Clustering of Ions in Organic Polymers. A Theoretical Approach

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ABSTRACT: Clustering of ions in organic polymers is treated from a theoretical point of view. It is shown that ions in organic media of low dielectric constant exist most probably as pairs or higher multiplets, even at relatively high temperatures. The maximum size of a noncrystalline and approximately spherical multiplet is shown to be determined by the surface areas and volumes of the participating chemical species and is of the order of eight ion pairs or less. At relatively low temperatures, the ionic multiplets can aggregate to form a cluster, the factors involved in cluster formation being the elasticity of the chains and the electrical work of cluster collapse. The clusters are assumed to be stable below a characteristic temperature T_c. By setting the elastic work involved in the cluster formation at T_c equal to the electrostatic work, an equation is derived which correlates the number of ion pairs in the cluster with the spacing of the ionic groups along the chain, the density, the dielectric constant, the root mean square end-to-end distance of the polymer chain, the size of the ions, the average multiplet size above T_c, and a calculable constant which is a function of the cluster geometry. No adjustable parameters are involved. Several simple geometries are assumed for ethylene–sodium methacrylate clusters, and the calculated average intercluster distance for 4.5 mol % of the ionic component ranges from 44 to 95 Å. The experimentally determined repeat distance is of the order of 83 Å.

I. Introduction

Although extensive studies of the bulk properties of ionic polymers have been undertaken, a divergence of opinion exists in regard to state of aggregation of the ions. One series of studies[1–5] postulates the existence of sizable regions of dimensions of *ca.* 100 Å in which the ions are clustered, the most direct evidence coming from small angle X-ray scattering,[1,4] while another group[6–8] arrives at the conclusion that the ions are dispersed throughout the sample in a very low state of aggregation, *i.e.*, either as ion pairs or ion quartets.

While the above-mentioned studies dealt primarily with the sodium salts of ethylene–methacrylic acid copolymers, other materials have also been investigated, notably carboxyl containing rubbers by Tobolsky, Lyons, and Hata[9] as well as ion containing copolymers of butadiene and vinyl pyridine by Otocka and Eirich,[10,11] leading also to divergent conclusions. Bonotto and Bonner[12] have proposed a model for ionic aggregates in ethylene–sodium methacrylate copolymers which has received considerable attention.

In this paper, the formation of ionic clusters in organic polymers will be explored from a theoretical point of view. It will be shown that both of the above pictures are correct for different concentrations of the ionic comonomer in the polymeric material. Specifically, it will be shown that while for high ion concentrations clustering is favored, a critical concentration must exist below which cluster formation is energetically unfavorable, so that below that concentration the ions should be dispersed as pairs or quartets. Furthermore, the theory will attempt a correlation between the size of the cluster and the distance between clusters with various chain parameters, with the aim of predicting effects which have not, as yet, been observed experimentally.

The work will first of all consider the association of ions in media of low dielectric constant. Associated pairs, triplets, quartets, etc, in which the charges are as close to each other as is physically possible, will be referred to in this paper as multiplets, and the factors which limit the size of the multiplets will be explored in some detail. Subsequently, the possibility of the association of multiplets to form larger clusters, in which the multiplets are separated by nonionic material, will be investigated, and an equation derived for the cluster size as a function of various chain parameters. This equation will be applied to several cluster geometries. Finally, an argument will be presented for the existence of a minimum ion concentration below which multiplets can exist but cluster formation is energetically unfavorable.

Since the experiments mentioned above[1–12] have been described very recently, no attempt will be made to review them here. However, before describing the theory itself, it might be very useful to explore briefly the behavior of ions in organic media, for instance, in materials such as copolymers of ethylene and sodium methacrylate.

No perfectly satisfactory quantitative model for such a system exists, since materials like sodium formate or acetate are not soluble in aliphatic hydrocarbons. One could, of course, draw some conclusions from the

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(1) R. Longworth and D. J. Vaughan, *Polym. Preprints*, **9**, 525 (1968).

(2) W. J. McKnight, L. W. McKenna, and B. E. Read, *J. Appl. Phys.*, **38**, 4208 (1968); W. J. McKnight, T. Kajiyama, and L. W. Read, *ibid., Preprints*, **9**, 534 (1968).

(3) W. J. McKnight, invited paper presented before the March Meeting of the American Physical Society, Philadelphia, Pa., 1969.

(4) B. W. Delft and W. J. McKnight, *Macromolecules*, **2**, 309 (1969).

(5) T. C. Ward and A. V. Tobolsky, *J. Appl. Polym. Sci.*, **11**, 2403 (1967).

(6) E. P. Otocka and T. K. Kwei, *Macromolecules*, **1**, 401 (1968).

(7) E. P. Otocka, invited paper presented before the March Meeting of the American Physical Society, Philadelphia, Pa., 1969.

(8) E. P. Otocka, M. Y. Hellman, and L. L. Blyler, submitted for publication.

(9) A. V. Tobolsky, P. F. Lyons, and N. Hata, submitted for publication.

(10) E. P. Otocka and F. R. Eirich, *J. Polym. Sci., Part A-2*, **6**, 921 (1968).

(11) E. P. Otocka and F. R. Eirich, *ibid., Part A-2*, **6**, 933 (1968).

