STRUCTURE AND VISCOELASTIC PROPERTIES OF ION-CONTAINING POLYMERS IN THE SOLID STATE

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Abstract—The evidence concerning the state of aggregation of the ions in organic ion-containing polymers is summarized. The bulk of the evidence, coming from small angle X-ray scattering, water uptake, glass transition, rheological and mechanical measurements, suggests that below a critical ion concentration the ions act as simple cross-links, whereas above that point more extensive clustering is encountered. Clustering manifests itself in the presence of a small angle X-ray peak at Bragg distances of *ca.* 20–100 Å, from the shape of which a model of a cluster has been proposed. Below the clustering region, styrene ionomers absorb at equilibrium *ca.* one water molecule per ion pair, while above that concentration more water is retained. Also, near the clustering region the glass transition shows a very rapid rise with ion content.

Clusters influence the mechanical properties profoundly. A dramatic broadening of the relaxation region is observed in stress relaxation, as well as the appearance of new tan δ peaks the position of which can also be correlated with ion concentration. The melt rheology is also affected; the temperature shift necessary to obtain superposition of various properties (such as G' vs ω for the ester and salt) exhibits sigmoidal behaviour near the clustering transition.

In general, ionic clusters act very much like fillers or crystallites, so that a sample containing only a small ion concentration behaves in many respects very much like a highly filled or highly crystalline material.

I. INTRODUCTION

Over the past few decades, extensive studies have been performed on a wide range of ion-containing polymers in aqueous solutions, i.e. the polyelectrolytes.[1,2] It is surprising, therefore, that very little attention has been devoted to the investigation of this important class of materials in the solid state. The first review of solid-state properties,[3] published in 1967, is devoted primarily to the polyphosphates; a more recent review[4] also includes studies on rubbery polymers and polyethylene. Very recently, a collection of reviews has appeared dealing with a range of solid state investigations.[5] However, in spite of all the recent work, the study of the solid state properties of ion-containing polymers lags far behind the solution studies.

Several possible reasons come to mind for this lag. In the area of applications, many more are known in which ion-containing polymers are used in dilute solution rather than in the solid state. As a matter of fact, the only material which is commercially successful in this field is an ionomer based on ethylene,[6] with a few other materials used only on a small scale as additives. For this reason, very little industrial effort has been devoted to this field. From a fundamental point of view, it has been known that ions aggregate in polymeric matrices, but the elucidation of both the extent of aggregation and the structure of the aggregate have presented very complex problems. This has possibly also contributed to the reluctance of workers to get into the field. In spite of these difficulties, several groups have studied the physical properties of ion-containing polymers in the solid state,[7–16] and a consensus is slowly emerging regarding the structure of the aggregates and their effect on viscoelastic properties, although no unanimity has, as yet, been achieved.[14,15] In this presentation an attempt will be made to review the present status of the field.

The first part of the presentation will concern itself with evidence for the type of ion aggregation encountered under various conditions that comes from several different experimental approaches other than rheological studies. These include small angle X-ray scattering, water uptake, and the glass transition. The second part will summarize the rheological evidence concerning ion aggregation, coming from such experimental approaches as dynamic mechanical and stress relaxation studies, as well as from melt rheology investigations.

Before proceeding with the main part of the discussion, it might be useful to recapitulate our current understanding of the structure of ion-containing polymers, which will provide a unifying background for the presentation of the experimental data.[17,18] It should be stressed that no unanimity exists, as yet for some of the views to be presented here, but the bulk of the evidence does seem to point in that direction.

In materials of low dielectric constant, even at low concentrations, the ions aggregate to some extent to form multiplets which act as transient crosslinks. These aggregates are quite small (several ion pairs), their lifetimes decreasing with increasing temperature. Above a certain concentration, a different type of ion aggregation is found. In this case, many ions come together, along with some non-ionic material, to give sizeable clusters which not only act as crosslinks, but, more precisely, like a re-enforcing filler or like microcrystallites. It is exceedingly difficult to estimate the sizes or separations of the clusters, but estimates of the order of 100 ion pairs separated by *ca.* 100 Å are typical. The concentration at which the transition between the multiplet and the cluster structure takes place depends on the host material. In polyethylene, clusters seem to exist exclusively even at the lowest concentrations which have been studied.[12] In polystyrene the transition takes place at 6 mol% of ionic comonomer (sodium methacrylate),[16] while in ionomers based on ethyl acrylate it lies at *ca.* 10% (see below).[19] In mixtures of poly (propylene oxide) and lithium perchlorate, which behave like ion-containing polymers due to the strong interaction between the ether oxygen and the cation,[20] the transition seems to lie at *ca.* 16%. Finally, in

the polyphosphates, even with complete neutralization, no clustering can be observed.[3]

