Matrix Polarity Effects on Ionic Aggregation in a Nitrated Styrene Ionomer

Mario Gauthier† and Adi Eisenberg*

Department of Chemistry, McGill University, Montreal, Quebec, Canada H3A 2K6.
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ABSTRACT: A styrene–methacrylic acid copolymer (7 mol % acid) was partially nitrated. The relaxed dielectric constant of the sodium-neutralized material was raised from 3.2 (nonnitrated) to 7.3 (32% nitrated). The tan δ peak associated with clusters in the sodium ionomer, as detected by dynamic mechanical measurements, was unaffected. In a parallel study, the styrene–sodium methacrylate ionomer was plasticized with nitrobenzene. Despite its high polarity, the diluent displayed the effects of typical nonpolar plasticizers, affecting the matrix and the ion-rich domains to the same extent. Comparison with previous results and consideration of cohesive energy density data suggest that specific interactions are an important factor in determining the plasticizing behavior of diluents, rather than the dielectric constant alone. A nitration technique is also suggested for polystyrene, which allows control of the degree of substitution in the 0–100% range and yields predominantly the para isomer.

Introduction

The addition of small amounts (up to ca. 15 mol %) of ions to organic polymers, by such means as copolymerization or postpolymerization modification, has led to new materials with modified properties[1,2] which are of ever growing industrial importance.[3] It is generally accepted that ionomers, as defined by Rees and Vaughan,[4] owe their peculiar properties to the aggregation of the ions introduced into the organic matrix. Two distinct types of aggregates, multiplets and clusters, are believed to be formed as a result of ionic associations in carboxylate and sulfonate systems.[5]

Some structural parameters of polymers are clearly known to affect the properties of ionomers. The effects of the variation of the type of counterion[6] or the placement[7] and nature[8] of pendant ions, for example, have been studied. The effect of the dielectric constant of the polymer matrix has also been explored to some extent. Eisenberg and King[2] pointed out that, while the rheological properties of ethylene-based ionomers ($\epsilon \approx 2.3$) are dominated by clustering even at ionic concentrations as low as 1%, similar styrene-based systems ($\epsilon \approx 2.5$) only show comparable effects starting at 4–6 mol % ions. Furthermore, acrylate-based systems ($\epsilon \approx 4$) display significant clustering effects only at ionic concentrations as high as about 10–15 mol %. Although a comparison of these results apparently suggests a significant effect of the polarity of the polymer matrix on ionic aggregation, one problem is evident. The three systems have pendant groups of a very different nature, possibly leading to different steric effects, as well as differences in specific molecular interactions.

In order to investigate more fully the influence of matrix polarity on ionic aggregation, there is an obvious need for a method that allows one to vary systematically the polarity without changing the nature of the backbone or the pendant ionic groups attached to it.

A tabulation of dielectric constants for organic liquids[9] reveals the high dielectric constant of nitrobenzene (ϵ = 34.8 at 25 °C). Nitration of aromatic compounds being an easy reaction, the controlled nitration of a styrene-based copolymer should provide the desired system.

Nitration of polystyrene is well-documented in the chemical literature. Unfortunately, little effort has been devoted to the production of polymers with low (0–50 mol %) nitration levels, the general tendency being to aim at high degrees of substitution (100–200%).[10-12] Even in cases where partial nitration is achieved, the reaction conditions suggested are, in general, not very flexible, leading to solubility problems for the polymer and yielding nonuniform products and irreproducible results when the proportions of solvent to nitric acid are changed.[12] It would nevertheless appear that one of the techniques suggested[10] might have a limited usefulness in controlling the degree of substitution of the products, although no such attempt was reported in the original paper.

A somewhat more interesting approach is the nitration by in situ generation of the nitronium ions from inorganic nitrates and trifluoroacetic anhydride.[13] That procedure, however, uses relatively high salt concentrations and leads to solubility problems for many inorganic nitrates as well as to sample contamination by salt residues, undesirable in the case of ionomers.

Since no known nitration technique could be applied directly to modify the ionomers in a controlled manner, a new approach was devised. The technique is applicable without modification to the degrees of substitution in the 0–100% range and leaves no nonvolatile residues. The products apparently contain mostly, and possibly exclusively, the para isomer. The technique was applied equally successfully to polystyrene homopolymer and to the PS–MAA copolymer used in the aggregation study. In this case, a styrene–methacrylic acid copolymer with 7 mol % acid and denoted as PS–0.07 MAA, according to the convention suggested by Eisenberg and King,[2] was used.

The aim of this study was to examine the effects on ionic aggregation of the systematic variation of the dielectric constant of the polymer matrix, via nitration. The choice of the nitro group is of particular relevance to this work. In spite of its high polarity, it is not significantly subject to specific interactions with ions, because the negative end of its dipole is delocalized on one nitrogen atom and two oxygen atoms.[14] It therefore becomes possible to separate dipolar and specific interaction effects on ionic aggregation. The results obtained for the dynamic mechanical properties of the nitrated sodium methacrylate ionomers were quite unexpected and suggested a comparative study of the effects of plasticization with nitrobenzene on the PS–MAA–Na system.

The work of Bazuin and Eisenberg[15] on plasticized PS–MAA–Na ionomers has already highlighted the importance of the nature of diluents on their plasticizer behavior. The effects of a nonpolar and a highly polar and hydrogen-bonded plasticizer were compared. While diethylbenzene affected the matrix and cluster aggregates to the same

* To whom correspondence should be addressed.
† Present address: Institut für Makromolekulare Chemie, Universität Freiburg, Stefan-Meier-Strasse 31, D-7800 Freiburg, Federal Republic of Germany.

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extent, glycerol, used in the same concentration range, clearly affected the ion-rich domains preferentially. This is discussed in greater detail below.

