. Alternatively, it could be argued that the single chains do not change their conformation as they move into different multimer structures. From considerations of excluded-volume interactions of the polymer backbone in a good solvent, such as the one used in this study, it would be expected that the ionomer chains show expansion with increasing temperature due to chain swelling. We saw previously that due to ionic interactions the single chain dimensions of the ionomer solutions are lower than those of the corresponding nonionic polymer, indicating poor solvent conditions.[24] However, even in that case an increase of the single chain dimensions would be expected with increasing temperature for nonionic polymer solutions. SANS single chain studies of polystyrene in a θ-solvent in the semidilute concentration regime have shown that the radius of gyration of the single chains remains almost constant with increasing temperature for a narrow temperature regime but that it increases with further increase in temperature following a theoretically predicted scaling law of $(^1/_8)$ with the reduced temperature.[49] An increase of the radius of gyration with temperature has also been observed in the concentrated solution regime.[50] On the other hand, the dissociation process that takes place in these solutions with increasing temperature should cause the chains to collapse in analogy with the effect of the extent of aggregation on the single chain dimensions.[24] Thus, the tendency of the single ionomer chains to satisfy these two criteria could be responsible for the result that the single ionomer chains remain unaffected by an increase in temperature.

It is of interest to note that despite the differences observed on the effect of temperature on the aggregates between the telechelic ionomer solutions studied here and reported data for random copolymer ionomer solutions, the impact of temperature on the single ionomer chains is very similar between the two systems. Both

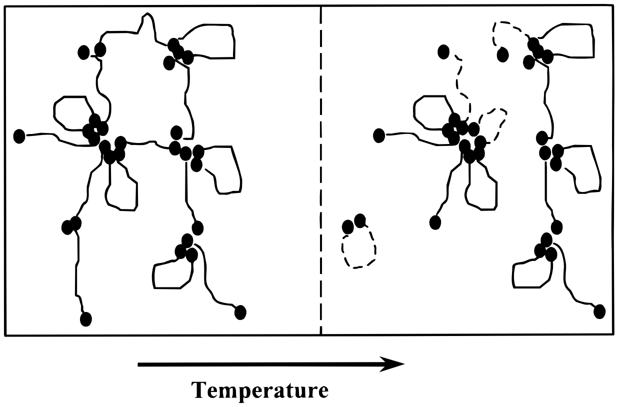

Figure 15. Schematic representation of the effect of temperature on the association structure of telechelic ionomer solutions. The arrow is directed toward increasing temperature. The ionomer chains are indicated as solid lines and the ionic groups as filled circles. Broken lines are used to indicate the ionomer chains inside a multimer where the thermal energy could weaken the ionic interactions, thus leading to multimer dissociation.

of these systems show that temperature has a negligible effect on the single chain dimensions. These results indicate that independent of whether multimer dissociation occurs or not with increasing temperature, the multiplets formed by the ionic pair aggregation are so strong that they do not allow any freedom in the chains connected to these multiplets to change their conformation, as this could disrupt the multiplet. It is energetically more probable that dissociation of the multimers with increasing temperature occurs via bridging chains that connect different multiplets or via chains that belong to the smallest multiplets rather than chains which have both ends connected to the same multiplet. The number of such chains that move into a different aggregation structure is expected to be significantly smaller than the number of chains remaining in the same configuration. Therefore, as SANS detects only the average chain conformation, a very slight or no change would be observed in this case. In the second paper of this series we proposed a schematic representation of the single chain conformation in associating telechelic ionomer solutions as a function of concentration and ionic content. The arguments displayed above based on this picture are schematically shown in Figure 15, which represents a molecular picture of the effect of temperature on the telechelic ionomer solution structure.

V. Conclusions

Increasing temperature has a significant impact on the structure of telechelic ionomer solutions, as revealed by a monotonic decrease of the total scattering intensity obtained via the technique of small-angle neutron scattering (SANS). For all ionic systems studied and for solutions with different extents of association, increasing temperature resulted in a monotonic decrease of both the apparent extent of association and the size of the associating particles. These results show that with increasing temperature dissociation occurs that results in multimers of a smaller number of chains and smaller size. Interestingly, the extent of association was observed to decrease by the same magnitude with respect to its value at 25 °C independent of the ionic system and concentration. It is therefore concluded that in telechelic ionomer solutions the apparent degree of aggregation is described as an independent function of temperature and concentration, according to the relationship $N_{\mathrm{agg}}(T,c) = f(T)\,g(c)$. This result indicates that the extent of association in these solutions can be controlled by either concentration or temperature in a similar way. It is observed that a reduction of the aggregation extent of 50% is achieved by 50 °C. This dramatic influence of temperature is unique to the telechelic ionomer solutions studied here as studies on random copolymer ionomer solutions have reported no significant effect of temperature on the ionomer solution structure.

Although dissociation takes place with increasing temperature, the supramolecular structure of the ionomer solutions was observed to remain unchanged with temperature. The fractal dimension of the ionomer solutions remains the same, indicating that the extended configuration proposed to describe the supramolecular structure of ionomers at 25 °C persists at higher temperatures. This is an indication that a significant extent of bridging between ionomer aggregates remains even though the associating particles undergo dissociation. The deGennes model was observed to fit the data very well at all temperatures studied, in analogy to the previous studies of the effect of concentration.[23,24] The Flory−Huggins ionomer solution interaction parameter is affected only slightly by temperature, decreasing with increasing temperature. In the semidilute solution regime the thermodynamic interaction parameter was observed to reach the critical value expected for a θ-state solution.

The contrast matching technique was successful in probing the single chain dimensions of the ionomer solutions as a function of temperature, in a way independent of the total scattering measurements. Both the wormlike chain model and the Debye functions fit the data very well, resulting in similar values for the single chain dimensions. Although dissociation was observed to take place in the ionomer solutions, the single chain dimensions were observed to not be influenced by temperature. It is proposed that the constancy of the radius of gyration with temperature is the result of two opposite tendencies: the tendency of the polymer backbone to swell upon increasing temperature and the tendency of the single chains to contract due to decrease in the extent of association and the preference of intramolecular interactions. The effect of temperature on the single chain dimensions is similar for telechelic and random copolymer ionomer solutions. On the basis of arguments of the energetics of the association phenomenon, a molecular picture is proposed for the effect of temperature on the structure of the telechelic ionomer solutions.

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