It is worth noting that the heterophase (cluster) model for the structure of organic ionomers is quite new. It was first proposed by Bonotto and Bonner,[9] and subsequently adopted, with some modifications, by several groups of investigators.[11,12,16] As a matter of fact, a very approximate theoretical treatment has appeared.[17]

II. NON-RHEOLOGICAL EVIDENCE FOR ION AGGREGATION

A. Small angle X-ray scattering

The most convincing single line of evidence pointing toward the existence of some type of heterogenieties comes from small angle X-ray scattering (SAXS). Small angle peaks have, by now, been observed in the ethylene ionomers,[21,22] and in ion-containing copolymers based on butadiene,[15,23] styrene,[16] and polytetrafluoroethylene.[24] They have also been found in poly (cesium acrylate) although at somewhat wider angles.[25] There is no doubt that the low angle peaks are ion associated, since a blank run on the parent acid shows no trace of a low angle peak. Furthermore, in polystyrene based ionomers, which have been investigated on both sides of the multiplet–cluster transition, no low angle peak appears below *ca.* 5 mol% of ionic repeat units, i.e. in the multiplet region, whereas it does appear above that point. The cation of choice here is cesium, since it is the heaviest of the alkali ions. Finally, in polyethylene, in which some contribution to the scattering might be expected from the crystal lamellae, the peak was found to persist even at temperatures far above the melting point. In the styrene based materials, no such problems exist. The Bragg spacings calculated from these peaks range from *ca.* 30–60 Å.

Even without a detailed analysis, it is clear that the small angle peaks must reflect electron density inhomogenieties which exist in the salts over distances of *ca.* 10–100 Å. Detailed interpretations of the data are difficult, however, since many models can be imagined which are in accord with the experimental scattering results. The most sophisticated analysis to date was carried out on the ethylene ionomers.[22] The proposed model features an ionic cluster with a radius of 3–13 Å (which presumably also contains some hydrocarbon component), surrounded by a hydrocarbon shell from which most of the ions have been excluded. The total size of the unit is of the order of 50–70 Å. This model is in satisfactorily agreement with all the features observed by SAXS.

B. Water uptake

The best correlation between ion aggregation and water uptake has been obtained again in the styrene ionomers[16] which as has been mentioned before, were investigated on both sides of the multiplet-cluster transition region. Figure 1 shows the equilibrium water uptake at room temperature for styrene-sodium methacrylate copolymers, plotted as the number of water molecules per ion pair against the ion concentration. While the total number of points is too small to be sure of the detailed shape of the line, the trend is very clear. At low ion concentrations, where the ions exist in the form of small multiplets surrounded by the hydrocarbon matrix, only selected sites on this multiplet are capable of retaining water, apparently one water molecule per ion pair. However, above the 5–6% region, where the ions aggregate to form clusters, a much larger amount of water can be retained.
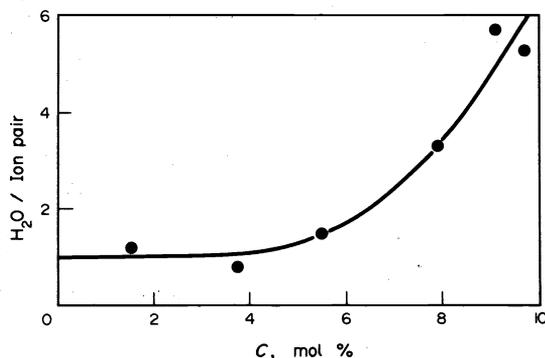

Fig. 1. Equilibrium water content (H_2O molecules per ion pair) in styrene ionomers at room temperature vs sodium methacrylate concentration in mol%.

Since the dielectric constant is, presumably, very much higher within the cluster than in the hydrocarbon region, many more water molecules can be accommodated. If it is recalled that not all the ions can possibly exist in the cluster, even at relatively high ion concentrations, it becomes clear that the water retention capability of the cluster must be very large.

