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Cluster Formation and Chain Extension in Ionomers

Emily Squires and Paul Painter*

Polymer Science Program, The Pennsylvania State University, University Park, Pennsylvania 16802

Stephen Howe

Department of Chemistry, Stanford University, Stanford, California 94305.

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ABSTRACT: Previous theoretical studies of ionomers have been largely concerned with cluster formation and predicted average sizes for these aggregates. Here we will describe a model that is capable of predicting the equilibrium distribution of cluster sizes. In the course of this work we reassessed the assumptions underlying various theoretical approaches and found various problems. The most important of these concerns the use of a chain extension term. We will argue that for ionomers with a truly random distribution of clusters, linked by subchains that obey Gaussian statistics, there is no chain extension term.

The nature and extent of ion association in ionomers remains an intriguing and important question. A number of models have been proposed, based largely on experimental (mainly scattering) studies.[1] Theoretical descriptions of these systems have not been as common, resting, until fairly recently, on the seminal analysis published by Eisenberg in 1970.[2] In this, and in most subsequent theoretical work, a balance between the energy and the entropy of ion association provides a thermodynamic conceptual framework. The minimization of the free energy of the system then allows the prediction of an average ion aggregate size.

Eisenberg introduced the terms multiplets and clusters, the former being closest contact ion aggregates while the latter are a result of clustering of these multiplets into domains that must also include (for steric reasons) hydrocarbon chain segments. It was assumed that the energy of association originates in dipole rather than electrostatic interactions and that the aggregation of ionic species results in chains extending or contracting from their most probable conformations. This generates a temperature-dependent elastic force that opposes the aggregation process. Subsequently, Forsman[3,4] made the important observation that an entropy of localization (or association) term must also be considered when expressions for the free energy are constructed. There have been other theoretical studies, by Datye et al.[5,6] and Dreyfus,[7] but these have been largely concerned with a more detailed formulation of an electrostatic energy term and the subsequent derivation of a model describing the arrangement of ionic species in a cluster.

Studies of ionomers in this laboratory have until now been concerned with the characterization of ethylene–methacrylic acid polymers using FTIR.[7,8] The spectroscopic data was consistent with the presence of relatively small (3–4 ion pairs), highly organized aggregates, in agreement with a SAXS study by Yarusso and Cooper.[10] In sulfonated polystyrene ionomers, however, these authors calculated that there were some 16–18 ion pairs per cluster, in broad agreement with most of the theoretical work mentioned above. Furthermore, these theories predict an average cluster size; in reality there is an equilibrium distribution of sizes. Accordingly, we reexamined ion clustering in ionomers using a simple statistical mechanical scheme so as to obtain results in terms of a distribution. In the process, we considered the chain extension term prevalent in most ionomer theories and found no justification for its existence. The experimental evidence for chain extension obtained from neutron scattering studies is conflicting[11-13] but (as we shall see) can be explained in a satisfactory manner when the effective chain size "seen" in neutron scattering experiments is considered.

This paper considers the case against chain extension first by showing why some of the previous theories predict it, second by presenting an analogy between ionomers and elastomeric networks, and third by considering the chain statistics in a short mathematical treatment. This is followed by a statistical treatment of the association entropy and energy involved in ionic aggregation in order to derive the equilibrium distribution of cluster sizes. We will not maintain Eisenbergs distinction between multiplets and clusters but simply define ionic aggregates as "clusters".

Chain Extension

Looked at in a certain way, it would seem obvious that end-to-end distances (between ionic units or cross-link points) would change as a function of aggregation. If we imagine that the aggregates are distributed on a lattice, with chains connecting only nearest-neighbor multiplets, then as the degree of aggregation or number of ionic units in each cluster increases, the average distance between aggregates, or end-to-end distance between cross-link points, should also increase. This type of argument is similar to that advanced by Eisenberg[2] and seems to have been implicitly accepted in subsequent theoretical work.[3-7] (Dreyfus[7] did calculate that the ratio of the distance between clusters to the end-to-end distance is a rather flat function in the "useful" range of concentration of charged monomer units, however. He concluded that the chains are extended, but not excessively so, and went on to discuss various ways in which the system could decrease the tension.)