(12) S. Bonotto and E. F. Bonner, *Polym. Preprints*, **9**, 537 (1968).

crystal structures of long-chain carboxylic acids, but to what extent crystal structure models are relevant here is unknown. Thus, for greater generality, it seems preferable to resort to previous studies of ions in media of low dielectric constant. One such study, by Pettit and Bruckenstein,[13] is particularly instructive in that it considers the energetics of association for ionic aggregates such as ion pairs, triplets, quartets, up to sextets (nomenclature of this article differs slightly from that employed by Pettit and Bruckenstein), and concludes that for salts such as Bu_4NCl, Bu_4NClO_4, Bu_4NBr, $NaClO_4$, $HClO_4$, KCl, and many others in solvents of dielectric constant between 2.27 and 7.38 ionic multiplets are perfectly feasible, as has been confirmed experimentally. The most direct observation of ion quartet formation for sodium carboxylate ions is that of Otocka, Hellman, and Blyler,[8] who deduce it from the fact that sodium salts of low molecular weight carboxy terminated butadiene rubbers exhibit the phenomenon of chain-end association both in the bulk and in solution, and yield simple linear chains of an apparently very high molecular weight for butadienes of relatively low molecular weight.

Although no higher multiplets seem to be present in that system, it will be shown that they are entirely feasible for a material possessing a higher concentration of ionic species. In view of the above, it is highly probable that quite generally in media of low dielectric constant, such as polyethylene (PE), the ions would exist at least as contact ion pairs (or even as higher multiplets) since the energy W needed to separate a contact ion pair into separate ions is

$$W = -e^2/(r4\pi\epsilon_0K) \tag{1}$$

where K is the dielectric constant of PE ($\simeq$2.3), $1/4\pi\epsilon_0 = 1$ dyn cm^2/statcoulomb^2, e is the electronic charge, and r the distance between the centers of positive and negative charge in the contact ion pair. For r = 1.5 Å (a reasonable value for a $-COO^- Na^+$ pair) the interaction energy is of the order of 7×10^{-12} ergs per ion pair, and since at room temperature kT is of the order of 4×10^{-14} ergs, the fraction of ion pairs existing as separated ions is exceedingly small. Moreover, it should be stressed that no steric factors are involved in the ion pair formation.

Can the ions at this point associate into ion triplets, quartets, or perhaps even higher multiplets? Undoubtedly, but here already we have to recall that the ions are attached to chains which, unless the ion pairs forming the quartet belong to the same polymer chain, will be stretched and thus utilize some of the electrostatic energy released in the quartet or higher multiplet formation.

Therefore, it becomes reasonable to inquire about the constraints affecting this ionic collapse to yield an ionic multiplet. These are (1) the dimensions of polymer chains and of the ion pairs, (2) the tension on the chains resulting from ionic aggregation if sequenial ion pairs (*i.e.*, those nearest each other along the same chain) become incorporated into different multiplets (the incorporation of sequential ion pairs into the same multiplet is an event which is statistically comparable to ring formation, and which can probably be neglected, with the errors introduced by this assumption decreasing as the spacing between ions along the chain increases[14]); (3) the electrostatic energy released upon multiplet formation. It will be seen that this last item is not a limiting factor for reasonable multiplet sizes.

In the next section we shall first explore ionic multiplet formation with regard to the spatial requirements involved since these are, as will be seen, the limiting factors. Although initially "amorphous" multiplets will be considered, later on more ordered structures will be utilized, but only for the sake of calculational simplicity. In still later sections, it will be shown that multiplets can associate as a result of weak ionic interactions to yield clusters, and that the energies involved in the extension of chains in the process of cluster formation are comparable to the electrostatic energies involved. As mentioned before, a general relation will be developed between the cluster size and the electrostatic and elastic energies involved and applied to several simplified cluster geometries.

It should be stressed that the theory presented here is only a first approximation theory. Clearly the models which will be utilized for the structures of the multiplets or of the clusters are rather arbitrary, and were chosen so as to make the final calculation as simple as possible, while maintaining physical reasonableness.

II. Multiplet Size and Separation

We shall first explore the effects of chain extension on multiplet formation since this is one of the constraints on multiplet size. It is clear that the larger the ionic multiplets, of whatever structure, the further apart they must be from each other. Since we assume that sequential ion ion pairs are not incorporated into the same multiplet, the maximum separation between multiplets cannot be greater than the length of the fully stretched chain between neighboring ion pairs. Evidently, a relationship must exist between the number of ions in a multiplet and the separation between them, with the upper limit of that separation being given by the fully stretched chain.

The multiplets are most probably distributed at random in the body of the material. However, for the sake of calculational simplicity, we shall assume that they are distributed on a cubic lattice, *i.e.*, that each is located at the body center of a cube, the dimensions of which are given by R_0. R_0 is obviously also the nearest neighbor distance between multiplets. If the number of ion pairs in a multiplet is n_0, then the average concentration of ions, c, in pairs per cubic centimeter, is given by

$$c = n_0/R_0^3 \tag{2}$$

From stoichiometric considerations, c can also be set equal to

$$c = \rho N_{Av}/M_c \tag{3}$$

where ρ is the density of the polymer, $N_{Av} = 6 \times 10^{23}$, and M_c is the molecular weight of the chain between

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[13] L. D. Pettit and S. Bruckenstein, *J. Amer. Chem. Soc.*, **88,** 4783 (1966).

