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Aggregation of Ion Pairs in Sodium Poly(styrenesulfonate) Ionomers: Theory and Experiment

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ABSTRACT: Theory of the effect of ion-pair clustering on chain dimensions was compared with mean-square radii of gyration determined on poly(styrenesulfonic acid) ionomers by small-angle neutron scattering (SANS). Reasonable agreement between theory and experiment was obtained by setting the surface energy of cluster formation (the only arbitrary parameter) equal to 8.9 kcal/mol of ion pairs. Since theory predicted more ion pairs per cluster than could be accommodated in spherical clusters, lamellar cluster formation was assumed. Theory predicted about 15 and 12 ion pairs per cluster for polymer containing 1.9 and 8.5 mol % ionic repeat units, respectively. The data suggest, however, that the clusters themselves may aggregate to form higher order structures for ionic concentrations greater than about 5–6 mol %. The theory was also compared with results from SANS chain dimension measurements on the acid precursor of the 1.9 mol% ionomer. Predictions of chain extension due to carboxyl–carboxyl hydrogen bonding were in good agreement with the reported value for the polymer if about 50% of the carboxyl groups participate in hydrogen bonding. The reported mean-square radius of gyration was not, however, known to sufficient accuracy to offer a critical test of the theory.

Introduction

An overwhelming body of experimental evidence indicates that there is aggregation of ion pairs in ionomers.[1] In spite of all of this evidence, however, there is still no clear picture of the nature of the aggregates. In this paper we suggest that measurements of chain dimensions by small-angle neutron scattering (SANS) interpreted in terms of recent theory will lend further insight to the nature of ionomer structure. The arguments will be illustrated by results from recent measurements of neutron scattering from a set of sodium poly(styrenesulfonate) ionomers prepared from polystyrene of 1.0×10^5 molecular weight.[2] Ion content varied from 1.9 to 8.5 mol %. Results were also reported for scattering experiments on a 1.9 mol % unneutralized acid sample. Polymer preparation and characterization and the scattering experiments are described in detail in a previous paper.[2]

Results of the neutron scattering experiments were incontrovertible; the *z*-average radius of gyration of the polymer molecules increased monotonically with increasing ion content. Although qualitative arguments were given associating this phenomenon with ion-pair association,[2] more detailed interpretation requires a theory framed in terms of molecular parameters that are, at least in principle, determinable from independent experiments. One of us recently published such a theory[3] based on the statistical mechanics of chain-like molecules and energy considerations of ionic interactions introduced by Eisenberg.[4] Statistical considerations alone indicate that clustering of ion pairs should indeed result in extension of the chain-like molecules, and a simple model (to be described later) gives a simple closed-form expression for chain extension as a function of the fraction of repeat units participating in cluster formation, the number of repeat units in each cluster, polymer concentration, and the statistics of the unperturbed polymer chains. By extending the theory to include entropy effects and a simple model for energy of cluster formation, the analysis gives a prediction of chain extension and number of repeat units per cluster as a function of one arbitrary parameter—the change in surface energy of a cluster associated with the addition of one repeat unit.

The theory was formulated for an assembly of monodisperse chains. Since the heterodispersity indices of the polymers used in the experiments were 1.05–1.06, it is reasonable to assume that any serious disagreement be-

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Table I
Chain Expansion of Sodium Poly(styrenesulfonate) Ionomers Prepared from Polymer of 1.00×10^5 Molecular Weight

mol % of sulfonate	$\langle S^2\rangle^{1/2}$, Å	α_S	Z
0	85.5 ± 1.4		
1.9 (acid)	92.0 ± 4.0	1.08 ± 0.02	0.12 ± 0.04
1.9 (salt)	106.7 ± 0.8	1.248 ± 0.022	0.56 ± 0.04
4.2 (salt)	110.7 ± 3.4	1.295 ± 0.045	0.68 ± 0.09
8.5 (salt)	122.7 ± 6.6	1.433 ± 0.080	1.06 ± 0.16