In some approaches, then, the conceptual basis for a chain extension term is a result of placing the aggregates on some sort of lattice, with chains connecting only nearest-neighbor multiplets (or clusters). Although it can be assumed that such a lattice is "disordered", with a distribution of distances between lattice points, just the fact that subchains are restricted to linking adjacent points leads to a bias in the argument and the subsequent derivation of a chain extension term. An alternative conceptual framework is that of a completely random system, where the process of aggregation would be analogous to cross-linking and network formation in polymers that have specific multifunctional cross-link points. Flory[15,16] argues that the formation of elastic networks does not change the distribution of chain end-to-end distances and makes the important distinction between topological neighbors, directly connected by one elementary chain, and spatial

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neighbors, connected by a longer path in the network. Neutron scattering studies seem to confirm Flory's view.[17,18]

We believe these points are qualitatively persuasive, but to make our case in a more compelling fashion the detailed mathematical arguments for chain extension advanced by Forsman[3,4] have to be examined, particularly as his predictions are in apparent agreement with a neutron scattering study.[12,13] Forsman compares the subchains in an ionomer to those in an unperturbed system, where they are free to assume a normal Gaussian-type distribution. The two ends of each subchain are assumed to be trapped within lattice volumes l^3 composed of s cells of size d along each side. The key assumption is that l is very small compared to the root mean square end-to-end distanct, so that, as Forsman says, "the distribution function $W_0(x)$ would vary only negligibly over a distance equal to l".

Upon cluster formation, the x components of two ends of a subchain are assumed to shift by amounts p and q, respectively. Because the chain ends are trapped inside a small volume, there is a distribution of net changes in end-to-end distances from permuting the random shifts of each of the chain ends. Forsman sets up a matrix of possible shifts that has s diagonal terms and shows that the distribution of shifts is s for $(p - q)$, $(s - 1)$ for $(p - q) \pm 1$, $(s - 2)$ for $(p - q) \pm 2$, etc. It should be noted that the assumption that any change in $W_0(x)$ over these distances is negligible is still in effect here.

This model changes every member of the distribution into minidistributions symmetric about each value of x. For example, before cluster formation there are, on average, $W_0(x)$ subchains with an end-to-end distance of x. Cluster formation superimposes a symmetric distribution upon this number, resulting in $W_0(x)(s/s^2)$ of the original chains being left with end-to-end distances of x, $W_0(x)$ $[(s - 1)/s^2]$ being changed to $(x + d)$, $W_0(x)$ $[(s - 1)/s^2]$ being changed to $(x - d)$, etc. The new distribution of end-to-end distances is thus the summation of the s^2 shifted distributions or

$$W(x) = \frac{\beta}{\pi^{1/2}s^2}[se^{-\beta^2x^2} + (s-1)e^{-\beta^2(x+d)^2} + (s-1)e^{-\beta^2(x-d)^2}...] \quad (1)$$

(upon averaging $(p - q) = 0$, so p and q are not represented in the distribution). When the above expression is used to calculate the mean square value of the x component of the chains, Forsman finds that the new x component is larger than that for an equivalent yet unperturbed chain. He then concludes that there is chain extension.

The problem with this approach is that it is not internally consistent. It is assumed that $W_0(x)$ varies negligibly over distances of the order of 1. Accordingly, $W_0(x) = W_0(x + d) = W_0(x - d) = ... = W_0(x + ds) = W_0(x - ds)$ and the sum in eq 1 should be

$$W(x) = \frac{\beta}{\pi^{1/2}s^2}[se^{-\beta^2x^2} + (s-1)e^{-\beta^2x^2} + (s-2)e^{-\beta^2x^2} + ...]$$

