Aggregate Modification via Plasticization of Ionomers—Dynamic Mechanical and Morphological Studies

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Received October 25, 1991; Revised Manuscript Received June 30, 1992

ABSTRACT: Plasticization of random styrene–(*N*-alkyl-4-vinylpyridinium iodide) ionomers was carried out using one of the following methods: quaternization of the vinylpyridine groups with *n*-iodoalkanes, alkylation of the styrene with 1-decene, or external plasticization with diethylbenzene. The materials thus prepared were analyzed using dynamic mechanical and small-angle X-ray scattering techniques. It was shown that plasticization of the styrene matrix induced clustering in these materials, while the ionomers in which the vinylpyridine groups were plasticized retained the characteristics of one-phase materials. The amount of material incorporated into the clusters was seen to vary depending on the mobility of the plasticizer, thus the fraction of clustered material in the externally plasticized ionomers was significantly greater than in the internally plasticized materials.

Introduction

The incorporation of ions into nonpolar matrices commonly leads to phase separation of the materials into ion-poor and ion-rich domains and results in materials with very different properties from their nonionic, one-phase precursors. Styrene-*co*-(sodium methacrylate) ionomers are good examples of this phenomenon. Even at very low ion concentrations, they show behavior significantly different from that of the parent acid copolymers in that the ionomers exhibit, for example, higher moduli at elevated temperatures and greatly increased melt viscosities.[1–5] All of these changes in the materials have been ascribed to the presence of phase-separated ionic and nonionic domains.

In the case of random ionomers, this phase separation into ionic aggregates is believed to result in entities known as multiplets and clusters. The existence of these two types of aggregates was first suggested in 1970;[6] however, there is still considerable controversy over the exact nature and structure of both multiplets and clusters.[7] As a consequence of this controversy, as well as the dramatic changes in properties resulting from ion incorporation, there is a growing body of experimental data from which the effects of this phase separation on the properties of ionomers can be assessed.

It is thought that multiplets are aggregates composed of a few ion pairs. With radii of the order of 5 Å, they are too small to behave as a phase distinct from the matrix. Rather, they act as thermolabile cross-links within it, thus serving to raise the glass transition temperature of the matrix.[1–3] In most random ionomers, multiplets are probably too small to be detectable by small-angle scattering techniques. They are, however, easily observed in the halatotelechelics,[8–11] where their average size is bigger (ca. 10 Å).

Clusters, by contrast, are believed to exist as a separate phase. Clusters contain many ion pairs as well as a significant proportion of chain material and are comparatively large. Consequently, clusters exhibit their own glass transition temperature and their effect on the T_g of the surrounding matrix may be expected to be quite complex.[1,2,12]

Both dynamic mechanical (DM) techniques and small-angle X-ray scattering (SAXS)[13,14] have been used extensively to observe aggregation in ionomers. In the first, the mechanical behavior of the materials as a function of temperature is under study. SAXS, on the other hand, probes the morphology of phase-separated domains. These two techniques explore different aspects of materials; dynamic mechanical experiments are frequency dependent and probe the molecular motions in the various phases, while SAXS is a static technique and probes average electron density differences. Thus, these two techniques are complementary, but are not necessarily sensitive to the same features of the aggregates.

In dynamic mechanical experiments, clustered ionomers are characterized by the presence of a rubbery inflection or plateau seen in the curve of storage modulus versus temperature. Furthermore, it is possible to determine the glass transition temperatures of both phases from the peaks seen in plots of the loss tangent against temperature.

The SAXS profile from an ionomer depicts the scattered intensity of the radiation, I, as a function of q ($q = 4\pi(\sin\theta)/\lambda$, with q the observation angle), which is related to the inverse of the average Bragg distance, and contains two features which are of interest. At very small q, ionomers generally exhibit an intensity upturn, whose meaning is at present unclear.[15] At slightly larger values of q, the profiles of clustered ionomers show a broad peak in the intensity, indicative of the presence of domains which interact with the radiation. It is not clear in all cases whether these peaks reflect shape or structure factors.[11] However, they have been used in both capacities to determine the scale of the aggregates.[8,13]

On the basis of the many studies which have been directed at an understanding of the phase separation encountered in ionomers, it is clear that there are a number of factors which influence ionic aggregation.[16] Only those four which are relevant to the present study will be introduced here, two pertaining to the ionic groups and the other two related to characteristics of the matrix.

Unquestionably, the ionic moieties present in ionomers determine many of the properties of the material. It is widely recognized that the concentration of ions markedly influences the aggregation in ionomers, with higher ion concentrations enhancing clustering, as seen in many mechanical studies.[1–3] The type of ion involved in the aggregation also appears to greatly affect clustering. Small

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ions, having a much higher charge density, enhance clustering,[12] while large ion pairs may even lead to a complete disruption of the clusters.[17,18]

The nature of the matrix influences the phase separation encountered in ionomers as well. Polymers which are composed of polar units are better able to solvate the ion pairs. As a result, matrices which are polar are less likely to show evidence of clustered domains.[19] Another aspect of the matrix which influences clustering behavior is the glass transition temperature. Experimental evidence indicates that ionomers with a lower T_g are more likely to be clustered than similar materials possessing a higher glass transition temperature.[20]

Thus, since a reduction in the glass transition temperature can enhance clustering, there is increasing interest in ionomers with lowered T_g's. To achieve this, plasticizers may be added to the materials as small molecule diluents or they may be chemically attached to the polymer chain via postpolymerization reactions. The former is considered an "external" plasticizer and the latter is denoted as "internal". There are certain advantages associated with each method. In the case of external plasticization, a very small amount of diluent makes a large difference in the properties of the material. Furthermore, a wide range of potential plasticizers is available and the introduction of the plasticizer is often relatively simple. The major disadvantage to using external plasticization is the mobility, especially the volatility, of the plasticizer. Attaching the plasticizer to the polymer chain obviously removes any problem with mobility. While this method of plasticization is not as effective as the use of external plasticizers in reducing the glass transition temperature, it clearly permits a greater amount of control. However, this technique, too, has some disadvantages. Postpolymerization reactions are associated with a number of problems, in particular the availability of reagents, possible unwanted side reactions, such as chain degradation or cross-linking, and the randomness of introduction of the new group. A third method of plasticization, monomer modification prior to polymerization, can also have its own disadvantages and will not be considered here.

