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Concentration and Counterion Dependence of Cluster Formation in Sulfonated Polystyrene

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Received June 23, 1983

ABSTRACT: Based on a crystal closest packing approach, models are developed which show that, in carboxylated ionomers, anion packing is determined by the counterion, while in sulfonated ionomers the anion packing is independent of cation. However, in sulfonated ionomers, there is a greater cluster density for divalent than for monovalent cations as a consequence of how the counterion coordinates to the sulfonate ions. SAXS data for the zinc and sodium salts of lightly sulfonated polystyrene (SPS) are analyzed in order to elucidate the cq/a relationship for these materials and to test the proposed model. Results suggest that there is a denser packing in the zinc salts.

Introduction

In the past 10 years several books, reviews, and symposia[1-5] have considered the structure and properties of ionomers. Much of the research on these materials has concentrated on the nature of the ionic cross-link, and evidence for microphase separation of ionic domains has come from a variety of experimental techniques, the most common being small-angle X-ray scattering (SAXS).[6-12] Many studies indicate that there is a certain critical concentration of ionic groups above which properties change, and this concentration is dependent upon the anion and cation used as well as the dielectric constant of the matrix polymer.[13-20]

Lundberg and Makowski[21] and Rigdahl and Eisenberg[22] have concluded from rheological studies that the effect on physical properties is several orders of magnitude stronger for the sulfonate ions than for carboxylate ions. Weiss and Agarwal[23] found that the melt viscosity of a propylene–acrylic acid graft copolymer was higher for the Na^+ than for the Zn^{2+} salts. In related work Navratil and Eisenberg[24] found that for styrene–methacrylic acid ionomers, the rate of stress relaxation was higher for the Ba^{2+} salts than for the Na^+ salts.

Otocka et al.[25] suggested that in mediums of low dielectric constant, such as a hydrocarbon matrix, salts with divalent cations would exist as simple contact ions while monovalent salts would exist as dipole–dipole pairs. It was further suggested that in the case of the monovalent salt the nature of the dipole–dipole attraction would be such that considerable separation could occur while preserving the integrity of the dipole–dipole bond. Otocka, as well as other researchers, predicted that one factor that would influence ionic bonding was the tendency of group 1 cations to six-coordination.

Eisenberg et al.[2] demonstrated that the critical concentration for various counterions could be related if the ratio cq/a, where c is the anion concentration, q is the charge on the cation, and a is the distance separating the centers of charge, is considered. For example, when the glass transition temperature, T_g, was plotted vs. cq/a for various counterions of ethylene–acrylic acid ionomers, the data were collinear. In a similar vein, Gierke, Munn, and Wilson[26] report that the SAXS peak intensity for group 1 cations of Nafion is a linear function of cq/a.

Using the results of past research on model compounds,[27] as well as our own results of SAXS studies of sulfonated polystyrene ionomers, we have developed a conceptual model that accounts for the observed differences in ionomer physical properties for several anions and cations. Schematic representations were developed to model the carboxylate and the sulfonate ions. The cations were considered to be hard spheres of the appropriate ionic radius. The various ways of bonding the anions and cations were considered and plots of SAXS data for the SPS salts were made for each type of bonding as a function of cq/a.

Discussion

The carboxylate anion is planar with only one edge available for bonding to a cation, as shown in Figure 1. Only one bonding length, 0.53 Å from the carbon atom to the midpoint between the oxygen atoms, need be considered. However, there are a number of ways the planar ions can be arranged in layers to coordinate with cations. At worst the ions might be randomly distributed with reference to each other. At best the ions will be equidistant from each other and from the cation.