$$W(x) = \frac{\beta}{\pi^{1/2}s^2}[s^2e^{-\beta^2x^2}]$$

$$W(x) = W_0(x) \quad (2)$$

which, obviously, gives no net change in end-to-end distance. In other words, if you assume initially that locating the subchain ends anywhere in particular (very small) lattice volumes gives no change in end-to-end distance, permuting random shifts around these volumes should also result in no change in the distribution function. As it turns out, even if we drop the assumption that $sW_0(x)$ is constant over l, we still predict no net change in end-to-end distance. In this case the probability distribution of shifts is given by $sW_0(x)$ for a shift of 0, $(s - 1)W_0(x + d)$ for a shift of $+d$, $(s - 1)W_0(x - d)$ for a shift of $-d$, etc. If the sum of this distribution is P, cluster formation reuslts in $sW_0(x)W_0(x)/P$ chains with end-to-end distances $= xW_0(x)(s - 1)W_0(x + d)/P$ chains with end-to-end distances $(x + d)$, etc. The new distribution $W(x)$ is again the s^2 shifted distributions:

$$W(x) = \frac{\beta}{\pi^{1/2}P}[se^{-\beta^2x^2}W_0(x) + (s-1)e^{-\beta^2}(x+d)^2W_0(x) + ...]$$

$$W(x) = \frac{W_0(x)}{P}[sW_0(x) + (s-1)W_3(x+d)...] \quad (3)$$

Thus,

$$W(x) = \frac{W_0(x)}{P}P = W_0(x) \quad (4)$$

again no change in this distribution after clustering, so that Forsman's model does *not* predict chain extension due to cluster formation, even when applied consistently. In fact this is true of any random system, as the following argument illustrates. Consider an ensemble of Gaussian subchains in an ionomer. Now let clusters form randomly throughout the system. To determine the effect of association, the mean square end-to-end distance is examined before and after cluster formation.

For a freely jointed chain, which of course has no preferential sites, the mean square end-to-end distance (r^2) is given by

$$\bar{r}^2 = \int_0^\infty r^2\, W_0(r)\, \mathrm{d}r \Big/ \int_0^\infty W_0(r)\, \mathrm{d}r = {}^3\!/_2\beta^2 \quad (5)$$

where $W_0(r)\,\mathrm{d}r = (\beta/\pi^{1/2})^3e^{-\beta^2r^2}\, 4\pi r^2\,\mathrm{d}r$ and is the probability of a chain having an end-to-end distance of r, irrespectively of direction. This expression can be considered as two parts: $(\beta/\pi^{1/2})^3e^{-\beta^2r^2}$ which is the probability that the subchain has extension r, and $4\pi r^2\,\mathrm{d}r$, which corresponds to the volume element available to a chain end at a distance r away from the other chain end.

We must now consider how being in a cluster affects the subchain ends. The simplest answer is that, due to the favorable energy exchange, the chain end stays in the cluster for (on average) a longer period of time than it does anywhere else. Because the number of clusters increases as $4\pi r^2\,\mathrm{d}r$, this changes the distribution to

$$W(r)\,\mathrm{d}r = (\beta/\pi^{1/2})^3e^{-\beta^2r^2}[(1-\rho)4\pi r^2 + \rho K4\pi r^2]\,\mathrm{d}r \quad (6)$$

where ρ = the molar density of clusters and K = a constant related to the strength of the interactions in the cluster.

The above equation represents the higher probability of finding a chain end in the portion of the spherical volume element (r from the origin) which contains clusters. Either before or after normalization, when eq 6 is used in the definition of r^2, the result is the same as for the freely jointed chain.

$$r^2 = \int_0^\infty W(r)\, r^2\, \mathrm{d}r \Big/ \int_0^\infty W(r)\, \mathrm{d}r = {}^3\!/_2\beta^2 \quad (7)$$

The terms introduced to increase the probability of a chain end being in a cluster cancel, so that in a truly random system of chains obeying Gaussian statistics, random clustering should not change the chain dimensions. As a corollary, if chain extension can be determined experimentally, then the system is not completely random. This leads us naturally into a consideration of the neutron scattering results.

