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to the density effects seen by Crabb et al.[7] The FCC and BCC models both have only one-bead elementary motions and therefore show the same scaling behavior as a function of the attractive potential.

The behavior of the chain dynamics in the Θ and collapse regions seem to be nicely explained by the formation of gel modes predicted by Brochard and de Gennes. At very large attractive values of the potential and corresponding high coil densities the differences in the values of the relaxation times of the three modes are becoming significantly smaller. The scaling exponent, γ_N, showed a nearly linear correlation with the coil density, ρ, independent of chain length and the value of the potential. This has not been previously observed. In future work, the lifetime of pair contacts will be measured to further investigate the existence of gel modes.

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Effect of Ionic Aggregation on Ionomer Chain Dimensions. 2. Sulfonated Polyurethanes

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I. Introduction

The effect of ionic aggregation on ionomer chain dimensions is an area into which much theoretical effort has flowed, but experimental work has been quite limited. In a parallel small-angle neutron scattering (SANS) study of carboxy-telechelic polystyrene ionomers, we found no change in the average chain dimension as a result of ionic aggregation.[1] This finding agrees with the theory of Squires et al.[2] but disagrees with the theories of Forsman[3] and Dreyfus,[4] both of which predict substantial chain expansion. Here, we examine a sulfonated polyurethane ionomer with labeled soft segments [poly(tetramethylene oxide) (PTMO)]. The polyurethane ionomer differs in three important ways from the telechelics. First, instead of bearing only one ionic group at each chain end, the polyurethane ionomer contains many pendant groups spaced along the chain, separated by the soft-segment units. Second, the ionic groups here are sulfonates rather than carboxylates; the former are known to be more strongly interacting.[5] Third, and perhaps most important, the ion content of the polyurethane ionomers is much greater than that of the telechelics: their equivalent weight is about 775 g/equiv vs 3500 g/equiv for the telechelics. Since the relative chain expansion is predicted to increase with ion content, some chain expansion may be discernible here, though it was not with the telechelics.

As a reference for the unperturbed dimensions of the soft segment, blends of the PTMO oligomers were used. Since these materials have low degrees of polymerization N and do not have a particularly narrow molecular weight distribution (MWD), a polydisperse wormlike chain model described earlier[1] was used to fit the data. The polydispersity introduces the possibility that the chains may not have their unperturbed conformations, even in bulk, due to swelling of the longer chains by the shorter ones, as has been noted previously for poly(dimethylsiloxane) in a solution of its oligomer.[6]

II. Experimental Section

The deuterous PTMO was synthesized as described previously[7] from fully deuterous monomer (99.5+ atom % D, Aldrich). The hydrogenous PTMO was a commercial sample (N_n = 14.03 by end-group titration). The MWD of the deuterous oligomer was determined by a high-performance liquid chromatographic (HPLC) method[7] and is shown in Figure 1 up to N = 51. For calculating moments of N and for the polydisperse wormlike chain model describing the coherent SANS, the MWD was extrapolated through N = 150 by fitting the data over the range N = 12–51 to a straight line in log(mole fraction) vs N. Moments of N and R_g^2, calculated with a (the Kuhn, or statistical segment, length) equal to both 18.8 and 24.1 Å, are listed in Table I. The choice of a values comes from the SANS results as described below. Blends of the two oligomers, with deuterous volume fractions v_D near 0.2 and 0.5, were prepared by blending the two oligomers in methanol (10 wt %) and stirring for 7 h. The methanol was then evaporated in an air oven at 80 °C for 5 h and finally in a vacuum oven at 40 °C for 9 h. The melting point of the oligomers is very close to room temperature, so to prevent any crystallization (which could also lead to

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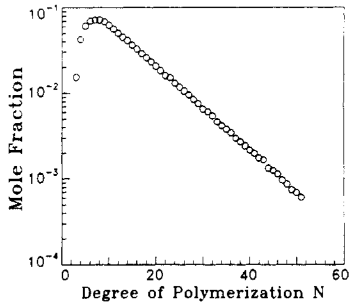

Figure 1. Molecular weight distribution for the deuterous PTMO oligomer obtained by HPLC.

Table I
Characteristics of Deuterous PTMO Oligomer

averaging moment	N	$(R_g^2)^{1/2}$, Å a = 18.8 Å	$(R_g^2)^{1/2}$, Å a = 24.1 Å
number	13.90	14.0	15.3
weight	19.90	18.3	20.4
z	27.45	22.3	25.1

isotopic segregation), the blends were kept at 40 °C until the time of measurement. The samples will be referred to as PT*xx*, where *xx* is the approximate deuterous volume percent.

