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Communications to the Editor

Chain Extension in Unoriented Ion-Containing Polymers—Does It Occur?

Introduction. Ionic aggregation or ion clustering is a well-known phenomenon which has been supported by numerous experimental evidence from small-angle X-ray and neutron scattering techniques (SAXS and SANS) and transmission electron microscopy.[1–7] However, the studies of the nature and the extent of ion association in ionomers lead to some intriguing and important questions. One of them is chain extension.

Several theoretical models of ionic aggregation have suggested the possibility of chain extension in ionomers.[8–10] These models have essentially considered a balance between coulombic interactions and chain deformation during the ionic aggregation. The models proposed by Forsman et al., Eisenberg, and Dreyfus suggest that the aggregation of ionic species could result in chains extending from their most probable conformations.[1,8,10] However, Squires et al. has stated that there is no theoretical justification for chain extension in ionomers having a random distribution of ionic clusters.[9]

Small-angle neutron scattering (SANS) has been carried out on some random ionomers, such as Nafion and sulfonated styrene ionomers, to study the chain extension.[2,3] However, conflicting results have been reported. For example, Pineri et al.[2] reported no change in the radius of gyration, $\langle R_g \rangle$, in Nafion ionomers. Earnest et al.[3] found that $\langle R_g \rangle$ regularly increased with increasing sulfonation content, which was suggested to result from chain extension. These differences in the SANS behavior might, of course, possibly arise as a result of the specific chain structure of the ionomer studied. In random ionomers, ionic groups are randomly placed on the polymer backbone; therefore, the segment length of the polymer chain between two ionic groups varies considerably. As a result, the distance between any two neighboring ionic groups on the same backbone varies, which can alter the Coulombic interaction between ionic groups. Consequently, the conformation of polymer segments between ionic groups might also possibly vary. Hence, it is difficult to determine local chain extension by monitoring the changes in the value of $\langle R_g \rangle$ for the overall chain for random ionomer systems.

Better definition of chain structure and ion-containing group location are more clearly addressed by use of telechelic or segmented ionomers. In the former, the ion-containing groups appear at the terminal points (or ends of the molecule), while for the segmented systems, the ion-containing groups are placed sequentially along the backbone. Hence, in the case of telechelic or segmented ionomers, the possible effects of chain extension, if they exist, might be expected to be more distinct due to a more regular chain structure with respect to placement of the ionic groups. As an example, Williams et al.[5] studied ionic aggregation in telechelic dicarboxylate polyisoprene 100% neutralized with magnesium cations. They reported that the interdomain spacing, d, of the ionic region increased *linearly* with increasing molecular weight. The linear molecular weight dependence was speculated to result from an extended-chain conformation. Recently, SANS studies have been carried out on telechelic polystyrene ionomers and sulfonated polyurethane ionomers by Register et al.[11,12] Their sulfonated polyurethane ionomers contained poly(tetramethylene oxide) (PTMO) as the soft segment consisting of about 12 repeat units. Their SANS results indicate that the PTMO soft segment $\langle R_g^2 \rangle$ increased 27% in length as a result of ionic aggregation.[12] For their telechelic polystyrene ionomers, there was no chain extension effect observed.[11] This might result from the relatively long styrene segments (ca. 70 repeat units) between ionic species in the telechelic styrene ionomers.

Recently, we have studied segmented PTMO-based ionene materials.[13,14] in which short single-unit doubly charged benzyl dihalide ionic hard segments are connected with dimethylamino-capped PTMO soft segments. The PTMO soft segment molecular weight distribution was also narrow. Due to strong ionic interactions and the very regular chain structure, a distinctly regular ionic domain structure along with a very high degree of microphase separation was observed in these systems by both SAXS and TEM.[7] These ionene systems, therefore, make rather ideal model systems for studies of chain extension. In this paper, we will discuss some experimental evidence which we believe to be related to the chain extension of the PTMO soft segments in these ionene polymers and will add further evidence to support some of our observations from the work of others on telechelic ionomer systems.