Pineri et al.[11] determined no change in the radius of gyration (R_g) in forming styrene–methacrylic acid and Nafion ionomers, in agreement with the theoretical analysis presented here. In contrast, Earnest et al.[12] determined changes of up to 40% in R_g for sulfonated polystyrenes. As Dreyfus[7] has pointed out, however, the reality of this effect is questionable as the molecular weight of the diffracting object increases simultaneously. In fact, if the values of R_g presented by Earnest et al. are divided by the square root of the reported molecular weights, then there appears to be little variation.

There are two aspects of the neutron scattering results of Earnest et al.[12] that should be considered. First, the protonated and deuteriated chains were mixed, sulfonated, and then checked for percent sulfonation. Since C–D reactions are often slower than those involving equivalent C–H groups, the perdeuteriated chains might not be sulfonated to nearly the same extent as the protonated ones. This should only affect subsequent comparisons of measured chain extension (if real) with the predictions of various models, however. A more fundamental question concerns a point that seems to have been generally ignored in neutron scattering studies of ionomers. If two deuteriated chains are joined by a cluster, can neutron scattering tell them apart? If they cannot be distinguished, then we would expect the measured R_g and molecular weight to *both* increase with not only salt content but also the fraction of deuteriated chains. Systematic changes in R_g are not apparent within the range of experimental error defined by Earnest et al., but there are significant changes in the calculated molecular weight, particularly for the high salt content polymers.

We presume that the probability of two deuteriated chains "visiting" the same cluster has previously been neglected because of an implicit assumption of random contacts. The central feature of ionomer morphology, however, is that there are specific loci of strong interaction and this leads to cluster formation. These clusters may be randomly arranged, but the number of contacts is no longer determined by calculations based on purely random mixing. Instead, it is proportional to the number of interacting sites and the number of units per cluster. It is relatively easy to show that this leads to significant contact between deuteriated chains for the higher salt content ionomers used in the neutron scattering studies. We initially consider a deuteriated chain participating in a cluster and ask "what is the probability that this chain is *NOT* joined through clusters to other deuteriated chains?" If, for example, there are 98% non-deuteriated chains (C_H) and, say 4 units per cluster (n), the probability that the other 3 chains are not deuteriated would be $(0.98)^3$ or $(C_H)^{(n-1)}$. Because each chain contains s salt groups, the probability $P(n)$ is $P(n) = (C_H)^{(n-1)s}$.

Applying this simple but reasonable calculation to the polymers used by Earnest et al., we find that for clusters of 4–8 units there are a significant number of contacts, ranging from 15% to 93% depending upon the specifics of the system, as shown in Table I. Accordingly, we believe that the neutron scattering results do not present "unequivocal" evidence for chain extension, as the authors claim. In this context it should be noted that Pineri et al.[11] obtained their results on systems where only 0.5% or 1% of the chains was deuteriated (compared to levels of 2.5% or 3% for Earnest et al.), so that the probability of detecting one deuteriated chain attached to another through a cluster would be far less in their study.

Table I
Probability That a Single Deuteriated Chain Is Not Joined through Clusters to Other Deuteriated Chains

mol % salt	salt groups/ s chain	% DPS	$P(8)^a$	$P(4)^a$
1.9	2.74	2.0	67.88	84.70
1.9	2.74	2.5	61.53	81.21
1.9	2.74	3.0	55.75	77.85
4.2	6.05	2.0	42.50	69.30
4.2	6.05	2.5	34.23	63.16
4.2	6.05	3.0	27.53	57.53
8.5	12.24	2.0	17.71	47.62
8.5	12.24	2.5	11.43	39.47
8.5	12.24	3.0	7.36	32.68

$^a P(n)$ = probability assuming a uniform cluster size of n salt groups/cluster. Calculations based on $M_n = 1.5 \times 10^4$ and the assumption that every salt group is in a cluster.

