with an insulating polymer film produces novel conducting polymer alloy films in which highly conducting PPy is mixed to form continuous conducting paths. The physical properties and the morphology were investigated by using PVC and PVDF–TrFE as insulating polymer films. The conductivity is greatly increased with the PPy amounts incorporated in the film. The alloying process does not change the mechanical property of the insulating film and improves the thermal stability of the film in a high-temperature region. The structure of alloy films has been revealed by SEM observation of extracted film, and the physical properties are closely related with the film morphology.

Registry No. PPy, 30604-81-0; PVC, 9002-86-2; (TrFE)-(PVDF) (copolymer), 28960-88-5.

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Vinylpyridinium Ionomers. 1. Influence of the Structure of the Ion on the State of Aggregation in Random Styrene-Based Systems[1]

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ABSTRACT: The thermal and dynamic mechanical properties of random styrene ionomers containing various vinylpyridinium groups have been examined. The properties of the materials were found to be independent of the structure of the ion. The glass transition temperatures of these ionomers were found to increase regularly with increasing ion content, at a rate of about 3.5 °C/(mol % ions). In contrast with styrene ionomers with pendant anionic groups studied before, the vinylpyridinium ionomers showed only one peak in their loss tangent curves, associated with the T_g of the matrix. The absence of a second, higher temperature peak suggests the absence of clusters in these ionomers, at least at temperatures above their T_g. The storage modulus curves are in agreement with this conclusion.

Introduction

Over the past few decades, ionomers have been the subject of a large number of investigations.[2,5] Early studies brought to light the unique properties of these materials and suggested a range of applications. This encouraged further research in an attempt to understand the phenomena responsible for these properties and thus enable researchers to produce materials capable of answering very specific needs.

Fundamental investigations have focused on relatively few types of backbones and even fewer kinds of ionic groups; these few systems have been studied extensively, using numerous techniques to probe different aspects of their behavior. Polyethylene, poly(tetrafluoroethylene), and polystyrene, as well as some elastomers, have probably been the most widely investigated backbones. A relatively new family of ionomers based on the polypentenamer backbone has also been investigated.[4] Other systems have been examined, although not as extensively. Variation of other parameters, such as the nature of the ion and the counterion, the ion content, and the position of the ion relative to the chain, has provided a better understanding of the factors influencing the properties of ionomers. Most of the studies have been conducted on salts of carboxylic acids, the most common being methacrylic and acrylic acids as well as carboxystyrene. Sulfonic acids have been introduced on certain backbones. Investigations of ionomers carrying a positive charge have been limited mostly to a few vinylpyridinium systems.

Ion Aggregation in Ionomers. It is well-known that ionic compounds have a tendency to aggregate in media of low dielectric constant.[6] A similar, but somewhat more complex behavior may be expected in ionomeric systems in the bulk, since the majority of the backbones studied are of relatively low polarity.

The first attempt made to describe this phenomenon theoretically is probably that of Eisenberg.[7] Several other treatments have been published more recently.[8–11] Briefly, Eisenberg suggests that aggregation is governed by two opposing tendencies, association between ion pairs ($\Delta G < 0$) and stretching of the polymeric chain segments when such an association between ion pairs occurs ($\Delta G > 0$). The formation of two different types of aggregates is postulated: multiplets and clusters. The association of ion pairs into multiplets is shown to be limited solely by spatial restrictions, as the electrostatic energy gained is much greater than the work done to deform the chains. Multiplets are thus considered to be an association of a relatively small number of ion pairs (<8) and to be completely coated with nonionic chain material. Clusters are suggested to result from the aggregation of multiplets; since the latter are completely coated with nonionic material, clusters are expected to include chain segments. In contrast with the multiplets, the difference between the electrostatic and the elastic forces involved in the forma-

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tion of clusters is smaller, and above a certain critical temperature the clusters decompose back to multiplets. More recent articles have refined the picture of ion aggregation considerably. Different models for the structure of clusters have been proposed and are discussed in a review article by MacKnight and Earnest.[4]