Experimental Section

Materials and Equipment. Styrene monomer (Aldrich, 99%, inhibited with *tert*-butylcatechol) was washed 3 times with a 5% aqueous sodium hydroxide solution and twice with distilled water, to remove the inhibitor. The monomer was dried over calcium hydride (Aldrich, 95+%, 40 mesh) overnight with stirring and distilled at reduced pressure (bp 47–48 °C/22 mmHg). Methacrylic acid monomer (Aldrich, 99%) was also distilled at reduced pressure (bp 67 °C/6 mmHg). Both monomers were stored for at most a few days in tightly stoppered flasks in a freezer (−20 °C) before use.

The solvents, nitrobenzene (Aldrich, 99%) and 1,2-dichloroethane (A&C American Chemicals, reagent), as well as the fuming nitric acid (Mallinckrodt, 90%) used in the nitration procedure were utilized without purification. The nitrobenzene used in the plasticization study was dried over phosphorus pentoxide (Anachemia, reagent) for 3 days and then decanted and distilled at reduced pressure (86 °C/7 mmHg). It was then transferred to oven-dried 2-mL ampules which were immediately sealed with a flame for later use. A benzene/methanol solution, 90:10 by volume, used in the neutralization procedure for the styrene-*co*-methacrylic acid polymer, was prepared from A&C American Chemicals reagent-grade solvents. Manipulations involving benzene were systematically performed in a ventilated hood, because of its known toxicity. The *N*,*N*-dimethylformamide (DMF) used as the solvent in the potentiometric titration of the nitrated PS–MAA polymers was also A&C American Chemicals reagent grade.

The ^{1}H nuclear magnetic resonance (NMR) spectra used to characterize the products were recorded on a Varian XL-200 Fourier transform instrument, with at least 64 transients acquired. The spectra of the polymers with degrees of nitration lower than 40% were recorded in deuterated chloroform (MSD Isotopes, 99.8% d) at room temperature. Deuterated dimethyl sulfoxide (MSD Isotopes, 99.9% d) was used at 70 °C for samples with higher degrees of substitution. Infrared (IR) spectra of polymer films were recorded on an Analect AQS-18 Fourier transform spectrometer with a resolution of 2 cm^{-1} in the 400–4400-cm^{-1} range; 64 transients were acquired for both the background and the sample.

Potentiometric titration curves were established by using a Corning 245 pH meter equipped with a general purpose combined glass/saturated calomel electrode.

A Perkin-Elmer DSC-2C differential scanning calorimeter (DSC) was used to determine the glass transition temperature of nitrated polystyrene samples as a function of the degree of nitration (as determined by NMR). A heating rate of 20 °C/min was used, and the instrument was calibrated with indium and tin samples. The relaxed and/or unrelaxed dielectric constants of some of the materials were measured using a General Radio 1621 precision capacitance measurement system. The dynamic mechanical properties of the samples were determined with a Polymer Laboratories Mark II dynamic mechanical thermal analyzer (DMTA) interfaced with an IBM PC-XT compatible computer. The instrument was used in the dual-cantilever bending mode at a frequency of 1 Hz. A heating rate of 1 °C/min was used, and the oven of the instrument was continuously purged with a flow of dry nitrogen. The data obtained were analyzed with programs initially developed by Susan Williams for an automated torsional pendulum (TP) system and described elsewhere.[16]

Synthesis. Styrene homopolymer and the copolymer with methacrylic acid (ca. 7.5% MAA mol/mol content) of molecular weight 10^5 g/mol were prepared via bulk polymerization with benzoyl peroxide (6.66 g/L) at 60 °C[17,18] using a technique already reported.[19] The exact methacrylic acid content of the copolymer was determined by titration of triplicate 0.4-g samples in benzene/methanol, 90/10 by volume, with a standard methanolic 0.05 N sodium hydroxide solution. The sample solution was titrated to the phenolphthalein end point, and a blank correction was included in the calculations.

Nitration tests were initially carried out on the styrene homopolymer, and the technique was later employed to nitrate the copolymers used in the ionic aggregation study. Although many different solvent systems were tested for the nitration reaction, a mixture of nitrobenzene with 1,2-dichloroethane, 3/1 by volume, provided the homogeneous solution conditions necessary for the uniform nitration of the polymers in the 0–100+% range. In a typical nitration test, polystyrene, 1.00 g, was first dissolved in 17.2 mL of the 3/1 nitrobenzene/1,2-dichloroethane solvent in a 50-mL, 3-neck flask. The flask was immersed in a stirred water bath at 20 °C, and fuming (90%) nitric acid, 2.8 mL, was slowly added dropwise with magnetic stirring in ca. 8 min, so that the temperature in the flask remained at 20.0 ± 0.5 °C. The resulting solution, 3 M nitric acid, was stirred for 60 min longer at 20 °C after the addition of the acid was completed. Distilled water (10 mL) was finally added to stop the reaction, and the polymer was recovered by precipitation of the organic phase in methanol. The light yellow solid was collected and air-dried on a Buchner funnel before drying in a vacuum oven at 60 °C overnight. The yield was 1.05 g of polymer with 27% substitution.

Sample Preparation and Analysis. The ratio of the integrated NMR peaks for the protons α to the nitro group (δ = 7.85 ppm) to those for the rest of the aromatic protons (δ = 7.10 and 6.55 ppm) was used to determine the degree of nitration. It should be noted that all the nitration and plasticization levels reported in this work are molar ratios. They are calculated from the molar ratio of aromatic rings bearing nitro groups to the total amount of rings present. In the case of plasticized samples, however, the weight fraction of plasticizer is also reported (between parentheses) for convenience. A curve relating the concentration of nitric acid to the degree of nitration under the conditions given above was constructed for the 0–44% substitution range from the NMR results.

The technique used for polystyrene was also used to nitrate the styrene–methacrylic acid (PS–MAA) copolymer. The degrees of substitution of those polymers were determined with the same NMR technique used for the styrene homopolymer. Nitration levels were also confirmed in this case from the equivalent weights determined by titrating 0.4-g samples potentiometrically in DMF with the standard 0.05 N sodium hydroxide solution. A more accurate estimate of the end point was obtained by fitting a sixth-order polynomial to the data obtained in the transition region using a computer and scanning the second derivative of the curve for the inflection point where $y''(x) = 0$.