[14] H. Jacobson and W. H. Stockmayer, *J. Chem. Phys.*, **18,** 1600 (1950).

ionic groups. Equating these two values of c we obtain

$$R_0 = \sqrt[3]{n_0M_c/(\rho N_{Av})} \qquad (4)$$

The spatial prerequisites to amorphous multiplet formation will now be explored, since they provide another and more stringent constraint on multiplet size. We assume that the multiplet can be represented as a spherical liquid drop consisting of ions only, and that the hydrocarbon chain segments are confined to the surface of the drop; we assume thus that we are dealing with a well-defined phase separation. The following terms need to be defined: let v_p = volume of an ion pair, r_m = radius of the multiplet, S_{ch} = area of hydrocarbon chain which must be in contact with the surface of the ion sphere. For the case of the ethylene–sodium methacrylate copolymers, this would be the segment $-CH_2CHCH_2-$, the carboxylate ion which penetrates into the sphere being attached to the central carbon atom. The surface of the multiplet would thus be

$$S_m = 4\pi r_m^2 \qquad (5)$$

and the volume of the multiplet

$$v_m = 4\pi r_m^3/3 \qquad (6)$$

The total number of ion pairs in the multiplet can thus be expressed either as the ratio of the surface of the multiplet (S_m) to the contact surface of a chain (S_{ch}) or the volume of the multiplet (v_m) to the volume of an ion pair, and these two ratios must equal each other, *i.e.*

$$n_0 = v_m/v_p = S_m/S_{ch} \qquad (7)$$

Inserting the values calculated above, we obtain

$$r_m = 3v_p/S_{ch} \qquad (8)$$

For an ethylene–sodium methacrylate copolymer, reasonable values for v_p and S_{ch} are 12 Å^3 and 12 Å^2, yielding $r_m \approx 3$ Å and $v_m \approx 100$ Å^3. Thus a maximum value of eight pairs is indicated for perfect volume occupation, but it is very likely that the number will be smaller than that since packing of $-COO^-Na^+$ groups cannot be expected to lead even approximately to complete volume occupation. It should be stressed that once this multiplet has been formed it is completely coated with nonionic chain material, so that no additional ion pair can contact it. This fact will become very significant when we discuss clustering of multiplets in the next sections. So far, nothing has yet been said about the electrostatic energies involved. In the case of multiplet formation they are very much larger than the energies of chain extension (as will become evident further on when clustering is discussed) so that only spatial constraints need to be considered.

III. Clustering of Multiplets

In the preceding section we saw that the maximum multiplet size for a liquid drop type of ionic aggregate was of the order of eight ion pairs and that beyond that point an additional ion pair could not contact the liquid drop since the surface of the drop is coated completely. One could regard this ionic drop as a 16 functional cross-link. At this point the multiplets can possibly aggregate to form clusters of a wide range of possible structures, each of which leads to a slightly different electrostatic interaction. For example, the ionic drop discussed above could act as a nucleus for ion pair clustering, in which the ion pairs might act as dipoles attracted to the sphere by electrostatic forces, to each other by dipolar forces, and separated from each other by the thickness of a polymer chain. These cluster geometries would be repeated throughout the sample. We shall discuss a modification of this model in detail below. Alternatively, it is possible that the liquid drops themselves aggregate to form some sort of cluster, possibly with some dipoles acting as tie points between drops, and again this cluster would be repeated throughout the sample; a version of this model involving ordered multiplets will also be discussed. Finally a completely different model based on amorphous but charged multiplets will be described. Clearly many other models are possible, among them rod-shaped or sheet-shaped aggregates of ions as well as many many others.

Before proceeding to a detailed calculation of the electrostatic interactions and elastic work for some of the above models, we shall first consider the factors which enter into this computation. They are the following.

1. Upon cluster formation, work is done to stretch the polymer chains (*i.e.*, segments between ionic groups) from the distance corresponding to the existence only of primary multiplets, R_0, to that corresponding to a cluster of size n. It is assumed that the chains connect only nearest neighbor multiplets. Equation 4 for distances between multiplets is also applicable to distances between clusters, and the work of chain stretching can be calculated from the equations of the theory of rubber elasticity.

2. Electrostatic energy is released when multiplets aggregate to form a cluster, the work depending on the geometry of the cluster and the dielectric constant of the medium.

3. The cluster is not infinitely stable. Presumably at some temperature T_c the cluster decomposes, and it is at that temperature that the elastic forces and the electrostatic forces just balance each other.

4. In contrast to the multiplet case, we assume here that half of all the sequential ion pairs incorporated into the same cluster do yield "rings." This assumption is based on the reasoning that "ring formation" is expected to occur only for one of the two chains emanating from an ion pair on the surface of a cluster, while probably both chains emanating from an ion pair in the center of a cluster would yield rings. The factor of 2 is arbitrary, it might well be somewhat larger or somewhat smaller, but in view of the other uncertainties inherent in the theory the inaccuracy which is introduced in this way is relatively minor. It is discussed quantitatively in section VI. Most ion pairs lie on the surface of a cluster. To illustrate this point, let us assume that the ion pairs in the cluster are distributed on a cubic lattice, s ion pairs on a side. A model in which this is the assumed structure is discussed in detail in section IV-A. The total number of unit cubes in the large cube (the cluster) is s^3 while the number of cubes constituting the surface of this cubic

cluster is $s^3 - (s-2)^3 = 6s^2 - 12s + 8$. Thus, the fraction of ion pairs on surface of the cluster is $(6s^2 - 12s + 8)/s^3$, and the fraction in the interior is $1 - (6s^2 - 12s + 8)/s^3$. Since the ion pairs which are on the surface of the cluster can be assumed to be involved in ring formation involving sequential ionic groups only to the extent of one of the two chains emanating from them, the error in assuming that this state of affairs continues throughout the cluster is, to a reasonable approximation, the fraction of ion pairs not in contact with the surface. For $s = 3$, $n = 27$ and the error is 3.7%; for $s = 4$, $n = 64$ and the error is 12.5%, while for $s = 5$, $n = 125$ and the error is 21.6%. As will be shown in section IV, typical cluster sizes are of the order of 100 so the error is negligible in comparison to the other approximations inherent in the theory.