The synthesis of polyurethane ionomers based on 1:1 alternating copolymers of PTMO and methylenebis(*p*-phenyl isocyanate) (MDI) has been described previously.[8] Approximately 6% excess MDI was used. Sulfonate groups are introduced by replacing the urethane hydrogens with sodium propanesulfonate branches. Ionomers were synthesized with all-hydrogenous soft segments (PUI00) and with an equimolar mixture of fully hydrogenous and fully deuterous soft segments (PUI50). Polymers synthesized by the same method[8] have been shown to have polystyrene-equivalent molecular weights in excess of 20 000. The ionization level was determined by elemental analysis for sulfur (Galbraith Laboratories) and found to be 95 and 101% for PUI00 and PUI50, respectively, indicating essentially complete replacement of the urethane hydrogens by sodium propanesulfonate groups. The same hydrogenous oligomer was used for both the PT*xx* and PUI*xx* samples, but the deuterous oligomer came from two different batches. However, the MWDs of the batch used for the oligomer blends (Figure 1) and for the ionomer[9] are virtually identical. The ionomers were compression molded into 2.54-cm-diameter disks at 120 °C and 95 MPa and allowed to cool in the mold to 40 °C during 1 h. Thicknesses were 1.29 and 2.10 mm for PUI00 and PUI50, chosen to given neutron transmittances of ca. 50%.

The methods used to acquire and reduce the SANS data, using the small-angle diffractometer at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory, as well as the small-angle X-ray scattering data, are detailed elsewhere.[1] For SANS, the PT*xx* specimens were held in a 1-mm-path quartz solution cell at ambient temperature. No crystallization occurred during the measurement or even for several days afterward. Scattering and transmittance of the solution cell were accounted for.

III. Results and Discussion

Figure 2 shows SAXS and SANS patterns for the two polyurethane ionomers. The SAXS patterns resemble those reported previously for similar materials:[8] a major peak is visible at a scattering vector magnitude q = 0.12 Å^{-1}, reflecting ionic aggregation ($q = (4\pi/\lambda)\sin\theta$, where 2θ is the scattering angle and λ is the radiation wavelength). Also visible in the SAXS data are a shoulder near 0.28 Å^{-1} and an upturn in scattered intensity near q = 0. The SANS data in Figure 2 also show the same peak and upturn, as expected. The SAXS peak intensities differ between the two samples, a reproducible but puzzling result, given the apparent similarity of the materials in all respects save isotopic composition. This may be due to some absorption of water vapor by the ionic aggregates in PUI00, which would lower the X-ray contrast. Nonetheless, the value of PUI00 data in this study is as a "blank" to subtract the interphase scattering[10] from PUI50, yielding the uncontaminated single-chain scattering. It is thus sufficient that the SAXS peaks in PUI00 and PUI50 be similar in shape only. A fraction of the PUI00 SANS was subtracted from the PUI50 SANS to visually eliminate the peak in a plot of ln I vs ln q. Because the aggregate composition is not known in detail, this fraction cannot be calculated a priori, but was determined visually to be 1.00. Since the aggregates are expected to contain MDI residues, as well as the sodium propanesulfonate groups, it is likely that in PUI00 the coherent scattering length density β for the aggregates exceeds that for the matrix, while for PUI50 the reverse is true. This suggests that labeling using about 25% deuterous soft segment would produce a "contrast-matched" specimen,[10] where no interphase SANS would be evident.

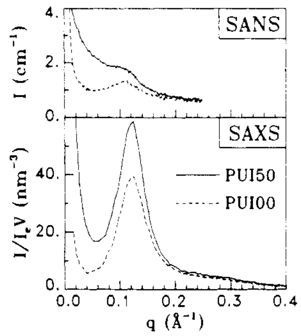

Figure 2. Bottom: desmeared SAXS patterns for samples PUI50 (—) and PUI00 (- - -). Top: SANS data for samples PUI50 (—) and PUI00 (- - -).

The polydisperse wormlike chain model used to describe the coherent SANS intensity is described elsewhere.[1] The parameters of the fit are the Kuhn length a, the coherent intensity scale factor K, and a background intensity multiplier to account for incoherent scattering. K is defined by

$$I(q) = \frac{(\Delta\beta)^2 m_0 v_L}{\rho N_A} S(q) \equiv KS(q) \tag{1}$$

where $\Delta\beta$ is the coherent scattering length density difference between hydrogenous and deuterous PTMO[11] (=6.82 × 10^{10} cm^{-2}), m_0 is the monomer molecular weight (72.11 g/mol), ρ is the amorphous PTMO mass density (0.98 g/cm^3), and N_A is Avogadro's number. v_L is the volume fraction of the chain that can be labeled; for the PTMO oligomers, v_L = 1, giving K = 0.568 cm^{-1}. Here, K was treated as a fitting parameter to account for any errors in the absolute intensity calibration. The monomer contour length l for PTMO is calculated to be 6.11 Å from tabulated bond lengths and angles.[12] The Flory interaction parameter χ was taken to be zero, in the absence of any other information. However, simulated scattering curves using reasonable values of χ found for hydrogenous–deuterous pairs of other polymers[13] were not discernibly different from those calculated with χ = 0, due to the low N of the PTMO. The MWD of the hydrogenous PTMO was taken to be identical with that of the deuterous PTMO, as both are synthesized in the same fashion.