In Figure 2a a scheme is shown in which the oxygen atoms of the anions are packed in two parallel hexagonally packed layers, with one layer being slightly displaced from the other. The scheme shown in Figure 2b is one in which the hexagonal layers are displaced so that one layer interweaves the other. In Figure 2a a univalent sodium cation fits into the six-coordinated trigonal-bypyramidal hole between the anion layers, as occurs in $NaH(CH_3CO_2)_2$,[27] while in Figure 2b a divalent zinc cation fits into the six-coordinated hole, similar to the structure of $Zn(CH_3CO_2)_2{\cdot}2H_2O$.[27]

Clearly, the array with the small divalent cation is more densely packed as the anions are both closer within a layer and between layers. However, when there is a 1:1 ratio of anions to cations, as in Figure 2a, more anions will have to be shared by cations in order to achieve six-coordination than when the anion to cation ratio is 2:1, as in Figure 2b. Therefore, when the cluster is stressed, more interactions need to be overcome to remove ions from the ionic cluster

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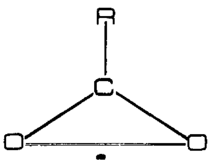

Figure 1. Carboxylate anion.

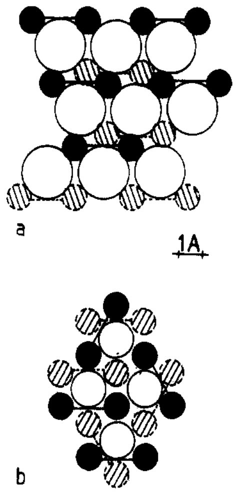

Figure 2. Close packing in carboxylate ionomer cluster: (a) sodium cation, view along bond; (b) zinc cation, view along bond. Small striped circles represent oxygen atoms below the plane of the paper; small dark circles are oxygen atoms above the plane of the paper. Lines connect oxygen atoms that come from the same carboxylate ion.

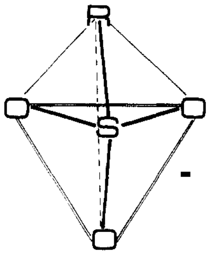

Figure 3. Sulfonate anion.

shown for the monovalent cation in Figure 2a, although the cross-link provided by the individual contact ions in the divalent salt may persist longer than the cross-link formed by dipole–dipole attraction in the monovalent salt. This interpretation is in agreement with experimental results that show that a monovalent Na^+ salt of propylene–acrylic acid has a higher melt viscosity[23] than a divalent Zn^{2+} salt and that the divalent Ba^{2+} salt of styrene–methacrylic acid has a higher rate of stress relaxation than the monovalent Na^+ salt, but a more pronounced rubbery plateau.[24]

Another aspect of the ionic packing schemes presented in Figure 2 concerns how additional ions could be added to the arrays. In Figure 2a the edges contain both uncoordinated anions and cations and thus new ion pairs can be added in virtually any orientation. In Figure 2b the edges contain only anions and thus new ions can be added only if the cation is properly oriented toward the cluster. Thus entropy considerations favor cluster enlargement more for the monovalent than for the divalent cation.

In contrast to the planar carboxylate anion, the sulfonate anion is tetrahedral,[27,28] as shown in Figure 3. This introduces the possibility of one bond length (0.82 Å) if the cation coordinates to the edges of the anion and another bond length (0.47 Å) if the cation coordinates to the face. Figure 4a depicts antiparallel overlapping layers of hexagonally packed anions with monovalent sodium cations fitting into the octahedral holes created by the anion edges; this correlates with the published structure of $Na_2(CH_2(SO_3)_2)$.[27] Figure 4b presents a scheme in which divalent zinc cations share faces between two antiparallel layers of hexagonally packed anions; this model is similar to that for $Zn(CH_3C_6H_4SO_3)_2{\cdot}6H_2O$.[27] Cations in both arrays are six-coordinated. No anions are shared by more than one cation in Figure 4b while a number of oxygen atoms are shared by one or more cations in Figure 4a. As in the case of the carboxylate salts, the array proposed for the monovalent cation has both anions and cations on the edges and new ion pairs can approach in any orientation. The scheme shown in Figure 4b for the divalent cation only presents anions on the edges. In fact, each contact ion pair is a separate unit with a positive center and a negative edge and within a cluster there will be both attractive and repulsive forces. Thus, both steric and energy considerations predict the type of structure shown in Figure 4a for monovalent sulfonate salts. In an EXAFS study of divalent salts of sulfonated polystyrene, Yarusso et al.[29] found each cation to have six oxygen and three cation neighbors; the array depicted in Figure 4b is in accordance with these results and thus is a reasonable structure for the divalent sulfonate salts.