The other aspect of plasticization of ionomers depends on the nature of the plasticizer. Because ionomers can be phase separated into polar and nonpolar regions, diluents of different dielectric constants should tend to plasticize particular areas, i.e. the matrix or the clusters. Some previous studies on the plasticization of ionomers have been concerned largely with the effects of plasticization of the clusters using highly polar diluents,[21-31] where it has been shown that this type of plasticization eliminates the features associated with clustered materials. The introduction of plasticizers with a polarity similar to that of the matrix depresses the glass transition temperature of the matrix.[27,29,32] and, at low loading levels, even favors clustering.[33] Recent studies[34] have shown that the interactions between the plasticizer and the polymer are very complex; thus, plasticization of an ionomer with plasticizers containing nitro groups, materials which are polar, but do not hydrogen bond, results in behavior characteristic of nonpolar plasticizers.

Ionomers consisting of styrene-*co*-(*N*-methyl-4-vinylpyridinium iodide) have been previously investigated.[18] They represent one series of a limited group of ionomers which do not exhibit evidence of clustering. It is thought that this lack of phase separation is due to the large size of the ion pairs and the high T_g of the matrix. The dynamic mechanical behavior of some styrene-*co*-(*N*-alkyl-4-vinylpyridinium iodide) ionomers, in which the alkyl group ranges in length from butyl (4) to decyl (10), have been previously reported and indicate that these materials also do not behave as if they were clustered.[35]

The aim of the present study is to show that plasticization, even in small amounts, can change an ionomer from an unclustered to a clustered system, accompanied by dramatic changes in its mechanical properties, i.e. tan δ, and morphology, as seen in SAXS, of the material. The differences in the effects of plasticization via internal or external methods using two nonpolar plasticizers are also explored. In addition, the effects of internal plasticization using nonionic and ionic pendant groups are compared. The results of this work also show that the inducement of clustering which was seen in acrylate-based vinylpyridinium ionomers[20] can be extended to styrene-based systems. For this purpose, three sets of samples have been investigated: (i) Sty–0.06VP(4–)-MeI, externally plasticized by diethylbenzene; (ii) Sty–xVP(4–)-RI, where x = 0.02, 0.07, and 0.10, and where R ranges from methyl to decyl, thus acting as a plasticizer for the ionic material; (iii) Sty[yC$_{10}$]–xVP(4–)-MeI, where x = 0.02, 0.06, 0.08, and 0.11, and y, the extent of alkylation by 1-decene, ranges from 0.1 to 0.9.

The ionomers under study here are composed of styrene-*co*-(*N*-methyl-4-vinylpyridinium iodide). They have been plasticized either externally or internally with nonpolar diluents, in order to reduce the glass transition temperature of the matrix and to determine if clustering is occurring with this reduction. Both dynamic mechanical and SAXS experiments were employed in these studies. The SAXS data for the previously studied styrene-*co*-(*N*-alkyl-4-vinylpyridinium iodide) materials are also reported and confirm that these materials do not appear to be clustered.

Experimental Section

Polymerization. Random copolymers of styrene and 4-vinylpyridine and a styrene homopolymer were prepared by free radical copolymerization in the bulk as previously described.[18] The conditions of polymerization are summarized here for convenience. Styrene (Aldrich, 98%) and 4-vinylpyridine (Aldrich, 97%) were fractionally distilled at reduced pressure (19 mmHg and 47 °C, 16 mmHg and 65 °C, respectively) and then stored for a few hours at low temperature until needed. The initiator, benzoyl peroxide, was used as received. The quantities of monomers required, for polymer compositions ranging between 0 and 12 mol % vinylpyridine were calculated. An arbitrary acceptable limit, 30%, to the compositional variation between the first and last chains polymerized determined the reaction time. The monomers were mixed, sufficient initiator was added for a M_n of 100 000, and the solution was transferred to an ampoule. After degassing, the ampule was sealed and refrigerated. Subsequently, the polymerization was carried out at 60 °C for approximately 11 h, resulting in a conversion of ca. 30%. The polymer solution was then diluted with toluene to 5 wt %, precipitated in a 10-fold volume excess of methanol, filtered, and washed with more methanol. It was dried in vacuum at ca. 60 °C to constant weight. The vinylpyridine content of the copolymers was determined both by titration of the samples in chlorobenzene solution with perchloric acid in acetic acid and from an analysis of the infrared spectra, using a previously prepared calibration curve.[18] The molecular weights of the polymers were not measured. However, under the conditions of polymerization, the initiator concentration was expected to yield materials with M_n of ca. 100 000,[18] and because of the free radical nature of the polymerization, the polydispersity was expected to be 2, resulting in an M_w of ca. 200 000.

The sequence of reactions employed following the polymerization depended on the method of plasticization used. Materials for the internal plasticization study were first alkylated and then quaternized. The samples for the external plasticization study were quaternized and then plasticized. The polymers that were plasticized using long *n*-iodalkanes were quaternized with these reagents as has been described earlier.[30]

Internal Plasticization. The styrene-*co*-4-vinylpyridine copolymers were plasticized to varying extents through the alkylation of different proportions of the phenyl rings through a Friedel–Crafts reaction, similar to one reported previously.[33] Before the polymers were alkylated with 1-decene (Aldrich, 96%), the reagent was purified by distillation under reduced pressure (12 mmHg and 61 °C) and then stored at reduced temperature.

