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Glass Temperature Enhancement in Ionomers

It has been reported[1,2] that the glass transition temperature, T_g, of an ionomer is considerably higher than that of the polymer matrix before the introduction of ions. For example, in the case of Nafion, T_g increases[3] by as much as 100 °K. It is intuitively obvious that ion pairs function as cross-links of some kind and lead to T_g enhancement, but the exact mechanism by which this takes place has not been fully established.

It has been conjectured[1] that T_g is the temperature at which ion pairs dissociate and hence is the temperature at which the thermal energy approaches the electrostatic binding energy of an ion pair. However, this explanation does not account for several of the experimental features, including the rise in T_g as the acid form of the ionomer is neutralized to the salt form[4] and the dependence of T_g on the water content of the ionomer.[4] Further, in an ionomer of the Nafion type it does not seem plausible that an individual ion pair can act as a cross-link since both ions are on the same polymer chain.

In this Communication, we suggest that the mechanism responsible for raising T_g is qualitatively different from the one proposed above. It is known from small-angle X-ray scattering,[5] neutron scattering,[6] and Mössbauer studies,[7] as well as from other experiments, that the ionic groups in an ionomer aggregate to form clusters of ion pairs or dipoles. We propose that an ionic cluster as a whole acts as a cross-link and that the glass transition in an ionomer corresponds to the onset of orientational disorder or "melting" in a cluster of dipoles, as against a dissociation or "breaking" of dipoles.

The driving force for clustering lies in the fact that the electrostatic energy is lowered when dipoles aggregate in orientations that minimize the dipole–dipole electrostatic energy. At low temperature the orientations of the dipoles are locked in the minimum-energy configuration. As the temperature is raised thermal energy destroys orientational order in the cluster, thereby weakening the attractive electrostatic forces that bind it and causing the cluster to break up. We believe this to be the mechanism underlying the glass transition in an ionomer.

The transition temperature that we obtain for an ionic cluster turns out to be considerably higher than that of the other relaxations in an ionomer, such as the glass transition of the matrix or the glass transition of the water in the ionic regions. The relaxation occurring at the highest temperature is generally taken to determine the glass transition temperature of the ionomer, since this corresponds to large-scale motions of polymer chains. It seems natural, therefore, to identify the T_g of the clusters to be the glass transition temperature of the ionomer.

We have carried out computer simulations on a first-principles model of a dipole cluster to determine the electrostatic binding energy of the assembly and to study the phenomenon of "melting" in clustered dipoles. In this Communication we will describe qualitative features of our model, leaving details of the calculation to be reported later.

Central to our model is a cluster of dipoles interacting electrostatically. By assuming that ion pairs act as point dipoles we find the electrostatic energy of a cluster to be

$$E_{\mathrm{es}} = \frac{1}{4\pi\epsilon} \sum_{j>i}^{N} \sum_{i=1}^{N} \left(\frac{\vec{p}_i \cdot \vec{p}_j}{|\vec{r}_i - \vec{r}_j|^3} - \frac{3(\vec{p}_i \cdot (\vec{r}_i - \vec{r}_j))(\vec{p}_j \cdot (\vec{r}_i - \vec{r}_j))}{|\vec{r}_i - \vec{r}_j|^5} \right) \tag{1}$$

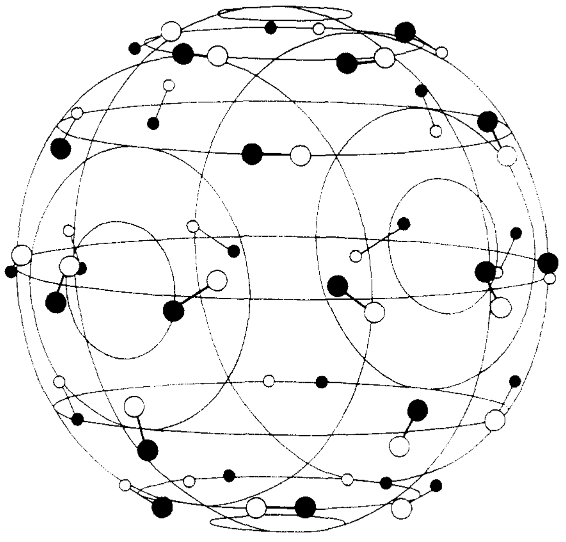

Figure 1.