Evidence for the occurrence of aggregation, whatever the structure of the aggregates, is plentiful. The increase in glass transition temperature of ionomers with ion content may be directly related to the presence of aggregates which are expected to diminish the mobility of the segments in a manner similar to that of covalent cross-links. The very large increase in the melt viscosity of ionomers with increasing ion content may be attributed to ionic interactions between the chains that persist even at temperatures far above the glass transition temperature of these systems.[12] The rate of stress relaxation has been found to decrease with ion content, and above a certain proportion of ions, the breakdown in time–temperature superposition in some systems indicates the occurrence of a secondary relaxation mechanism that has been related to the presence of clusters. Dynamic mechanical measurements also display features that may be attributed to the presence of aggregates. The loss tangent curves usually show an additional peak at a temperature above the T_g of the system that has been associated with a transition of the ion-rich phase. There is also a decrease in the slope of the storage modulus curves with increasing ion content.

Styrene Ionomers. Styrene ionomers have been studied extensively in this laboratory. The majority of the studies were performed on the sodium salts of copolymers of methacrylic acid.[13-16] The dynamic mechanical investigations[16] revealed a shift of the loss tangent as well as the storage and loss moduli (G' and G'') curves to higher temperature with increasing ion content, confirming the increase in the glass transition temperature with increasing ion content detected by DSC.[14] This was accompanied by a decrease in the slope of the G' and G'' curves in the transition region and, above a certain ion content, the appearance of a second, high-temperature peak in the loss tangent curves; these changes were interpreted as evidence for the presence of ion-rich phase-separated microdomains or clusters.

The effect of the position of the ion relative to the chain on the properties of ionomers has been investigated by comparing the properties of the sodium salts of para-carboxylated styrene copolymers with those of the methacrylate system.[17] The effect of the nature of the anion carried by the backbone has been the subject of several investigations. The melt rheology of sodium salts of styrene–*p*-carboxystyrene and styrene–para-sulfonated styrene copolymers was investigated by Lundberg and Makowski;[18,19] the dynamic mechanical properties of these ionomers were measured in this laboratory.[20] These studies seem to show that while the strength of the clusters is related to the nature of the anionic group their size depends upon the position of the ions relative to the backbone. A recent study of styrene–alkoxide ionomers[21] has shown that the clusters present in the sodium salts of styrene–*p*-hydroxystyrene copolymers are weaker and of smaller size than the clusters found in other anionic systems.

In view of these results it seemed interesting to investigate the properties of ionomers bearing a positive charge by studying styrene–vinylpyridinium copolymers. Relatively few investigations have been conducted on vinylpyridinium ionomers. The viscosity and conductance of nitromethane–dioxane solutions of styrene–4-vinylpyridine copolymers quaternized with *n*-butyl bromide were determined by Fuoss and Cathers.[22,23] The mechanical properties of butadiene–2-methyl-5-vinylpyridine copolymers quaternized with methyl iodide were studied by Otocka and Eirich.[24,25] DSC measurements showed a large increase of T_g with ion content, of about 8 °C/(mol % ionic groups). Curves of the variation of Young's modulus with temperature exhibited the second inflection point at high modulus values usually observed in ionomeric systems, as well as the decrease in slope with ion content. Finally, styrene–butadiene–4-vinylpyridine terpolymers complexed with ferric or nickel chloride salts have been studied by Meyer and Pineri.[26-28]

In view of the paucity of data on ionomers bearing a cationic charge, an investigation of a variety of vinylpyridinium ionomers was undertaken in this laboratory. The first investigation is devoted to the influence of the structure of the pyridinium ion on the bulk properties of styrene-based ionomers. The thermal and dynamic mechanical properties of ionomers of styrene with 4-vinylpyridinium, 2-vinylpyridinium, and 2-methyl-5-vinylpyridinium have been investigated and are the subject of this publication. The influence of the copolymer architecture on the state of aggregation was examined in a study of styrene–4-vinylpyridinium ABA block ionomers. This investigation is presented in the following paper in this issue. Finally, the influence of the T_g and the dielectric constant of the matrix was investigated by examining ethyl acrylate-, butyl acrylate-, and methyl methacrylate-based vinylpyridinium ionomers and will be the subject of two future publications.