In polyethylene, in which the ions are clustered over the entire concentration region, the water uptake is consistently high.[15] However, meaningful correlations with styrene are difficult, primarily because of the fact that the glass transition of the styrene ionomers is above 100°C, while that of polyethylene is below 0°C; the water uptake experiments are usually performed at room temperature, which means that each of the polymers is in a different region relative to its glass transition.

C. The glass transition

Although the glass transitions in several systems have been investigated, only two will be discussed here since only in these have both sides of the multiplet–cluster transition been studied. The ethyl acrylate–metal acrylate system has been studied over almost the entire concentration region with a wide range of metal cations. Independent of the ion, the rise of T_g with ion concentration is initially linear; somewhere between 5 and 15% of the ionic comonomer (depending on the ion) the line curves upward, and at some still higher concentration (10–35%, again depending on the ion) it becomes linear again with a slope somewhat lower than in the low concentration region. Preliminary rheological studies suggest that the sigmoidal region is associated with the existence of clusters.

If the glass transition is plotted not against the concentration, c, itself, but against cq/a, where q is the cation charge and a the distance between centers of charge in the ion pair, then a single line is obtained for all the cations studied. This plot is shown in Fig. 2. The superposition of all the lines on this plot is not surprising if it is recalled that in the polyphosphates or silicates all the T_g results for all cations also fall on a straight line if T_g is plotted against q/a.

In a study of the glass transitions in styrene-sodium methacrylate copolymers with up to 10 mol% of the ionic component, no sigmoidal behavior was noticed in spite of the fact that X-ray and rheological evidence suggests a transition at *ca.* 5–6%. This result possibly indicates that the glass transition behaves in a non-linear fashion only after a large concentration of clusters has been built-up, rather than upon the onset of clustering as determined
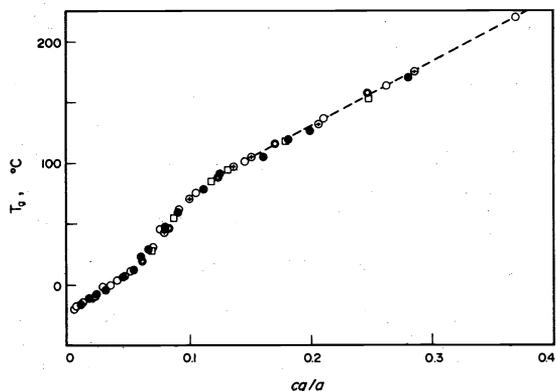
Fig. 2. Glass transition in ethyl acrylate ionomers (°C) vs metal acrylate concentration, c, times the ratio of cation charge, q, to the distance between centers of charge, a, q is the units of electrons and a in Å. Symbols: ●Cs; ○K; ○Na; ○Li; ■Ba; ○Ca.

rheologically. A more extensive rheological study of the ethyl acrylate ionomers is needed, however, before this possibility is confirmed.

III. RHEOLOGICAL EVIDENCE FOR ION AGGREGATION

A. Stress relaxation

Of all the ionomers, the styrene based materials have been investigated most extensively by the technique of stress relaxation both above and below the clustering transition.[16] The ethylene-based materials were also studied,[11] but in that case the presence of crystallinity makes the interpretation of the results much more difficult. Figure 3 shows the stress relaxation master curves for polystyrene and two styrene ionomers of 3.8 and 7.7 mol% sodium methacrylate, all drawn at $T = T_g$. The parent polymer, as might be expected, shows only one inflection point at log $E \approx 6.5$, which is related to the entanglement spacing in the material. In the 3.8% sample, two inflection points are evident, on at the same E value as in pure styrene and another at log $E \approx 7.5$ This second inflection point is a function of the ion concentration, and for $c < 6\%$ correlates well with the modulus of elasticity calculated by assuming that each ion pair acts as a crosslink. For this ion concentration, as well as for all the
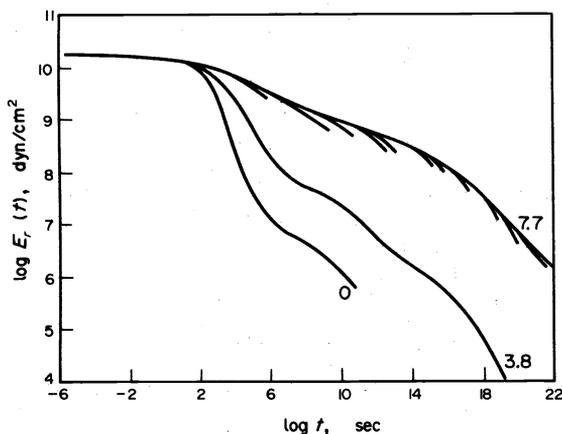
others below 6%, time–temperature superposition is applicable over the entire temperature and modulus range that was studied. A comparison of the two curves for 0 and 3.8% of ions shows also that the transition region is broadened considerably, i.e. that if ions are present, more time is required at T_g for the modulus to drop to a particular value than in the absence of ions.