We shall first attempt to calculate the elastic forces involved in cluster formation. If the fundamental multiplets consist of four or more ions, it is evident that they would act as crosslinks. If these multiplets now form clusters, then, as was pointed out above, some chains will be extended while others will contract, unless we postulate a very rapid reorganization within the multiplet and subsequent "ring" formation, *i.e.*, the incorporation of sequential ion pairs within the same multiplet. Otocka, Hellman, and Blyler[8] find no evidence for rapid quartet reorganization around room temperature, which means that elastic forces must play a significant part in cluster formation, at least for multiplets of four or more ions.

The elastic force, f, acting on the two ends of a polymer chain is[15]

$$f = 3kTh/\overline{h^2} \qquad (9)$$

where $\overline{h^2}$ is the mean square end to end distance for the free chain and h the actual separation of the ends. The work of stretching a polymer chain from a distance R_0 to R, the distance corresponding to a cluster size of n is

$$W = \int_{R_0}^{R} f\,\mathrm{d}h = \int_{R_0}^{R} (3kT/\overline{h^2})h\,\mathrm{d}h = (3kT/2\overline{h^2})(R^2 - R_0^2) \qquad (10)$$

where R as a function of n is given by eq 4.

The work of contracting a chain from a distance of R_0 to 0 is

$$W = \int_{R_0}^{0} f\,\mathrm{d}h = \int_{R_0}^{0} (3kT/\overline{h^2})h\,\mathrm{d}h = -(3kT/2\overline{h^2})R_0^2 \qquad (11)$$

Since, as was mentioned before, it is taken that half the chains expand from R_0 to R while the other half collapse from R_0 to 0, the net work, per chain, done upon cluster collapse is simply the average of the two expressions for expansion and contraction, *i.e.*

$$W_{\mathrm{ch}} = (3kt/4h^2)(R^2 - 2R_0^2) \qquad (12)$$

It is convenient to express $\overline{h^2}$ in terms of the mean square end-to-end distance of a freely jointed chain, $\overline{h_0^2}$, *i.e.*

$$\overline{h^2} = \overline{h_0^2}(\overline{h^2}/\overline{h_0^2}) \qquad (13)$$

where

$$\overline{h_0^2} = l^2(M_c/M_0) \qquad (14)$$

l being the length of a C–C bond and (M_c/M_0) the average number of C–C links in a chain between ionic groups. Substitution of these relationships into the equation for W_{ch} yields

$$W_{\mathrm{ch}} = (3kT/4l^2)(M_0/M_c)(\overline{h_0^2}/\overline{h^2})(R^2 - 2R_0^2) \qquad (15)$$

where $(\overline{h_0^2}/\overline{h^2})$ is a number smaller than one which indicates how much smaller the mean square end to end distance of a freely jointed chain is than the real chain. For instance, for polyethylene the number would be one-eighth.[16] Inserting the values for R we obtain

$$W_{\mathrm{ch}} = \frac{3kT}{4l^2}\frac{M_0}{M_c}\frac{\overline{h_0^2}}{\overline{h^2}}\left[\left(\frac{nM_c}{\rho N_{\mathrm{Av}}}\right)^{2/3} - 2\left(\frac{n_0M_c}{\rho N_{\mathrm{Av}}}\right)^{2/3}\right] \qquad (16)$$

The electrostatic energy per ion pair released upon cluster collapse is, as was mentioned before, a function of the geometry of the cluster. Several geometries will be considered below, but for now we shall express the energy in the most general terms as a fraction, k', of the energy released upon formation of an ion pair from isolated ions for the particular system under consideration. The energy of ion pair formation was given as

$$W = -e^2/(r4\pi\epsilon_0K) \qquad (1)$$

Therefore, the electrostatic energy per ion pair upon cluster formation is given by

$$W' = k'e^2/(r4\pi\epsilon_0K) \qquad (17)$$

At some temperature T_c the cluster becomes thermodynamically unstable, and at that temperature the elastic force and the electrostatic forces just balance each other. Since the elastic force was calculated per chain and the electrostatic force per ion pair, W_{ch} can be set equal to W' at T_c, and we obtain

$$\frac{k'}{K}\frac{1}{4\pi\epsilon_0}\frac{e^2}{r} = \frac{3}{4}\frac{kT_c}{l^2}\frac{M_0}{M_c}\frac{\overline{h_0^2}}{\overline{h^2}}\left[\left(\frac{nM_c}{\rho N_{\mathrm{Av}}}\right)^{2/3} - 2\left(\frac{n_0M_c}{\rho N_{\mathrm{Av}}}\right)^{2/3}\right] \qquad (18)$$

which can now be solved for n. The result is

$$n = \frac{\rho N_{\mathrm{Av}}}{M_c}\left[\frac{4l^2}{3kT_c}\frac{\overline{h^2}}{\overline{h_0^2}}\frac{M_c}{M_0}\frac{k'}{K}\frac{1}{4\pi\epsilon_0}\frac{e^2}{r} + 2\left(\frac{n_0M_c}{\rho N_{\mathrm{Av}}}\right)^{2/3}\right]^{3/2} \qquad (19)$$

Since T_c can, in principle, be determined experimentally and k' calculated for any particular cluster geometry, n and R can be calculated. This will be done below. Also, several predictions can be made about the relationship of n or R to various experimental parameters such as the spacing of ions along the chain or the di-

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(15) M. V. Volkenstein, "Configurational Statistics of Polymer Chains," John Wiley & Sons, Inc., New York, N. Y., 1963, 501 eq 8.153.

