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Ionic Aggregation in Model Ionomers[†]

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ABSTRACT: A series of halato-telechelic butadiene and isoprene polymers have been studied as model compounds for the more complex ionomers. Small-angle X-ray scattering (SAXS) measurements have been conducted over a wide scattering vector range as a function of the metal cation, degree of neutralization, swelling by both polar and nonpolar solvents, molecular weight, and temperature. It has been found that the characteristic SAXS intensity profile is governed principally by the configuration of the polymer molecule between the ionic groups located at the ends of each chain whereas the nature of the cation plays only a secondary role. Provided the chain length is well-defined, i.e., provided there is a narrow molecular weight distribution, there is a nearly complete microphase separation between the ionic groups and the hydrocarbon chain. The ionic aggregates can be adequately described as multiplets that are surrounded by a volume from which other ionic domains are excluded and are arranged in a liquid-like manner in space. No evidence was found for ionic clusters or a critical concentration and temperature of multiplet formation.

Introduction

One of the outstanding problems in the physics of ionomers is the description of the structure of these compounds. Although there is little doubt that ionic aggregation is responsible for their unique physical properties, no detailed picture of the aggregates and of their organization in bulk or in solution has emerged. Are they multiplets or clusters?[1,2] Is their shape spherical, lamellar, or more complex? Are they randomly distributed, are they organized in a liquid-like manner, or do they show paracrystalline order? It is difficult to give an unambiguous answer to these questions. All the structural models[3,4] based principally on small-angle X-ray scattering (SAXS) results from a wide variety of ion-containing polymers can be adjusted to account for the observed data but are unable to give an unequivocal description of the morphology. The limited amount of characteristic features in the SAXS data, i.e., one broad scattering maximum, and the number of parameters involved in the model calculations contribute, in large measure, to this ambiguity. For instance, although all models consider the ionic aggregate as the basic scattering unit, they attribute the origin of the characteristic maximum, the so-called "ionomer peak", to either an interference between small interacting aggregates or to the internal structure of independent complex ionic particles. In addition, the molecular properties for most of the ionomers studied to date are usually not well-defined. The ionizable groups are often located on pendant side chains randomly spaced along the main chain.

In order to understand the process of ion aggregation and to elucidate the parameters governing the morphology of ionic polymers, it is important to study model ionomers with well-defined molecular characteristics and to follow the evolution of the structure as a function of controlled molecular parameters. Comprehending the structure in these model systems can lead to an understanding of the structure of the more complex ionomers and a relation to the physical properties. Halato-telechelic polymers (HTP) were chosen as such model compounds. Of critical importance is the fact that the ion pairs are located at each end of short chains with a characteristic separation distance. Furthermore, their molecular charactersistics are well-defined and can be varied as desired.[5-11]

We report here a structural investigation of a series of dicarboxy-telechelic polybutadiene and polyisoprene using SAXS. The use of synchrotron radiation made possible the collection of a large quantity of high-quality data, extending over a large scattering vector range as a function of the metal cation species, extent of neutralization, swelling by polar (water) or nonpolar solvent, distance between ionic pairs, and temperature. In the light of the results obtained, a simple model has emerged where the chain between ionic pairs plays an important role in the overall structure.

Experimental Section

Polymer Preparation. Carboxy-telechelic polybutadiene commercially available from BFGoodrich (Hycar CTB 2000 × 156) with $\bar{M}_n = 4600$, $\bar{M}_w/\bar{M}_n = 1.8$, functionality = 2.01, and cis/trans/vinyl ratio = 20/65/15 was used in this study unless specified otherwise. Carboxy-telechelic polyisoprenes of different molecular weights (6000, 10 000, 17 000, 24 000, 30 000, and 37 000) were anionically prepared in tetrahydrofuran (THF) at −78 °C. Tetramer of sodium α-methylstyrene was used as a difunctional initiator of the isoprene (10 wt %) polymerization. This monomer was dried over calcium hydride at room temperature, distilled under reduced pressure, mixed with *n*-butyllithium, and redistilled just prior to polymerization. THF was dried by refluxing over benzophenone–sodium and distilled under a nitrogen atmosphere. Polymerization was performed in previously flamed and nitrogen-purged flasks equipped with rubber septums. Hypodermic syringes and stainless steel capillaries were used to handle carefully dried products under a nitrogen atmosphere. The living macrodianions were deactivated by excess anhydrous carbon dioxide, and the final polymer was recovered by precipitation into acidified methanol containing an antioxidant (Irganox 1010). Polyisoprene microstructure was characterized by 65% 3,4 units and 35% 1,2 units, $\bar{M}_w/\bar{M}_n < 1.2$, and the mean number of carboxylic acid groups per chain (functionality) was ca. 1.95. This functionality was determined via potentiometric titration of the acid end groups with tetramethylammonium hydroxide in a 90% benzene/10% methanol mixture.

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Carboxy-telechelic polydienes were quantitatively neutralized in toluene under strictly anhydrous conditions by using stoichiometric amounts of highly reactive metal alkoxides or alkyl metals. The polymer was initially dried by three successive azeotropic distillations of benzene and finally dissolved in toluene (5% w/v) previously dried by refluxing over calcium hydride. When the appropriate amount of metal alkoxides dissolved in dry alcohol (or alkyl metals in toluene) was added dropwise into the prepolymer solution, the solvent was partly distilled off under reduced pressure. Freshly dried toluene was added into the reaction medium and a further distillation was performed. After a third distillation of toluene, the polymer was dried under vacuum until there was no weight reduction. As reported elsewhere,[9] titanium and zirconium alkoxides were used in excess compared to the carboxylic acid end groups (two alkoxy groups per carboxylic acid group). The unreacted alkoxy groups attached at the chain ends were hydrolyzed into metal oxohydroxide moieties before the solvent was removed and the polymer was dried to constant weight.