A 3% solution of the polymer in carbon disulfide was prepared. The number of moles of 1-decene added was determined from the moles of styrene units present in solution; the molar ratio of alkylating agent to styrene was 2:1. After the addition of 1-decene, the solution was heated to refluxing. Anhydrous aluminum trichloride (Anachemia, reagent grade), was added as a 20% slurry in 1-nitropropane so that the ratio of moles of $AlCl_3$ to styrene was 1:1. For example, in a solution containing 6.00 g of styrene units (0.0576 mol), 0.115 mol of 1-decene (16.2 g) and 0.0576 mol of aluminum trichloride 7.68 g) would be added. The extent of alkylation depended on the reaction time; for lower levels of alkylation a few hours of reflux were sufficient, but the reaction was carried out for 24 h for maximum alkylation. The alkylated polymer was recovered after precipitation into a 10-fold volume excess of methanol.

It was important to purify the polymer in order to forestall any complications from cross-linking due to remaining traces of the catalyst. A 1% solution of the polymer in chlorobenzene was prepared and 0.01 and 0.05% of 2-propanol and distilled water, respectively, were added. This mixture was refluxed for another 24 h and then washed with distilled water. The polymer was precipitated into a 20-fold excess of methanol, filtered, and dried under vacuum at 60 °C for a few days. A series of similar materials was prepared via the partial alkylation of the styrene homopolymer with 1-decene. The method employed was identical to that described above for the styrene–vinylpyridine copolymers.

The extent of alkylation was determined from ^1H NMR spectra obtained on a Varian XL-200. The ratios of the aromatic and aliphatic peaks were determined in relation to the amount of styrene and vinylpyridine known to be present. The pyridine group is essentially unreactive to Friedel–Crafts alkylation under the conditions used,[36] thus all of the alkylation was believed to have taken place on the phenyl rings.

The alkylated samples were quaternized with iodomethane (Aldrich, 99%). This reagent was distilled under nitrogen at 41–43 °C shortly before use. The quaternization was performed in tetrahydrofuran (THF) which had been previously dried over potassium–benzophenone complex until the purple color persisted and was then distilled.

The samples to be quaternized were dissolved in sufficient dry THF under nitrogen to make a 5% solution. A 5-fold molar excess of iodomethane was added, and the resulting light yellow solution was refluxed for 90 min. The polymers were recovered by precipitation into 20-fold excess volume of hexanes; then they were filtered and dried in vacuum at 60 °C to remove residual solvent.

External Plasticization. The ionomer samples for the external plasticization studies were first quaternized with iodomethane as described above. Subsequently, they were redissolved in benzene/methanol (90/10 v/v) and freeze-dried. The polymers were kept in vacuum at 60 °C until needed. Apart from quaternization, the styrene homopolymer was treated in the same fashion.

Diethylbenzene (Aldrich, 97%, a mixture of ortho, meta, and para isomers) was used as the diluent in these studies. It was chosen because, in addition to its structural similarity to styrene, diethylbenzene has an exceptionally low vapor pressure for an organic compound of its molecular weight. The diluent was purified before the plasticization experiments by distillation under reduced pressure (10 mmHg and 55 °C). Dry ampules were each filled with approximately 2 mL and sealed.

For each plasticization experiment, a sample of the freeze-dried polymer, weighing from 0.9 to 1.2 g, was used. The contents of two ampules of diethylbenzene were added to the sample in an aluminum weighing pan lined with Teflon. To get a uniform distribution of the diluent in the sample, the following procedure was used. The sample was placed in a desiccator under vacuum for 1 h, then moved to a drying pistol, and heated to ca. 100 °C under nitrogen for another 1 h. The drying pistol was cooled to about 56 °C (boiling acetone) and placed again under vacuum. The samples were removed after different lengths of time to yield different plasticizer contents. For example, a sample evacuated for about 5 h contained approximately 10% diethylbenzene by weight. This tedious procedure of mixing the plasticizers and the polymer was chosen because it was important to ensure that the plasticizer was evenly distributed throughout the sample. Freeze-dried samples dissolved quickly in the plasticizer, and the removal of the diethylbenzene from the polymers was relatively slow. Finally, prior to study, the samples were compression moulded at temperatures slightly above T_g (less than 100 C°) for 15 min. Any variation of diluent concentration within the sample was thus expected to be negligible, and the samples appeared homogeneous on visual inspection.

The actual amount of plasticizer contained within the samples was determined only for those samples used for the dynamic mechanical experiments. The polymer was weighed first after molding, then after the experiment, and then placed in a drying pistol at approximately 100 °C under vacuum until it reached constant weight. Plasticizer loss during the DMTA run was negligible, and in the cases where the sample adhered to the DMTA frame, it was still possible to calculate the diethylbenzene content. From the initial samples, a calibration curve (length of drying time for a given plasticizer content) was prepared, and twin samples for the small-angle X-ray scattering studies were prepared following it. One of these samples was used in the SAXS study and the other was dried to constant weight, so as to get a better approximation of the plasticizer content in the sample.

Dynamic Mechanical Experiments. The samples for the dynamic mechanical experiments were compression moulded into rectangular slabs at elevated temperatures and 2 GPa pressure. The average dimensions of the moulded slabs were 12 × 35 × 2 mm. In the external plasticization studies, as described above, the samples were weighed before the experiment. The samples were run in a dynamic mechanical thermal analyzer (DMTA, Polymer Laboratories) in dual cantilever bending mode at a heating rate of 0.5 °C min^{-1} in a nitrogen atmosphere. Data were obtained concurrently for five frequencies ranging from 0.3 to 30 Hz.

The dynamic mechanical experiments were stopped at temperatures not greater than 170 °C for two reasons. There are problems with dequaternization of the *N*-methylvinylpyridinium iodide ion pairs on prolonged exposures to temperatures above about 160 °C. Furthermore, in the case of the external plasticization studies, the boiling point of diethylbenzene is 180–2 °C.