tween theory and the results of the SANS experiments could not be attributed to molecular weight distribution. We thus consider the polymer to be monodisperse and express the chain dimensions in terms of an expansion factor α_S

$$\alpha_S^2 = \langle S^2\rangle / \langle S^2\rangle_0 \tag{1}$$

where $\langle S^2\rangle$ and $\langle S^2\rangle_0$ are the mean-square radii of gyration of the ionomer or acid precursor and the unsubstituted polymer of the same degree of polymerization. Degree of substitution, radii of gyration, and expansion factors of the polymers studied by SANS are given in Table I.

Theory[3] is developed in terms of a different expansion factor, α_L, defined by

$$\alpha_L^2 = \langle L^2\rangle / \langle L^2\rangle_0 \tag{2}$$

where $\langle L^2\rangle$ and $\langle L^2\rangle_0$ are the mean-square lengths of the vectors connecting ionic or acid groups and the analogous repeat units in the unsubstituted polymer. It is demonstrated in the Appendix, however, that the two expansion factors are identical for flexible polymer molecules of sufficiently high molecular weight—which is the case for the polymers considered in this paper. It is thus appropriate to write

$$\alpha_S^2 = \alpha_L^2 \tag{3}$$

Comparing Theory and Experiment

Theory. The theory[3] describing the effect on chain dimensions of aggregation of ionic or acid groups into clusters is based on a number of assumptions: (1) Repeat units that participate in aggregation are equally spaced along the chain backbone. (2) Gaussian statistics apply to the subchains connecting substituted repeat units as well as to entire chainlike molecules. (3) Every aggregate contains the same number of interacting repeat units. (4) Each aggregate is formed only from those interacting repeat units which would be near neighbors in the absence of aggregate formation.

The distribution function for the x component of the vector connecting two contiguous repeat carrying ion pairs on an unperturbed chain is given by

$$W(x) = (\beta/\pi^{1/2}) \exp(-\beta^2 x^2) \tag{4}$$

It was further assumed that the aggregates lie within the lattice volumes of a cubic lattice of unit cell length l, which is given by

$$l = mM_0/CN_A f \tag{5}$$

where m is the number of repeat units per aggregate, M_0 is the molecular weight of an unsubstituted repeat unit, C is the concentration of polymer (for bulk polymer, C is replaced by the density ρ), N_A is Avogadro's number, and f is the fraction of repeat units that are participating in aggregate formation. This lattice model implies that each cluster is centered at the same position in each lattice volume. It is not assumed, however, that each cluster is oriented in the same way relative to the lattice.

Detailed analytical and numerical analysis[5] of the theoretical formulation[3] shows that

$$\alpha^2 = F_1(\beta l) + (\psi/6)f^{2/3}F_2(\beta l) \tag{6}$$

where

$$\begin{aligned} F_1(\beta l) &= 1 + (\beta l)^2/3 \qquad F_1 \le 1.73 \\ &= (2/\pi^{1/2})(\beta l) \qquad F_1 > 1.73 \end{aligned} \tag{7}$$

and

$$F_2(\beta l) = 2(\beta l)^2 \tag{8}$$

The term $F_1(\beta l)$ in eq 6 is the contribution to α^2 from localizing each repeat unit carrying an ion pair at a given point, i.e., formation of what we might call primitive point clusters. The term $(\psi/6)f^{2/3}F_2(\beta l)$ is the addition contribution to α^2 associated with the notion that any repeat unit carrying an ion pair would have an equal probability of being located anywhere within the volume occupied by its cluster. The parameter ψ is determined by the shape of the clusters and is equal to 0.770 for spheres, 1.00 for oriented cubes, and is greater than 1.00 for asymmetric aggregates such as lamellae. The second term is negligible for sufficiently small f; when this is the case the clusters are adequately described as point cluster.

