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# Elastic Theory for Ionic Clustering in Perfluorinated Ionomers[†]

**William Y. Hsu* and Timothy D. Gierke**[‡]

*Central Research and Development Department, E. I. du Pont de Nemours and Co., Inc., Wilmington, Delaware 19898.* *Received June 8, 1981*

ABSTRACT: A semiphenomenological elastic theory for ionic clustering is proposed. The free energy of the system is obtained by assuming the elastic energy necessary to create the volume in the matrix for the hydrated cluster is balanced by the energy produced by the favorable hydrophilic interactions at the surface and in the cluster interior. An expression for the cluster diameter is obtained by minimizing this free energy. This expression correctly describes the experimental variation in cluster diameter with cation form, equivalent weight, and water content which has been reported recently for one perfluorinated ionomer.[1] The model also predicts that short channels connecting adjacent clusters are thermodynamically stable, in support of the cluster-network model proposed by us earlier.[2]

## I. Introduction

In many ion-containing polymers, the ion exchange sites are observed to aggregate and form microphase-separated domains, or clusters.[3] The existence of ionic clusters in perfluorinated ionomers is well established,[1,2,4-8] and the clustering has a marked effect on the mechanical[4] and transport properties[2,9-12] of the polymer. In addition, the unique chemical properties of these perfluorinated ionomers have suggested many novel applications of ion-containing polymers not suitable for hydrocarbon ionomers. These include applications in electrochemical processes,[13-15] in catalysis,[16-18] and as polymer electrodes.[19] In many of these applications, the perfluorinated ionomer plays an active role, and the effect of ionic clustering is important. It is useful, therefore, to understand the forces that control the structure of these aggregates.

Several models of ionic clustering in perfluorinated ionomers have been reported in the literature. Gierke[2] has proposed a phenomenological model, the cluster-network model, which is consistent with his experimental observations, and used the model to explain the performance of the resin as a membrane in chlor-alkali cells. In this model, the phase-separated domains are assumed to be spherical inverted micellar structures connected by short narrow channels. Cluster dimensions were obtained by comparison with experimental observations, but details about the forces controlling these dimensions were not considered.

Mauritz, Hora, and Hopfinger[20,21] have reported a fundamental theory to describe the process of ionic clustering based on first principles. In this theory they consider the balance in energy between the elastic deformation of the matrix and the various molecular interactions that exist in the polymer. This theory depends on many molecular parameters (24), which are estimated from a combination of experimental bulk thermodynamic data and molecular structure calculations employing both molecular and quantum mechanics. This model semiquantitatively reproduces water adsorption, polymer density, and number of waters per exchange site, but the calculated cluster diameters (2.0 nm) and number of exchange sites per cluster (10-15) are smaller than those observed experimentally.[22]

Table I
Interactions Assumed before Hydration of Hypothetical Cluster

| type interaction | strength |
|---|---|
| $SO_3^-/CF_2$ | $B_1N_p$ |
| $SO_3^-/SO_3^-$ | $-B_2N_p$ |
| $H_2O/H_2O$ | $-B_3N_w$ |
| elastic energy[a] | $A(\pi/6)d_0^3G(c)$ |

[a] Reference 24.

In this paper we report a simple elastic theory for ionic clustering. In this theory, the cluster dimensions are determined by a consideration of the energetics involved, similar to the work of Mauritz et al. We, however, do not attempt to calculate all of the interactions. We adopt a semiphenomenological approach to obtain an expression for the equilibrium cluster diameter by minimizing the total free energy of the system, which contains an elastic term, a condensation or bulk term, and a hydrophilic surface term. Our approach is similar to that reported recently by Fedors[23] to describe water absorption by a polymer that contains liquid-soluble inclusions. The present theory is tested by comparison to the results of a recently reported small-angle X-ray study.[1] In general, our results are consistent with experimental observation.

## II. Model

We begin by assuming that in a fully hydrated ionomer the ionic clusters exist as spherical domains with an inverted micellar structure.[2] Our goal is to determine the average equilibrium diameter of such a cluster by considering the energetics associated with its growth. The starting point is a hypothetical dry cluster that contains $N_p$ ion exchange sites and that is imbedded in a *swollen* polymer; i.e., all the other hydrated clusters have been formed. We now consider the change in free energy associated with the growth of this hypothetical cluster, with $N_p$ held constant.