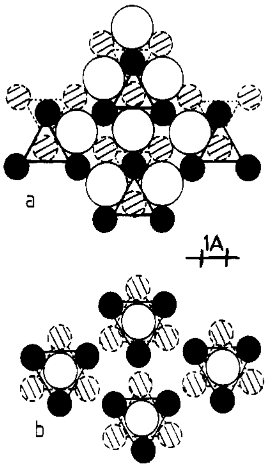

Figure 4. Close packing in sulfonate ionomer cluster: (a) sodium cation, view along bond; (b) zinc cation, view along bond. Small striped circles represent oxygen atoms below the plane of the paper; small dark circles are oxygen atoms above the plane of the paper. Lines connect oxygen atoms that come from the same sulfonate ion.

Table I
Intensity of Na-SPS SAXS Peaks as a Function of cq/a

c	cq/a face a = 1.44 Å	 edge a = 1.79 Å	I/I_e, eu/Å^3
1.38	0.96	0.77	0.06
2.25	1.56	1.26	0.15
3.24	2.25	1.81	0.32
5.5	3.84	3.09	0.77

To test this hypothesis, we considered our previously reported SAXS data on Na-SPS and Zn-SPS.[12] In evaluating SAXS peak intensity as a function of cq/a, we treated the data for values of a corresponding to both face-sharing and edge-sharing coordination. The SAXS data for Na-SPS are presented in Table I and those for Zn-SPS are contained in Table II. The SAXS peak intensity vs. cq/a is plotted in Figure 5 for both salts. As expected, regardless of coordination, intensity increases as cq/a increases.

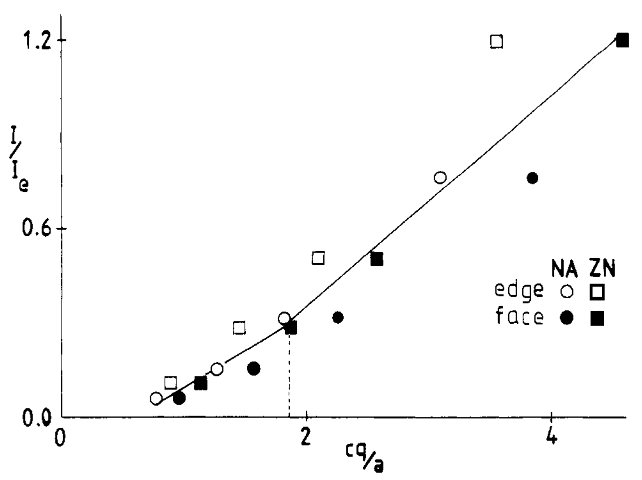

Figure 5. cq/a vs. SAXS intensity for sulfonated polystyrene. Data contained in Tables I and II.

Table II
Intensity of Zn-SPS SAXS Peaks as a Function of cq/a

c	cq/a face a = 2.42 Å	 edge a = 3.12 Å	I/I_e, eu/Å^3
1.38	1.14	0.88	0.11
2.25	1.86	1.44	0.28
3.24	2.68	2.08	0.50
5.53	4.57	3.54	1.20

On the basis of the previous findings of Eisenberg,[2] one expects that the relationship depicted in Figure 5 should be independent of cation, and therefore the data as plotted vs. cq/a should be collinear. In Figure 5 the data plotted for the Na^+ salt in the edge-sharing conformation are collinear with those of the Zn salt in the face-sharing array. This suggests that Figure 4a may represent the microstructure in Na-SPS ionic clusters, while Figure 4b may be indicative of the cluster microstructure in Zn-SPS. If the line defined by these data points is taken to be the accurate cq/a relationship, then it will be noted that this line changes slope at a value of cq/a of about 2.