The glass transition temperature (T_g) of the nitrated polystyrene samples was measured as a function of the degree of nitration on the Perkin-Elmer differential scanning calorimeter. The values reported were obtained in the second run, after leaving the samples at T_g + 15 °C for a few minutes, followed by quick quenching (320 °C/min or the maximum attained by the instrument).

The polymer films used in IR spectroscopy were obtained by compression molding at ca. 10 MPa of 0.05 g of material between two aluminum plates covered with aluminum foil. The temperature was maintained for at least 5 min at 200 ● 10 °C. Infrared spectra were recorded for 103% nitrated polystyrene, 100% nitrated PS–MAA copolymer (based on the benzene rings), and 32% nitrated PS–MAA.

The nitrated PS–MAA samples used for dynamic mechanical measurements were prepared by weighing precisely 1.5-g batches of material in 250-mL, round-bottomed flasks, dissolving them in 100 mL of 90/10 benzene/methanol, and adding a proper amount of 0.05 N methanolic NaOH solution for complete neutralization, according to the predetermined equivalent weights of the materials. The samples were then freeze-dried, and sample drying was completed by putting 1.30 g of the freeze-dried materials in a vacuum oven at 100 °C for at least 14 days prior to molding. Each sample was compression molded in a preheated mold at 220 °C. The temperature was maintained at 220 ± 5 °C and the pressure at 20 MPa for 10 min. The pressure was then very slowly released, and the mold was allowed to cool on the press to 5–10 °C below the matrix glass transition temperature of the polymer (as estimated from the DSC results) before it was taken out of the mold. Typical DMTA sample dimensions were 36-mm length × 12-mm width × 2.5-mm thickness. The exact dimensions were measured to ±0.01 mm with a micrometer immediately before mounting on the DMTA for dynamic mechanical measurements.

The PS–MAA samples containing nitrobenzene as an external plasticizer were prepared by drying appropriate amounts of freeze-dried PS–MAA, fully neutralized with sodium hydroxide, in vacuo at 100 °C for at least 14 days, as before. The sample weights were calculated so that the total weight, after removal of excess nitrobenzene, would be 1.30 g. The dry samples were then impregnated with 4 mL of dry nitrobenzene and transferred quantitatively to small boats made from Teflon sheets. Each sample was left to soak for 1 h in a desiccator at room temperature and then transferred to a drying pistol at 100 °C (water), purged with dry nitrogen, for 1 h longer. The temperature was decreased to 56 °C (boiling acetone), and the excess nitrobenzene was slowly pumped out until the proper sample weight was reached. Molding of the plasticized samples was done as in the case of the nitrated samples, except that the temperature was kept at 200 °C while the pressure was applied, so as not to lose significant amounts of nitrobenzene (bp 214 °C/760 mmHg).

Two samples, containing about 10% and 30% nitrobenzene, mole/mole, respectively, were prepared with the technique described above. The molded 30% sample was weighed precisely (±0.1 mg) before and after the run, to evaluate the amount of plasticizer lost during the run. It was then brought to constant weight in a drying pistol at 150 °C (boiling *N,N*-dimethylformamide) under vacuum, to evaluate the amount of plasticizer originally present. The effect of temperature on plasticizer loss was explored in a more detailed manner by preparing an extra sample containing about 10% nitrobenzene. The sample was set up in the DMTA for a fake run at 1 °C/min and taken out for weighing at a temperature of 185 °C, which is of particular interest to this study.

For dielectric measurements, dried nonnitrated and 32% nitrated PS–MAA–Na samples were molded at 210 °C/20 MPa for 10 min in a circular mold (ca. 19-mm diameter × 1.5-mm thickness). The mold was lined with aluminum foil at the bottom and on the plunger, to serve as electrical contacts for the measurements. The capacitances of the samples at 100 Hz were measured with the General Radio capacitance bridge to determine both their unrelaxed (room temperature) and relaxed (ca. 200 °C) dielectric constants.

Results and Discussion

Synthesis and Sample Analysis. The methacrylic acid content of the copolymer was determined, by titration in benzene/methanol, to be 7.0% ± 0.1% on a mole/mole basis. The uncertainty in the MAA content was evaluated from an error of 2 drops, or 0.05 mL, on the titrant volumes used for both the sample and the blank, arising from the somewhat diffuse end point observed in titrations in organic solvents. Titrant volumes of 6.0 mL were typically used for the samples, yielding a relative error of 1.7%.

The curve relating the degree of nitration obtained (as determined by NMR) to the concentration of fuming nitric acid used is given in Figure 1. The solid curve was fitted to the data with a second-order polynomial (correlation coefficient $r^2 = 0.995$) and may be used to approximate the degree of substitution X (mol %) as

$$X \text{ (mol \%)} = 8.18M^2 - 20.9M + 17.0 \qquad (1)$$

where M represents the HNO_3 molarity. The usefulness of this nitration technique lies in the fact that a homogeneous system is obtained in all proportions with nitric acid, making it possible to control smoothly the nitration level in the 0–100+% range. Although the values shown in Figure 1 only refer to degrees of substitution of less than about 50%, samples were prepared (in less accurately temperature-controlled conditions) with up to 106% substitution, by increasing the nitric acid concentration and/or temperature.