Before hydration, the energetics of the dry cluster are described by the interactions listed in Table I. $N_w$ is the number of water molecules that eventually will be absorbed by the cluster, $d_0$ is the initial diameter of the dry cluster, $G(c)$ is the tensile modulus of the swollen matrix with water content $c$, $B_i$ are the strengths of each interaction, and $A$ is a geometric constant of order unity. For the spherical geometry, $A = {}^2/_3$.[24] Note the interaction energy of the water molecules outside the membrane is explicitly taken into account. This is important because this term is necessary if we are to understand the variation in cluster diameter with the water content of the membrane. The validity of a continuum description of the elastic contribution may not be obvious a priori, but good agreements between theory and data offer justification posteriorly.

We now consider the hydrated cluster shown schematically in Figure 1. There, $d_c$ is the diameter of the hydrated cluster and $\sigma_w$ is the diameter of a water molecule.

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[†] Contribution No. 2894.

[‡] Present address: E. I. du Pont de Nemours and Co., Polymer Products Department, Washington Works, B21, Parkersburg, WV 26101.

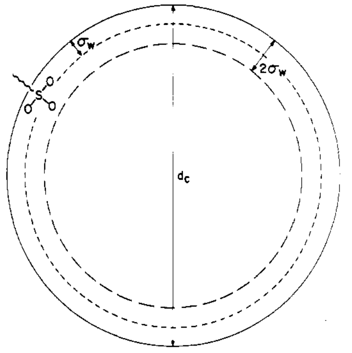


**Figure 1.** Schematic of a hydrated ion cluster, where $d_c$ and $\sigma_w$ are diameters of the hydrated cluster and a water molecule, respectively. The water molecules at the outer surface of the cluster interact with the fluorocarbon matrix, the sulfonate ion exchange sites, and other molecules, the water molecules in the next layer below the outside surface interact with the ion exchange sites and surrounding water, and the remaining water molecules interact with other water molecules only.

Table II
Interactions Assumed after Hydration of Hypothetical Cluster

| type interaction | strength |
|---|---|
| $SO_3^-/CF_2$ | $A_1N_p$ |
| $H_2O$ at surface | $-A_2N_w'$ |
| $H_2O$ in second layer | $-A_3N_w''$ |
| $H_2O$ in bulk | $-A_4(N_w - N_w' - N_w'')$ |
| elastic energy [a] | $AG(c)(\pi/6)d_c^3[1 - 3\,(d_0/d_c)^2 + 2\,(d_0/d_c)^3]$ |

[a] Reference 24.

The water molecules at the outer surface of the cluster interact with the fluorocarbon matrix, the ion exchange sites, and other water molecules. We assume that these molecules, which number $N_w'$, can be characterized by an average interaction parameter $A_2$. Similarly, the water molecules in the next layer below the outside surface, which number $N_w''$, interact with the ion exchange sites and surrounding water and are characterized by the interaction parameter $A_3$. The remaining water molecules, numbering $N_w - N_w' - N_w''$, interact only with other water molecules and are characterized by the interaction parameter $A_4$. The dependence of the energetics on cation form is implicitly contained in the tensile modulus, $G(c)$, which depends on the water content of the swollen polymer,[25] and water content is affected by cation form. We expect any further effect of cation form on the hydration of our final hypothetical cluster to be minimal. The energetics for the hydrated cluster are summarized in Table II.

The change in free energy that accompanies hydration, $\Delta F$, is then given by

$$\begin{aligned}\Delta F &= (\text{energetics after}) - (\text{energetics before}) \\ &= N_p(A_1 + B_2 - B_1) - AG(c)(\pi/6)d_0^3 + N_w(B_3 - A_4) - N_w'(A_2 - A_4) - N_w''(A_3 - A_4) + AG(c)(\pi/6)d_c^3[1 - 3(d_0/d_c)^2 + 2(d_0/d_c)^3]\end{aligned} \tag{1}$$