It is anticipated, based on the degree of packing and the number of cations with which the anion oxygens coordinate, that the monovalent and divalent sulfonate salts will exhibit the same differences in physical properties found in carboxylate salts. While there are some data in the literature that appear to agree with this hypothesis, notably the work described in ref 30 and 31, the agreement is not absolute. In rheological work done in our laboratory the storage modulus (measured with a Rheovibron viscoelastometer at a frequency of 110 Hz) for the Na^+ salt of SPS is higher than that for the Zn^{2+} salt, but, as shown in Figure 6, the rubbery plateau is broader for the divalent salt. A comprehensive study of the effect of the cation on the properties of sulfonate ionomers is clearly warranted in order to evaluate this hypothesis.

Conclusions

In carboxylated ionomers the packing within anion layers is determined by the counterion; a denser packing occurs with a small divalent cation. In sulfonated ionomers the anion packing is independent of the counterion. Small divalent cations appear to share faces between layers while larger monovalent cations share the larger spaces created by the anion edges. However, with both anions the monovalent cation has more interactions with the anions than does the divalent cation. On the basis of models postulated here, SAXS results on two different salts of SPS suggest a critical cq/q value of about 2.0, above which changes in properties may occur.

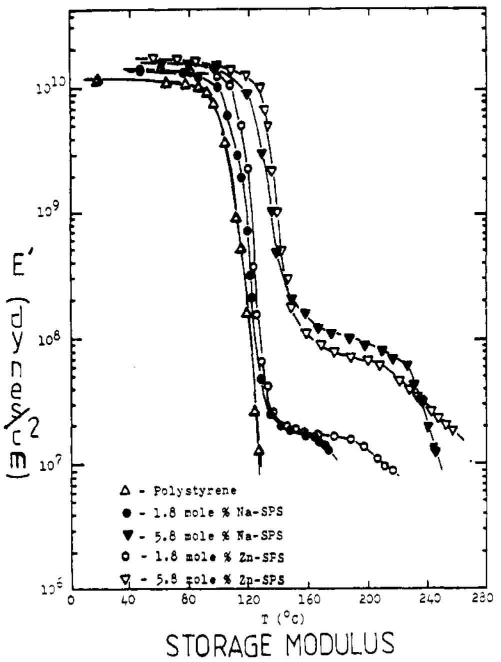

Figure 6. Storage modulus of Na-SPS and Zn-SPS.

Acknowledgment. We thank Dr. J. S. Lin and the staff at Oak Ridge National Laboratory NCSASR for their generous assistance and acknowledge support from the National Science Foundation under Grant No. DMR-8108333. We also express our appreciation to Abner Wang for the dynamic mechanical data.

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Excimer Fluorescence as a Molecular Probe of Polymer Blend Miscibility. 6. Effect of Molecular Weight in Blends of Poly(2-vinylnaphthalene) with Poly(methyl methacrylate)

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Received May 19, 1983

ABSTRACT: Excimer fluorescence is employed to determine the influence of molecular weight and concentration on the miscibility of blends of poly(2-vinylnaphthalene) (P2VN) with poly(methyl methacrylate) (PMMA). Three P2VN guests of molecular weights 21 000, 70 000, and 265 000 and concentrations between 0.3 and 35% are blended by solvent casting from toluene with nine PMMA hosts having molecular weights ranging from 1100 to 350 000. Fluorescence measurements are shown to be more sensitive to the existence of phase separation than either the visual observation of turbidity or the observation of two glass transition temperatures by differential scanning calorimetry. The fluorescence results are used with Flory–Huggins lattice theory to yield a consistent value of the binary interaction parameter of 0.07 ± 0.015 for P2VN/PMMA blends.