Further analysis of the data was made possible after the run using a curve-fitting and peak-finding routine written for this laboratory by S. Williams. In the cases where this program was not suitable, the glass transition temperatures were estimated by visual inspection of the peak maxima.

Small-Angle X-ray Scattering Experiments. The samples for the SAXS experiments were also compression moulded, under temperatures and pressures similar to those used in the moulding of the DM samples, into disks of a typical diameter 12 mm and thickness 1 mm. Because these samples were moulded several weeks before the experiments were run, they were protected from the atmosphere in the interim. The samples that were plasticized internally, either with a nonpolar group, as in the alkylated materials, or with a polar one, i.e. those samples quaternized with the *n*-iodoalkanes, were kept under vacuum. The samples that were plasticized with diethylbenzene were sealed in individual ampules.

The small-angle X-ray scattering experiments were run on the D-22 beamline at LURE, using synchrotron radiation. This line is characterized by moderate flux and high resolution. The energy of the beam was 8500 eV. The samples were positioned in air either 818 or 830 mm from the 1-D position-sensitive detector, depending on the sample holder used, the rest of the beam path being evacuated, and spectra were collected for 1200 s. The analysis of the data was performed using software written by O. Lyon. The spectra were corrected for background scattering of a polystyrene blank, sample absorption, and sample thickness,

Table I
Relative Plasticization Levels of Samples

A. Internally Plasticized Samples

starting material	duration of alkylation reaction (min)	extent of alkylation (mol % styrene)
polystyrene	60	10
	275	33
	480	48
Sty–0.0265VP(4–)	1515	92
Sty–0.0508VP(4–)	1455	77
Sty–0.0622VP(4–)	70	11
	135	20
	335	32
Sty–0.0791VP(4–)	1410	84
Sty–0.106VP(4–)	1870	73

B. Externally Plasticized Samples

starting material	length of time evacuated (min)	diethylbenzene content (mol % sty)
polystyrene		0
	300	8
Sty–0.0193VP(4–)	190	10
Sty–0.0622VP(4–)		0
	705	5
	315	7
	260	9
	125	15
Sty–0.121VP(4–)	190	4

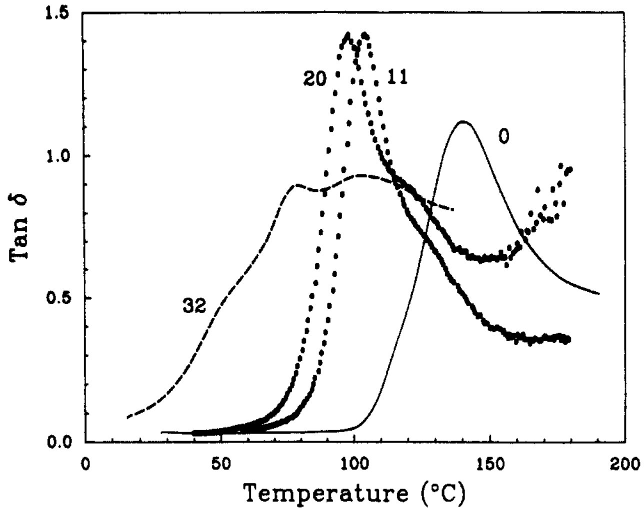

Figure 1. Loss tangent at 1 Hz as a function of temperature for internally plasticized Sty–0.06VP(4–)-MeI ionomers. Numbers refer to the level of alkylation as a function of the mole percent plasticized styrene.

where possible. Indeed, in the case of the highly alkylated samples, only the material of highest ion content was sufficiently below its T_g for the thickness to be measured with precision. The externally plasticized samples were sealed in ampules before it was recognized that the thickness measurement was important, and the thickness could not be determined afterward. Therefore the intensities scattered by the samples cannot be compared directly.

Results

The levels of plasticization of different materials were determined by different techniques. ^{1}H NMR spectroscopy was used to determine the extent of alkylation in the samples plasticized with 1-decene, while the amount of diethylbenzene in the externally plasticized materials was determined by weight loss; the polymers that were quaternized by *n*-iodoalkanes were judged to be fully quaternized when the infrared peak at 1414 cm^{-1} disappeared completely. The ionomers prepared for this study, along with their relative plasticization levels, are shown in Table I.

The dynamic mechanical behavior of the materials depended on the type and the amount of plasticization employed, in addition to the expected dependence on ion content. For the sake of clarity, the earlier results[30] for the samples quaternized with *n*-iodoalkanes are first briefly recapitulated. This is followed by a description of the results observed for the alkylated and externally plasticized samples.

Quaternization of random styrene-*co*-4-vinylpyridine copolymers with *n*-iodoalkanes can be considered a type of internal plasticization of the polymer groups by the attached alkyl chains. The styrene-*co*-(*N*-alkyl-4-vinylpyridinium iodide) ionomers all resemble a styrene homopolymer of comparable molecular weight in their mechanical behavior. The principal difference is an increase in the glass transition temperature with increasing ion content. However, as the length of the attached alkyl chain increases, the effect of increasing plasticizer content offsets that of ion content. The single T_g varies linearly with ion concentration and alkyl chain length over the vinylpyridine content and iodoalkane range studied. For such styrene–vinylpyridinium ionomers, it was shown that it was possible to relate the glass transition temperature to the alkyl chain length and vinylpyridine content using a simple equation. The absence of a second peak in the loss tangent versus temperature curves indicates that these materials are not clustered.

By contrast, the internal plasticization of the nonpolar matrix in styrene-*co*-(*N*-methyl-4-vinylpyridinium iodide) ionomers, via alkylation of the phenyl groups, significantly alters the mechanical properties. When alkylated to a moderate degree, a shoulder is clearly evident on the high-temperature side of the peak in the tan δ vs temperature plots. The shoulder is attributed to the glass transition of a second, clustered phase, as has been done for other clustered systems. As the level of alkylation increases to above 30 mol %, the shape of this curve changes markedly and both peaks are of comparable magnitude. This is shown in Figure 1. In the samples with much higher levels of alkylation, it is unclear whether there is a second peak in the loss tangent because of the large scatter in the data. The storage modulus (G') curves do not have a second inflection point in any of these samples; however, the materials which are clustered have much broader transitions.