Results and Discussion. From SAXS and TEM measurements,[7] a very regular ionic domain *lamellar*-like structure possessing a very sharp interphase region exists in the ionene systems. The length (L) between the ends of a PTMO soft segment which connects two ionic hard segments was *estimated* from the SAXS data using eq 1. In eq 1, d is the interdomain spacing calculated from the

$$L = d - D \tag{1}$$

desmeared SAXS profile, and D is the ionic domain size which is ca. 1.1 nm estimated from the benzyl dihalide ionic segment length. In order to note if a perturbation exists in the end-to-end distance for the soft segment, the values of L have also been compared with the PTMO segment length calculated by assuming either a *fully extended* chain or a *Gaussian* type chain. For the former, the segment length denoted as Ls is calculated by eq 2. Here, N is the number of repeat units per PTMO soft

$$Ls = N\sum n_i l_i \sin(\theta_i/2) \tag{2}$$

segment, and n is number of ith bonds per repeat unit. The parameters l and θ represent the ith bond length and bond angle, respectively. For a Gaussian type chain, the average end-to-end length is calculated by the root-mean-square end-to-end distance (RMS) as follows:

$$\mathrm{RMS} = (C_\infty N\sum n_i l_i)^{1/2} \tag{3}$$

In eq 3, C_∞ is the characteristic ratio for PTMO. Although some differences exist in the reported value of C_∞,[15,16] we have utilized 5.8.[15] It might be pointed out that the value

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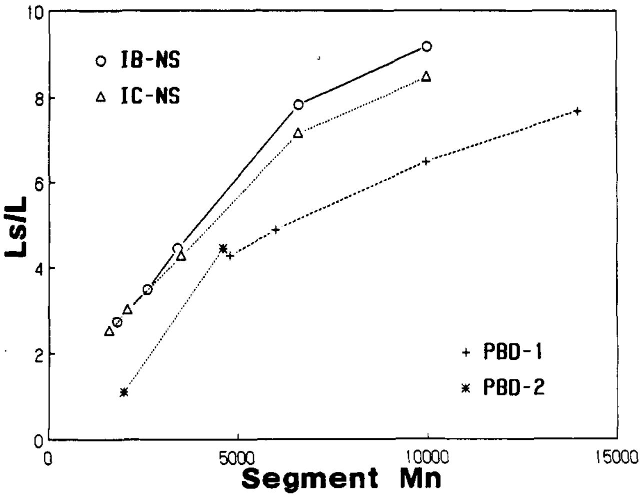

Figure 1. Relationship between Ls/L and the PTMO segment molecular weight for the ionene polymers addressed in the text as well as two polybutadiene ionenes and PBD telechelic ionomers. The data for the PBD-1 and PBD-2 materials were obtained from refs 4 and 17, respectively.

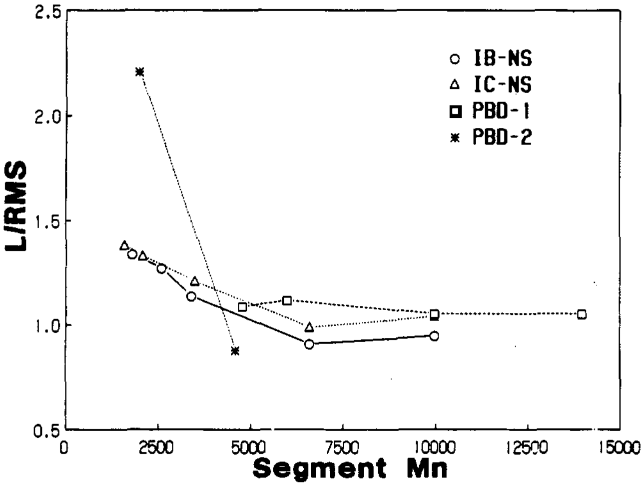

Figure 2. Relationship of L/RMS and the average segment molecular weight between ion-containing groups for the different segmented ionene ionomers and the two telechelic ionomers addressed in Figure 1. The difference between the IB-NS and IC-NS materials is believed to be experimentally significant.

of C_∞ becomes independent of molecular weight somewhat above about 50 bonds.[16] This requirement is well met by all of the soft-segment or telechelic chains discussed within this paper.