Metal (K, Mg, Ba) methoxides were freshly prepared just before use by reaction of the pure metal with anhydrous methanol. Alcohol was dried by refluxing over sodium. Di-*n*-butylberyllium was obtained by reacting *n*-BuLi with $BeBr_2$, prepared according to the procedure of Richards and Burgers for $MgBr_2$.[12] The synthesis of $BeBr_2$ was, however, carried out in refluxing THF. Titanium isopropoxide (Aldrich) and zirconium *n*-propoxide (Ventron) were used as received. Copper(II) isopropoxide was prepared by reacting completely dehydrated copper(II) chloride[13] with a stoichiometric amount of lithium isopropoxide in anhydrous 2-propanol.[14] A green precipitate of copper isopropoxide formed, which turned blue as the mixture was shaken. The supernatant solution was removed under a nitrogen atmosphere (through a stainless steel capillary), and the precipitate was repeatedly washed with dry 2-propanol until this solvent remained colorless. (The LiCl reaction subproduct and the unreacted $CuCl_2$ are soluble in 2-propanol.) Copper isopropoxide was used as a suspension into dry 2-propanol at a rate of 0.1 mol/L. Iron(III) isopropoxide was prepared at 0 °C by bubbling ammonia into a solution of anhydrous ferric chloride in a mixture of dry benzene and 2-propanol.[15] After completion of the exothermic reaction, the volatile components were evaporated under reduced pressure. The residue of ferric isopropoxide and ammonium chloride was extracted with dry benzene, which is a selective solvent for the alkoxide. Ferric isopropoxide was used as a 0.05 mol/L solution in dry benzene. When required, halato-telechelic polydienes were molded into 1-mm-thick disks at temperatures ranging from 80 to 110 °C. All solid samples were kept under atmospheric conditions and protected from light.

When studied in solution, the HTP were examined as prepared. The concentration was adjusted by variation of solvent content. Concentrations were determined by evaporation of the solvent from a known volume of solution and weighing the remaining dried polymer.

SAXS. Most SAXS experiments were performed at the Stanford Synchrotron Radiation Laboratory (SSRL) using the SAXS camera at beam line I-4. Preliminary experiments were conducted at LURE-DCI, Orsay, at beam line D-11. Both facilities have been described elsewhere.[16,17] Briefly, at SSRL, the beam is horizontally focused and monochromated by a bent asymmetrically cut silicon (111) crystal. It is also focused vertically by a float glass mirror so that the beam size at focus several centimeters before the detector is ca. 150 × 400 μm. Two detectors placed immediately before and after the specimen monitor the beam decay and the sample absorption coefficient. The scattering profiles were recorded with a one-dimensional self-scanning photodiode array having a spatial resolution of 25 μm and a time resolution on the order of 1 s. Two sample-to-detector distances were used, covering a scattering vector or q range from 0.008 to 0.32 Å^{-1} ($q = (4\pi/\lambda)\sin(\epsilon/2)$, where ϵ is the observation angle and λ, the wavelength, was 1.412 Å). The data corrected for dark current, detector homogeneity, parasitic scattering, and sample absorption were matched in the region of overlap.

D-11 at LURE, of similar design, uses a bent asymmetrically cut germanium (111) monochromator (λ = 1.608 Å) but no mirror, so that the beam size is ca. 500 × 1000 μm at the detector. A gas-filled, one-dimensional, position-sensitive proportional counter with a spatial resolution of 150 μm was used to detect the scattered radiation.[18]

Scattering profiles are presented as normalized intensities vs. scattering vector q. Conversion to absolute scattering units involves a simple multiplicative factor. Smearing effects due to the finite size of the counting elements of the detector were found to be of importance only at very small scattering vectors and, consequently, were ignored. Experiments involving temperature scanning or swelling were performed in real time either as the temperature was changed or as the swelling solvent was introduced.

Data Analysis

We start with the assumption that there exists a two-phase morphology with an arbitrary electron density difference between the phases. We make no assumptions concerning the spatial distribution of the ions, the size and shape of the phases, or the spatial correlations between the domains. With this premise, standard scattering theories[19] for a two-phase system can be used to analyze the SAXS profiles. Hence, characteristic lengths pertaining to the morphology of the samples have been obtained.

(i) Assuming a constant electron density in each of two phases separated by a sharp interface, Porod[20] and Debye[21] have derived the asymptotic form of the scattered intensity:

$$\frac{\lim_{q\to\infty} I(q)q^4}{\int_0^\infty I(q)q^2\,dq} = \frac{K_P}{Q} = \frac{1}{\pi\phi(1-\phi)}\frac{S}{V} \qquad (1)$$

where K_P is the Porod constant, Q is the scattering invariant, ϕ is the volume fraction of one of the phases, and S/V is the specific interfacial area. Equation 1, which does not require absolute intensities, provides a direct measurement of the surface/volume ratio of the scattering entities. Knowing ϕ and assuming a spherical shape of the ionic domains permit an approximate calculation of the radius of the ionic domains, R_D.

(ii) If the interface between domains is diffuse, the scattered intensity decreases more rapidly with increasing scattering vector than predicted by Porod (negative deviations). Assuming that the diffuse phase boundary can be described by a step function convoluted with a Gaussian smoothing function with a standard deviation of σ, then[22,23]

$$I(q) = \frac{(2\pi)^4 K_P}{q^4}\exp(-\sigma^2 q^2) \qquad (2)$$

The diffuse phase boundary thickness, E, can be approximated as $(12\sigma)^{1/2}$.