Association

Forsman[3,4] made a major contribution to the study of ionomers when he realized that the association of units into a cluster is an important part of the entropy of the system. As in the case of the chain extension term, however, we again believe that the analysis was internally inconsistent, leading to an erroneous result. In order to obtain an expression for the entropy of localization (or association), Forsman first determined the number of configurations associated with putting m unassociated interacting units on a lattice of size N

$$\Omega = N(N-1)(N-2)...(N+1-m) \qquad (8)$$

Defined in this way the units are distinguishable among themselves, which can perhaps be more easily seen if eq 8 is rewritten in the form

$$\Omega = N!/(n-m)! \qquad (9)$$

When the number of configurations associated with putting the cluster of size m on the lattice was determined, however, the following equation was used:

$$\Omega = N/m \qquad (10)$$

In this expression the m units are indistinguishable among themselves. It is easy to show that it does not matter whether the units are considered to be distinguishable or indistinguishable, as long as the distinguishability is not changed during the analysis. If the terms are mixed, however, the final expression is incorrect. We shall not pursue this point here or derive an expression for the probability of association, P_A, using Forsman's model (it can be shown that $P_A = (m-1)!(N-m)!/(N-1)!$), because this approach assumes that the interacting units are arranged on a lattice. Instead, we will consider the a priori probability of having a cluster of m interacting groups in a system of N total number of units, with f being the fraction of N units which are interacting. For large N, the probability is approximated as

$$P_A = f^{(m-1)}(1-f) \qquad (11)$$

The probability of having an interacting unit next to the first is $(fN-1)/(N-1)$. That for a third unit being next to the first two is $(fN-2)/(N-2)$. The probability of a noninteracting unit following is given by $((1-f)N - 3/N - 3)$. For large N the probability approaches eq 11. This approach is not rigorous, in that the three-dimensional aspects of the problem are ignored. The inclusion of a coordination number would lead to a much more complicated theory, however, and of necessity include at least one additional parameter that would have to be determined from experimental data. Forsman also ignores this aspect of the problem of determining the entropy of association, and in order to formulate an initial generalized

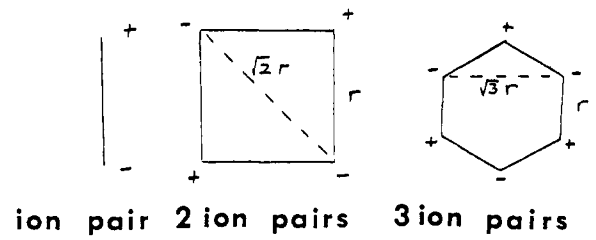

Figure 1. Coordination structures used in the calculation of the energy of interaction by Broze et al.[19]

Table II
Energies Calculated by Broze et al.[19]

no. of ion pairs	$(\Delta E)_{\min}$ (e^2/Dr_d)	$(\Delta E)_{\min}$ per ion pair (e^2/Dr_d)
1	-0.855	-0.855
2	-1.221	-1.026
3	-3.227	-1.076

model, we do not believe that this simplification is unreasonable.

Energies

Both Eisenberg[2] and Dreyfus[7] observed that ion pair formation releases a lot of energy, sufficient to totally dominate any entropy term in an equilibrium scheme. Accordingly, both of these authors and Datye et al.[5,6] assumed dipole–dipole interactions between ion pairs. Experimental evidence cited previously in this paper, however, indicates that there are small locally ordered domains that have the character of ionic crystals. In this context, it is not the formation of an ion pair itself that leads to aggregation and physical cross-linking (at least when monovalent cations are used to form the ionomer). Rather, it is the capability for further aggregation that is important. Consequently, we do not need to consider the energy of ion pair formation but instead consider the additional energy that such ion pairs release when clusters are formed.