Experimental Section

The desired vinylpyridinium ionomers were obtained by quaternization of styrene–vinylpyridine random copolymers with methyl iodide. The nonionic copolymers were obtained by bulk free-radical copolymerization of the monomers initiated with benzoyl peroxide. The r_1 (vinylpyridine) and r_2 (styrene) values for the different systems are given in Tables I–III. The polymerization was stopped below 40% conversion to ensure reasonable compositional homogeneity of the samples. Mixtures of different monomer ratios were prepared to obtain polymers of different vinylpyridine contents, ranging from 2 to 13 mol %.

Materials. Styrene (Aldrich, 99%, inhibited with 10–15 ppm of *p-tert*-butylcatechol) was washed 3 times with a 5% aqueous solution of sodium hydroxide to remove the inhibitor, washed 5 times with water to a neutral pH, and dried over calcium hydride overnight. It was then distilled under reduced pressure (21–22 mmHg) at 47–48 °C, discarding the first and last 10% of the monomer.

4-Vinylpyridine (4VP) (Aldrich, 98%) was dried over calcium hydride overnight and fractionally distilled under reduced pressure (15 mmHg) at 68–69 °C, discarding the first and last 10% of the monomer. 2-Vinylpyridine (2VP) (Aldrich, 97%) and 2-methyl-5-vinylpyridine (2Me5VP) (Aldrich 97%) were treated similarly but distilled at 75–77 °C (27 mmHg) and 79–82 °C (29 mmHg), respectively.

Benzoyl peroxide (99%, Baker) was used without further purification.

Polymerization. For each mixture, the desired amount of vinylpyridine was transferred to an Erlenmeyer flask to which 100 g of styrene was added. The amount of benzoyl peroxide (about 6.66 $g \cdot L^{-1}$) necessary to yield copolymers of the desired molecular weight ($\sim 1 \times 10^5$ $g \cdot mol^{-1}$) was accurately weighed and added to the Erlenmeyer. Each mixture was transferred with a syringe into an ampule, the liquid was degassed by three freeze–thaw cycles, and the ampules were sealed under vacuum. They were immersed in a 60 °C bath for 11 h to achieve about 30–40% conversion. The polymerization mixture was then diluted with toluene to obtain a 5% solution and precipitated into 10 volumes of rapidly stirred methanol. The white polymer strands were soaked in fresh methanol overnight, filtered, dried by suction, and freed of residual solvents by heating in a vacuum oven at 70

Table I
Bulk Polymerization of Styrene and 4-Vinylpyridine[a]

[4VP] in mixture, mol %	[4VP] in polymer, mol %	convrsn, %
1.1	1.9	29
3.0	5.2	33
4.4	7.2	36
6.4	9.7	39

[a] Temperature, 60 °C; time, 11 h; [initiator], 6.66 g/L. r_1(4-vinylpyridine) = 0.70. r_2(styrene) = 0.50.

Table II
Bulk Polymerization of Styrene and 2-Vinylpyridine[a]

[2VP] in mixture, mol %	[2VP] in polymer, mol %	convrsn, %
1.1	1.9	39
2.9	4.4	36
4.5	6.6	40
6.2	9.1	43

[a] Temperature, 60 °C; time, 11 h; [initiator], 6.66 g/L. r_1(2-vinylpyridine) = 0.55. r_2(styrene) = 0.9.