Analysis of the SANS data of sodium poly(styrenesulfonate) ionomers[3] indicates that $F_1 < 1.73$ for all cases. The second term in eq 6 is small but not negligible. It is thus possible to write eq 6 in the following form which best illustrates the effect of molecular parameters:

$$Z \equiv \alpha^2 - 1 = \phi f^{1/3} m^{2/3}(1 + \psi f^{2/3}) \tag{9}$$

where

$$\phi = (\rho N_A)^{-2/3} M_0^{-1/3} (2\kappa)^{-1} \tag{10}$$

The parameter κ is the proportionality factor between molecular weight and mean-square end-to-end distance of an assembly of the unsubstituted polymer molecules.

Equation 6 (or eq 9) predicts the value of α one would observe experimentally if a fraction of repeat units f (presumably carrying ion pairs) were to associate into m repeat units per aggregate with a given geometry. It does not, of course, predict m and α as functions of f. At least one example can, however, be analyzed by use of eq 6 (or eq 9) alone—dimerization of repeat units. If there were reason to believe that a fraction f of the repeat units all exist as dimers but there is no further aggregation, α as a function of f can be predicted from eq 9 by setting $m = 2$ and estimating ψ for the dimers. This would presumably not be the case for ionomers, but would likely apply to their acid precursors.

In general, however, theory must be developed beyond an expression for α as a function of m and f (for given ψ) to give it predictive capability. This was done by using eq 9 along with a model for free energy of cluster formation which incorporates molecular parameters. Rubber elasticity theory was used to quantify conformational entropy decrease with aggregation of repeat units. An additional entropy decrease accompanying localization of repeat units during aggregation was included as well as an energy of aggregation which was a function of aggregate geometry. The three terms were then added to give the free energy change associated with aggregation of repeat units, and the minimum free energy was taken as the equilibrium state.

It was shown that for both spherical and lamellar aggregates the controlling energy was the change in surface energy in adding an additional ion pair to the cluster. In dimensionless form, the surface energy was denoted as θ_2;

in energy units per mole of ion pairs it is expressed as θ_2RT. Given the cluster geometry, the theory then gives both m and α as functions of f with one adjustable parameter, θ_2, which, in principle, could be determined independently.

Precision and Accuracy of Experimental Results. Before comparing theoretical predictions with experimental results, it is useful to look more carefully at the uncertainty of the radius of gyration measurements reported for the polymers considered in this paper.[3] The errors reported by Earnest et al. in their Table II were not all calculated on the same basis. Data for experiments with unmodified polystyrene and one experiment with an acid polymer containing 1.9 mol % sulfonic acid were reduced by linear regression. Errors reported for these $\langle S^2\rangle^{1/2}$ determinations were obtained from the standard deviation of the slopes of the Zimm plots. Errors quoted for the sodium salts, however, are maximum errors that could be consistent with the scattering data. It is useful here to put all the errors on as common a basis as possible. There is, of course, less uncertainty in $\langle S^2\rangle^{1/2}$ for the unsubstituted polymer than reflected in Table II of Earnest et al.[2]

Two scattering experiments were performed giving root-mean-square radii of gyration of 84 and 87 Å with an expected standard deviation of 2 Å for each (from the confidence level of the slopes). The inference is thus that, for this polymer, $\langle S^2\rangle^{1/2} = 85.5 \pm 1.4$ Å to a 70% confidence level. Since only one scattering experiment was performed on the 1.9 mol % acid polymer, we must accept the rather uncertain $\langle S^2\rangle^{1/2}$ value of 92 ± 4 Å at the same confidence interval. All of the ionomer samples were, however, run in triplicate, so the maximum errors reported previously can be disregarded and errors at the 70% confidence interval calculated by the usual statistical treatment. The results are given in Table I.