This is an approach used by Broze et al.[19] in their treatment of halato-telechelic polymers and is in turn based on Pettit and Bruckenstein's[20] extension of the Denison–Ramsey treatment of ion pair formation. Neglecting the minor contribution from induced dipoles, the potential energy E can be written

$$\Delta E = -e^2/Dr + B/r^n \qquad (12)$$

where e is the electrostatic charge, D is the dielectric constant, and r is the distance between the contact ion pairs. The term B/r^n is used to express various other forces. Pettit and Brukenstein[20] empirically assigned a value of 6.9 to n, based on a study of alkali metal halide ion pairs. Broze et al.[19] obtained B by minimizing the energy expression for dimers

$$[\partial(\Delta E)/\partial r]_{r=r_d} = e^2/Dr_d^2 - 6.9B/r_d^{7.9} = 0$$

$$B = r_d^{5.9}e^2/6.9D \qquad (13)$$

Upon substituting in eq 12

$$(\Delta E)_{\min} = 0.855e^2/Dr_d \qquad (14)$$

This general approach was applied to the structures illustrated in Figure 1. For simplicity, we will confine our analysis to ionomers involving monovalent cations, although Broze et al. also considered some simple structures that might be formed by using divalent cations. The calculated energies, expressed in multiples of e^2/Dr_d, are reproduced in Table II. We have extended this treatment to the larger structures shown in Figure 2, and the energies are listed in Table III. The quantities required for this analysis are not the absolute energies but are the energy differences per ion pair. It can be seen from the last column of Tables II and III that the energy per ion pair increases at a decreasing rate as the cluster size increases, and the energy differences are small compared to the energy of formation of the ion pair.

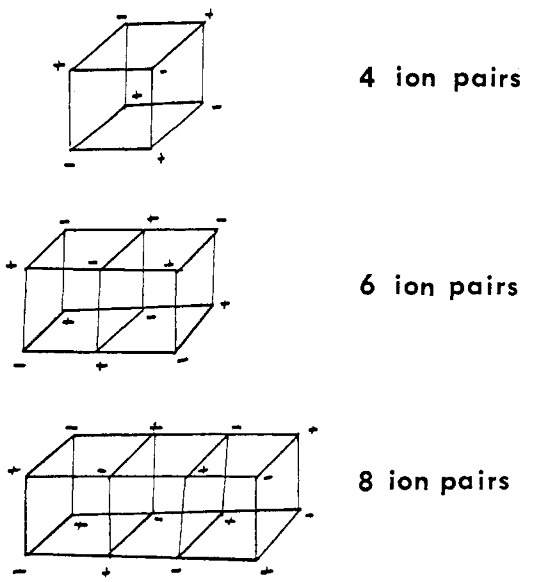

Figure 2. Additional structures considered in this study.

Table III
Energies for Larger Structures

no. of ion pairs	$(\Delta E)_{\min}$ (e^2/Dr_d)	$(\Delta E)_{\min}$ per ion pair (e^2/Dr_d)
4	-4.41	-1.10
6	-6.727	-1.121
8	-9.07	-1.13

Calculation and Discussion

The terms composing the partition function must now be correctly combined to yield the probability of multiplets of different size. Each term is adjusted to reflect the probabilities and energies in terms of one unit. We will assume that there is total and instantaneous formation of ion pairs when an acid copolymer is converted to an ionomer, so that the ion pair energy is the ground-state energy. The energy of an ion pair in a cluster of size s is equal to the cluster energy divided by s (see Tables II and III). The difference between this energy and the ground-state energy, E_s, is the gain in energy per ion pair due to cluster formation and the quantity required for use in the partition function.

Knowing a rough estimate of both the a priori probability and resulting energy change, the Boltzmann distribution can be utilized to predict the equilibrium distribution of cluster sizes. The Boltzmann distribution is

$$n_s/n = P_s e^{-\Delta E_s/kT} \qquad (15)$$

where the partition function $Q = \sum_s P_s e^{-\Delta E_s/kT}$, n_s/n = the proportion of interacting units in clusters of size s, P_s = the a priori probability of finding an interaction unit in a cluster of size s, ΔE_s = the change in energy of an interacting unit upon being included in a cluster of size s, k = Boltzmann constant, and T = temperature.