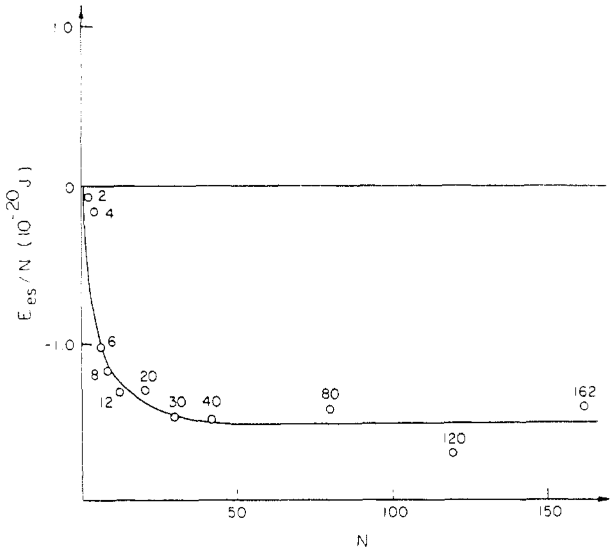

Figure 2.

where N is the number of dipoles in the cluster, $\vec{p}_i$ is the dipole moment of the ith dipole, located at $\vec{r}_i$, and ϵ is the dielectric constant of the medium. The location of dipoles within a cluster is not known from experiment. As a starting point, we assume that the dipoles are distributed uniformly on the surface of a spherical cluster and form a close-packed arrangement, the nearest-neighbor distance being determined by the molecular pair potential. This close-packing constraint determines the radius r of a cluster of N dipoles. The geometry that we have assumed above is clearly a simplifying assumption of our model, and we intend to study other geometries in the future. However, we do not expect geometry to alter qualitatively the results that we will obtain. The cluster geometry that we have chosen is motivated by the inverted micelle model proposed by Gierke.[8] In that model it is assumed that the ionic clusters are not interpenetrated by fluorocarbon chains. While retaining this assumption in our calculations, we point out that it is in no way crucial to our model. Allowing fluorocarbon chains to penetrate an ionic cluster would change the polarizability of the intervening medium and would alter the numerical value of T_g, but the qualitative results that we obtain would not change. The number of dipoles N in a cluster is determined by parameters such as the equivalent weight of the ionomer and the flexibility of the polymer chains and can be obtained from a first-principles calculation.[9] However, in this Communication, we will simply treat N as an input parameter to

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be obtained from experiment.

We have performed computer simulations on clusters of dipoles to determine which orientations of the dipoles minimize the electrostatic energy and hence to obtain the ground state ($T = 0$) energy of the cluster. Starting with a completely random distribution of orientations, we allow the dipoles to relax into a self-consistently stable arrangement. This ground state is highly degenerate as a consequence of the symmetry of the array, and so different initial conditions lead to various final orientations. Figure 1 shows a ground-state configuration for a cluster of 30 dipoles. Figure 2 is a plot of the electrostatic energy per dipole as a function of the number of dipoles in a cluster; typical values have been assumed for the parameters that enter our model. We see that the binding energy per dipole, E_{es}/N, initially increases with N and then reaches a constant value for $N \gtrsim 30$.