Application of aggregation theory requires the parameter κ (eq 10). Since $\langle L^2\rangle_0 = 6\langle S^2\rangle_0$ for unsubstituted unperturbed polymers, we could use the SANS measurements to determine κ. The measure of $\langle S^2\rangle_0^{1/2}$ for the unsubstituted polymer, 85.5 ± 1.4 Å, is in good agreement with the value of 87 Å reported by Benoit et al.[6] Root-mean-square radii of gyration of polystyrene of the same molecular weight in Θ solvents are 86.7 and 88.4 Å at 20 and 100 °C, respectively.[7] Good agreement between the two SANS experiments and the 20 °C solution measurements notwithstanding, it will be argued that the SANS measurements at 20 °C actually reflect unperturbed chain dimension near the glass transition, or about 100 °C. The fact that the SANS measurements of $\langle S^2\rangle^{1/2}$ would then be 1.5–3.3% lower than those predicted from Θ solvent measurements hardly does violence either to the concept that conformational statistics in bulk are the same as in Θ solvents at the same temperature or to the accuracy with which any of the experimental data are determined. But because of the difference, which may easily be due to calibration of scattering equipment, we elected to take the Θ solvent value at 100 °C, $\langle S^2\rangle^{1/2} = 88.4$ Å, in determining κ. This, along with a density of 1.05 g/cm^3 gives a value of ϕ of 0.318.

Chain Dimensions of Acid Precursor. It is reasonable to assume that the sulfonic acid groups in the precursor for the sodium sulfonate ionomers would be highly dimerized, and theory predicts that dimerization would effect chain extension. SANS experiments on the precursor containing 1.9 mol % sulfonic acid groups does indeed show such an effect; $\alpha = 1.06 \pm 0.02$ or $Z = 0.12 \pm 0.04$.

Chain expansion is predicted by eq 9 by setting $m = 2$ and picking suitable values for f and ψ. If all of the sulfonic acid groups were dimerized f would equal 0.019; we have, however, considered the possibility that only 20–80% of the acid groups participate in dimer formation. We have not yet calculated ψ from the geometry of a sulfonic acid dimer, but it would very likely be between 0.770 for spheres and 1.26 for rectangular parallelepipeds with an aspect ratio of 2. All of these values were used to estimate Z from eq 9, and the results are shown in Table II.

Table II
Predicted Expansion of Chains in Styrene-Styrenesulfonic Acid Copolymer with 1.9 mol % Acid Groups

		Z from theory^b	
%SAGD^a	f	$\psi = 0.770$	$\psi = 1.26$
100	0.019	0.14	0.15
80	0.015	0.13	0.13
60	0.011	0.12	0.12
40	0.0076	0.10	0.10
20	0.0038	0.080	0.081

[a] %SAGD = percent of sulfonic acid groups dimerized.
[b] Z from SANS = 0.12 ± 0.04.

The calculated values of Z are insensitive to the values of both f and ψ over the ranges selected. One is tempted to assert that the theory is in good agreement with experiment for dimerization of acid groups. Indeed, if the theory is a reasonable description of the dimerization process one is even tempted to conclude that comparing theoretical and experimental expansion factors suggests that about 60% of the acid groups are dimerized. Considering the error in the experimental value of Z, it is, however, difficult to quantify these statements.

One cannot discount the possibility that aggregates of more than two sulfonic acid groups might be present in the precursor polymer. If, then, we assume that the average number of sulfonic acid groups per aggregate is 3, 4, or 6, the theoretical prediction of Z would be obtained by multiplying the values in Table II by 1.31, 1.59, and 2.08, respectively. If such higher order aggregates are, in fact, present in the precursor polymer, the experimental value of Z would be substantially smaller than the value predicted by theory. Additional SANS data and independent physical chemical evidence for the nature of the aggregates of sulfonic acid groups in the precursor polymer would be required for a critical test of the theory.