The infrared spectrum of a 103% nitrated polystyrene sample showed para substitution on the rings, in the form of a characteristic doublet pattern[20] at 1800 and 1925 cm^{-1} (5.56 and 5.19 μm, overtones) and a strong band appearing

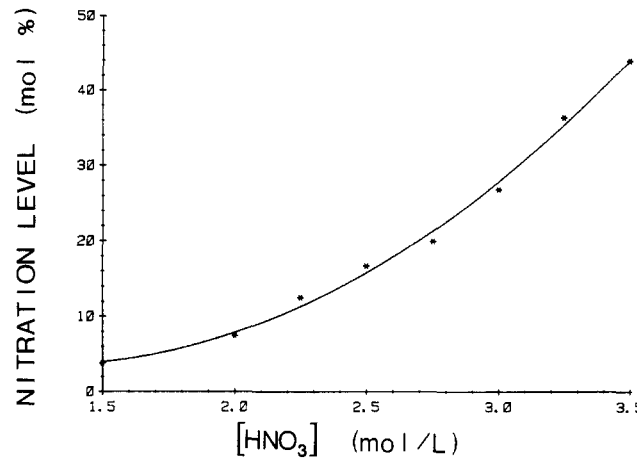

Figure 1. Nitration of polystyrene in 3:1 nitrobenzene/1,2-dichloroethane with fuming nitric acid at 20 °C after 60 min.

at 830 cm^{-1} (12.05 μm, out-of-plane bending). The weaker but still present bands at 710 and 750 cm^{-1} (14.1 and 13.3 μm, out-of-plane bending) for monosubstituted benzene rings also indicate that not all the styrene units may be nitrated. It seems likely, considering the nitration level determined by NMR (103%), that small amounts of the 2,4-dinitro isomer are also present. However, the associated IR bands are apparently too weak to be detected in the 1650–2000-cm^{-1} (5–6.1-μm) region. The comparison of the NMR spectra of the nitrated polymers with model compounds likewise did not reveal the presence of significant amounts of dinitro isomers. The presence of other isomers in the complete nitration of polystyrene with nitric acid has already been confirmed in oxidation studies of the products, the para isomer being predominant.[21]

The infrared spectrum of 30% nitrated polystyrene was, as expected, closer to polystyrene than to the 103% nitrated sample, showing the usual quadruplet structure in the 1650–2000-cm^{-1} region (5–6.1 μm) for monosubstitution of the ring, as well as the features, though less pronounced, already described for the fully nitrated sample. Infrared spectra of 32% and 100% nitrated PS–MAA copolymers were essentially identical with those obtained for the corresponding nitrated styrene polymers, except for an additional carbonyl band at 1740 cm^{-1} (5.75 μm).

It should be noted that the predominant para nitration observed in the samples supports the assumption, used in the calculations from the NMR integrals, that the nitro group introduced has two neighboring protons on the ring. The assumption would, of course, be invalid if significant amounts of the ortho isomer, or disubstituted species, were present.

The degree of substitution, X, of the PS–MAA samples was also calculated from the equivalent weights (EW) of the copolymers as determined by titration with the standard 0.05 N NaOH solution, according to the equation

$$X = \frac{(\text{EW} - 1470)100\%}{598} \qquad (2)$$

where 1470 represents the equivalent weight of PS–0.07 MAA and 598 represents the equivalent weight difference between 100% and 0% nitrated polymers. The good agreement between the values determined from the equivalent weight and the NMR results (Table I) provides further support for the assumptions made and indicates that the methacrylic acid groups were unaffected in the reaction. The accuracy of the NMR technique, resulting from the variations observed in the integrals due to spectrum phasing errors, was estimated to be about 5%

Table I
Comparison of the Nitration Levels Determined by NMR and by Titration (Recalculated from the EW) of Nitrated PS–0.07 MAA Copolymers

% NO_2	
NMR	titration
16.0 ± 0.8	15 ± 9
40 ± 2	38 ± 9
74 ± 4	74 ± 9

of the values determined. The larger errors obtained with the equivalent weights technique arise from the subtraction of the EW of the nitrated material from the EW of PS–0.07 MAA, both of similar magnitudes and with relative errors of 1.7%.

Physical Properties. The glass transition temperature (T_g) of nitrated polystyrene samples, as determined by DSC, increased monotonically in the 0–100% range (correlation coefficient $r^2 = 0.9994$) with the degree of substitution, X:

$$T_g\ (°C) = 106.4 + 0.850X \quad (3)$$

Cross-linking problems were first observed on the DSC when samples were left at temperatures of the order of T_g + 50 °C for about 15 min. The T_g of the samples increased by a few degrees, and they became insoluble in DMF. The tendency of nitrated polystyrene samples to cross-link increased with the degree of substitution, as well as with the MAA content, in the case of the copolymers.

The cross-linking problems encountered made it critical to choose the optimum methacrylic acid content for the study. The styrene–sodium methacrylate system is well characterized, with a cluster T_g increasing more rapidly than the matrix T_g, particularly at ion contents greater than 5 mol %.[22] Nitration, on the other hand, shifts the matrix T_g of the materials to higher temperatures, eventually causing the two loss maxima in the tan δ verge temperature curve to merge when the degree of nitration is increased. It would therefore seem preferable to use a PS–MAA sample with a higher ion content for the study, e.g., 10%, with a matrix T_g of 145 °C and a cluster T_g of 220 °C, according to torsional pendulum measurements.[22] Preliminary work, however, showed that 50% nitrated PS–0.10 MAA–Na samples cross-linked when heated to 80 °C for a few hours.

The particular choice of 7% MAA content, with a matrix T_g of ca. 135 °C and a cluster T_g of ca. 185 °C,[22] therefore, represents a compromise between the better spacing of the loss maxima observed at higher ion contents and the cross-linking tendency of the samples. A range of 0–32% nitration was used in this work, but extended drying periods (2 weeks) at relatively low temperature (100 °C) were needed in order to prevent cross-linking. The equivalence of the extended sample drying periods at a lower temperature with shorter periods at higher temperature (4 days at 150 °C) was demonstrated by comparison of two DMTA runs for the nonnitrated ionomer, which yielded identical results.