Figure 3 shows the background-subtracted data for the PT*xx* samples, along with the best-fit lines from the polydisperse wormlike chain model. For comparison, earlier SANS data given by Miller and Cooper[9] (MC) for a 10%

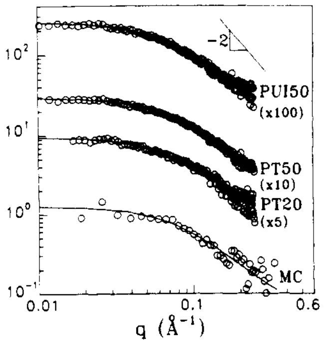

Figure 3. Background-subtracted SANS data (O) and best fit of polydisperse wormlike chain model (—). Top to bottom: PUI50 (×100), PT50 (×10), PT20 (×5), MC. Intensities have been multiplied by the indicated factors for clarity; for PUI50, the interphase scattering has also been subtracted. Inset shows limiting power-law slope of −2 expected for the Debye function.

Table II
SANS Modeling Results

sample	v_D	a ± SD, Å	K ± SD, cm^{-1}
PT50	0.530	18.5 ± 0.5	0.604 ± 0.005
PT20	0.205	19.6 ± 1.1	0.605 ± 0.009
MC	0.100	15.9 ± 3.9	0.715 ± 0.044
PUI50	0.563	24.1 ± 1.0	0.527 ± 0.006

labeled blend of virtually identical oligomers is also shown. On the basis of these data, MC concluded that the oligomers possessed their unperturbed conformations. However, the MC approach had several shortcomings, including poor statistical quality of the data, using a Debye function rather than wormlike chain scattering to describe the data, and incorrect computation of mean-square radius of gyration R_g^2 moments from the best-fit R_g^2. The best-fit parameters to these data sets are listed in Table II, along with their standard deviations in the fit, which may be considered lower bounds on the errors in the parameters. The average value of a from PT50 and PT20, weighted inversely to their standard deviations, is 18.8 Å. This value also falls within the standard error found for a in the MC data, though the standard error there is much larger due to the noisier data. The similarity of a and K in the PT20 and PT50 fits provides a posteriori justification for assuming the same MWD for the hydrogenous and deuterous PTMO, as both parameters would be affected by any mismatch. Also, the inset in Figure 3 shows that no region of the data is described by a power-law slope of −2, as would be expected for the high-q portion of the Debye function. This further emphasizes the need to use a wormlike chain model to describe such short-chain polymers.

Evans and Huglin[14] performed intrinsic viscosity measurements on high-N PTMO fractions in three Θ-solvents. Using the value of $\Phi = 0.0025$ dL/(Å^3·mol) for the universal viscometric constant, one can calculate an average value of $a = 11.7$ Å from their values of $[\langle r^2\rangle_0/M]^{1/2}$. This is far outside the error limits for a in the current investigation. The PTMO oligomers are substantially swollen from their unperturbed dimensions, in contrast with the conclusion of MC. This is because the short chains are swelling the longer chains, since the relation[15] $N_{\text{short}} \gg (N_{\text{long}})^{1/2}$ does not hold for the entire MWD shown in Figure 1. It should be noted that expansion of the chain is an excluded volume effect, and the polydisperse wormlike coil model assumes random-walk statistics, i.e., no excluded volume. However, the primary effect of excluded volume on the SANS data is the overall expansion of the chain,[16] which is satisfactorily modeled by "stiffening" the chain through an increased a, since the data extend only to $q \simeq 5/a$. While excluded volume will also modify the segmental density distribution within the coil, any such effect is apparently too subtle to be noted in the SANS data.