As expected, the alkylation of the styrene homopolymer to varying extents with 1-decene resulted in materials with reduced glass transition temperatures. Only one glass transition temperature was observed for all plasticizer contents, although the materials were opaque. In contrast, all of the plasticized ionomers were clear. The opacity may be due to contamination by residual 2-propanol, the immiscibility of the alkane in styrene, or possibly side chain crystallization. However, since phase separation in nonionic systems was not the principal aim of this study, this observation was not followed up.

The plasticization of the styrene-*co*-(*N*-methyl-4-vinylpyridinium iodide) ionomer with diethylbenzene may result also in a material with properties very different from those of the unplasticized precursor ionomer. In addition to the dependence of the phenomena on the amount of plasticizer involved, the ion content proved to be important; thus the ionomers containing very low (ca. 2 mol %) and very high (ca. 12 mol %) vinylpyridine contents did not exhibit any behavior associated with phase separation upon plasticization. In general, for ionomers

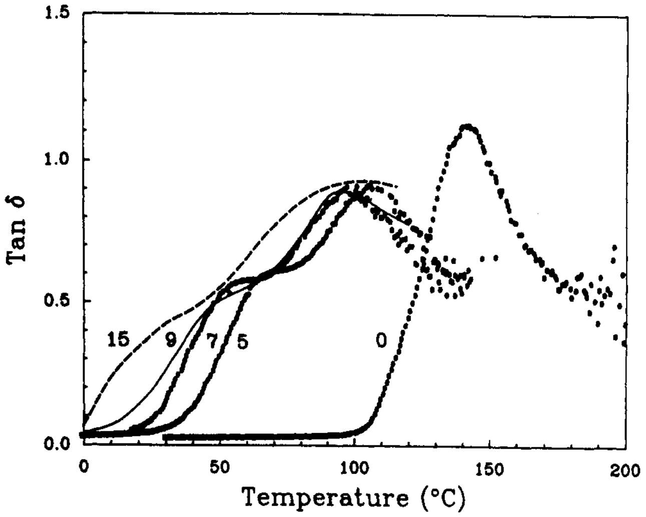

Figure 2. Loss tangent at 1 Hz as a function of temperature for externally plasticized Sty–0.06VP(4–)-MeI ionomers. Numbers refer to the level of plasticization as a function of the mole percent plasticized styrene.

of moderate vinylpyridine content and at the low levels of plasticization studied, the reduction in the glass transition temperature is much more pronounced for these samples than for the internally plasticized ones. A higher temperature peak, attributed again to clusters, is also clearly observed in the loss tangent–temperature curves of the 6 mol % ionomer, as shown in Figure 2. It is unlikely that this second peak is due to uneven plasticization, which would result in areas of unplasticized ionomer, because the positions of both peaks depend on the amount of diethylbenzene present, and a gradation in plasticizer concentration would result in a single, very broad T_g. Rather, the presence of two glass transitions suggests that clustering has occurred also in these ionomers, although here the higher T_g, that of the clusters, is predominant even at very low plasticizer contents.

The equivalent plasticization of the styrene homopolymer with diethylbenzene also depressed the T_g of the material. As in the internal plasticization of polystyrene, no second tan δ peak is observed. However, unlike the alkylated homopolymer, the samples in these plasticization experiments were transparent.

The results from the dynamic mechanical experiments on these ionomers are summarized in Table II. The glass transition temperatures, the peak half-widths, and the activation energies calculated for the different materials are listed. A comparison of the loss tangent data for the different methods of plasticization is shown in Figure 3.

The other series of experiments performed on these ionomers used small-angle X-ray scattering. The results from the SAXS studies indicate that significant changes in the morphology of the ionomers accompany the reduction of the glass transition temperature. The results of the SAXS studies, i.e. the peak positions and intensities for the above mentioned samples, are also listed in Table II.

The SAXS profiles of the ionomers quaternized with *n*-iodoalkanes did not have a peak in intensity over the observed *q* range, and thus, there was no evidence of aggregation in these samples. This is consistent with the dynamic mechanical results on these materials.[35] The investigation of the SAXS diffraction of the highly alkylated styrene-*co*-(*N*-methyl-4-vinylpyridinium iodide) ionomers yielded rather different results. While there is no conclusive evidence of phase separation in the mechanical studies because of the low modulus above the T_g of the highly plasticized systems, the internally plasticized materials of higher ion content have very distinct peaks in their SAXS profiles, demonstrating that they are phase separated. The externally plasticized samples all had peaks in their SAXS profiles. With the exception of the 10% sample, in which the peak was a shoulder on the small-angle upturn, all the peaks were well resolved, although weaker in intensity than those found in the internally plasticized materials. The upturn at small angles, however, was present in all samples, regardless of their method of plasticization. An example of the small-angle X-ray scattering profile observed for each plasticization scheme is shown in Figure 4.

Discussion

Previous studies have demonstrated that clustering in ionomers can be dramatically influenced by the choice of plasticizer. Thus, it is possible to "fine-tune" the properties of ionomers through selective plasticization. For example, one way to reduce or obliterate the mechanical features associated with clustering is to reduce the strength of the ionic interactions within the cluster,[21-31] for example by the addition of highly interacting plasticizers to the polar domains of the ionomers. The clusters may retain their identity; however they no longer exert an effect on the rheological properties of the material. It has also been shown that the addition of a very large amount of nonpolar plasticizers ultimately destroys much of the mechanical behavior associated with clustering.[33] The opposite effect, the enhancement of aggregation, has been achieved through the addition of moderate amounts of nonpolar plasticizers.[20,33] Finally, there are some plasticizers which do not have very much effect on the phase separation in ionomers. In this study, the plasticizers either induced two-phase behavior, i.e. clustering, into one-phase materials, or were ineffective, in which case the material retained the characteristics of a one-phase system. The one-phase materials, which for the purposes of this study are the least interesting, will be discussed first, and the final section of the discussion will deal with the two-phase, or clustered, ionomers.