A nitration level of 32% raised the relaxed dielectric constant of the PS–0.07 MAA–Na ionomer (measured at 200 °C) from 3.2 to 7.3. The corresponding unrelaxed dielectric constants (at room temperature) were 2.9 and 3.7 for the nonnitrated and 32% nitrated ionomers, respectively. The unrelaxed dielectric constant ($\epsilon = 2.9$) obtained for the PS–0.07 MAA–Na sample is consistent with dielectric data varying from $\epsilon = 2.7$ to 3.2 reported by Hodge and Eisenberg[23] for the same materials with MAA contents from 2 to 9 mol %. Ishida,[24] in his dielectric relaxation study of acrylate polymers, reported relaxed and unrelaxed dielectric constants of 7.1 and 4.7 for poly(methyl acrylate) at 100 Hz and temperatures of 46.5 and 14.5 °C, respectively. The added nitro groups therefore increase the polarity of the styrene matrix to raise it to a level comparable to the acrylate polymers.

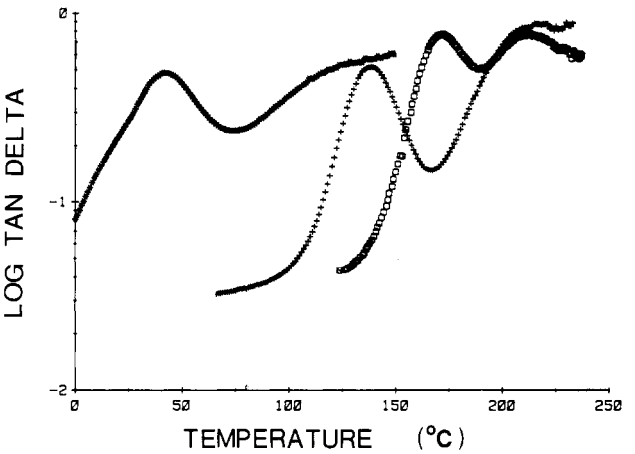

Figure 2. Dynamic loss tangent curves of (+) PS–0.07 MAA–Na, (□) PS–0.07 MAA–Na 32% nitrated, and (*) PS–0.07 MAA–Na plasticized with 25% mol/mol (30% w/w) nitrobenzene.

Stress relaxation studies of ethyl acrylate based ionomer systems[25] have revealed that time–temperature superposition breaks down at ionic concentrations of the order of 12–16%. More recently, dynamic mechanical studies of the same materials[18] have shown that the high-temperature loss tangent maximum becomes predominant at ion concentrations of the order of 10–15%. The higher ion content observed in the acrylate ionomers as the onset of cluster-dominated rheological properties, compared to the styrene systems (4–6%), was attributed to their higher dielectric constant.

It therefore seemed reasonable to expect that, if matrix polarity was an important parameter affecting ion aggregation, an increase caused by partial nitration of the matrix should affect aggregation in a similar manner. The higher polarity of the nitrated materials was expected to decrease the proportion of ionic material included in the clusters in favor of the multiplets, affecting at the same time the relative intensities of the two associated loss maxima.

The dynamic mechanical measurements yielded, on the contrary, surprisingly different results. The matrix T_g of the nitrated PS–MAA–Na samples increased, as expected, with increasing nitro group content (Figure 2), but the cluster T_g was essentially unaffected, both in shape and in position, by the highly polar nitro groups, even at the upper nitration level. It therefore seems that the polarity of the polymer matrix is not, in itself, a predominant parameter affecting ionic aggregation.

As noted earlier, Bazuin and Eisenberg, in their plasticization study,[15] explored the effects of two diluents of a very different nature on the PS–MAA–Na system. Diethylbenzene (DEB), a nonpolar diluent, affected the tan δ peaks associated with the matrix and with the clusters to a similar extent, as demonstrated by the similar decrease in both T_g's observed with increasing DEB concentration (Figure 3). Glycerol, a very polar ($\epsilon = 42.5$ at 25 °C)[9] and strongly hydrogen-bonded diluent, on the contrary, affected preferentially the cluster peak. Considerations of the different nature of nitrobenzene, compared to glycerol, and the unexpected results obtained for the dynamic mechanical properties of the nitrated polymers led to a plasticization study with that particular diluent. Nitrobenzene is a substance which, apart from its lack of hydrogen-bonding ability, has a high dielectric constant (ϵ

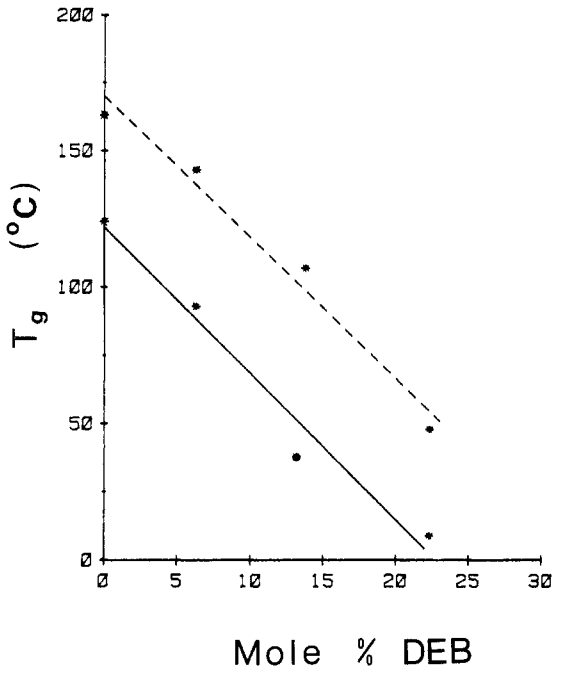

Figure 3. Matrix (—) and cluster (- - -) glass transition temperatures of PS–0.05 MAA–Na ionomers plasticized with diethylbenzene, as estimated from ref 15.

= 34.8 at 25 °C and 20.8 at 130 °C),[9] comparable to glycerol. It is also similar in structure to the nitrated polymer, apart from its additional mobility.