(16) T. M. Birshtein and O. B. Ptitsyn, "Conformations of Molecules," John Wiley & Sons, Inc., New York, N. Y., 1966, p 205.

electric constant, and these will also be discussed in detail below.

IV. Calculation of k' for Three Structures for Ethylene–Sodium Methacrylate Copolymers

As was shown before, the maximum size for a spherical "liquid" ionic drop was of the order of eight ion pairs, and beyond that point an additional ion pair could not contact the ionic material since the drop was covered with a hydrocarbon surface consisting of 16 three-carbon chain segments. Any additional ion pair which would find it possible to join the cluster would have to do so at a distance of a chain thickness; this new ion pair, it should be recalled, would drag along with it two more chains, so that it would also contribute to the nonionic surface coating. Possibly ion quartets or even octets might join the original liquid drop, at a distance of a hydrocarbon chain, but the joining of very high multiplets is improbable.

A realistic picture of the cluster might therefore be the following: a central ionic drop consisting of up to eight ion pairs, coated with a nonionic skin. Ion pairs and higher multiplets surround this drop, attracted to it by electrostatic forces acting through a minimum thickness of a polymer chain, the whole cluster now acting as a cross-link. While the picture presented above might be realistic, it is extremely difficult if not impossible to handle quantitatively. It is therefore necessary to introduce some simplifying assumptions, concerned primarily with the geometry of the clusters. We shall assume three different geometries and calculate k' (and therewith also n and R) for all. The first of these will be called the "pure pair" model, and the second will be named the "octet-pair" model. The third model is based on amorphous multiplets which contain an excess charge, and are thus attracted electrostatically.

A. The "Pure Pair" Model. While this model is probably not physically accurate since quartets or octets represent a more stable situation thermodynamically, it is perhaps instructive to treat it quantitatively in order to obtain some idea of the relationship between n and the interaction parameter k', although, admittedly, for a model which represents a structural extreme.

The important features of this model are the following.

1. As will be seen below, for reasonable concentrations of the ionic comonomer the clusters are of the order of 100 ion pairs. Numerically, therefore, the contribution of the central liquid drop to the total is small. Thus we assume that the ionic drop does not exist, and that the only multiplets present in the cluster are ion pairs. This may be a serious conceptual imperfection, but the effects of introducing higher multiplets will be shown to have only a moderate effect numerically on the cluster size or spacing.

2. The only disruptive forces acting on the cluster are the temperature-dependent elastic forces of the chains which tend to pull the ion pairs out of the cluster. Upon disruption, only isolated ion pairs are present in the material.

3. The ion pairs act as dipoles, the dipole moment being given by the actual separation of the centers of charge in a $-COO^-Na^+$ pair multiplied by the electronic charge. The orientation of the dipoles within the cluster is probably such as to maximize the interaction energy between them. For the sake of a first calculation, a simple cubic array will be assumed in which the dipoles are in a head-to-tail arrangement along any one row and antiparallel in neighboring rows.

4. The interaction energy between coplanar dipoles is proportional to the inverse cube of the distance between them and is given by[17]

$$W_d = -(\mu^2/d^3)(1/4\pi\epsilon_0)(1/K)(2\cos\theta_A\cos\theta_B - \sin\theta_A\sin\theta_B) \quad (20)$$

where θ_A and θ_B are the angles made by the two dipoles with the line joining their centers. This is a well-known relation for dipoles separated by distances which are large by comparison to the charge separation within the dipoles.

5. The dipoles are separated from each other by the thickness of a polymer chain (not in its planar zigzag form but in the one most likely to encountered in a liquid). This distance may be too small for eq 20 to apply precisely, since the distance between dipoles is not very much larger than the charge separation within the dipole; it should still be an acceptable approximation, however.

One can now calculate k' for this geometry. To obtain a reasonably precise value, it is necessary to sum all the interactions of a dipole with all of its successively more distant neighbors. This represents a Madelung constant calculation for a dipolar lattice, and was performed before;[18,19] however, due to the small size of the cluster in the present case, it is preferable to redo the computation. If the nearest neighbors are taken to be at a distance d, the next nearest will be at $\sqrt{2}d$, the third at $\sqrt{3}d$, etc. Not all the dipoles which are at the same distance will yield the same interaction. For instance, of the six nearest neighbors, two are in a head-to-tail arrangement around the central dipole, while the four others are in an antiparallel arrangement. Taking all factors into account and going out to the seventh nearest neighbor at a distance of $\sqrt{8}d$, we obtain for the total interaction of any dipole with all of its neighbors

$$W = (-6\mu^2/d^3)(1/4\pi\epsilon_0 K) \quad (21)$$

To avoid counting each interaction twice, the energy *per* dipole in cluster formation is

$$W' = -(3\mu^2/d^3)(1/4\pi\epsilon_0 K) \quad (22)$$

Now, as was mentioned in section III, most of the ion pairs are on the surface of a cluster, so the factor of 3 is probably an overestimate. A factor of 2 seems more reasonable, and it will be adopted for a first calculation. Since the interaction energy for an ion pair is

$$W = -e^2/r4\pi\epsilon_0 K \quad (1)$$

we obtain

$$k' = W'/W = (2\mu^2/d^3)/(e^2/r) \quad (23)$$

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[17] E. A. Moelwyn-Hughes "Physical Chemistry," 2nd ed, Pergamon Press, Inc., New York, N. Y., 1961, p 306.