The appropriate cluster diameter, $d_c$, is the one that will minimize $\Delta F$. To find the value of $d_c$, we must find expressions that relate $N_w$, $N_w'$, and $N_w''$ to $d_c$. We assume that the exchange sites possess a specific volume $V_p$ and that the water molecules have specific volume $V_w$. The volume of the hydrated cluster then becomes

$$(\pi/6)d_c^3 = N_wV_w + N_pV_p \tag{2}$$

which provides a relation for $N_w$:

$$N_w = [(\pi/6)d_c^3 - N_pV_p]V_w^{-1} \tag{3}$$

Similarly, the volume of the outer shell of the cluster with the thickness of the water molecule $\sigma_w$ is given by

$$[(\pi/6)d_c^3 - (\pi/6)(d_c - 2\sigma_w)^3] = N_w'V_w + N_pV_p' \tag{4}$$

where we have represented the volume that the exchange sites occupy in the outer shell by $N_pV_p'$. Equation 4 provides a relation for $N_w'$

$$N_w' = [(\pi/6)d_c^3 - (\pi/6)(d_c - 2\sigma_w)^3 - N_pV_p']V_w^{-1} \tag{5}$$

A relation for $N_w''$ is obtained in a similar manner:

$$N_w'' = [(\pi/6)(d_c - 2\sigma_w)^3 - (\pi/6) \times (d_c - 4\sigma_w)^3 - N_p(V_p - V_p')]V_w^{-1} \tag{6}$$

An expression for $d_c$ can now be derived by minimizing $\Delta F$ and using eq 3, 5, and 6. To a good approximation the result is

$$d_c = \frac{4\sigma_wK_s}{[AG(c)(1 - d_0^2/d_c^2) + K_1]} - 2\sigma_w' \tag{7}$$

where

$$K_s = K_2 + K_3 \tag{8}$$

$$K_1 = (B_3 - A_4)V_w^{-1} \tag{9}$$

$$K_2 = (A_2 - A_4)V_w^{-1} \tag{10}$$

$$K_3 = (A_3 - A_4)V_w^{-1} \tag{11}$$

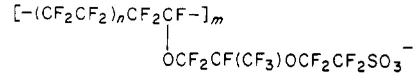
$$\sigma_w' = [1 + (1/2)K_a/K_s]\sigma_w \tag{12}$$

$$K_a = K_3 - K_2 \tag{13}$$

In eq 7, $K_s$ represents a surface term and is expected to increase with increasing hydrophilicity of the exchange sites. Interestingly, the expression for $d_c$ does not explicitly depend on $N_p$, the number of exchange sites in the cluster. There is, however, an implicit dependence since $d_0$ depends on $N_p$. $K_1$ depends on the energy of the water molecules before hydration through $B_3$; thus the cluster diameter will depend on the chemical potential of the water with which the ionomer equilibrates. $\sigma_w'$ should be slightly smaller than $\sigma_w$ because $K_3$ would be slightly smaller than $K_2$, which is affected more strongly by direct water-exchange site interactions. Qualitatively, eq 7 suggests, in accord with intuitive arguments, that larger clusters will be obtained by increasing the hydrophilicity of the exchange site, reducing the tensile modulus of the fluorocarbon matrix, or increasing the chemical potential of the external water source, i.e., decreasing $B_3$.

## III. Comparison with Experiment

Gierke, Munn, and Wilson[1] have recently reported a fairly detailed small-angle X-ray study of ionic clustering in the perfluorinated ionomer with the chemical structure



$$[-(CF_2CF_2)_nCF_2\underset{\displaystyle |\atop \displaystyle OCF_2CF(CF_3)OCF_2CF_2SO_3^-}{CF}-]_m$$

I

Some of the results reported in this paper include the variation of cluster diameter with the equivalent weight (EW), cation form, and water content of the polymer. In this section, we compare the model developed above with these experimental results.