Because cluster structures are known to be highly water-sensitive, the nitrobenzene was carefully dried over phosphorus pentoxide and sealed immediately afterward in dry ampules, to avoid absorption of water vapor in the atmosphere. The freeze-dried PS–MAA–Na samples were, like the nitrated ones, further dried at 100 °C for 14 days. One reason to provide the same treatment to the samples is obviously the need for identical sample history. Another reason, less obvious, is that at 100 °C, which is lower than the T_g of the material (ca. 135 °C), the freeze-dried material does not compact and therefore absorbs the plasticizer more readily and ensures its even distribution.

The effect of nitrobenzene, as compared to nitration, on the glass transition temperatures of the matrix and ion-rich regions is illustrated in Figure 4. Nitrobenzene concentrations of 9.5% and 25% mol/mol were determined from the sample weight difference before the DMTA run and after drying to constant weight in a drying pistol at 150 °C (DMF) under vacuum. The plasticizer behavior of nitrobenzene is somewhat surprising, when compared to the results of Bazuin and Eisenberg.[15] Nitrobenzene seems to affect the matrix and cluster regions to the same extent, as in the case of diethylbenzene (Figure 3). This is particularly interesting, because of the comparable dielectric constants of nitrobenzene and glycerol (ϵ = 34.8 versus 42.5, respectively, at 25 °C). Thus, nitrobenzene, in spite of its high dielectric constant, acts essentially like a nonpolar plasticizer (diethylbenzene). The plasticizer behavior of nitrobenzene is in marked contrast with glycerol which, apart from depressing the matrix T_g slightly, virtually eliminated the clusters, causing a quick drop in G' above T_g with increasing glycerol concentration.

A graphic approach, described in a more detailed manner elsewhere,[16] is used to subtract a linear or polynomial base line from a portion of the tan δ curve in the data-analysis program.

The value of the storage modulus E'_{in} at the inflection point of the rubberlike plateau was used to calculate the

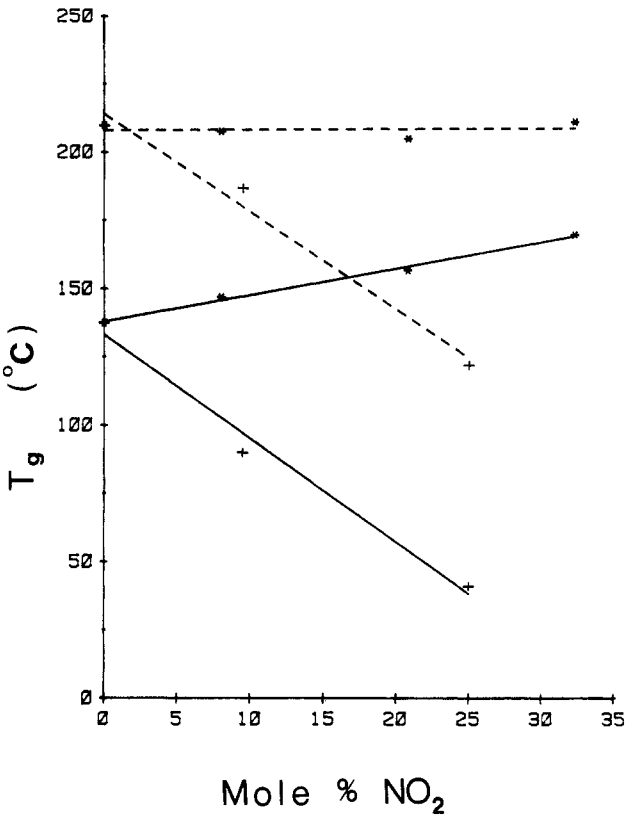

Figure 4. Peak positions of the dynamic loss tangent maxima in PS–0.07 MAA–Na nitrated (*) and plasticized with nitrobenzene (+) for the matrix (—) and ion-rich domains (- - -).

Table II
Average Molecular Weight between Cross-Links Calculated from the Storage Modulus at the Inflection Point of the Rubberlike Plateau for Nitrated and Plasticized PS–0.07 MAA-Na Ionomers

nitrated		plasticized	
% NO_2, mol/mol	M_c, g/mol	% NO_2, mol/mol	M_c, g/mol
8.0	460	0	300
21	370	9.5	430
32	490	25	760

average molecular weight between cross-links according to the equation[26]

$$M_c = \frac{3\rho R T_{in} v_2^{1/3}}{E'_{in}} \quad (4)$$

as reported in Table II. The value $\rho = 1.05 \times 10^3$ kg/m^3 for the density of polystyrene[27] was used as an approximation for the ionomers. The correction factor involving v_2 (volume fraction of polymer) was used for the plasticized samples.

The theoretical M_c value calculated for strictly multiplet-type interactions was 1470 g/mol. The experimental values reported in Table II show no significant trend for the nitrated ionomers. This is consistent with the constant appearance of the cluster peak observed in the loss tangent curves of both the 32% nitrated and the nonnitrated PS–0.07 MAA–Na ionomers (Figure 2) and reflects a comparable relative distribution of ions in the matrix and ion-rich phases of both samples. The plasticized ionomers, however, show a clearly increasing trend for M_c. This is similar to the observations made by Bazuin and Eisenberg[15] for PS–0.05 MAA–Na samples plasticized with diethylbenzene and attributed to the progressive destruction of the network by dilution with the plasticizer.

The plasticizer loss studies show significant losses of nitrobenzene by the end of the run. The 25% mol/mol (30% w/w) sample, which was tested in the 60–250 °C range at a heating rate of 1 °C/min, had lost, by the end of the run (250 °C), 42% of the plasticizer initially present. The more detailed study performed on another 10% plasticized sample (actually 10.3% mol/mol), however, showed that by the time the sample reached 185 °C, which is the glass transition temperature associated with the ion-rich domains at 1 Hz, only 25% of the plasticizer was lost. The losses should have been even less important by the time the 25% plasticized PS–MAA–Na sample reached its cluster T_g (122 °C).

The results obtained for both the nitrated and the nitrobenzene-plasticized PS–MAA–Na systems can be rationalized in terms of the relative importance of polarity versus specific interaction effects.