One-Phase Ionomers. The quaternization of styrene–vinylpyridine copolymers with *n*-iodoalkanes is an example of plasticization which has no effect on the phase separation in these materials. Plasticization via this technique enlarges the ionic group. This results in a mild depression of the T_g, but there is no evidence of phase separation either in dynamic mechanical or SAXS studies.

The 2 mol % styrene–(*N*-methyl-4-vinylpyridinium iodide) systems are another example of one-phase materials in which no evidence for clustering has been found, even when the ionomers have been alkylated with 1-decene or plasticized with diethylbenzene. The behavior of these materials is thus unlike that seen for ca. 2 mol % styrene–(sodium methacrylate) ionomers, in which behavior characteristic of two-phase systems has been observed using dynamic mechanical techniques[12] and Raman spectroscopy.[37]

Two-Phase Ionomers. The addition of moderate amounts of a nonpolar plasticizer has been seen to enhance or even induce clustering in several systems.[20,33] The phenomenon of inducing clustering through plasticization has been observed in materials of already rather low T_g, such as ethyl acrylate, and in the present study this observation is extended to styrene-based vinylpyridinium ionomers. A number of factors suggest that in the styrene-based systems clustering should be easier to achieve than in the acrylate systems. One such factor is the much lower

Table II
Results from Dynamic Mechanical and SAXS Experiments

sample	mole % plasticizer	T_g (low) @ 1 Hz (°C)	T_g (high) @ 1 Hz (°C)	E_{act} (low) (kJ·mol^{-1})	E_{act} (high) (kJ·mol^{-1})	q_{max} (Å^{-1})	intensity (normalized)
		A. Internally Plasticized Samples					
polystyrene[a,b]	9.9	98.5		470			
	32.8	51.8		500			
	47.9	34		240			
Sty–0.0265VP(4–)-MeI[a,c]	91.7	15.5		190			
Sty–0.0622VP(4–)-MeI	11.4	104.4	128.5	400	280	0.181	
	19.7	98.3	124.7	400	250	0.172	
	32.3	53.1	112.4	390	310	0.153	
Sty–0.0791VP(4–)-MeI[a]	83.6	20		200		0.165	3E–3
Sty–0.106VP(4–)-MeI[a]	73.3	41		230		0.182	2.3E–3
		B. Externally Plasticized Samples					
polystyrene[a,b]	0	115.6		490			
	7.9	46.3		310			
Sty–0.0193VP(4–)-MeI[a,b]	10.1	37.5		350			
Sty–0.0622VP(4–)-MeI[a,c]	0	140.5		580			
Sty–0.0622VP(4–)-MeI[d]	2.5					0.129	5E–4
	5					0.133	3.75E–4
Sty–0.0622VP(4$^-$)-MeI[b]	5.3	63.7	105.6	340	480		
	7.0	51.1	96	280	260		
	9.4	44.6	98.6	300	280		
Sty–O.06VP(4–)-MeI[d]	10					0.134	6E–4
Sty–0.0622VP(4–)-MeI[b]	15.2	20.9	88.2	400	220		
Sty–0.0622VP(4–)-MeI[d]	20					0.130	4E–4
Sty–0.121VP(4–)-MeI[a,b]	3.8	114.4		390			

[a] No second peak in DM experiments. [b] SAXS not run on sample. [c] No peak in SAXS. [d] SAXS sample only; DM experiments not run.

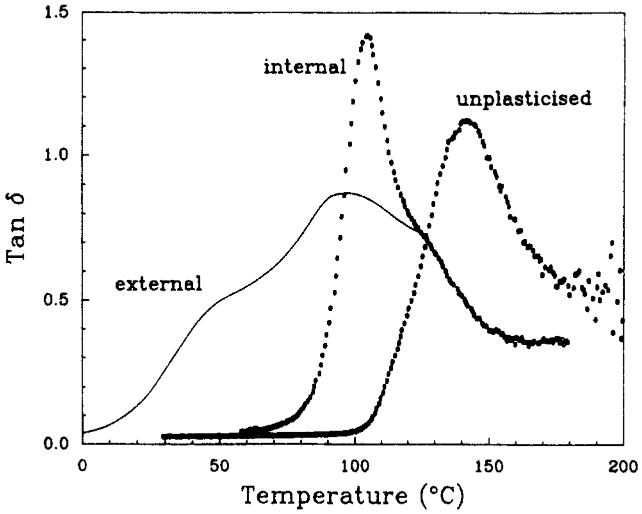

Figure 3. Comparison of the loss tangents at 1 Hz as a function of temperature for unplasticized and approximately 10% plasticized Sty–0.06VP(4–)-MeI ionomers.

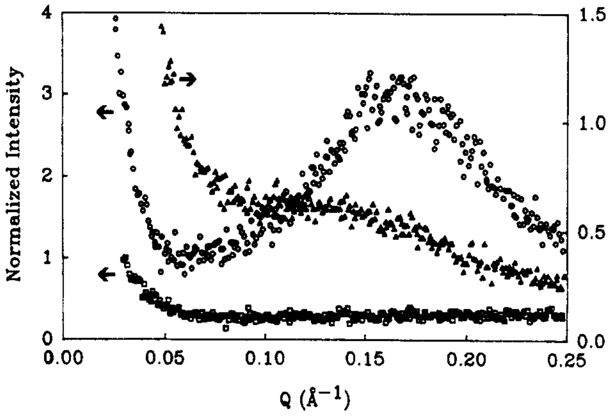

Figure 4. Small-angle X-ray scattering profiles for plasticized ionomers: Sty–0.07VP(4–)-DeI (□), Sty[0.8p-C$_{10}$]–0.06VP-MeI (○), Sty–0.06VP(4–)-MeI + 10% diethylbenzene (▲).