Table III
Bulk Polymerization of Styrene and 2-Methyl-5-vinylpyridine[a]

[2Me5VP] in mixture, mol %	[2Me5VP] in polymer, mol %	convrsn, %
1.6	1.9	32
3.9	4.5	31
5.2	5.9	33
7.5	8.5	30
12.3	13.3	33

[a] Temperature, 60 °C; time, 11 h; [initiator], 6.66 g/L. r_1(2-methyl-5-vinylpyridine) = 0.91. r_2(styrene) = 0.81.

°C for about 24 h. The relevant polymerization parameters are given in Tables I–III.

Characterization. (a) Analysis. The vinylpyridine content of the copolymers was determined following the procedure described by Burleigh et al.[29] for the characterization of butadiene–4-vinylpyridine copolymers involving titration with a perchloric acid solution in glacial acetic acid.

(b) Molecular Weight. An approximate molecular weight was obtained by measuring the intrinsic viscosity of the copolymers in toluene solutions and using the K and a values for polystyrene ($K = 7.5 \times 10^{-5}$ g·dL^{-1}, $a = 0.75$). The measurements were made at 25 °C (4VP, 2VP) and 30 °C (2Me5VP) with Ubbelohde viscometers. Five different concentrations were used, ranging from 0.05 to 0.25 g/dL. The intrinsic viscosities were found to range between 0.5 and 0.65 dL/g, corresponding to molecular weights of (1.3–1.7) × 10^5 g·mol^{-1}.

Quaternization with Methyl Iodide. (a) Materials. The polymer was dried at about 70 °C in a three-neck flask overnight, in a vacuum oven. Methyl iodide was fractionally distilled under nitrogen, a few hours before use. Tetrahydrofuran was dried by refluxing over potassium metal until the purple, characteristic of the potassium–benzophenone complex, persisted. It was then distilled directly into the flask containing the polymer.

(b) Procedure. The quaternization procedure adopted was a combination of the methods described by Selb and Gallot[30] and Otocka and Eirich.[24] The 4VP copolymers were quaternized by adding a 5-fold excess of methyl iodide to a 5% solution of the polymer in dry THF and refluxing under nitrogen for 1.5 h. Since only about 20% quaternization of the 2VP units was achieved when the above procedure was followed, more severe conditions were required to quaternize the 2Me5VP and 2VP copolymers fully. A 7-fold excess of methyl iodide was used for the 2Me5VP copolymers, and the solutions were refluxed for 4 h. The 2VP copolymers were quaternized with a 25-fold excess of methyl iodide and refluxing overnight. For all three types of polymers, the solution turned yellow a few minutes after the addition of methyl iodide. This yellow is also encountered with monomeric 4-substituted pyridinium salts.[31] Colorless quaternized copolymers were obtained by Gallot's group[32] by conducting the quaternization reaction under vacuum with solvents and reagents that had been purified and stored under vacuum. As only traces of the side product responsible for this coloration should be present[31] and were not expected to influence or interfere with the measurement of the mechanical properties of these polymers, it was judged unnecessary to follow the more elaborate procedure described by Gallot to obtain colorless materials. Clouding of the solution occurred during quaternization of the samples of highest vinylpyridine content due to some precipitation of the polymer which was redissolved by adding small amounts of absolute ethanol to the THF solution while the quaternization was progressing.

It was found that even slight exposure of the reaction mixture to the air deepened the coloration of the solution and yielded highly colored polymers. The quaternized materials were thus recovered by aspirating the cooled reaction mixture in a syringe and allowing the solution to drop in a fine stream into 20 volumes of rapidly stirred hexanes to precipitate the polymer. The strands were filtered and dried by suction; complete removal of solvents was achieved by heating in a vacuum oven at about 80 °C overnight.