This comparison is facilitated by rearranging eq 7 to the following form:

$$AG(c)(1 - d_0^2/d_c^2) = 4\sigma_wK_s(d_c + 2\sigma_w')^{-1} - K_1 \tag{14}$$

Table III
Water Uptake, Cluster Diameter, and Modulus Data for $SO_3^-$ Polymers of Different Equivalent Weights ($Na^+$ Form)

| EW | $d_c$, nm | $10^2\Delta m$ | $G/G_0$ | $(d_c + 2\sigma_W)^{-1}$, nm$^{-1}$ |
|---|---|---|---|---|
| 944 | 5.09 | 42.0 | 0.200 | 0.177 |
| 971 | 4.97 | 37.5 | 0.237 | 0.179 |
| 1100 | 4.31 | 23.8 | 0.429 | 0.203 |
| 1200 | 3.88 | 17.1 | 0.605 | 0.222 |
| 1600 | 3.03 | 8.1 | 1.419 | 0.274 |
| 1790 | 2.74 | 6.3 | 2.196 | 0.298 |

Table IV
Water Uptake, Cluster Diameter, and Modulus Data for 1200 EW $SO_3^-$ of Different Ion Forms

| ion form | $d_c$, nm | $10^2\Delta m$ | $G/G_0$ | $(d_c + 2\sigma_W)^{-1}$, nm$^{-1}$ |
|---|---|---|---|---|
| $H^+$ | 4.74 | 33.6 | 0.372 | 0.187 |
| $Li^+$ | 4.49 | 29.7 | 0.418 | 0.196 |
| $Na^+$ | 4.21 | 21.0 | 0.533 | 0.207 |
| $K^+$ | 3.45 | 8.7 | 0.774 | 0.246 |
| $Rb^+$ | 3.56 | 8.1 | 0.788 | 0.239 |
| $Cs^+$ | 3.50 | 5.9 | 0.841 | 0.243 |

Table V
Water Uptake, Cluster Diameter, and Modulus Data for 1200 EW $SO_3H$ Polymer vs $H_2O$ Content

| $d_c$, nm | $10^2\Delta m$ | $G/G_0$ | $(d_c + 2\sigma_W)^{-1}$, nm$^{-1}$ |
|---|---|---|---|
| 4.08 | 19.4 | 0.565 | 0.213 |
| 3.94 | 18.5 | 0.580 | 0.219 |
| 3.70 | 15.3 | 0.638 | 0.231 |
| 3.38 | 12.9 | 0.684 | 0.250 |
| 3.27 | 12.0 | 0.703 | 0.257 |
| 2.97 | 8.6 | 0.777 | 0.278 |
| 2.52 | 6.3 | 0.831 | 0.318 |
| 2.52 | 5.4 | 0.853 | 0.318 |

In addition, the tensile modulus of polymer I has been reported;[13] it obeys the following empirical relation:

$$G(c)/G_0 = \exp[-\alpha(c + 1200 - \mathrm{EW})/20] \qquad (15)$$

In eq 15, $G_0$ is a temperature-dependent term equal to 275 J/cm$^3$ at room temperature, $\alpha = 0.0294$, $c$ is the water content of the swollen polymer in grams of water per 100 g of dry polymer, and EW is the equivalent weight of the polymer. With eq 15, eq 14 may be written

$$[G(c)/G_0](1 - d_0^2/d_c^2) = 4\sigma_w(K_s/AG_0)(d_c + 2\sigma_w')^{-1} - (K_1/AG_0) \qquad (16)$$

Equation 16 indicates that a plot of the quantity $[G(c)/G_0](1 - d_0^2/d_c^2)$ vs. the quantity $(d_c + 2\sigma_w')^{-1}$ will be a straight line with a slope given by $(4\sigma_w K_s/AG_0)$ and intercept given by $-(K_1/AG_0)$.

The appropriate results from the X-ray studies and eq 15 are summarized in Tables III–V and plotted according to eq 16 in Figure 2. We have assumed a value of 0.31 nm for $\sigma_w'$. This corresponds to the diameter of the water molecule.[26] We have also employed a value for $d_0 = 2.0$ nm, which is in accord with experimental observation.[1] Figure 2 suggests that the variation of cluster diameter with equivalent weight and cation form of the polymer is properly described by the elastic model, eq 16. From the least-squares fit we find

$$K_s = 917 \text{ J/cm}^3$$

$$K_1 = 170 \text{ J/cm}^3$$

However, before we can account for the variation of $d_c$ with water content, a brief examination of how these data were obtained[1] is in order.