A computer program was written to calculate the probability of cluster formation as a function of the fraction of interacting units present and the cluster energies. These vary with the dielectric constant of the medium, D, and the assumed distance apart of the ion pair, r_d. A plot of the relative distribution of cluster sizes as a function of Dr_d is shown in Figure 3. In this example, the fraction

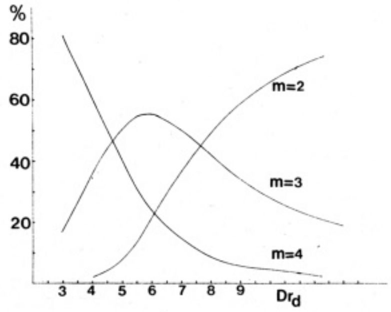

Figure 3. Plot of the percent distribution of clusters of size on ion pairs as a function of the energy of interaction, expressed in terms of the parameter Dr_d. Calculations were made for a system with a fraction of 0.04 interacting units at a temperature of 300 K.

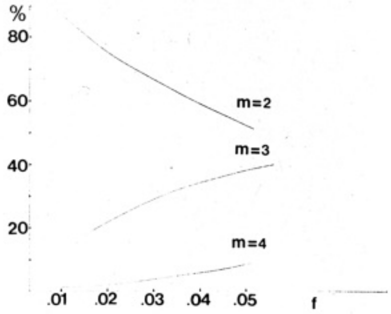

Figure 4. Plot of the effect of changing the fraction of interacting units on the percent distribution of cluster sizes.

of interacting units is 0.04 and the temperature is 300 K. It can be seen that in the range of Dr_d characteristic of ethylene–methacrylic acid copolymers (about 6–9 units on this plot), practically all the units are distributed in clusters of only moderate size, between 2 and 4 units.

The effect of changing the fraction of interacting units is shown in Figure 4, where a value of $Dr_d = 9$ units and a temperature of 300 K are assumed. Dimers, trimers, and tetramers dominate the distribution, with a preponderance of dimers at lower fractions of interacting units. The effect of temperature on the same system is illustrated in Figure 5. As might be expected, smaller cluster sizes are predicted at higher temperatures.

The surprising aspect of these results is the large affect that the entropy of localization has in limiting the size of the clusters. In one sense this is a very satisfying result, in that only relatively small clusters are predicted, in broad agreement with some recent experimental work for ethylene–methacrylic acid copolymers.[8,9,14] It is clear, however, that the calculated distributions are heavily dependent upon the exact form of the energy term, particularly differences between one structure and another, and therefore very model dependent. Accordingly, these results can at present only be taken as an illustration of trends. We need to have a much more complete description of the forces of association if we are to obtain results that we can compare to experiment with any degree of confidence. Here we have considered only electrostatic forces, because we initially assumed that they are large compared to dipole interactions. But, as a result of relating energies to a ground state that consists of an ion pair, the values of E_s used in the partition function are much smaller than the forces between ion pairs. Consequently, a model that incorporates both ionic and dipole interactions should be considered in the future.

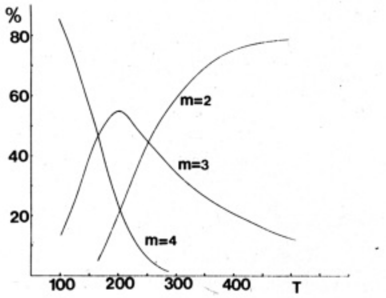

Figure 5. Effect of temperature on the percent distribution of cluster sizes.

Conclusions

A model that is capable of predicting the equilibrium distribution of cluster sizes in ionomers has been developed. The predicted distribution depends heavily on the precise form of the energy term, however, and in its present form is probably only useful for illustrating trends. A much more important result of this study is the reassessment of terms used in previous studies. In particular, we believe there is no theoretical justification for chain extension in ionomers with a random distribution of clusters.

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