Introduction

This report is part of a series of studies on the application of fluorescence techniques to the study of polymer blends.[1-6] Previous work has demonstrated that excimer fluorescence can be used to detect immiscibility in polymer blends at an earlier stage than is possible by measurements of optical clarity[4,5] or differential scanning calorimetry.[5,6] In addition, it has been shown that the simple Flory–Huggins mixing theory could be used to predict the points of immiscibility arising from increases in guest or host molecular weight in blends of poly(2-vinylnaphthalene) (P2VN) with polystyrene (PS).[3] In this paper, the influence of molecular weight is examined for blends of P2VN with poly(methyl methacrylate) (PMMA), which is known to be less miscible than the P2VN/PS series.[1,2]

The first objective of this work is to demonstrate the generality of the method of interpreting excimer fluorescence of blends containing P2VN, which was developed earlier.[6] In so doing we will determine a consistent value of the binary interaction parameter from fluorescence measurements. The second objective is to compare the interaction parameters for P2VN in PS and PMMA extracted from the fluorescence data with those predicted by the regular solution theory of Hildebrand and Scott.[7,8]

The reliability of regular solution theory depends heavily on the accuracy of values of the solubility parameter, δ, which are used to calculate the binary interaction parameter for the blend. In order to obtain δ values which reflect the possibility of specific chemical interactions between guest and host polymers, a separate study has been performed in which δ has been evaluated from intrinsic viscosity measurements of P2VN, PS, and PMMA, each in several classes of solvents.[9] For dilute P2VN/PS blends, the appropriate values should be $\delta_{\mathrm{P2VN}} = 9.5 \pm 0.2$ cal$^{1/2}$/cm$^{3/2}$ and $\delta_{\mathrm{PS}} = 9.20 \pm 0.05$ cal$^{1/2}$/cm$^{3/2}$. For dilute P2VN/PMMA blends, we have proposed that $\delta_{\mathrm{P2VN}} = 9.0 \pm 0.2$ cal$^{1/2}$/cm$^{3/2}$ and $\delta_{\mathrm{PMMA}} = 9.4 \pm 0.2$ cal$^{1/2}$/cm$^{3/2}$, where the change in the effective solubility parameter of P2VN results from the change in matrix from an aromatic to an ester character. In this work, the values of χ_{AB} for P2VN/PS and P2VN/PMMA predicted by the intrinsic viscosity results as well as those predicted by a molar group additivity scheme are compared to the values determined from the fluorescence measurements.

Table I
Description of Commercial Polymers

sample(MW)	$M_{\mathrm{w}}/M_{\mathrm{n}}$	synthesis	supplier	ID or lot no.
PMMA(1100)[a]	1.1	*c*	*e*	QR-537
PMMA(2500)[a]	1.1	*c*	*e*	QR-635
PMMA(12 000)[a]		*d*	*f*	02
PMMA(20 000)[a]		*d*	*e*	Acryloid A-101
PMMA(54 000)[b]	1.07	*c*	*g*	
PMMA(79 000)[b]	1.06	*c*	*g*	
PMMA(92 000)[b]	1.06	*c*	*g*	
PMMA(180 000)[b]	1.1	*c*	*g*	
PMMA(350 000)[b]	1.15	*c*	*g*	

[a] Weight-average molecular weight. [b] Number-average molecular weight. [c] Anionic synthesis. [d] Free radical synthesis. [e] Experimental samples were provided by Dr. D. J. McDonald, Rohm and Haas Co. [f] Scientific Polymer Products, catalog no. 424. [g] Pressure Chemical Co.

Experimental Section

The PS(2200), P2VN(21 000), P2VN(70 000), and P2VN(265 000) samples have been described previously.[3] The PMMA samples, having molecular weights ranging from 1100 to 350 000, are described in detail in Table I. The tacticity of the PMMA samples is unknown, but we have no reason to believe that there

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