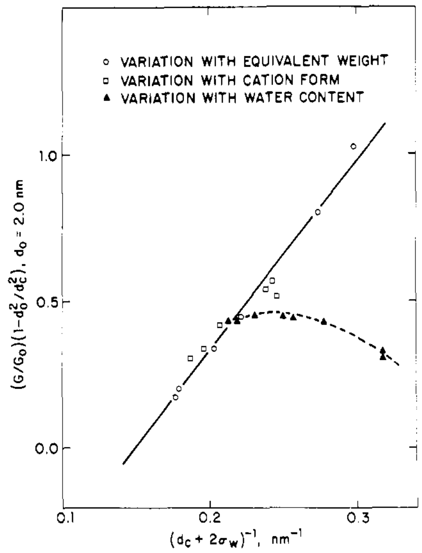


**Figure 2.** Variation of the cluster diameter, $d_c$, with equivalent weight, cation form, and water content. The data are plotted in a form that facilitates comparison with the prediction of our elastic theory. The solid line is a least-squares fit of eq 16 to the variation of $d_c$ with equivalent weight and cation form. The variation with water content is accounted for in Figure 4 by the inclusion of change in the chemical potential of water.

The variation in water content, at fixed equivalent weight, was obtained by allowing a totally swollen membrane to desorb water, or a dry membrane to absorb water, for a variable amount of time. After such time, the sample was sealed in a polypropylene bag and the X-ray data were obtained. During the X-ray scan, the polymer is in equilibrium with an atmosphere of some relative humidity, RH, characteristic of the internal water content of the polymer. Because this RH value changes with water content, $K_1$ is a variable in these experiments; nevertheless, its dependence on the water content of the membrane can be deduced. If the water vapor atmosphere under the polypropylene bag is treated like an ideal gas, the difference in free energy, $\Delta F_w$, between water vapor at a relative humidity, RH and pure water, RH = 1.00, is given by

$$\Delta F_w = RT \ln (\mathrm{RH}) = -\Delta B_3 \qquad (17)$$

This change in free energy produces a comparable change in the interaction parameter $B_3$, which in turn leads to a change in $K_1$ according to eq 9:

$$\Delta K_1 = -(RT/18) \ln (\mathrm{RH}) \qquad (18)$$

where we have used the value of 18 cm$^3$/mol for the molar volume of water, $V_w$.

The vapor sorption isotherm for 1200 EW polymer has been measured by Munn,[27] and the results are shown in Figure 3. From this curve, the value of the relative humidity, RH, of the atmosphere that equilibrates with the polymer of water content c can be obtained. Using eq 18, $\Delta K$ can be calculated for this value of RH, and the quantity $K_1/AG_0$ can be adjusted according to

$$(K_1/AG_0)_{\mathrm{RH}} = (K_1/AG_0)_{\mathrm{RH}=1.0} + (\Delta K_1/AG_0) \qquad (19)$$

The results of this calculation are listed in Table VI, using $^2/_3$ for the quantity $A$[24] and the value of $G_0$ given above. Also shown in Table VI are the cluster diameters calculated with eq 7 using the value for $K_s$ obtained from fitting the equivalent weight and ion form data to eq 16. The results correspond closely to the experimental values in Table V. By accounting for the change in the chemical

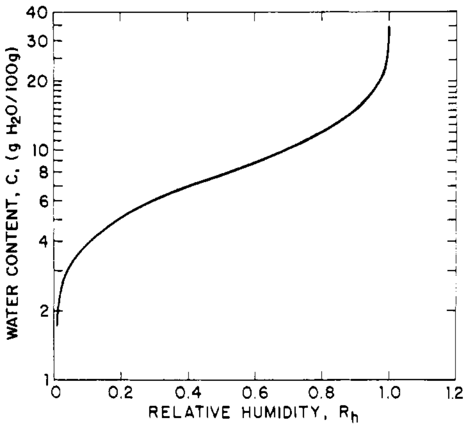


**Figure 3.** Water vapor sorption isotherm for 1200 EW samples of polymer I.

Table VI
Results for Calculated Variation of Cluster Diameter with Water Content in 1200 EW $SO_3H$ Polymer, $A = {}^2/_3$