(iii) Fluctuations of electron density within the phases contribute a background to the scattering curve, I_{fl}. It arises from thermal density fluctuations and also from the presence of isolated ions randomly distributed in the nonionic matrix or of organic monomers in the ionic phase (Laue scattering). Over the scattering vector range of interest in this study, I_{fl} can be assumed constant as a function of angle. I_{fl} is then evaluated from a plot of $I(q)q^4$ vs. q^4 and must be subtracted from the scattering curve before any further analysis can be performed.

(iv) In most of the specimens investigated, a significant amount of excess scattering was observed at small scattering vectors. Attempts to estimate a size scale of the entity giving rise to this scattering via a Guinier analysis[24] were unsuccessful. Plots of ln $(I(q))$ vs. q^2 were nonlinear and, consequently, only a lower bound could be set on the particle size via this method. As an alternate approach, a Debye–Bueche correlation function analysis[21] was used. For an isotropic system where heterogeneities are randomly

Table I
SAXS Data for α,ω-Dicarboxylatopolybutadiene Neutralized with Different Cations[a]

cation	R_{ionic}	v	d, Å	R_D, Å	E, Å	$(d - 2R_D)$	I_{fl}
K	1.33	+1	71.6	11.1	5.8	49	818.7
Be	0.34	+2	59.8	9.15	2.6	41.5	210.6
Mg	0.74	+2	63.0	7.75	0.75	47.5	149.6
Cu	0.80	+2	54.3	6.2	1.5	41.9	225.0
Ba	1.38	+2	75.3	6.9	2.0	61	126.2
Fe	0.67	+3	56.1	6.1	1.6	44	363.9
Ti	0.64	+4	57.8	7.65	0.8	42.5	209.2

[a] R_{ionic} is the ionic radius of the metal, v its valency, d the distance between domains obtained by applying Bragg's law to the position of the intensity maximum, R_D the domain radius, E the diffuse phase boundary between the ionic domain and the hydrocarbon matrix, and I_{fl} the background due to a random distribution of ions in the organic matrix and thermal density fluctuations (in arbitrary units). Estimates of errors in the values of d are ±2 Å, of R_D ±3 Å (given the assumptions made in the text), and of E ±2 Å. It should be noted that E, for all samples except the K cation results, is zero to within experimental error.

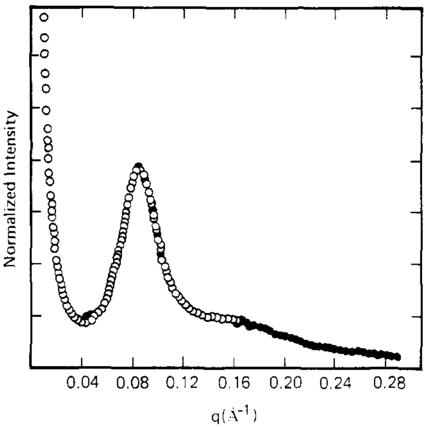

Figure 1. Normalized small-angle X-ray scattering profile for α,ω-dicarboxylatopolybutadiene neutralized with barium. The data shown are the superpositioning of scattering data taken at two different sample-to-detector distances. This figure also shows the quality of a typical scattering profile and the range over which the data overlapped.

arranged in space and assuming that the spatial correlation function is given by

$$\gamma(r) = \exp(-r/a) \qquad (3)$$

where a, the correlation length, characterizes the average size of the heterogeneities. A plot of $I(q)^{-1/2}$ vs. q^2 will yield the correlation length from the slope-to-intercept ratio. Considering the approximations made in such an analysis, the uncertainty in the origins of the very low-angle scattering, and the limited q range, it is difficult to interpret precisely the correlation length. It should be noted that this "zero-order scattering" cannot originate from individual ionic domains but rather from large-scale heterogeneities (>100 Å) encompassing numerous ionic domains. A more detailed analysis of this "zero-order scattering" will be the subject of a forthcoming paper.

(v) Spatial correlation of the ionic domains gives rise to a broad interference maximum in the scattering profile. Numerous models have been used to interpret this scattering maximum with limited success as stated previously. In order to avoid such ambiguities, Bragg's law was applied to the value of q at the maximum intensity. This corresponds to a distance d between the ionic domains which could be correlated to the variation of well-controlled parameters. It should be recalled here that Bragg's law is approximate for a structure without long-range order and only gives an estimate of the actual separation distance.

Results and Discussion

Nature of the Cation. The SAXS profile for the barium salt of dicarboxypolybutadiene (PBD-Ba) containing 2.4 mol % of charged monomers (acid groups) is shown in Figure 1. This scattering profile typifies the characteristic features of all the HTP's investigated in this study. All show the broad maximum, centered around q = 0.1 Å^{-1}, characteristic of ionomers which is usually taken as evidence for ionic aggregation. This maximum is not seen in the acid form, however. Two other features of importance are, first, the shouldering on the high-q side of the main peak, not usually observed in other systems and interpreted as a second-order effect and, second, a scattering at very small scattering angles often neglected in the interpretation of the data. The relative contributions of these different features will vary with the type of specimen investigated and the method of preparation.

As described previously, the α,ω-diacid polymers have been neutralized by alkali, alkaline earth, transition, trivalent, and tetravalent metal II, III, and IV cations with valencies (v) ranging from 1 to 4 and ionic radii varying from 0.34 to 1.38 Å. Variation of the valency of the cation essentially changes the basic architecture of the chains before aggregation. For v = 1, the ionic monomers and cations are at the extremities of short chains, for v = 2, the divalent cations act as chain extenders equally spaced along the chain, and for $v \geq 3$, the trivalent cations act as the cross-links of a three-dimensional network. The results summarized in Table I for carboxy-telechelic polybutadiene ($\bar{M}_n$ = 4600) show the following.