Chain Dimensions of Sodium Poly(styrenesulfonate) Ionomers. Table I lists the expansion factors and values of Z for the sodium poly(styrenesulfonate) ionomers, and Figure 1 shows Z as a function of f. Since it is assumed that all ion pairs participate in aggregate formation, f is taken equal to 0.019, 0.042, and 0.085. Figure 1 also shows theoretical predictions of Z as a function of f. The asymmetry factor ψ is taken as 1.0, corresponding to nearly cubic lamellar aggregates. Curves are shown for surface energies of cluster formation of $\theta_2 = 10$, 12, and 15. The numbers next to the small solid points on the theoretical curves represent the closest whole number of ion pairs per cluster computed from theory at those points.

Interpretation of the results requires consideration of sample preparation. Films for the SANS experiments were cooled slowly from 150 °C to room temperature; in a few instances they were annealed at 133 °C for 20 h before cooling. Identical SANS results were obtained with both treatments. As long as the temperature is sufficiently above the glass transition, the number of ion pairs per cluster may change as the polymer films are cooled. Indeed, the number of ion pairs per cluster may or may not remain at its equilibrium value during cooling, depending upon how rapidly the temperature is decreased. As the

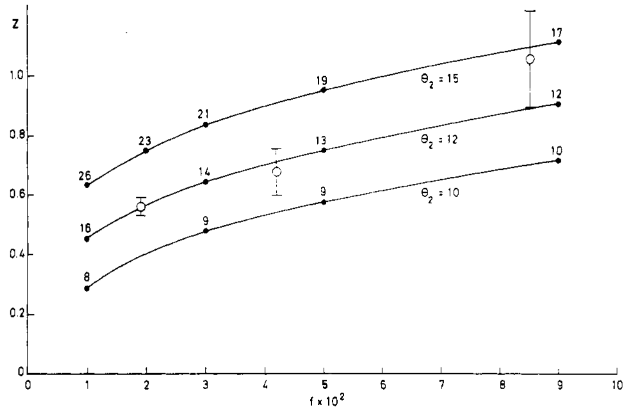

Figure 1. Chain expansion as measured by $Z = \alpha^2 - 1$ as a function of fraction of ionic repeat units for sodium poly(styrenesulfonate) ionomer. The open circles are experimental values and the error bars represent a 70% confidence interval. The curves show theoretical predictions for lamellar aggregates with dimensionless surface energies θ_2 of 10, 12, and 15. Numbers next to the small, filled circles on the theoretical curves represent the predicted nearest whole number of ion pairs per aggregate for various values of f and θ_2.

films are cooled to, or slightly below, their glass transitions, however, one would expect long-range reorganizations to cease. The structure of the ion-pair clusters and chain extension at room temperature, where most of the SANS experiments were done, would thus actually reflect equilibrium values near the glass transitions, i.e., about 100 °C. Given this premise, the values of θ_2 taken for the theoretical curves would thus correspond to 7.4, 8.9, and 11.1 kcal/mol of ion pairs. These values are quite reasonable for the dipole–dipole interaction being considered.

The radius of gyration of the ionomer containing 4.2% sodium salt was measured both at room temperature and 160 °C with nearly identical results. If we take θ_2 for this polymer to be 12.0 at 100 °C, the value of θ_2 is 10.3 at the higher temperature. Figure 1 shows that this change in temperature corresponds to a change in the theoretical prediction of Z that is just within the experimental accuracy. It is not surprising, therefore, that little difference in chain dimensions was detected at the two temperatures. We suggest, however, that repeated measurements (with appropriate statistical treatment) would document a small decrease of α^2 with increasing temperature.

We should like to call special attention to the experimental point for $f = 0.85$ in Figure 1. On the one hand, considering the experimental error inherent in the SANS experiment, it could easily belong with the other two experimental points in scattering about the theoretical curve for $\theta_2 = 12$ and correspond to about 12 ion pairs per aggregate. On the other hand, it is tempting to argue that Z increases faster with f than predicted by theory for $f >$ 0.05 or 0.06. Eisenberg has shown that there is evidence for a change in the nature of ion-pair aggregation in polystyrene sodium carboxylate ionomers above about 4 mol % salt content. Possibly, the same applies to the sulfonate ionomers. Following Eisenberg's arguments, we suggest that, in the lower concentration regime, the clusters consist mainly of multiplets—spherical or lamellar aggregates as described in this paper and by theory.[3] At the higher concentrations, however, the dipole–dipole interactions between clusters (multiplets) might induce ordering of the clusters themselves. Whether or not this effect should be considered as formation of well-defined higher level clusters—clusters of multiplets as described by Eisenberg—or less well-defined structure such as association of solute molecules in liquid solutions is not clear. In either case, however, the higher level structure would increase chain extension beyond that predicted by theory.