| water content $10^2\Delta m$ | equiv rel humidity | calcd $K_1/AG_0$ | calcd diam $d_c$, nm |
|---|---|---|---|
| 19.4 | 0.99 | 0.927 | 3.99 |
| 18.5 | 0.96 | 0.951 | 3.90 |
| 15.3 | 0.90 | 0.999 | 3.69 |
| 12.9 | 0.84 | 1.051 | 3.55 |
| 12.0 | 0.80 | 1.088 | 3.47 |
| 8.6 | 0.60 | 1.306 | 2.99 |
| 6.3 | 0.34 | 1.724 | 2.44 |
| 5.4 | 0.22 | 2.063 | 2.01 |

potential of the water with which the polymer equilibrates, we have shown that our model is consistent with the observed variation in cluster diameter with water content. This is demonstrated more graphically in Figure 4. In summary, the model correctly describes the variation of cluster diameter with equivalent weight, cation form, and water content.

It is interesting to examine the magnitude of the parameters $K_1$ and $K_s$ that we have deduced from the experimental data; $K_1$ = 170 J/cm$^3$ and $K_s$ = 917 J/cm$^3$. These values may be compared with the heat of vaporization of water, 2260 J/cm$^3$, the thermal energy at 300 K ($RT/V_w$), 138 J/cm$^3$, and the free energy of formation of ($H_2O\cdots H_2O$) bonds,[21] 418 J/cm$^3$. The fact that $K_1$ is small and positive indicates that the free energy of the "bulk" water inside the membrane is slightly larger than that for pure water. This result is consistent with the observation that the hydrogen bonding of the absorbed water is significantly weaker than normal water.[28] This positive $K_1$ effect is more than offset by the much larger lowering in free energy produced by the surface interactions, $K_s$. According to the current model, the cluster diameters observed in the perfluorinated ionomer I are determined predominantly by a balance between the surface interactions, $K_s$, and the energy of elastic deformation.

## IV. Cluster-Network Model[2]

The success of this simple elastic theory in describing the results of small-angle X-ray studies is encouraging. As noted earlier, the phenomenological cluster–network model proposed by us to explain ion transport in these polymers assumes the clusters are connected by short narrow channels. The thermodynamic stability of such channels is a question that can be examined with the present theory. We, of course, do not propose that the current theory can be used to confirm the existence of channels, but only that the results of such an examination will be illuminating.

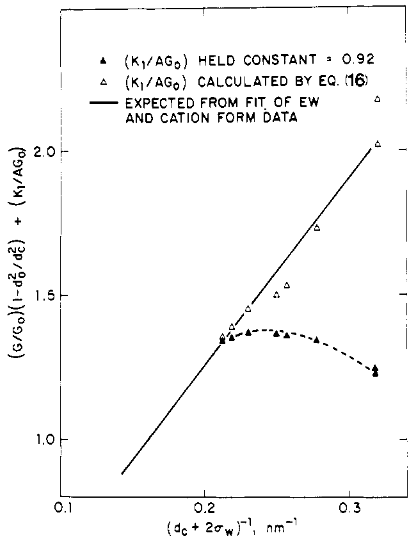


**Figure 4.** Comparisons of the prediction of eq 16 with the observed variation in $d_c$ with water content before (closed triangles) and after (open triangles) the inclusion of change in the chemical potential of the water with which polymer I equilibrates.

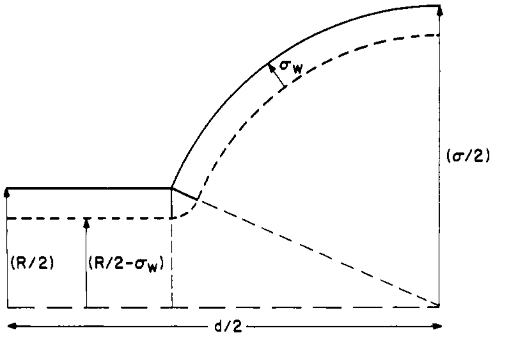


**Figure 5.** Schematic for two equivalent clusters of diameter $\sigma$ connected by a channel of diameter $R$. The center-to-center separation of the clusters is $d$, and $\sigma_w$ is the diameter of a water molecule.