(1) With the exception of the K cation, the only monovalent ion studied, the ionic domains are *small* (R_D = 6–9 Å) and their dimensions do not vary significantly to within experimental error, estimated at ±10%. R_D does not appear to be strongly related to the ionic radius of the cation. However, in the alkaline earth series (Be, Mg, Ba), R_D decreases slightly as the ionic radius increases. A more systematic study of this series would be necessary to confirm this weak dependence.

(2) The phase boundary between an ionic domain and the organic matrix is *sharp*. The values of E reported are effectively zero to within experimental error. Again, PBD-K is an exception.

(3) The distance between scattering domains varies little with the nature of the ion. The linear dimension of the hydrocarbon phase between two ionic domains, $d - 2R_D$, is constant except for BaPB. To within experimental accuracy, d is of the same order as the root mean square end-to-end distance of 70 Å for the 71% trans, 25% cis, 4% vinyl polybutadiene chain.[25]

It is interesting to note here that although the average size of the ionic domains is shown to be independent of the ionic radius of the cation, the functionality and size of the ionic cross-links responsible for the viscoelastic properties are strongly dependent on the cation size, at least for the alkaline earth series.[10,11] This apparent discrepancy may be associated with the assumed spherical

Table II
SAXS Data for Magnesium α,ω-Dicarboxylatopolyisoprene of Different Molecular Weights

$\bar{M}_n$	R_D, Å	E, Å	$\phi_{Mg} \times 10^3$	I_{fl}
6500	5.5	2.0	1.95	30.7
10000	6.9	2.0	1.27	11.8
24000	5.3	2.7	0.53	16.8
30000	5.4	1.1	0.42	28.6

[a] ϕ_{Mg} is the volume fraction of Mg multiplets derived from the scattering invariant, assuming that the density of the multiplets is that of pure Mg. Thus, ϕ_{Mg} corresponds to the volume fraction of the ionic domains. Error estimates on the values of R_D and E are ±3 Å and ±2 Å, respectively.

shape of the domains in the SAXS analysis or may be due to nonuniform spatial distribution of the ionic domains.

Molecular Weight. Samples of dicarboxylatopolyisoprene of low polydispersity, 100% neutralized with Mg (PIP-Mg), with $\bar{M}_n$ ranging from 6000 to 37000 were investigated. The ion content, expressed as the number of ionizable groups per 100 monomers, was varied from 0.37 to 2.12. The maximum in the scattering profile was found to move to smaller angles as the molecular weight was increased and was visible only as a shoulder on the intense zero-order scattering for $\bar{M}_n = 30000$. For $\bar{M}_n = 37000$, only a very weak zero-order scattering appeared and, consequently, could not be analyzed quantitatively.

The results are summarized in Table II. The ionic domain radius R and the diffuse phase boundary thickness E were independent of $\bar{M}_n$. The volume fraction of the domains, measured by the scattering invariant Q, decreased as $\bar{M}_n$ increased. The level of electron density fluctuation I_{fl} was very low in comparison to that of PBD-Mg, where the polydispersity was much higher, indicating that very few ionic groups were isolated in the hydrocarbon matrix outside the ionic domains. The correlation length derived from a Debye–Bueche analysis of the zero-order scattering was found to increase with molecular weight, indicating that the size scale of the heterogeneities giving rise to this scattering increased. Taken together, these results clearly show that there is no discontinuity in any of the physical quantities measured as a function of molecular weight. This would reflect an invariance in size and/or organization of the ionic domains. Therefore, a simple picture emerges where only the *distance* between ionic domains, but not the overall organization, changes as the molecular weight between ionic groups is varied.

The marked dependence of the separation distance between ionic domains upon the molecular weight suggests that the molecular configuration of the polyisoprene molecule strongly influences the morphology. A previous study[7] suggested an extended configuration of the chain as evidenced by a linear increase of the separation distance d with M. A coiled configuration would give a slower variation of d with M, depending on the domain morphology. According to predictions in block copolymer theory,[26,27] for a lamellar morphology $d \ \alpha \ M^{1/3}$ ($q_{max} \ \alpha \ M^{-1/3}$) and for a spherical morphology $d \ \alpha \ M^{1/2}$ ($q_{max} \ \alpha \ M^{-1/2}$). Also, an $M^{1/3}$ variation would ensure a constant density of domains throughout the sample since their size was found to be independent of M. Accordingly, the data for four molecular weights where a distinct scattering maximum was observed were plotted as a function of M^{-1}, $M^{-1/2}$, and $M^{-1/3}$ in Figure 2. Owing to the limited molecular weight range, all of the plots appear to be linear within experimental error. However, in the limit of infinite molecular weight q_{max} must be zero. As can be seen, this corresponds more closely to the $M^{-1/2}$ dependence, where the intercept of the best fit line is closer to the origin. Evaluation of the exponent from a plot of ln (q_{max}) vs. ln (M) yields a slope of −0.45, which is between the two extremes of −0.33 and −0.5. While it is clear that the data do not rule out the formation of lamellar structures, the variation in d with M more closely agrees with the spherical domain description.