Also shown in Figure 3 are the data for PUI50, with the background and interphase scattering subtracted. The position of the "knee" in the curve near 0.06 Å^{-1} is noticeably different from that for the PTxx samples, and the best-fit $a = 24.1$ Å is substantially different as well. This indicates that the soft-segment $(R_g^2)_z$ increases 27% as a result of ionic aggregation, assuming that the oligomer SANS data are a suitable surrogate for those from the soft segments in the nonionic polyurethane. To compare this with Forsman's theory,[3,17] assuming $\kappa = 0.318$ as for polystyrene and 20 ionic groups per aggregate, an expansion of ca. 130% is calculated, much higher than observed. On the other hand, the current results are also inconsistent with the no-expansion result predicted by Squires et al.[2]

The theories of Forsman, Dreyfus, and Squires essentially consider the process of ionic aggregation as a balance between enthalpic (Coulombic attraction) and entropic (chain localization at the aggregates and chain deformation) forces. The subchains connecting ionic aggregates are always considered to be Gaussian, but in fact they may be extended near the ionic aggregates. de Gennes[18] has treated theoretically the case of two interacting surfaces with a high density of end-grafted chains immersed in a melt of the same polymer; the chains must stretch to maintain a uniform segment density. de Gennes[18] noted the similarity of this model to microphase-separated block copolymers; in fact, block copolymers with a spherical morphology have been shown[19] to possess a "corona" of matrix material surrounding the dispersed spheres. This corona defines the radius of closest approach between spheres and also excludes matrix homopolymer;[20] these observations strongly suggest that the corona chain segments are extended. For ionomers, a radius of closest approach greater than the aggregate radius was postulated earlier by Yarusso and Cooper[21] in modeling ionomer SAXS data.

Because of the higher ion content in these polyurethane ionomers than in the telechelics studied earlier,[1] the fraction of chain segments in the corona surrounding the aggregates and thus their contribution to the overall chain expansion should be greater. It is also possible that the ratio of corona to aggregate material differs between the two types of ionomer, depending on the internal organization of the aggregates. This reconciles the null result found for the telechelics with the mild extension found here. Future theories of ionomer chain dimensions should consider this effect in their formulation.

Finally, the K values found for PT20 and PT50 are in good agreement with each other but are 6.4% greater than the calculated K. This small discrepancy is within the error limits of the absolute intensity calibration and instrumental drift. The data of Miller and Cooper,[9] which were collected 6 years ago, are not expected to have a comparable K value, as their calibration was based on the incoherent scattering from H_2O, which is known to be a less accurate method of calibration[22] than the partially labeled polystyrene standard now in use at IPNS. The K value for PUI50 is 13% lower than for the PTxx samples, which is due[1] to the volume fraction $(1 - v_L)$ occupied by the MDI residues and propanesulfonate branches, which are unlabeled and thus do not contribute to the single-chain scattering. These units form 34%

of the mass of PUI50, but since they are expected to be localized in regions of higher mass density (the ionic aggregates), they should occupy a volume fraction smaller than their weight fraction. However, to bring the numbers above into perfect agreement would require the aggregates to have a mass density of 3.6 g/cm^3, which seems rather large. This point requires further investigation, preferably using a contrast-matched sample to eliminate the subtraction method used here.

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Communications to the Editor

Novel Initiator Systems for the End-Functionalization of Poly(vinyl ethers)

The extensive investigation of the living cationic polymerization of vinyl ethers by Higashimura and co-workers[1–4] and others[5,6] has paved the way to the molecular engineering of this type of polymer. Of particular interest is the synthesis of end-functionalized and telechelic poly(vinyl ethers) (PVE) as precursors of newer materials such as multisegmented copolymers.

ω-Functional and α,ω-functional PVEs can be prepared along different reaction pathways. One of the approaches involves essentially a preliminary synthesis of the functionalized vinyl ether monomer and use of its HI adduct as an initiator for vinyl ether polymerization in the presence of a Lewis acid activator. Thus, for instance, the HI adducts of 2-(vinyloxy)ethyl methacrylate and diethyl 2-(vinyloxy)ethylmalonate have been successfully used[7,8] to initiate the polymerization of vinyl ethers. Both of these have been prepared by reaction of chloroethyl vinyl ether with sodium methacrylate and sodium malonate, respectively.

A second pathway relies upon the reaction of the living poly(vinyl ether) chains with a nucleophilic functional compound as a terminating agent. Butylamine or the sodium salt of malonic esters[9–11] have been used effectively as terminating agents with the formation of ω-functional polymers. A combination of the first and second pathways allows symmetric or asymmetric telechelic poly(vinyl ethers) to be prepared.

As an extension of the second pathway, a symmetric telechelic polymer has also been obtained by using 1,4-bis(vinyloxy)butane as a bifunctional initiator followed by the termination of the living polymer by a nucleophilic functional reagent.

Presently, we are reporting briefly a new method of the end-functionalization of vinyl ethers by making use of the HI adducts of some conventional vinyl monomers to initiate the EVE polymerization in toluene at −40 °C. This type of end-functionalization is in sharp contrast to the reports by Nuyken and co-workers[6] or Higashimura and co-workers[7,8] in that the vinyl monomers used to prepare the initiator cannot be polymerized under the conditions used for the polymerization of vinyl ethers.

I. Addition of HI to Conventional Vinyl Monomers. The addition of a stoichiometric quantity of HI (0.4 molar solution) to conventional vinyl monomers (0.04