The 7.7% sample shows this time slowdown to be even more drastic. In addition, however, it can be seen that time–temperature superposition fails. This is indicated by the many lines which emanate from the main line, and is a result of optimizing superposition in the short-time region. This type of behavior is general not only for all polystyrene samples above ca. 6% of ions, but also for all other clustered samples which have been investigated by this technique, i.e. sodium methacrylate and the poly (tetrafluoroethylene) based ionomers.

Figure 4 shows the shift factors for the styrene ionomers with up to 10 mol% ionic material. A sharp discontinuity is evident between 5 and 6%, which correlates with the onset of clustering. It should be noted that the shifting of the curves above 6% has been done so as to maximize overlap in the short time region. The result can properly be called a pseudo-master curve.

As might be expected, changes in the molecular weight for $c \leqslant 6\%$ affect the stress relaxation behavior only below log $E = 6.5$, in pretty much the same way as non-ionic samples are affected. However, for $c > 6\%$, above ca. 180°C, the low molecular weight samples do exhibit time–temperature superposition, in contrast to those of high molecular weight. This is possibly due to the effect of molecular weight on the cluster size or life-time at those temperatures, and might even indicate a complete cluster decomposition; this is unlikely however, in view of the melt rheology results. Changes in the cation have only minor effects. Cesium exhibits a slightly lower ionic inflection point than sodium, with the lifetimes of the aggregates being also somewhat shorter; barium, on the other hand, suggests a somewhat longer lifetime.

Figure 5 illustrates the similarity of ionomer stress relaxation curves independent of the type of parent polymer. The three ionomer samples shown in (a), (b) and
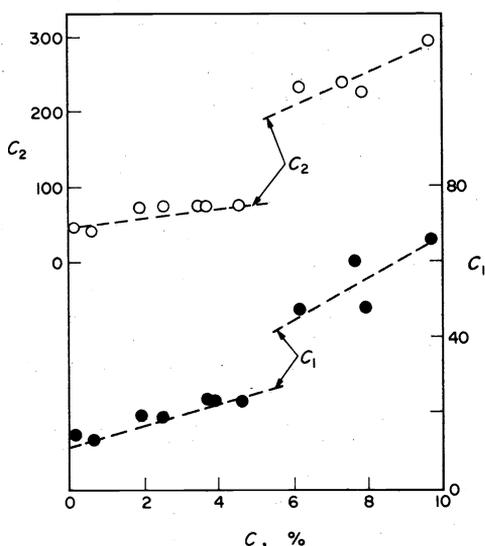

Fig. 3. Stress relaxation master curves for polystyrene and a 3.8 mol% styrene ionomer, and a pseudo master curve for a 7.7% ionomer. Log E vs log time.

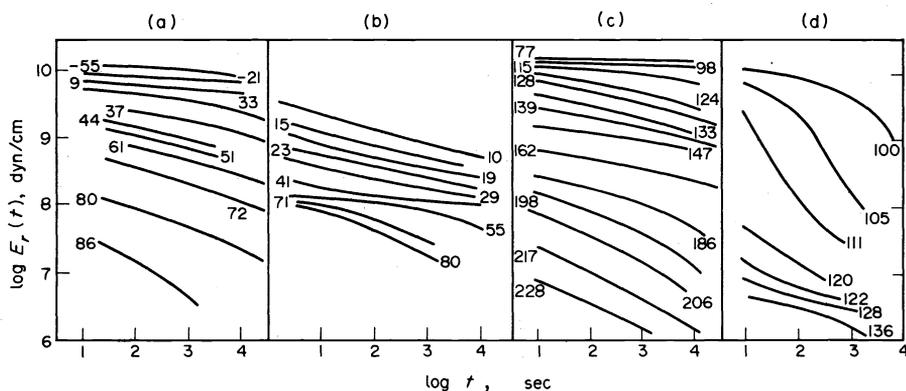Fig. 4. The WLF constants C_1 and C_2 for styrene ionomers at $T_{ref} = T_g$ as a function of ion content.