(c) Analysis. The extent of quaternization was determined by FTIR of thin films of the materials. The disappearance of the pyridine band at 1414 cm^{-1} for 4VP, at 1472 cm^{-1} for 2VP, and at 1527 cm^{-1} for 2Me5VP was taken as evidence for complete quaternization of the vinylpyridine units. The extent of quaternization could not be determined by elemental analysis due to the very small weight percentage of nitrogen present. A sample containing 10 mol % of quaternized 4VP units, for example, contains only about 1% by weight of nitrogen, a value well within experimental error. In addition, the reproducibility of iodine analyses was found to be very poor. The infrared technique was thus judged to be the most sensitive and reliable method.

Physical Properties. (a) Thermal Properties. The glass transition temperature of polystyrene and either poly(4VP) or poly(2Me5VP) differ by about 40 °C. A study of the composition dependence of the T_gs of the nonionic copolymers was thus conducted. The glass transition temperatures of the nonionic materials were measured by differential scanning calorimetry on a Perkin-Elmer DSC II. The samples were heated on the DSC head at a temperature of about 150 °C for 5 min, cooled rapidly to 50 °C, and scanned at a rate of 20 °C/min. Duplicate determinations were made for each sample. Because the T_g of poly(2-vinylpyridine) is about the same (100 °C) as that of polystyrene (106 °C), the thermal properties of the nonionic copolymers were not studied as there should be no change in the glass transition temperature of these copolymers with 2VP content.

The glass transition temperatures of the ionomers were also determined on the DSC. Aluminum pans were filled and the materials dried under vacuum at 80 °C for 3 days before measurement. They were heated on the DSC head at about 150 °C for 5 min, cooled to 50 °C, and scanned at 20 °C/min. Duplicate determinations were made for each sample. When these measurements were performed on the 2VP ionomers, it was found that these readily undergo dequaternization at around 135 °C. The T_g of these samples was thus determined without prior drying or annealing. The first scans were stopped about 10 °C after the appearance of the transition; the samples were immediately cooled to 50 °C and scanned again to obtain duplicate determinations.

(b) Dynamic Mechanical Properties. The dynamic mechanical properties of the ionomers were measured on a torsion pendulum. Because of the occurrence of dequaternization at relatively low temperatures, the dynamic mechanical properties of the 2VP ionomers were not studied. A polystyrene sample was also measured as a reference.

Rectangular prisms were obtained by compression molding at a temperature of $T_g + 30$ °C. The samples were dried for 3 days under vacuum at 80 °C. The measurements were performed under nitrogen or helium atmosphere. The dynamic mechanical measurements on the 4VP ionomers were performed under helium. It was found subsequently that because of its high thermal conductivity, the use of helium introduced a 6 °C difference between the thermocouple and the sample, at the heating rates used. For example, the glass transition of polystyrene determined from a loss tangent curve obtained under helium was 112 °C instead of 106 °C. The curves obtained under helium are thus shifted by

Table IV
Variation of T_g with Ion Content

4VP ion content, mol %	4VP T_g, °C	2VP ion content, mol %	2VP T_g, °C	2Me5VP ion content, mol %	2Me5VP T_g, °C
0.0	106				
1.9	111	1.9	113	1.9	112
5.2	116	4.4	120	5.8	125
7.2	125	6.6	128	8.5	135
9.7	139			13.3	153

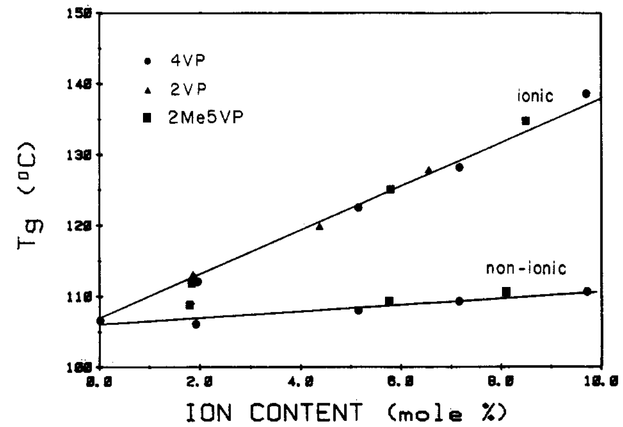

Figure 1. Variation of T_g with ion content for styrene-vinylpyridinium copolymers of different ion contents.