[18] J. A. Sauer, *Phys. Rev.*, 57, 142 (1940).

[19] J. M. Luttinger and L. Tisza, *ibid.*, 70, 954 (1946).

Let us apply this result to the case of an ethylene–sodium methacrylate copolymer containing 4.5 mol % of the salt. The following values are assumed to hold: $\rho = 1$ g/cm^3, $M_c = (100/4.5)28 = 620$, $l = 1.5 \times 10^{-8}$ cm, $T_c = 330$°K. A peak in tan δ was found at *ca.* 50° by both Otocka and Kwei[6] and by McKnight,[3] and tentatively ascribed to the breakdown of the association between salt groups. This does not constitute a proof that this is indeed T_c, but the value is a reasonable one and is used for the sample calculation in the absence of a better value. The persistence of diffraction effects up to 300° described in ref 1 is believed to be due to the multiplets and not to clusters

$$\frac{\overline{h^2}}{h_0^2} = 8$$

(This is the factor by which the real mean square end-to-end distance of a polyethylene chain differs from that of a freely jointed chain of l = 1.5 Å and the same number of links. Birshtein and Ptitsyn[16] give a factor of 4 over a freely rotating chain, and the additional factor of 2 represents the difference between the freely rotating and freely jointed chain). $r = 1.5 \times 10^{-8}$ cm, $M_0 = 14$ g/mol, $\mu = 1.5 \times 10^{-8}$ cm $\times$ 4.8×10^{-19} statcoulomb. (The distance of 1.5 Å is assumed to represent the separation between the sodium nucleus and the center of negative charge on the carboxyl group). $d = 7.0 \times 10^{-8}$ $\times$ cm (the dipoles are assumed to be separated by the thickness of a chain, $\simeq$5 Å; the separation of the center of the dipoles is thus one chain thickness *plus* the thickness of a sodium carboxylate dipole, $\simeq$2 Å). $1/4\pi\epsilon_0 = 1$ dyn cm/statcoulomb^2. $K = 2.5$ (the value of 2.3 for PE[20] is raised arbitrarily by 0.2 to take the sodium acrylate groups into account).

Insertion of these values into the equation for k' yields $k' = 0.020$ and this, in turn, when inserted into eq 19 for n (taking $n_0 = 1$ and the other values given above) yields $n = 160$ ion pairs which yields for the distance between clusters R = 55 Å. It should be recalled that X-ray studies[3] revealed a periodicity of *ca.* 83 Å for this material. Following this model to its logical conclusion, we note that the volume occupied by the dipoles, *i.e.*, the volume of one cluster is approximately $160\ (7 \times 10^{-8})^3 \simeq 55{,}000$ Å^3. By comparison, the volume of sample containing this cluster is of the order of $R^3 \simeq 165{,}000$ Å^3. Thus, the ionic "phase" occupies *ca.* 30% of the total volume. It should be stressed that crystallinity has been neglected entirely in this computation. No limits of error are given in these or any of the subsequent calculations because of the highly approximate nature of all of the models proposed. Indeed, the range of values for n and R encountered in all of the models might be taken as a range of uncertainty for the theory.

B. The "Octet-Pair" Model. The model, which is again quite arbitrary, assumes that above T_c half of the ionic groups exist as ion octets, *i.e*,, four pairs in closest proximity at the corners of a cube, and the other half in the form of ion pairs. Below T_c a cluster would be formed from the octets with the pairs acting as ties between octets, *i.e.*, connecting corners on an extension of a body diagonal; one pair sharing two corners of two octets, the closest approach between the pair and the octet being again one chain thickness. The geometry of this particular model is such that k' can again be evaluated easily, using classical electrostatics. For any pair interacting with a neighboring octet, the interaction energy can be calculated as $-e^2 \times 0.042 \times 10^8$. Since each pair is shared by two octets, the total interaction energy per free (tie) pair would be $-2e^2(0.042 \times 10^8)$. However, since only half of all the ion pairs are free, the other half being incorporated into octets, the last value has to be divided by two to obtain the interaction energy per pair (of any kind). Thus (neglecting interactions between octets themselves)

$$W' = -0.042e^2 \times 10^8/K$$

and since energy of ion pair formation is

$$W = -e^2/1.5 \times 10^{-8}K$$

we obtain

$$k' = W'/W = [e^2(0.042 \times 10^8)]/ \times (e^2/1.5 \times 10^{-8}) = 0.063$$

A calculation of n and R for 4.5 mol % of ionic groups yields n = 800 and R = 95 Å. We must keep in mind that in this case $n_0 \simeq 1.6$ since half of all the pairs are in octets.