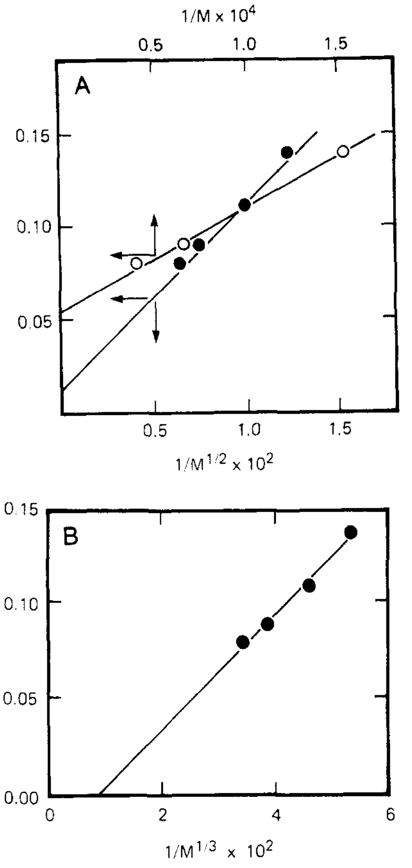

Figure 2. Scattering vector corresponding to the peak position plotted as a function of M^{-1} and $M^{-1/2}$ (A) and as a function of $M^{-1/3}$ (B).

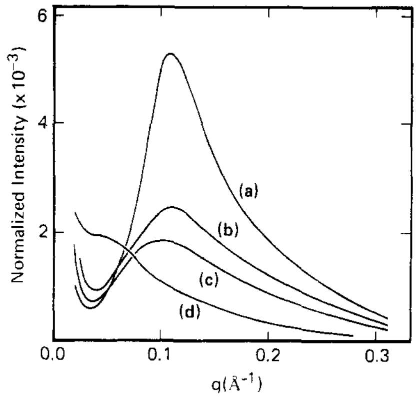

Figure 3. Small-angle X-ray scattering of PBD-Ti in the presence of toluene. The scattering profiles correspond to different volume fractions of PBD-Ti: (a) dry; (b) 0.9; (c) 0.6; (d) 0.2.

Toluene Swelling and Gel Studies. For a system composed of ionic domains dispersed in a hydrocarbon matrix, an organic solvent should preferentially swell the hydrocarbon phase and be excluded from the ionic domains. Consequently, swelling with an organic solvent provides a means of varying the distance between the ionic domains and, also, the characteristics of the morphology. Two parallel experiments were conducted. The first involved the immersion of the bulk specimen in toluene, a

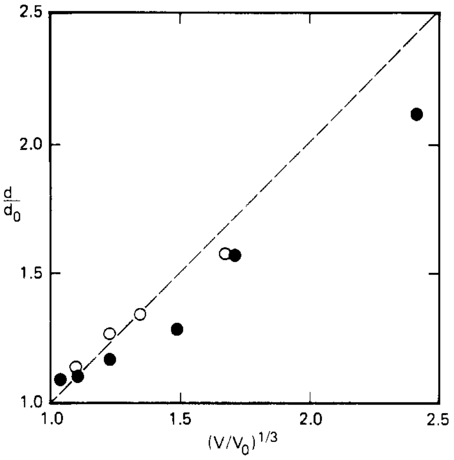

Figure 4. Equilibrium swelling of PBD-Ti where the relative change in the separation distance of the ionic domains (d/d_0) is shown as a function of the macroscopic increase in volume. The $^1/_3$ power was used to reduce the volumetric swelling to a linear dimension assuming an isotropic swelling. The two different data sets are for a bulk sample swollen with toluene (○) and a gel prepared at fixed concentrations in toluene (●).

Table III
SAXS Data for Gels of PBD-Ti in Toluene

ϕ	R_D, Å	E, Å	q_{max}, Å^{-1}	Q	I_{fl}/ϕ
0.07	6.9	1.8	<0.08	.58	520.5
0.2	6.0	1.7	0.08	.78	243
0.3	5.4	1.9	0.09	1.68	179.5
0.6	5.1	2.2	0.106	2.01	100
0.75	5.3	1.9	0.098	1.56	69
0.9	5.3	1.7	0.104	2.14	70
1	5.6	1.8	0.117	3.19	62

good solvent for polybutadiene with a low dielectric constant, and, in the second, a series of gels prepared at fixed concentrations by evaporation of solvent from dilute solutions were studied. In the former case, measurements over a fixed q range were performed as the solvent was injected into the sample cell under atmospheric conditions (Figure 3), whereas in the latter case, solutions between 7×10^{-2} and 9×10^{-1} g/cm,^{3} prepared under strictly anhydrous conditions, were studied over a larger q range with better statistics. The microscopic swelling, measured by the displacement of the SAXS peak d/d_0, was first compared to the macroscopic swelling $(V/V_0)^{1/3}$, measured by the change in linear dimensions of the sample or the volume fraction of solvent in the solution. As shown in Figure 4 for PBD-Ti, the deformation was affine except at very high degrees of swelling. (Similar results were obtained with PBD-Mg.) For the gels prepared at fixed concentrations, it was observed that (Table III) the SAXS invariant, Q, proportional to the polymer volume fraction ϕ, increased with increasing ϕ, while R_D and E were independent of ϕ, indicating that the size of the ionic domains remains constant. The breadth of the SAXS intensity maximum relative to its position $\Delta q/q_{max}$ increases as ϕ decreases, indicating a broader distribution of interdomain distances and a network distortion. Concurrently, the relative electron density fluctuation I_{fl}/ϕ increases, most likely resulting from some chains ends being forced into the hydrocarbon matrix. At higher dilutions the SAXS profiles were skewed toward the higher scattering vectors, as the contribution to the SAXS from the zero-order scattering increases. It was also observed that the scattering maximum was still visible even when the volume had increased by a factor of 14!

It is interesting to remark that the materials were somewhat brittle in the swollen state, in that they easily fractured during handling. Also, provided the swelling ratio was less than 1.5, the effects of swelling were reversible in that removal of the solvent was found to restore the original morphology of the specimen.