about +6 °C on the temperature axis compared to those obtained under nitrogen. For this reason, all of the measurements on the 2Me5VP ionomers were performed under nitrogen, which minimizes this difference. The chamber was heated at a rate of 30 °C/h, and the values of the loss tangent, G', and G'' were determined at periodic intervals. The frequency of the oscillations varied with the modulus of the polymer and ranged from about 5 Hz below T_g to about 10^{-1} Hz above T_g.

Results and Discussion

Thermal Properties. (a) Glass Transition Temperature. The DSC results for the 2-, 4-, and 2-methyl-5-vinylpyridine copolymers quaternized with methyl iodide are presented in Table IV and plotted in Figure 1. The variation of T_g with ion content is of about 3.5 °C/(mol %), a value comparable to that found for the anionic styrene ionomers;[14,17,20,21] this is a somewhat surprising result. The increase in T_g with ion content has been suggested to be proportional to $cq/\mathbf{a}$[33], where c is the concentration of ions, q is the magnitude of the charge, and **a** is the interionic distance. As the interionic distance in the pyridinium system is greater than in the carboxylated one, dT_g/dc of the pyridinium copolymers was expected to be smaller than that of the carboxylated materials. This behavior is difficult to explain on the basis of the thermal data alone. Dynamic mechanical measurements, however, offer an explanation for this high value of dT_g/dc.

(b) Dequaternization Phenomenon. In the course of the investigation of the thermal properties of the styrene–vinylpyridinium ionomers, a large endotherm around 160–190 °C was detected in all cases, in addition to the usual change in heat capacity associated with the glass transition. An infrared study performed in parallel on the 4-vinylpyridinium ionomers indicated that substantial dequaternization occurred under vacuum at temperatures as low as 100 °C when the samples were subjected to this heat treatment for time periods of the order of 24 h. The dequaternization was monitored by the increase in intensity of the 1414-cm^{-1} pyridine band with prolonged heating.

In light of these results, a systematic calorimetric study of the styrene-based vinylpyridinium iodide ionomers was undertaken, which led to the following observations. When the samples were left for short periods of time (e.g., 60–180 s) at a temperature close to that of the endotherm, their glass transition temperatures were found to be the same as those of the unquaternized materials, indicating the essentially complete dequaternization of the materials. In the case of the 2-vinylpyridinium ionomers, the endotherm was found to be very close to the glass transition of the material of highest ion content. It was thus concluded that torsion pendulum experiments could not be performed on these materials because of the longer time scale of the experiments. By contrast, the endotherm for the 4VP ionomers was found at a higher temperature. As expected, FTIR analysis of the 4VP ionomers after the torsion pendulum experiments showed negligible dequaternization of the materials. It was assumed, based on these results, that the 2-methyl-5-vinylpyridinium ionomers also remained fully quaternized during the torsional pendulum experiments. It is believed that the dequaternization process occurs at comparable rates at lower temperatures for the 2VP ionomers than for the 4VP and 2Me5VP systems because the 2VP ion is more sterically hindered. This is in agreement with the fact that the 2-vinylpyridine unit was much more difficult to quaternize.

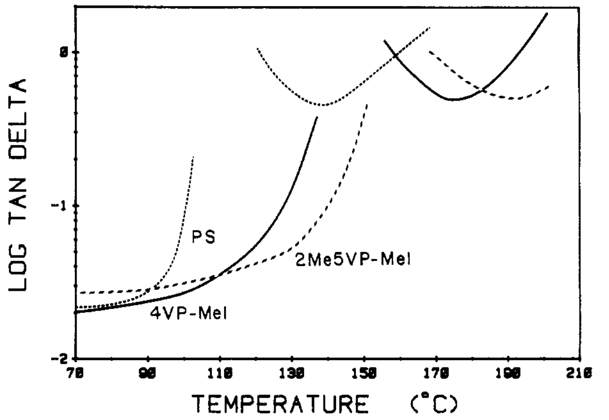

Figure 2. Variation of loss tangent with temperature for polystyrene, for a styrene–4-vinylpyridinium ionomer (9.7 mol %) and a styrene–2-methyl-5-vinylpyridinium ionomer (13.3 mol %).