Fig. 5. Stress relaxation master curves (log E vs log t) for (a) an ethylene ionomer (8% acid, 47% neutralized), (b) and ethyl acrylate ionomer (12% sodium acrylate), (c) a styrene ionomer (7.7% sodium methacrylate) and (d) polystyrene.

(c), are, respectively a copolymer of ethylene containing 8.0 mol% acidic comonomer (neutralized to 47%),[11] a copolymer of ethyl acrylate with 12% ionic groups,[26] and a copolymer of styrene with 7.7% sodium methacrylate.[16] All these materials are presumably in the clustered region, and clearly resemble each other very much. Part (d) of this figure shows the stress relaxation results for pure polystyrene. It is evident that a styrene ionomer with only 7.7% ions resembles an ethylene ionomer (and therewith also ethylene, since the last two are very similar) and an ethyl acrylate ionomer much more than its parent polymer.

B. Melt rheology

Only two types of materials were investigated to any extent by this technique, the ionomers based on ethylene[27] and on styrene.[28] In the ethylene ionomers, it was found that a sample of 4.1 mol% ionic comonomer neutralized to the extent of 56–59% failed to show time–temperature superposition, both for sodium and calcium ions; by contrast, in the unneutralized acid samples, time–temperature superposition was applicable. The ethylene ionomers, it should be recalled, are clustered at all ion concentrations, and only one ion concentration was studied. A subsequent investigation was devoted to the styrene ionomers over a narrow modulus region, but over a broad range of ion concentrations. It was found that in the range of $10^4 \leq G' \leq 10^6$ dyn/cm^2, the G' vs ω plots for the acid, the esterified sample, and the salt could be made to superimpose by a careful selection of the test temperature (or by a temperature shift). As might be expected, salt samples, or for that matter ester samples, of different concentrations could not be made to superpose. Figure 6 shows the temperature differences between ester and salt as a function of carboxylate content. As can be seen, the rise is rapid initially, levels off between 2 and 4%, and then rises rapidly again. This behavior clearly suggests a change in the structure of the ionic aggregates above 4%. Thus, since other evidence points to the existence of clusters above ca. 5–6%, while melt rheology shows a discontinuity already at 4%, it seems that the latter technique is most sensitive to changes in the morphology of the ionic aggregates.

C. Dynamic mechanical properties

Again, a wide range of similarities emerge when one compares the dynamic mechanical properties of ionomers, and, as with stress relaxation, the similarities tend to be
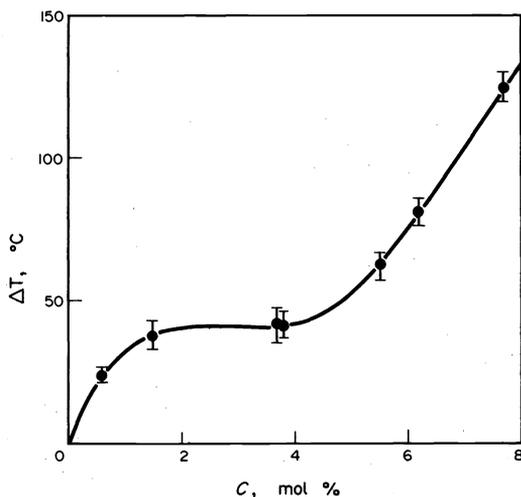

Fig. 6. The temperature shift, ΔT(°C), needed to obtain superposition between ester samples and corresponding styrene ionomer samples as a function of the sodium methacrylate content, c.

greater than those between an ionomer and its parent polymer. Figure 7 shows tan δ (ca. 1 Hz) for three types of materials. The uppermost set of curves reproduces the data for styrene and for two ionomers,[16] i.e. 7.7 and 7.9%. The next line gives the results for and ethyl acrylate copolymer containing 18.1 mol% sodium acrylate,[29] while the lowest set of curves presents the data for polyethylene and two ionomers[14] of 2.26 and 2.78%. All the ionomers are clustered, and the similarities are evident. The low temperature peak in all cases represents probably the glass transition of the predominantly non-ionic regions, while the peak at higher temperatures is due to the glass transition of the predominantly ionic microphase. The high temperature peak, in all cases, has the higher tan δ value. In the multiplet region, the polystyrene ionomers also show a peak above T_g, but that peak is very small by comparison to the main peak and moves only slightly with ion concentration. By contrast, the "ionic" peak is strongly temperature dependent, the variation being of the order of 20°/mol% ionic comonomer in styrene and ethylene.