Some insight into the nature of the proposed higher level structure can be gained by considering the geometric factors involved. For $f = 0.085$ and $m = 12$, the lattice distance given by eq 2 is 28.5 Å. In addition, one can estimate the length of an edge of one of the (hypothetical) cubic lamellar clusters. On the basis of handbook values of molecular and ionic volumes and assuming that the $SO_3^-\cdots Na^+$ ion pairs pack with the same efficiency in clusters as they do in the bisulfate crystal, the volume occupied by 12 ion pairs is estimated to be 8.3×10^{-22} cm³. This corresponds to lamellar clusters of 9.4 Å on each edge. We thus find that, for $f = 0.085$ and $m = 12$, l is only 3 times the edge length of the lamellar clusters. Considering the relative proximity of the clusters, it would therefore not be surprising if they did aggregate, at least to some extent, into higher order structures.

Appendix

α_S vs. α_L. It is well-known that the conformational statistics of flexible chain-like molecules of sufficiently high molecular weight can be formulated in terms of the random-flight model. According to this model, the backbone is thought of as being made up of a set of contiguous vectors, sometimes referred to as statistical segments, with the mass of the molecule located at the junctions of the vectors. If a linear or branched molecular chain is divided up into n statistical segments, its mass would then be thought of as being equally divided between the $n + 1$ points at the junctions. The mean square of the x-component of the end-to-end distance of the ith statistical segment is written $\langle x_i^2 \rangle$, but since they are all assumed to be characterized by the same distribution function, all $\langle x_i^2 \rangle$ are equal and are simply denoted as $\langle x^2 \rangle$. For most purposes the components of the statistical segments are assumed to obey Gaussian statistics, and for Θ conditions or bulk polymer

$$\langle X^2 \rangle_0 = n \langle x^2 \rangle_0 \tag{A-1}$$

where $\langle X^2 \rangle_0$ is the unperturbed mean square of the x-component of the end-to-end distance vector. Furthermore

$$\langle S_x^2 \rangle_0 = (1/6) \langle X^2 \rangle_0 = (n/6) \langle x^2 \rangle_0 \tag{A-2}$$

where $\langle S_x^2 \rangle_0$ is the mean square of the x-component of the radius of gyration, i.e.

$$\langle S^2 \rangle = \langle S_x^2 \rangle + \langle S_y^2 \rangle + \langle S_z^2 \rangle \tag{A-3}$$

For many problems in the statistical mechanics of chain molecules, the three orthoginal directions are indistinguishable, and one can write

$$\langle S^2 \rangle = 3 \langle S_x^2 \rangle \tag{A-4}$$

In order to compare the conformational statistics of ionomers and acid precursors with those for unsubstituted polymer, we will define the statistical segments as the vectors connecting the repeat units bearing the acid or salt group for the substituted polymer and the analogous repeat units for the unsubstituted polymer. It has already been shown that if the ion pairs undergo aggregation the statistical segments deviate from Gaussian statistics.[3] Nonetheless, regardless of the distribution of the x_i, one can write the following expression for an assembly of monodisperse chains:[8,9]

$$(n + 1)^2 S_x^2 = \mathbf{x}^{\mathrm{T}} \mathbf{F} \mathbf{x} \tag{A-5}$$

where $\mathbf{F}$ is an nXn symmetric matrix with elements that depend upon the branching (if any) and $\mathbf{x}$ is an nth order column matrix with elements x_i. It is thus always possible to effect an orthoginal transformation