Most of the information needed in order to make qualitative predictions about T_g is contained in Figure 2. For example, if the average number of dipoles per cluster is known, we can obtain an estimate for T_g^{cluster} from

$$-E_{\mathrm{es}} = \tfrac{3}{2} N k_{\mathrm{B}} T_g^{\mathrm{cluster}} \qquad (2)$$

where k_{B} is Boltzmann's constant. We have argued earlier that T_g^{cluster} can be identified with the glass transition temperature of the ionomer. Hence we will drop the superscript in T_g^{cluster} and simply denote this quantity by T_g. The glass transition temperature could be determined more precisely by carrying out Monte Carlo simulations to study the behavior of thermodynamic quantities such as the specific heat as a function of temperature; for the present purposes, however, eq 2 will suffice since we are interested only in qualitative trends. We point out that eq 2 overestimates T_g since we have neglected the elastic contribution to the ground-state energy of the system. When dipoles aggregate to form clusters, the polymer chains to which the fixed ions are attached become deformed, and these conformational deformations give rise to an elastic energy that raises the ground-state energy of the system above that given by Figure 2. However, this contributes a constant term which we will ignore at this point since it does not qualitatively alter the behavior of our system.

We see from eq 2 that a plot of T_g as a function of N, the number of dipoles in the system, is simply the negative of the curve shown in Figure 2. This looks very similar to experimental plots[4] of T_g for Nafion-Cs as a function of Cs^+ content when the ionomer is neutralized from the acid form to the salt form. It is known that the degree of aggregation increases[2] as an ionomer is neutralized, and hence we believe that the mechanism in Figure 2 is responsible for the observed variation of T_g with increasing neutralization. We point out that the conventional explanation predicts $T_g \propto q/a$, where q is the charge of the counterion and a is the sum of the ionic radii of the ions that form a dipole. This leads, in contradiction with experiment, to a decrease in T_g as neutralization increases, since the charge of Cs^+ is the same as that of H^+ while the ionic radius of Cs^+ is larger than that of H^+. We also point out that our model predicts that the glass transition in an ionomer occurs over a broad temperature range, as is experimentally observed.[4] This is because in a real system we expect to find a distribution of clusters of different sizes, each of which "melts" at its own temperature.

This analysis also lends itself to a discussion of the effect of water absorption and counterion type on the glass transition temperature. Our model predicts that T_g decreases as water content increases, since water that is absorbed in the hydrophilic ionic regions causes the dielectric constant to increase, thereby reducing the electrostatic binding energy. Similarly, we would expect that T_g will decrease as counterion radius increases, because the dipole length a increases with counterion radius and it can be seen by a dimensional argument that $E_{\mathrm{es}} \propto 1/a$. Both the above predictions appear to be consistent with experiment.

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Group-Transfer Polymerization. 3. Lewis Acid Catalysis

Anionic polymerization of methacrylates is widely recognized as being capable of producing living polymers with controlled molecular weight and narrow molecular weight distribution (MWD). Simple alkyl acrylates, on the other hand, have been found[1] to behave quite differently from methacrylates in anionic polymerization, generally giving poor conversion, broad MWD, and loss of living ends so that block copolymer formation fails. We have chosen to address the problem of controlled polymerization of acrylates by the use of group-transfer polymerization (GTP). A recent report[2] has described the anion-catalyzed, ketene silyl acetal initiated polymerization of acrylic monomers. In this communication we describe the use of zinc halides and dialkylaluminum halides and oxides as Lewis acid catalysts for GTP and demonstrate their particular advantage in the preparation of polyacrylates of narrow MWD.

Zinc halides[3a–c] and dialkylaluminum chlorides[3d] have been widely used as catalysts for alkylations and other reactions of silyl enol ethers and ketene silyl acetals. We find that zinc chloride, bromide, and iodide and dialkylaluminum chlorides and oxides are effective catalysts for GTP of acrylates and methacrylates with initiation by the ketene silyl acetal (1, Scheme I). The resulting polyacrylates and -methacrylates have a narrow MWD, and the degree of polymerization is controlled by the ratio of monomer to initiator used (see Tables I and II). The MWD of polyacrylates prepared by GTP with the Lewis acid catalysts is generally narrower than that of polyacrylates prepared by GTP using anion catalysts such as

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