Our approach, in considering the thermodynamic stability of channels, is very similar to that used in section II. We recognize that the applicability of macroscopic concepts to channels 10 Å in size may be questionable, but we believe our results will be suggestive and interesting. The initial state consists of two equivalent clusters of diameter $d_c$ separated by a distance $d$. Now suppose we allow a channel of diameter $R$ to form between these two clusters at constant volume. The new cluster diameter is designated by $\sigma$. This configuration is shown in Figure 5. The change in free energy, $\Delta F$, that results will be a function of the final channel diameter, $R$. Using arguments like those used in deriving eq 1, we obtain

$$\frac{\partial \Delta F}{\partial R} = 0 = (K_2 - K_3)\frac{\partial V'}{\partial R} + K_3\frac{\partial V''}{\partial R} - \frac{\pi}{2}AG(c)d_0^2\frac{\partial \sigma}{\partial R} \quad (20)$$

where $V'$ is the volume containing all the water molecules except those at the surface of type $N_w'$ and $V''$ is the volume containing all the "bulk" water molecules, that is, excluding the water molecules of type $N_w'$ and $N_w''$. When expressions for $V'$ and $V''$ are obtained, the derivatives evaluated, and the results substituted into eq 20, we obtain a very complex result, which can be written

$$\sum_i A_i(R/\sigma)^i = 0 \quad (21)$$

The expansion coefficients in eq 21 are functions of $\sigma$, $d$, $AG(c)$, $K_s$, and $K_a = K_3 - K_2$, all of which are known except $K_s$. We have solved eq 21 numerically for various choices

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of $K_a$ and find that for 1200 EW polymer

$$R = 1.4 \pm 0.2 \text{ nm} \tag{22}$$

for $-1 < K_a/K_s < 0$. This value is in agreement with the value of 1.2–1.3 nm deduced from water transport experiments.[2] The change in free energy that results from the formation of the channel is only $-11$ J/cm$^3$; thus our elastic theory suggests the channels are continually forming and unforming at ambient temperatures. This is consistent with the previously proposed cluster–network model.

## V. Conclusion

We have derived a semiphenomenological expression for the diameter of ionic clusters in ionomers and demonstrated that this expression correctly describes the variation in cluster diameter in one perfluorinated ionomer with water content, equivalent weight, and cation form. We find the cluster diameter is dominated by a balance between hydrophilic surface interactions with the ion exchange sites and the energy of elastic deformation. The model also predicts that short channels connecting adjacent clusters are thermodynamically stable, in support of the cluster–network model proposed by us earlier. The current elastic theory should generally apply to other ionomers, including hydrocarbon analogues and a comparison of the phenomenological parameters $K_s$ and $K_l$ for various ionomers should be instructive and interesting.

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# Properties of Low Molecular Weight Block Copolymers. 1. Differential Scanning Calorimetry of Styrene–Dimethylsiloxane Diblock Copolymers[1]

**Sonja Krause,* Magdy Iskandar,[2] and Mohammad Iqbal[3]**

*Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181.*

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ABSTRACT: The glass transition temperature, $T_g$, the width of the glass transition interval, $\Delta T_g$, and the change in specific heat at $T_g$, $\Delta C_p$, were obtained by differential scanning calorimetry for both microphases in a series of phase-separated styrene–dimethylsiloxane (S–DMS) diblock copolymers and were compared with the same quantities obtained on styrene (S) and on dimethylsiloxane (DMS) homopolymers of comparable molecular weight. In S–DMS samples with S block molecular weights $\geq 3.90 \times 10^4$, the S phases had properties very similar to those of S homopolymer. At lower S block molecular weights, the S phase properties diverged from those of S homopolymers of comparable weight; large divergences occurred when the S block molecular weight was $\leq 0.82 \times 10^4$. Various interpretations of the data are considered.

## Introduction

Recently, we[4] reported a comparison of the glass transition temperatures ($T_g$'s) of the styrene (S) microphases in styrene–dimethylsiloxane (S–DMS) diblock copolymers, in styrene–isoprene diblock and triblock copolymers, and in styrene–ethylene oxide diblock and triblock copolymers. In that work, it appeared that the magnitudes of the $T_g$'s of the S microphases in all these systems were approximately the same as long as S microphases made up of equal molecular weight blocks were compared. We concluded, therefore, that the chemical nature of the other block or blocks that are attached to the styrene blocks has no effect

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