$$\mathbf{x} = \mathbf{B}\eta \tag{A-6}$$

to a set of normal coordinates η_i and express eq A-5 as

$$(n + 1)^2 S_x^2 = \eta^{\mathrm{T}}\lambda\eta \tag{A-7}$$

where λ is a diagonal matrix given by

$$\lambda = \mathbf{B}^{\mathrm{T}}\mathbf{F}\mathbf{B} \tag{A-8}$$

Equation A-7 then can be written

$$(n + 1)^2\langle S_x^2\rangle = \sum_{i=1}^{n}\lambda_i\langle\eta_i^2\rangle \tag{A-9}$$

Determining $\langle S_x^2\rangle$ is thus reduced to diagonalizing F and finding the values of $\langle\eta_i^2\rangle$ from the distribution function for the x_i or its moments. Since

$$\eta_i = \sum_{i=1}^{n} b_{ji}x_i \tag{A-10}$$

one can use the moment theorem[10] to find $\langle\eta_i^2\rangle$. The result is

$$\langle\eta_i^2\rangle = \sum_{j=1}^{n} b_{ij}(\langle x_j^2\rangle - \langle x_j\rangle^2) - [\sum_{j=1}^{n} b_{ij}\langle x_j\rangle]^2 \tag{A-11}$$

But since all $\langle x\rangle = 0$, all the $\langle x_j^2\rangle$ are equal, and

$$\sum_{j=1}^{n} b_{ij}^2 = 1 \tag{A-12}$$

Equation A-11 reduces to

$$\langle\eta_i^2\rangle = \langle x^2\rangle \tag{A-13}$$

regardless of the distribution of the x_j.

Equation A-9 then becomes

$$\langle S_x^2\rangle = (n + 1)^{-2}\langle x^2\rangle\sum_{i=1}^{n}\lambda_i \tag{A-14}$$

or

$$\langle S^2\rangle = 3(n + 1)^{-2}\langle x^2\rangle\sum_{i=1}^{n}\lambda_i \tag{A-15}$$

For the unsubstituted, unperturbed chain

$$\langle S^2\rangle_0 = 3(n + 1)^{-2}\langle x^2\rangle_0\sum_{i=1}^{n}\lambda_i \tag{A-16}$$

or

$$\alpha_S^2 = \langle x^2\rangle/\langle x^2\rangle_0 = \alpha_L^2 \tag{A-17}$$

For this type of perturbation from random-flight statistics the expansion factors for radius of gyration and end-to-end distance are identical. The treatment that leads to eq A-17 should *not* be confused with the classical excluded volume problem for chains in dilute solution. In that case the two expansion factors are not equal. The distinction between the two examples in clear; eq A-17 applies when only the ends of the statistical segments (located at the ionic or acid groups) interact with each other and are moved from their (otherwise) equilibrium positions to allow for aggregate formation. Within the framework of the same model, the excluded volume problem deals with intramolecular interaction among all of the $n + 1$ masses and their environment.

Equation A-17 should be an adequate description of the polymers considered in this paper. In its development, however, it was tacitly assumed that the ionomer molecules were terminated with ionic groups since two of the $n + 1$ masses terminate linear chains in the statistical-segment model. This would not be the case for real ionomers or their acid precursors. Indeed most of these chain ends would not be terminated by substituted groups. One should thus correct eq A-17 for a chain-end effect not unlike that for rubber elasticity. It is easy to show, however, that the chain-end correction is negligible for the high molecular weight polymers used in experiments discussed here.[2]

In addition, applying the statistical-segment model implies that the ionic groups are equally spaced along the backbone—indeed the theory of cluster formation is formulated on that same assumption.[3] At present we offer no suggestion as to the seriousness of this assumption, either in the adequacy of eq A-17 or with respect to the theory of cluster formation itself.[3]

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