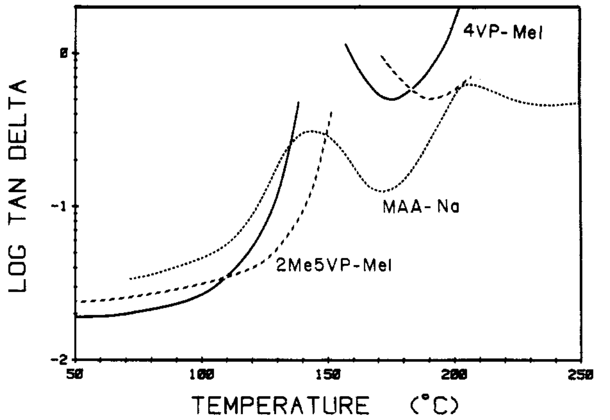

Figure 3. Variation of loss tangent with temperature for pyridinium (10 and 13 mol %) and sodium methacrylate (10 mol %) styrene ionomers.

Dynamic Mechanical Properties. The variation of loss tangent with temperature for the materials of highest 4-vinylpyridinium and 2-methyl-5-vinylpyridinium ion contents are shown in Figure 2 along with the curve obtained for polystyrene. As can be seen, the loss tangent curves for these ionomers are very similar to that of polystyrene, except for a shift to higher temperatures.

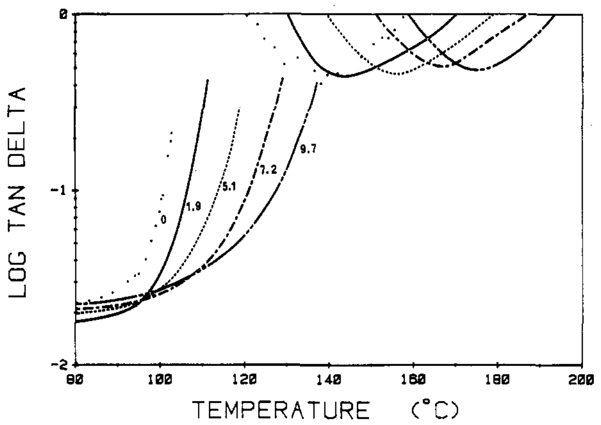

Figure 4. Variation of loss tangent with temperature for styrene–4-vinylpyridinium ionomers of various ion contents.

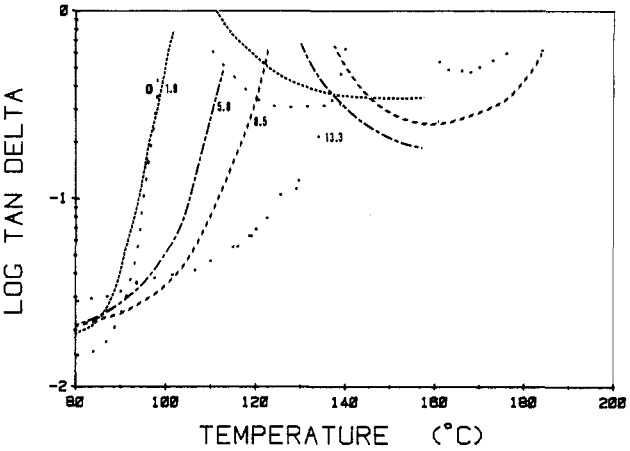

Figure 5. Variation of loss tangent with temperature for styrene–2-methyl-5-vinylpyridinium ionomers of various ion contents.