C. Amorphous Charged Multiplets. One other model is worth investigating. It is based on the idea that amorphous multiplets might not contain exactly the same number of anions and cations, but an excess of one or more charges. This has been found in the past for nonpolymeric ions.[13] Such multiplets could aggregate by simple ionic interactions which, however, are much weaker than those involved in ion pairs due to the greater distances involved. For the purposes of a first calculation, let us assume an amorphous multiplet of the type discussed in section II with approximately eight ion pairs in it, but with one excess ion of either charge. Let us further assume that the multiplets arrange themselves on a cubic lattice, the positive and negative multiplets alternating in three dimensions. The precise interaction energy of each multiplet will depend on the detailed cluster arrangement and size, but we can still compute k' for various geometries by simply computing the total interaction energy for a particular cluster, and dividing value by the total number of ion pairs involved times the interaction energy for the formation of an ion pair. We assume that the average multiplet radius is 3 Å, and that each multiplet is surrounded by a "skin" of 5 Å thickness. The closest approach of the centers of charge would thus be 15 Å, and the following values of k' are obtained: for two multiplets, k' = 0.006; for three multiplets (linear arrangement), k' = 0.006; for four multiplets (square planar arrangement), k' = 0.008; for eight multiplets (cubic arrangement), $k;$ = 0.009. For a first calculation, 0.008 is taken. The results are n = 82 and R = 44 Å.

If n_0 is taken as 4 rather than 8, k' would double, and n and R would increase accordingly.

D. Further Possibilities. Obviously many other more or less simple models could be calculated. The preceding examples are designed to demonstrate the

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(20) J. Brandrup and E. H. Immergut "Polymer Handbook," John Wiley & Sons, New York, N. Y., 1966, p VI43.

fact that clusters of reasonable size can be obtained from relatively simple geometries, and, most important, that the detailed geometry does not influence the cluster size profoundly provided that some type of weak bonding is operative. This may be achieved if a sufficient fraction of ion pairs are present outside of compact multiplets to provide relatively weak interactions, or if ionic bonds can be effected through relatively large distances between charged amorphous multiplets.

A further quantitative improvement on the present theory may be possible but would probably involve enormous complications. One has to consider the facts that above T_c a distribution of multiplets sizes probably exists, and that the energy level of these multiplets depends not only on their size but (due to the elastic nature of polymer chains and the increase in separation between multiplets with increasing size) also on the size of their neighbors. The multiplets would presumably exhibit a size distribution and geometrical spacing which would minimize the total energy, including both electrostatic and elastic. With decreasing temperature, the multiplets would collapse into clusters not at one temperature but over a temperature range. Finally, even if the structure for such a system is characterized, the evaluation of k' seems quite difficult. Therefore, no extension of the theory is attempted here.

V. Minimum Ion Concentration for Clustering

Since our knowledge of the multiplet or cluster geometry is very tenuous, only a qualitative argument will be presented to illustrate the need for a minimum concentration of ionic groups for the observation of clustering.

Under normal circumstances, *i.e.*, the presence of ions at frequent intervals along a chain of high molecular weight, clustering is to be expected as described in the preceeding sections. However, let us consider the following situation: the spacing of ionic groups along the chain has decreased considerably, to the point of less than one ion per distance between physical entanglements, and the multiplets that are formed (possibly quartets) are also relatively far apart in the body of the material. The multiplets are still subject to the same attractive forces that were operative before, however, in an attempt to approach each other they have to move over fairly large distances. This is prevented by the presence of physical entangelements acting as crosslinks as well as by the multiplets themselves, which also act as crosslinks if $n_0 > 1$. In other words, if the attractive forces between multiplets are smaller than the elastic forces which prevent the multiplets from approaching each other, no cluster formation is to be expected. The critical concentration will naturally depend on the structure of the multiplets and the nature of the polymer chain (insofar as the latter influences elasticity and entangelement spacing).

VI. Concluding Comments

An inspection of the equations for n and R reveals the following correlations: $n \propto M_c^{1/2}$, $T_c^{-3/2}$, $K^{-3/2}$, $k'^{+3/2}$, and $(\overline{h^2}/\overline{h_0^2})^{3/2}$; similarly, $R \propto M_c^{1/2}$, $T_c^{-1/2}$, $K^{-1/2}$, $k'^{1/2}$, and $(\overline{h^2}/\overline{h_0^2})^{1/2}$; these are all subject to experimental verification.

As was pointed out in section III, the assumption was made that one-half of all the chains form bridges between clusters while the other half form intracluster loops. The figure of one-half is, of course, quite arbitrary, although the number is most probably greater than one-fourth and smaller than three-fourths. It is of interest, therefore, to see how n and R would be affected if these numbers were chosen. If three-fourths of the chains form intramolecular loops, n would increase by a factor of approximately 2.8, while R, due to the cube root dependence of n on R, would increase by only 40%. Should only one-fourth of the chains form intramolecular loops, then the effect would go in the opposite direction, *i.e.*, n would decrease by a factor of *ca.* 0.55, while R would diminish by only 18%.

In the above derivations it was assumed that the spacing of the ionic groups along the chain was uniform. Within the framework of the theory (Gaussian chain approximation, etc.) it is believed that a random distribution of ionic groups would not affect the results appreciably; however, their presence in blocks might alter the picture drastically. If the ionic blocks were of a sufficient length, several possible events might occur. One distinct possibility would be microscopic phase separation; on a somewhat smaller scale this might take the form of large multiplets formation, the multiplet being too far apart to interact. Several other possibilities are, of course, conceivable, but the one mentioned above is believed to be the most probable.