dielectric constant of the styrene systems. Another is the unfavorable solubility parameter, χ, between styrene and vinylpyridinium.[38] Thus the styrene–vinylpyridinium ionomers are materials that, in the unplasticized state, appear to be prevented from clustering only because of the high matrix glass transition temperature. The present experimental results indicate that styrene–vinylpyridinium ionomers would tend to cluster easily if the T_g were lower. The addition of only 5% diethylbenzene lowers the glass transition temperature of the matrix sufficiently to cause a large amount of the material to cluster, and yet this T_g (63.7 °C) is still much higher than that of an unplasticized (ethyl acrylate)–vinylpyridinium ionomer of a similar ion content (ca. 5 °C).

Although both externally and internally plasticized styrene–(N-methyl-4-vinylpyridinium iodide) ionomers are phase separated, there are a number of differences in both the dynamic mechanical behavior and the SAXS profiles between materials plasticized using the two methods of plasticization. For convenience, the ways in which the internally and externally plasticized ionomers respond differently to the dynamic mechanical and small-angle X-ray scattering experiments are summarised in Table III.

An important difference between the two plasticizers lies in their structures, which influences how they interact with the matrix. Clearly, 1-decene is much less miscible with polystyrene than is diethylbenzene. However, given that the alkyl group is attached to the styrene, and thus cannot move out, it is believed that for the two-phase systems in this study, the differences in the results obtained are due to the change in mobility of the plasticizer, rather than the structure of the additive.

It is known that the mobility of a plasticizer determines its effectiveness in reducing the T_g. Clearly, an external plasticizer, being unattached in any way to the polymer chain, introduces more free volume than can a comparable amount of attached plasticizer. Thus, materials which have been plasticized with a small molecule diluent have glass transition temperatures which are generally much lower than materials plasticized with comparable amounts of internal plasticizers. This difference in the efficiency of plasticization is also seen in the results of this study;

Table III
Comparison of the Phase Behavior Resulting from Internal and External Plasticization

	internal	external
predominant T_g	lower T_g predominates at low plasticization; upper T_g of comparable importance at plasticization levels >30%	upper T_g always predominant
shift in T_g	both T_g's depressed as plasticizer is added, linear relationship	initially, both T_g's drastically lowered; depression slows but is always greater than internally plasticized
SAXS peak position	q_{max} @ ca. 0.18 Å^{-1}	q_{max} @ ca. 0.13 Å^{-1}
SAXS peak maximum I	4×10^{-3}	1.5×10^{-3}

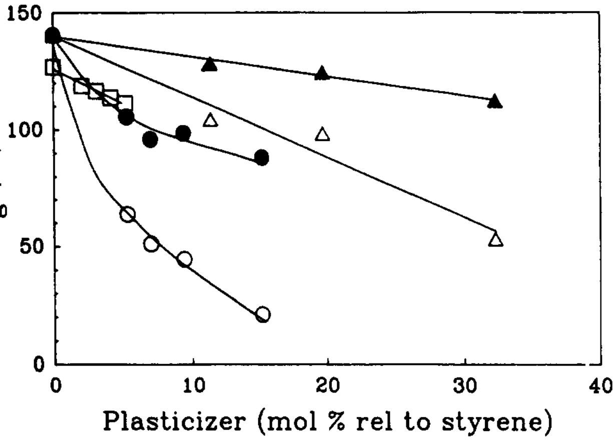

Figure 5. Relative depressions of glass transition temperatures of styrene–vinylpyridinium ionomers as a function of plasticizer. 2–10 mol % VP-MeI, quaternized with *n*-iodoalkanes (□); 6 mol % VP-MeI, internally plasticized by alkylation (○); 6 mol % VP-MeI, externally plasticized with diethylbenzene (△). Filled symbols indicate the upper T_g in materials which exhibited two glass transitions.

if approximately 10 mol % plasticizer has been incorporated internally, the T_g of the matrix is reduced by about 35 °C, whereas the same amount of external plasticizer depresses the matrix glass transition temperature by ca. 100 °C. It is also worth noting that when two phases are present in one of these ionomers, the difference between the two T_g's is also dependent on the type of plasticization used. To continue with the previous example, the difference in the glass transition temperatures of the two phases is about 20 °C for the 10 mol % alkylated sample, but is already ca. 40 °C for the externally plasticized materials. These variations in behavior may be seen in Figure 5. (For the ionomers quaternized by *n*-iodoalkanes, the values were obtained in the following steps. First, the vinylpyridine content was recalculated in terms of the styrene content alone and the appropriate ion content chosen. The vinylpyridine content also determined the maximum plasticization possible, based on 100% quaternization with iododecane. The other points are the glass transition temperatures of the same vinylpyridine content material, but with their alkyl chain length normalized to 10 carbons.)

Another difference between the dynamic mechanical data for the internally and externally plasticized samples is seen in the relative heights of the loss tangent peaks for the separate phases. It has been suggested that the areas underneath such peaks reflect the relative amounts of material present in each phase.[12,39,40] Thus, it appears that for the internally plasticized samples, initially relatively little material is incorporated into the clustered regions at low plasticizer contents. Only when the alkylation level is much higher, i.e. ca. 30%, does the amount of material in the cluster phase approach that in the multiplet-containing phase. In contrast, in the cases of the externally plasticized ionomers, the glass transition peak at higher temperatures is always substantially larger. This suggests that the phase responsible for this transition predominates in these materials.

The SAXS data show that other differences, in the positions and intensities of the peaks, exist between the internally and externally plasticized materials. Most notably, the highly alkylated materials have peaks at significantly larger *q* than the materials plasticized by small molecules. This implies that either the phase-separated regions are much closer together in the internally plasticized ionomers or that, in these systems, these domains are smaller. The ambiguity in this interpretation reflects the current uncertainty in understanding the small-angle X-ray scattering profiles of random ionomers, because of the difficulty in attributing such SAXS peaks to structure or shape factors.