By comparing the value of Ls or RMS to the measured value of L, the chain conformation can be estimated. For example, if the ratio of Ls/L reaches unity, the chain would be fully extended. Also, the ratio of L/RMS would be greater than 1. On the other hand, if the value of L/RMS lies close to unity and the value of Ls/L is much greater than 1, the chain would appear to be more in the form of a Gaussian coil.

Figures 1 and 2 illustrate the relationship between Ls/L and L/RMS as a function of the PTMO segment molecular weight for the ionene systems. Some additional data from other sources are also included which will be discussed shortly. As shown in Figure 1, the values of Ls/L decrease regularly with a decrease in the PTMO segment molecular weight while the L/RMS values increase as the molecular weight decreases (Figure 2). These data imply that the PTMO chain becomes more extended when the PTMO segment molecular weight decreases. Since these ionene systems contain only single-unit ionic hard segments, the ion content will increase as the PTMO soft-segment molecular weight decreases. As a result, the level of ionic interactions becomes greater. Consequently, this may promote a greater extension due to a larger Coulombic interaction energy per unit volume.

Figures 1 and 2 also show that the ionenes with chloride cations (IC-NS series) have slightly higher values of L/RMS and lower values of Ls/L than the analogous bromide ionenes (IB-NS series). This result suggests that the PTMO chains in the chloride ionenes are somewhat more extended than in the bromide ionenes. Since the chloride ion has a higher electronegativity than a bromide ion, the Coulombic interactions in chloride ionenes will be stronger.

In addition, we have also applied the same treatment above (eqs 1–3) to the published results of two telechelic polybutadiene (PBD) systems, PBD-1 and PBD-2. The polybutadiene molecular weight was in a range from 4600 to 14 000 for the PBD-1 system.[4] In the system denoted as PBD-2, the molecular weight of the polybutadiene segments was either 2000 and 4000.[17] Both systems were fully neutralized with Ba cations. These specific PBD systems have been chosen because they have at least two scattering peaks in their SAXS profiles which have been suggested to result from an ordered ionic domain structure. An average domain size of 1.1 nm calculated by Williams et al.[5] on similar PBD systems has been used for the value of D. The values of Ls/L and L/RMS for these telechelic systems are also plotted in Figures 1 and 2. It is clearly seen that the telechelic systems behave very similarly to the ionene systems. That is, the values of Ls/L increase with an increase in molecular weight, while the corresponding values of L/RMS decrease and are close to unity as the molecular weight decreases even though the telechelic systems have a higher molecular weight range than the ionene systems. Again, we believe this behavior may be at least in part explained as the result of partial chain extension. In view of our results, it should be pointed out that phase separation of block copolymers of the AB or ABA type has also shown partial chain extension in lamellar systems, and in fact it is expected.[18] Hence, our data in some respects are in line with these observations. However, we suggest that since not all of our systems are not necessarily lamellar in nature and since the "hard phase" is particularly "thin", direct application of the usual block copolymer theory cannot be assumed to directly apply without further justification. We therefore hope this work will help stimulate additional theoretical efforts. Certainly, further determination of the radius of gyration of SANS measurements using labeled segmented ionene materials would be of interest in order to further verify or disprove this explanation given above.

Summary. A strong molecular weight dependence of the interdomain spacing in model segmented PTMO ionene systems is observed. Based on calculated values of Gaussian and extended-chain calculations compared to the experimental results, the observed molecular weight dependence is believed to result from partial chain extension in these systems. Similar conclusions have been reached on a series of elastomeric telechelic ionomers by the same analysis. To verify our analysis, further SANS studies on the segmented PTMO ionene systems and related systems are needed.

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(19) Present address: Amoco Chemical Co., Naperville, IL 60566.

Daan Feng[19] and Garth L. Wilkes*

Department of Chemical Engineering and
Polymer Materials Interfaces Laboratory
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061-0211

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