D. Modulus–temperature data

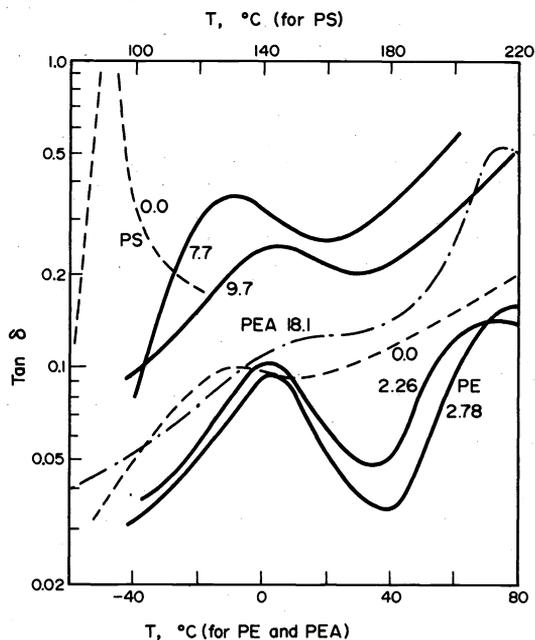Figure 8 shows the variation of the 10 sec modulus with temperature for styrene and two ionomers with 1.9 and

Fig. 7. Tan δ vs temperature for polystyrene, two styrene ionomers (7.7 and 9.7 mol%), an ethyl acrylate ionomer (18.1 mol%), polyethylene, and two ethylene ionomers (2.26 and 2.78 mol%).
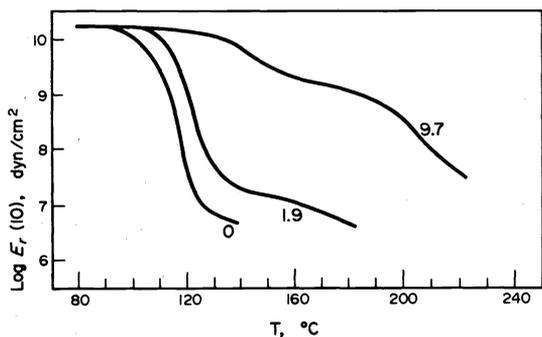

Fig. 8. Isochronal (10 sec) relaxation modulus vs temperature (°C) for polystyrene and two styrene ionomers (1.9 and 9.7 mol%).

9.7 mol% sodium methacrylate.[16] While the 1.9 sample, in which only multiplets are present, shows no unusual features, the 9.7 material, which is clustered, looks very much like a phase-separated block copolymer system. A superficial inspection of the plot for the last sample might suggest that the total amount of the high temperature block is very large, i.e. ca. 60–80%, with the T_g of that block being of the order of 200°C. This feature suggests that a substantial volume of the non-ionic polymer is incorporated into the ionic regions.

A study of samples of closely spaced ion content reveals no abrupt changes in the shape of the modulus–temperature curves. Therefore this technique is not the best for a study of the onset of clustering. However, it does reveal very dramatically the profound changes in polymer properties which can be achieved with less than 10% of ionic material.

IV. CONCLUSION

The preceeding discussion has attempted to present, briefly, the evidence for the existence of different types of ionic aggregates i.e. clusters and multiplets. Which of the

two is encountered under various circumstances depends entirely on the ion concentration and the nature of the host polymer. It was shown that a wide range of polymer properties is affected by the presence of ionic clusters, notably small angle X-ray scattering, water uptake, and the glass transition.

Special emphasis was placed on the effect of ionic aggregation on viscoelastic properties, as measured by stress relaxation, dynamic melt rheology, the torsional pendulum, and modulus–temperature behavior. Of these, the dynamic melt study gives perhaps the clearest indication of a charge in the nature of ion aggregation as a function of ion concentration, with stress relaxation also providing quite a sensitive test. Dynamic properties at constant frequency in the glass transition region show the existence of two peaks, which correlate well with modulus–temperature data. For clustered materials, both indicate a range of properties which are quite similar to those of the phase separated block copolymer systems.

It is of particular interest to note that in both dynamic mechanical and stress relaxation studies, clustered samples of styrene, ethyl acrylate and ethylene resemble each other much more strongly than, for example, pure styrene and a styrene ionomer.

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