As pointed out earlier, the delocalization of the negative end of the dipole on the nitro group has been suggested to explain the poor ion-solvating ability of compounds like nitrobenzene.[14] In a first attempt to rationalize the present results, classifications of solvents in terms of their solvating power were identified. Although many empirical scales have been suggested,[28] there is no general systematic approach to the problem. In particular, most of the suggested scales are derived from the study of very specific systems and have the tendency not to distinguish between polarity and specific interaction contributions to solvation. The relative importance of polarity in affecting the course of chemical reactions—often including a partly or completely ionic transition state—was very much disparaged by Dack.[29] His argument is that the polarity felt by polar or ionic species on a microscopic level is very different from the bulk property measured. This phenomenon, referred to as dielectric saturation, occurs when an ion, for example, is solvated by a polar solvent. The dipoles of the solvent molecules align themselves around the ion and partly cancel each other's contribution. Theoretical calculations by Ritson and Hasted[30] based on a few models have shown that, while the bulk dielectric constant of water is 78.54, its microscopic dielectric constant within 1.5 Å (0.15 nm) of an ion is about 5. The bulk value is regained at about 4 Å (0.4 nm) from the ion. The same alignment phenomenon may cause solvent molecules as different as methanol (ϵ = 32.6) and acetone (ϵ = 20.7) to have very similar microscopic dielectric constants.[29]

It seemed therefore preferable to try to separate, as much as possible, polarity effects from specific interactions, which is not achieved with the empirical scales mentioned above. A more quantitative measure of the relative importance of polar versus specific interaction effects may be obtained from cohesive energy density (CED) data for solvents, in the form of three-dimensional solubility parameters,[31] of which several relevant examples are given in Table III. The total CED (δ_0) is actually a measure of the energy required to vaporize 1 mL (10^{-6} m^3) of the solvent at zero pressure, i.e., without PV work. It may be decomposed into three components, related to dispersive forces (δ_d), polar contributions (δ_p), and specific interaction or hydrogen-bonding (δ_h) contributions related to δ_0 through the equation

$$\text{CED} = \delta_0^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (5)$$

A comparison of the δ_0 values reported for hexane, benzene, ethyl acetate, methanol, and water shows an intuitively expected increase in δ_0 but also points at the considerable variations encountered in the relative magnitudes of the δ_d, δ_p, and δ_h parameters. While specific interaction effects account for less than 2% of the total CED (δ_0^2) of benzene, they account for more than 50% of the CED of methanol. Although three-dimensional solubility parameters are not available for polymers, the value of δ_0 = 39.1 for poly(ethyl acrylate) is very comparable to δ_0 = 38.1 for ethyl acetate. The comparison of ethyl acetate, as a model compound for poly(ethyl acrylate), to nitrobenzene (δ_0 = 44.4) shows a similar overall CED. The individual components are, however, quite different. While the two substances have comparable dispersive force components, the balance of the polarity and specific interaction-associated effects is mostly due to polarity in the case of nitrobenzene and to specific interactions for ethyl acetate.

Table III
Solubility Parameters of Solvents and Polymers[a]

substance	δ_0	δ_d	δ_p	δ_h
hexane	30.3	30.2	0	0
benzene	38.3	37.4	2.1	4.2
ethyl acetate	38.1	31.1	10.9	18.8
nitrobenzene	44.4	36.0	25.1	8.4
methanol	61.9	31.0	25.1	45.6
glycerol	88.3	35.4	?	?
water	98.3	25.1	62.8	69.9
polyethylene	33.1			
polystyrene	38.1			
poly(ethyl acrylate)	39.1			

[a] In 10^{-3}(J·m^{-3})$^{1/2}$ (from ref 31).

Further support for the specific interactions concept can be found in the literature. Kay et al.[32] used conductometry to study alkali perchlorate solutions in acetonitrile and compared them with similar measurements in alcohols. They concluded that, in the case of small ions (e.g., sodium), the acid/base (or donor/acceptor) character of the solvent was predominant in determining the extent of ion solvation. For larger ions such as cesium, the greater ability of the solvent molecules to approach cations makes ion–dipole interactions more important in the solvation process. The donor/acceptor character of solvents was also found important by Mayer et al.[33] in their study of the dissociation of quinuclidinium chloride in different solvents, including nitrobenzene. The exceptionally low dissociation constant observed in nitrobenzene was attributed to its weak donor and acceptor character.

It seems likely, from the data presented above, that the unexpected effects observed in both the nitrated and nitrobenzene-plasticized PS–MAA–Na ionomers are a direct result of the low degree of specific interactions, rather than due to polarity effects. Apart from specific interactions, it seems reasonable to assume that another factor not examined here, namely structural (steric) effects, may have some influence on clustering.

Conclusions

The results of this work have shown that the dielectric constant of the polymer matrix is not, by itself, a predominant factor controlling ionic aggregation. The nitration of styrene–sodium methacrylate copolymers has no effect on clustering in the 8–32% range, in spite of the increased dielectric constant of the materials (ϵ = 7.3 at 200 °C for 32% NO_2).

A parallel plasticization study with nitrobenzene indicated that the ion-rich domains were affected to the same extent as the matrix, as already reported for nonpolar plasticizers. In spite of its high polarity, nitrobenzene behaves very differently from glycerol, also a polar substance which plasticizes the ion-rich domains much more than the matrix. The presence of specific interactions, therefore, seems to be a more important parameter than

polarity alone in determining the plasticizer effect of added diluents.

A nitration technique was also suggested which allows control of the degree of nitration in the 0–100% range for polystyrene and styrene–methacrylic acid copolymers. The T_g of nitrated polystyrene increased linearly with the nitration level.

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Registry No. (S)(MAA) (copolymer, sodium salt), 31227-13-1; nitrobenzene, 98-95-3.