Table IV
SAXS Data for Magnesium α,ω-Dicarboxylatopolybutadiene Swollen in Water

sample	R_D, Å	E, Å	Q	I_{fl}	d, Å
PBD-Mg 100					
dry	6.2	1.2	1.37	34.8	62
swollen	11.5	1.8	0.47	67.6	87
PBD-Mg 80					
dry	5.8	2.1	0.97	23.5	65
swollen	13.6	2.4	0.13	18.9	87

Effect of Water. Water has been known to alter dramatically the morphology in bulk ionomers. It would be expected that water would reside preferentially in the ionic domains and be excluded from the organic matrix. In order for swelling to occur, transport of the water through the organic matrix to the ionic domains requires some mechanism by which this may easily occur. Since the HTP is rubbery, it is evident that the ionic domains cannot be topologically continuous throughout the sample. Therefore, the presence of isolated ionic groups in the matrix, i.e., incomplete aggregation of the ionic groups, must facilitate this process. Consequently, the amount of water uptake and the location of water in the bulk specimen can reveal some important morphological information.

Three samples (PIP-Mg totally neutralized and PBD-Mg neutralized to 80% and 100%) were immersed in water at room temperature for several hours. The initially transparent samples were found to become opaque after immersion in water. Visual observation of cross sections of the specimens revealed a dramatic difference between the PIP and PBD specimens. For PIP, even after immersion for 1 month, only a thin layer of the sample near its surface became turbid, whereas the core of the specimen remained unchanged. For PBD, however, no distinct inhomogeneous swelling characteristics were found and a uniform uptake of water was evident. Also, the 80% neutralized PBD-Mg appeared to swell more rapidly than the 100% neutralized samples.

With all specimens studied, the SAXS maximum was displaced to lower q values. A 7% increase in the Bragg spacing was found for the PIP-Mg compared to a 25% increase for PBD-Mg neutralized to 80% and 100%. In addition, the SAXS reflection sharpened but the total integrated scattering decreased. The zero-order scattering was also found to decrease. As expected, the water uptake was accompanied by an increase in the domain radius from 6.2 to 11.5 Å for the PBD-Mg (100%) and from 5.8 to 13.6 Å for the PBD-Mg (80%). The diffuse phase boundary, however, showed only a slight increase. Results of the experiments on PBD-Mg are given in Table IV.

From these observations, several important conclusions can be drawn. The very slow rate of water uptake for all samples shows that the ionic domains are not easily accessible to a polar solvent and are isolated from one another. The difference in the water uptake behavior between the PIP-Mg and PBD-Mg can be related to the polydispersity (note that the rate at which water diffuses into the polymers is low for both). Since the chain length distribution is narrower for the PIP, the contour length between ionic groups is more uniform. This would lead to a better separation between ionic and nonionic monomers, consistent with the level of fluctuation scattering observed for these different specimens. If ionic "impurities" facilitate the transport of water, as suggested

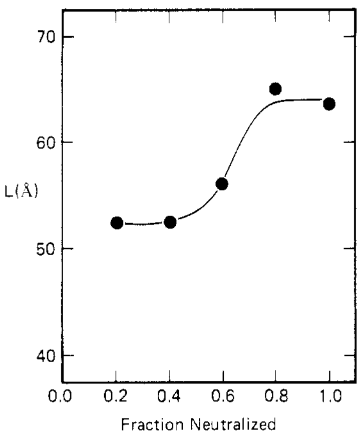

Figure 5. Bragg spacing corresponding to the position of the SAXS maximum for PBD-Mg as a function of the degree of neutralization.

earlier, the samples with fewer isolated ions in the organic matrix will have poorer water transport properties. Similarly for the 80% neutralized PBD-Mg, the incomplete neutralization leads to a higher amount of dissolved acid end groups in the matrix and, consequently, to an improved water transport.

It is also evident from the data in Table IV that while the ionic domain size increases, the separation distance $d - 2R_D$ (not the long period) does not change dramatically, indicating that the root mean square end-to-end distance of the chain is remaining relatively constant. Consequently, the water appears to be solvating the ionic domains preferentially. This leads to a reduction in the electron density of the domains and, hence, a reduced total scattering. The invariance of the diffuse phase boundary is surprising though.

Degree of Neutralization. A critical parameter in the development of the morphology in HTP's is the ion content of the polymer. This can be varied by changing the molecular weight of the polymer, i.e., by varying the distance between the ionic end groups, or by partial neutralization of the acid end groups. The former case has been discussed previously with the result that only the distance between ionic domains changes, whereas the conformation of the chain and the size of the domains remained constant. Partial neutralization, however, is more complex since, depending upon the degree of neutralization, a single chain may be terminated by zero, one, or two salt moieties.

Figure 5 shows a striking effect for PBD-Mg where the degree of neutralization was increased from 20% to 100%. This corresponds to an increase in the ion content from 0.47 to 2.33 salt groups per 100 monomer units. In general, the Bragg spacing increased following an S-shaped curve similar to that of a titration curve. In addition, the domain radius and the fluctuation scattering, normalized to the volume fraction of ionic groups, were found to be independent of the degree of neutralization. The zero-order scattering, on the other hand, increased at low ion content levels.

An identical study on PBD-Fe^{3+}, neutralized from 50% to 100%, did not show a change in the d spacing, R_D, or the normalized fluctuation scattering. These results are similar to those for the PBD-Mg at neutralizations greater than 60%.