In this theory crystallinity was completely neglected. Also, multiply charged cations were not considered since the simplest neutral unit (a linear arrangement) would already have a quadrupole moment which would make calculations much more difficult. It is conceiveable that the structure of the clusters in those cases might consist of a cation surrounded by several carboxylic residues, perhaps in excess of those needed for neutralization. This grouping would act as a large negative ion, and these negative units would be held together by the remaining cations not involved in the direct anion–cation multiplets. This model might even hold for monovalent cations as was suggested by Wilson, Longworth, and Vaughan,[1] but the calculation of k' for such a model would also be quite difficult.

Although clustering was not discussed here from a free energy point of view, it should be evident that this is strictly a thermodynamic theory. The enthalpy is related to the electrostatic work while the chain elasticity is related to the entropy. At T_c, which in this theory bears a formal resemblance to a thermodynamic transition, the two factors (*i.e.*, ΔH and $T\Delta S$) are equal. The theory could, with only a slight change in the formalism, have been recast into classical thermodynamic terminology.

It should be pointed out that since this is a thermodynamic theory, no conclusions can be drawn from it regarding the viscoelastic properties of materials, even in temperature regions in which clusters are known to exist. It is conceivable that the relaxation times which affect viscoelastic properties might be very much longer than the life times of the clusters, and thus, from the rheological point of view over the usual time scales, the clusters might be of no imporance even if X-rays indicate that they do exist. The opposite is, of course, also possible.

Finally, it should be stressed that the theory has two conceptual errors built into it which, fortunately, act in opposite directions. Since the classical theory of elasticity is employed, it is mathematically quite feasible to obtain intercluster distances greater than the fully stretched length of a polymer chain; this is physically unreasonable. However, the tacit assumption is also made that chains are stretched between centers of clusters rather than between their surfaces. Since the latter possibility is much more likely, intercluster distances may well be greater than fully stretched chains without loss of physical reasonableness.

Symbols Used

d	distance between multiplets in cluster
e	electron charge
f	force needed to keep polymer chain at end-to-end distance h
h	end-to-end distance of polymer chain
$\overline{h^2}$	mean square end-to-end distance of polymer chain
$\overline{h_0^2}$	mean square end-to-end distance of freely jointed chain
K	dielectric constant of polymer
k	Boltzmann's constant
k'	($= W'/W$), dimensionless geometry-dependent factor giving the magnitude of the electrostatic energy released per ion pair in cluster formation.
l	length of repeat unit (1.54 Å for C–C bond)
M_c	average molecular weight of chain between ionic groups
M_0	molecular weight of repeat unit
N_{Av}	Avogadro's number
n	average number of ion pairs in cluster
n_0	average number of ion pairs in multiplet
r	distance between centers of charge in ion pair
r_m	radius of "amorphous" multiplet sphere
R	average distance between clusters
R_0	average distance between multiplets above cluster decomposition temperature T_c
s	number of ion pairs along one edge of a hypothetical cubic cluster
S_{ch}	area of hydrocarbon chain in contact with surface of "amorphous" multiplet
S_m	surface of amorphous multiplet of radius r_m
T_c	cluster decomposition temperature or cluster formation temperature
v_m	volume of multiplet of radius r_m
v_p	volume of ion pair
W	electrostatic work of ion-pair formation
W'	electrostatic work per ion pair in cluster collapse
W_{ch}	elastic work per chain in cluster formation
$1/(4\pi\epsilon_0)$	1 dyn cm^2/statcoulomb^2
ρ	density of polymer

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Interactions of Sodium and Potassium Ions with Sodium and Potassium Alginate in Aqueous Solution with and without Added Salt

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ABSTRACT: The interaction of sodium and potassium ions with sodium and potassium alginate were investigated by measuring the counterion activity coefficients in aqueous solutions of the polyelectrolytes with and without added simple electrolyte at 25°. In salt-free solutions, the counterion activity coefficients were found to increase with increasing dilution and the activity coefficients of potassium ions were higher than those of sodium ions throughout the concentration range. Counterion activity coefficients decreased with increasing polyelectrolyte concentration at constant simple salt concentration and decreased with decreasing salt concentration at a constant polyelectrolyte concentration. Deviations from the additivity rule were most pronounced when the salt and polymer concentrations were approximately equal. Good agreement was obtained when Manning's line-charge polyelectrolyte model was compared with the experimental results for the lowest simple salt concentration.

A previous publication[2] was devoted to an experimental study of the interactions of Na^+ and K^+ ions with κ-carrageenan and λ-carrageenan in aqueous solutions with and without added simple salt. Cation activity coefficients were determined using ion-selective glass electrodes. In the present paper, results of similar experiments are reported for the Na and K salts of alginic acid. The alginic acid used in this study was derived from *Macrocystes pyrifera*, a giant kelp which is extensively found in the coastal waters off the western United States. Structural investigations[3,4] have shown that alginic acid is a linear polymer of D-mannuronic

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(1) Taken from a portion of the Ph.D. thesis of T. J. P., Seton Hall University, 1968.

(2) T. Podlas and P. Ander, *Macromolecules*, **2**, 432 (1969).

(3) R. L. Whistler and W. M. Corbett in "The Carbohydrates, Chemistry, Biochemistry, Physiology," W. Pigman, Ed., Academic Press, New York, N. Y., 1957, Chapter 12.

(4) E. T. Davidson, "Carbohydrate Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1967.