References and Notes

(1) (a) *Ionic Polymers*; Holliday, L., Ed.; Applied Science: London, 1975. (b) Bazuin, C. G.; Eisenberg, A. *Ind. Eng. Chem. prod. Res. Dev.* **1981**, *20*, 271. (c) MacKnight, W. J.; Earnest, T. R., Jr. *J. Polym. Sci., Macromol. Rev.* **1981**, *16*, 41.
(2) Eisenberg, A.; King, M. *Ion-Containing Polymers*; Academic: New York, 1977.
(3) (a) Weiss, R. A.; MacKnight, W. J.; Lundberg, R. D.; Mauritz, K. A.; Thies, C.; Brant, D. A. In *Coulombic Interactions in Macromolecular Systems*; Eisenberg, A., Bailey, F. E., Eds.; ACS Symposium Series 302; American Chemical Society: Washington, DC, 1986; pp 2–19. (b) Lundberg, R. D. In *Structure and Properties of Ionomers*; Pineri, M.; Eisenberg, A., Eds.; NATO ASI Series C; Reidel: Dordrecht, Holland, 1987; Vol. 198, pp 429–438. (c) Tan, J. S. *Ibid.* pp 439–451.
(4) (a) Rees, R. W.; Vaughan, D. J. *Polym. Prepr.—Am. Chem. Soc., Div. Polym. Chem.* **1965**, *6*(1), 287. (b) Rees, R. W.; Vaughan, D. J. *Ibid.* **1965**, *6*(1), 296.
(5) Eisenberg, A. *Macromolecules* **1970**, *3*, 147.
(6) (a) Navratil, M.; Eisenberg, A. *Macromolecules* **1974**, *7*, 84. (b) Makowski, H. S.; Lundberg, R. D.; Westerman, L.; Bock, J. In *Ions in polymers*; Eisenberg, A., Ed.; Advances in Chemistry 187; American Chemical Society: Washington, DC, 1980; pp 3–19.
(7) Brockman, N. L.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1145.
(8) (a) Lundberg, R. D.; Makowski, H. S. In *Ions in polymers*; Eisenberg, A., Ed.; Advances in Chemistry 187; American Chemical Society: Washington, DC, 1980; pp 21–36. (b) Rigdahl, M.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1641. (c) Fitzgerald, J. J.; Weiss, R. A. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1988**, *C28*, 99.
(9) *CRC Handbook of Chemistry and Physics*, 61st ed.; Weast, R. C., Astle, M. J., Eds.; Chemical Rubber Company: Boca Raton, FL, 1981; p E-56.
(10) Seliger, H. *Makromol. Chem.* **1973**, *169*, 83.
(11) (a) Bachman, G. B.; Hellman, H.; Robinson, K. R.; Finholt, R. W.; Kahler, E. J.; Filar, L. J.; Heisey, L. V.; Lewis, L. L.; Micucci, D. D. *J. Org. Chem.* **1947**, *12*, 108. (b) Zenftman, H. *J. Chem. Soc.* **1950**, 982. (c) Blanchette, J. A.; Cotman, J. D., Jr. *J. Org. Chem.* **1958**, *23*, 1117.
(12) Bajaj, I.; Kapoor, S. K.; Chatterjee, S. R. *Def. Sci. J.* **1968**, *18*, 89.
(13) (a) Crivello, J. V. *J. Org.* Chem. **1981**, *46*, 3056. (b) Crivello, J. V. U.S. Patent 3 715 323, 1973; *Chem. Abstr.* **1973**, *78*, 111976c.
(14) Burgess, J. *Metal ions in solution*; Ellis Horwood: Chichester, 1978; p 30.
(15) Bazuin, C. G.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 1137.
(16) Gauthier, M. Ph.D. Thesis, McGill University, Montreal, Jan 1989.
(17) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University: Ithaca, NY, 1953; p 140.
(18) Simmons, A. H. M.Sc. Thesis, McGill University, Montreal, Oct 1986.
(19) Navratil, M.; Eisenberg, A. *Macromolecules* **1973**, *6*, 604.
(20) Pasto, D. J.; Johnson, C. R. *Organic Structure Determination*; Prentice-Hall: Englewood Cliffs, NJ, 1969; Chapter 4.
(21) (a) Rafikov, S. R.; Ergozhin, E. E. *Dokl. Chem. (Engl. Transl.)* **1968**, *181*, 708; *Dokl. Akad. Nauk SSSR* **1968**, *181*, 899. (b) Rondestvedt, C. S., Jr.; Jeffrey, J. R.; Miller, J. E. *Ind. Eng. Chem. Prod. Res. Dev.* **1977**, *16*, 309.
(22) Navratil, M.; Eisenberg, A. *Macromolecules* **1974**, *7*, 90.
(23) Hodge, I. M.; Eisenberg, A. *Macromolecules* **1978**, *11*, 283.
(24) Ishida, Y. *Kolloid Z.* **1961**, *174*, 124.
(25) Eisenberg, A.; Matsuura, H.; Tsutsui, T. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 479.
(26) Treloar, L. R. G. *The Physics of Rubber Elasticity*; Oxford University: Oxford, 1958; Chapter 9.
(27) Rudd, F. J. In *Polymer Handbook*, 2nd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1974; p V-59.
(28) Reichardt, C. *Angew. Chem. Int. Ed. Engl.* **1965**, *4*, 29.
(29) Dack, M. R. J. Solutions and Solubilities. In *Techniques of Chemistry*; Dack, M. R. J., Ed.; Wiley: New York, 1976; Part 2, Vol. 8.
(30) Ritson, D. M.; Hasted, J. B. *J. Chem. Phys.* **1948**, *16*, 11.
(31) Burrell, H. In *Polymer Handbook*, 2nd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1974; p IV-337.
(32) Kay, R. L.; Hales, B. J.; Cunningham, G. P. *J. Phys. Chem.* **1967**, *71*, 3925.
(33) Mayer, U.; Gutmann, V.; Kösters, K. *Monatsh. Chem.* **1976**, *107*, 845.