Although a quantitative interpretation of the data is difficult at this point, it is apparent that a homogeneous network is formed at high levels of neutralization when most of the chain ends are included in the ionic domains.[28]

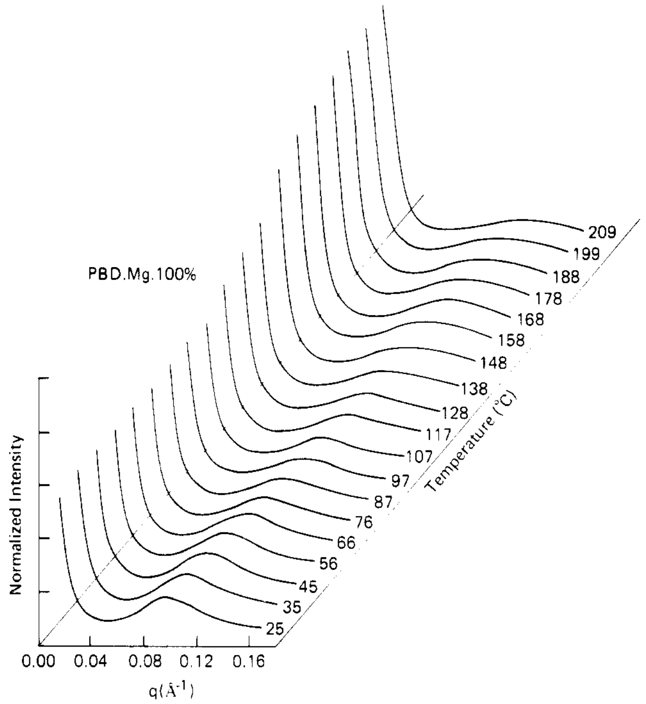

Figure 6. Real-time SAXS for PBD-Mg during a heating of the specimen up to 200 °C at 5 °C/min. Scattering profiles were collected every minute corresponding to a 5 °C temperature increment. The SAXS data were averaged over this interval. The annealing temperature of the specimen was 100 °C.

As the valency of the cation increases, it is possible that homogenization occurs at lower degrees of neutralization. However, the ionic aggregates formed do not depend on the extent of neturalization. Note that a similar effect has been reported[29] for a potassium-neutralized poly(tetramethylene glycol) where the separation distance between domains increased as the degree of neutralization was varied from 50% to 100%. In that case, it was accompanied by a slight decrease in aggregate size.

Temperature. Heating the specimens to 100 °C, the annealing temperature, does not significantly change the scattering profile as shown in Figure 6. Above 100 °C and up to 200 °C, when degradation of the polymer sets in, the zero-order scattering increases, the fluctuation scattering increases, and the distance, given by the peak, increases. The maximum is less intense and much broader but still exists at the highest temperature. These effects are reversible if degradation of the polymer has not occurred. Differential scanning calorimetry studies also show a weak, but distinct, endotherm over the temperature range studied. The domains become smaller and the distribution of separation distances broadens. Some aggregation, however, is still present at 200 °C.

Discussion

One key conclusion of this systematic study of HTP's is that the principal factor governing the morphology of these ionomers is the chain configuration between ionic monomers. The nature of the cation is only of secondary importance. This statement deserves some discussion since it can explain why so many structural models have been proposed.

First, the average distance between domains is determined by the molecular weight of the subchain between domains which adopts a coiled configuration. Indeed, it was found that the distance between ionic domains is of the same order of magnitude as the root mean square end-to-end distance of the chain and increased with molecular weight, obeying a power law that can be approximated by $d \propto \bar{M}_n^{1/2}$. Furthermore, the large swelling ratios observed before disruption of the domains when the specimens were immersed in toluene rules out a fully extended configuration of the chain and points to a chain configuration similar to that of an elastomeric network. This result is in general agreement with theoretical calculations[2,30] predicting only a moderate increase of the radius of gyration of long chains with ionic groups either regularly or randomly spaced along the backbone and spatially confined to aggregates. However, quantitative comparison with the theory can only be obtained from forthcoming neutron scattering experiments with partially deuterated specimens, where the radius of gyration of individual chains can be measured directly. Since the subchains between ionic groups do not necessarily link nearest-neighbor domains or may form loops, the distance between neighboring ionic domains afforded by SAXS is only an indication of the chain configuration.

Second, it was found that if the polydispersity is small, the microphase separation between the ionic and organic moieties is complete. In other words, it is possible to obtain a morphology where very few ionic monomers (or dimers) are dissolved in the organic matrix. Indeed, the ionic and organic phases are separated by a sharp boundary. In comparison to the PBD polymers, the fluctuation scattering is negligible for the PIP polymers, where the molecular weight distribution is narrower. A parallel study of the same carboxylatopolybutadienes by EXAFS (extended X-ray absorption fine structure), investigating the local environment of different cations,[30,34] has shown that the cations are surrounded by a first coordination shell of oxygen atoms, more numerous than for isolated ionic groups, i.e., larger than 4 for a divalent metal, at a distance corresponding to a metal–oxygen bond in model compounds. More importantly, the cations are surrounded by a well-defined second shell of cations. Thus, it was found that most of the cations are included in multiplets characterized by a relatively high degree of local order. The effect of swelling by polar and nonpolar solvents and the different water-uptake behavior of the investigated samples can also be explained by a similar picture.

It is also very likely that the "cross section" of the chain determines the equilibrium size of the domains. In our case, it was found to be only weakly dependent on the cation and on the same order of magnitude whether the backbone was polybutadiene or polyisoprene. Although no systematic study has been done on a wide variety of chains, it is possible to compare our data with those reported recently for two other halato-telechelic polymers. A domain size of 11 Å has been reported for poly(tetramethylene glycol)-K, a chain of similar diameter,[29] whereas polyisobutylene-based sulfonated polymers, having a bulky chain, appeared to contain very small multiplets.[35] In a model where all the chains originate from the surface of the ionic domains, the maximum size will be related to the specific volume of the organic monomers compared with that of the ionic pair.