Almost as striking in the SAXS profiles is the difference in the intensities of the peaks observed in the alkylated samples compared with those of the externally plasticized ionomers. The intensities of the internally plasticized materials are some 40 times the latter. This may, in part, be due to the differences in plasticizer concentrations (70–80 mol % for the alkylated materials vs <20 mol % for the externally plasticized ionomers); however, there is no similar increase in the maximum peak intensities in the series of externally plasticized materials with increasing diethylbenzene content. Thus, it is suggested that the differences in the mobilities of the plasticizers are responsible for the differences in peak intensities.

Differences in the plasticizer polarity might contribute to the ease of phase separation in these ionomers. However, the difference in polarity between the two plasticizers is much less than the polarity difference between either plasticizer and the ionic methylvinylpyridinium iodide unit. Two-phase behavior has been observed in (ethyl acrylate)–(methylvinylpyridinium iodide) ionomers plasticized with dimethyl malonate,[20] a plasticizer even more polar than those used in these studies. Consequently, the effects of plasticizer polarity are not considered to be as pronounced as the effects of plasticizer mobility for the ionomers used in this study.

It is possible to explain all of the differences listed above and in Table III as a consequence of the relative plasticizer mobilities. It is expected that the alkylation of the phenyl groups in the styrene–vinylpyridine copolymers occurs randomly along the chain, and therefore, in the solid state, the internal plasticizer should be distributed evenly throughout both phases. Because the glass transition temperatures are quite close in the internally plasticized systems, it appears that the only factor differentiating the clusters from the matrix is the presence in the former of a proportionately larger number of ions. If the peaks in small-angle X-ray scattering can be attributed to the dimensions of the scattering bodies, then these peak positions of the alkylated ionomers indicate that the domains are small, and the intensities of these peaks suggest that the domains and the matrix have very different electron densities. The assumption of small domain sizes is also in agreement with the relative peak heights in the dynamic mechanical results. These data are all consistent with a material which contains rather small and well-organized clusters.

The situation in the externally plasticized materials is quite different because, in this case, the plasticizer is free to move away from the ion-rich areas. Because of the mobility of the diethylbenzene, the matrix is expected to contain most of the plasticizer, and thus the clusters would be expected to have a T_g higher than that observed for the ion-rich regions in similar internally plasticized ionomers. In fact, the glass transition temperatures of the clustered phases of the externally plasticized ionomers are lower than those of the comparable internally plasticized materials. The additional reduction in the T_g can be attributed to a "soft-wall" effect which has been seen in other phase-separated systems.[41] However, the differences between the glass transition temperatures of the cluster and multiplet-containing phases are still markedly larger in the externally plasticized ionomers than in the alkylated materials. These larger differences indicate that, as expected, the concentration of diethylbenzene is not uniform throughout the material as a result of the presence of ions. In externally plasticized ionomers, therefore, the clusters should be different from the matrix on the basis of both average ion content and plasticizer content. The large size of the cluster peak in the loss tangent–temperature curves suggests that these domains are predominant in these materials. If it is again assumed that the small-angle X-ray scattering profiles are indicative of the domain size, then in the diethylbenzene-containing samples these clusters are larger than the domains found in the internally plasticized ionomers. The low relative intensity of the SAXS peak and the observed depression in the glass transition temperature of the clusters relative to that of the internally plasticized materials imply that, in addition to being large, these domains are rather poorly organized.

Recent studies[42] indicate that cluster size in normally clustered ionomers is unchanged by internal plasticization. Thus, the differences observed here in apparent cluster sizes may be due to the plasticizers used, or the differences may be a special feature of styrene–(methylvinylpyridinium iodide) systems.

It is clear that the externally plasticized 6 mol % styrene–vinylpyridinium ionomer is a highly clustered material. Thus, the absence of evidence for two-phase behavior in the externally plasticized 12 mol % *N*-methyl-4-vinylpyridinium iodide ionomer deserves special comment. The one-phase behavior suggests the following two possibilities. Either the material is truly unclustered or it contains a single phase of high ion concentration, i.e., all clustered. In this connection, it is worth recalling that styrene-*co*-(sodium methacrylate) ionomers have been seen to become almost entirely clustered at ion contents of ca. 13 mol % with only a very small peak due to the low T_g phase,[12] thus, it is conceivable that the same situation also exists for the plasticized styrene-*co*-(*N*-methyl-4-vinylpyridinium iodide) ionomers at high vinylpyridinium contents. In addition, the loss tangent peak of the cluster phase is clearly dominant already in the 6 mol % samples. Thus, although no samples were run between 6 and 12 mol % vinylpyridine concentration, which would confirm this trend to a completely clustered system, on the basis of the results in other systems, complete clustering seems most likely in the externally plasticized 12 mol % sample.

Conclusions

The plasticization of styrene–(*N*-methyl-4-vinylpyridinium iodide) ionomers by the incorporation of either an internal (attached) or an external (mobile) nonpolar additive yields phase-separated materials above 2 mol % ion content. At very high vinylpyridinium content, the entire material appears to be clustered. While the clustering observed in the styrene–vinylpyridinium ionomers is clearly a consequence of the reduction in the glass transition temperature of the material, the different methods of plasticization result in different cluster sizes on the basis of evidence from both dynamic mechanical and small-angle X-ray scattering. When these ionomers have been internally plasticized with 1-decene, the material thus produced appears to contain small, well-organized domains. In contrast, the introduction of diethylbenzene into these ionomers yields a material in which the clusters are relatively large and poorly organized.

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Registry No. (Sty)(4-VP) (copolymer)·xCH$_3$I, 84516-62-1; diethylbenzene, 25340-17-4.