Ionic aggregation evidenced by the SAXS peak has been found in all the neutralized HTP's down to 0.45% of charged monomers. In the acid form, however, no aggregation was observed. The concept of ionic multiplets, i.e., ionic domains containing a few ionic pairs and no organic monomers, adequately describes the type of aggregation observed here. However, the multiplets are larger than predicted by Eisenberg or Dreyfus. An estimation for PBD-Cu, where EXAFS indicates that the basic building block is a dihydrated copper acetate dimer, shows that a multiplet could contain from 10 to 12 divalent cations.

While a spherical shape has been assumed to derive a domain size from the SAXS data, the exact shape cannot be known. However, no experimental evidence was found in this study to support an extended lamellar configuration. If one takes into account the similarities between the HTP's and block copolymers or micellar systems, the volume ratio of ionic groups to organic monomers of these ionomers would lead to a prediction of spherical domains. Subsequent to the completion of this work, an electron microscopic investigation on thin films of these materials[36] showed the existence of domains, smaller than 20 Å, which appeared spherical, supporting the assumptions made here. However, due to the "crystal-like" nature of these aggregates, it is possible that the domains would appear as small platelets at higher resolution.[37]

Once formed, the ionic aggregates are very stable. Water does not destroy the domains but only solvates the cations, and dissolution in a nonpolar solvent would take days. A critical temperature for dissociation of the aggregates[3] has not been observed up to the temperature at which the polymer degrades. Instead, a gradual, reversible disruption of the ionic domains was observed. No evidence was found to support the formation of clusters, i.e., a further aggregation of several multiplets including organic material.

The absence of higher order reflections, other than a second-order shouldering in the scattering pattern, leads us to believe that each multiplet is surrounded by a correlation hole from which all other ionic domains are excluded. The magnitude of volume is, however, related to the configuration of the chain. The domains are then organized in a liquid-like manner as proposed by Yarusso and Copper.[38] A crystalline order, such as that proposed by Dreyfus,[2] is less likely since it would necessitate very pronounced lattice distortions in order to eliminate the high order Bragg reflections.

It is important to notice that, in this model, the size of the domains is determined by the relative sizes of the organic monomer to that of the ionic group, and the average distance between domains is fixed by the length of the chain. These two conditions are incompatible with a uniform distribution of the domains throughout the specimen. For instance, the distance should vary as $M^{1/3}$ for constant density whereas the end-to-end distance of the chains varies as $M^{1/2}$. Inhomogeneities of a characteristic size much larger than the interdomain distance should exist in all HTP's and could be the origin of the strong forward scattering observed in many ionomers and even stronger in the HTP's. This will be discussed in more detail in a forthcoming paper.

Conclusion

The use of halato-telechelic polymers as model compounds for the more complex ionomers has proven useful in gaining insight into the processes of ion aggregation and in evaluating the relevant parameters that govern the overall morphology of the specimen. The importance of the chain configuration has been clearly demonstrated. If the chain length is well-defined, there is complete microphase separation between the organic monomers and the ionic groups which are incorporated into multiplets. The size of these and, therefore, the functionality of the cross-links are a function of the size of the ionic groups and of the organic monomers. No evidence was found to support the formation of clusters, i.e., the aggregation of several multiplets. In addition, neither critical concentration of ions necessary to form multiplets nor a critical temperature of domain formation was observed.

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Communications to the Editor

Oligomers as Molecular Probes of Orientational Order in Strained Elastomeric Networks

In the past few years deuterium magnetic resonance (^{2}H NMR) has proven to be a valuable technique in the study of orientational order in elastomeric networks created by uniaxial strain. A measure of orientational order is the quadrupolar splitting of the ^{2}H NMR signal of a deuterated probe molecule generated by the orientational field in the strained network. This was first exploited by Deloche and Samulski,[1] who interpreted the quadrupolar splitting of deuterated solvent molecules used as swelling agents in terms of short-range orientational correlations between solvent molcules and polymer segments. The segmental order was probed directly by use of deuterated networks.[2-4] Gronski et al.[3] showed that in addition to the order parameter obtained from the quadrupolar splitting at maximum signal height characterizing the average segmental orientation, additional information can be obtained about the orientational behavior of the chain length distribution in the network by an analysis of the line shape of the ^{2}H NMR signal. The utility of selective deuteration was demonstrated for the case of chemically cross-linked networks[3] and thermoplastic elastomers.[4] Networks selectively deuterated at network junctions showed that chain segments attached to network junctions are oriented to a higher extent than the average. In a recent communication Samulski et al.[6] contrasted the quadrupolar splitting $\Delta\nu_s$ of deuterated solvent pobe molecules and the quadrupolar splitting $\Delta\nu_p$ of deuterated network chains at the same degree of swelling. The former was found to be smaller than the latter, which was explained by the structural dissimilarity between the probe and a hypothetical polymer segment. It was anticipated that $\Delta\nu_s/\Delta\nu_p \rightarrow 1$ if structurally similar molecules, i.e., oligomers of the same structure, were used as probe molecules. Using oligomers of increasing chain length, as the authors suggested, might provide a means of quantifying the ill-defined quantity of the hypothetical segment. In this communication we describe the main results of such an investigation.

The orientation behavior of four oligobutadienes with P_n = 10, 20, 40, and 80 (OB-10, OB-20, OB-40, and OB-80) in strained polybutadiene networks of various cross-link densities at different degrees of swelling was investigated. The oligomers were prepared by anionic polymerization from butadiene deuterated at the CH_2 groups in the 1,4 position and possess about equimolar 1,4 cis/trans structure and ca. 5–11% 1,2 monomer units. The networks were made from anionically prepared precursor chains by

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