Figure 3 shows a comparison of the variation of the loss tangent with temperature for styrene–sodium methacrylate (10 mol %), styrene–*N*-methyl-4-vinylpyridinium iodide (10 mol %), and styrene–*N*-methyl-2-methyl-5-vinylpyridinium iodide (13 mol %) copolymers. The styrene–sodium methacrylate system had been studied before in this laboratory by Navratil[16] but no high-temperature peak had been found at that time for the higher ion contents, due to instrumental limitations. In order to be able to compare the pyridinium systems with the well-known methacrylate ionomers, it was decided to repeat the experiments with the much improved instrumentation. The recently obtained loss tangent curve, which is presented in Figure 3, exhibits the additional high-temperature peak found for some ionomers. The curves obtained for the pyridinium systems are seen to be quite different from that of the methacrylate ionomer and do not show this second peak. The curves obtained for the 4-vinylpyridinium and 2-methyl-5-vinylpyridinium ionomers of different ion contents are collected in Figures 4 and 5.

The variation of the storage modulus, G', with temperature for the 4-vinylpyridinium (9.7 mol %) and the 2-methyl-5-vinylpyridinium (13.3 mol %) ionomer is presented in Figure 6 along with the curve obtained for polystyrene; the three curves are, again, very similar. The variation of the storage modulus with temperature for the methacrylate (10 mol %) and vinylpyridinium ionomers (10 and 13 mol %) is shown in Figure 7. The G' curves obtained for the 4-vinylpyridinium and the 2-methyl-5-vinylpyridinium samples of different ion contents are presented in Figures 8 and 9. As can be observed from these plots, the decrease in slope with ion content generally

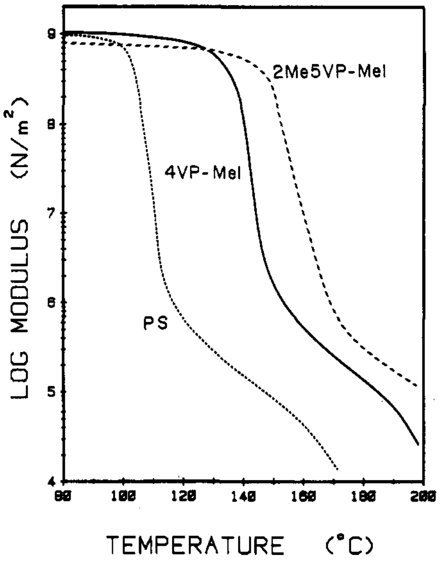

Figure 6. Variation of the storage modulus with temperature for a styrene–4-vinylpyridinium ionomer (9.7 mol %) and a styrene–2-methyl-5-vinylpyridinium ionomer (13.3 mol %).

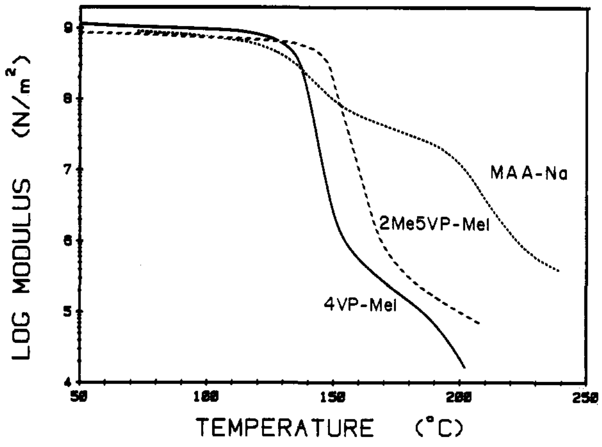

Figure 7. Variation of the storage modulus with temperature for sodium methacrylate (10 mol %) and vinylpyridinium (10 and 13 mol %) styrene ionomers containing about 10 mol % ions.

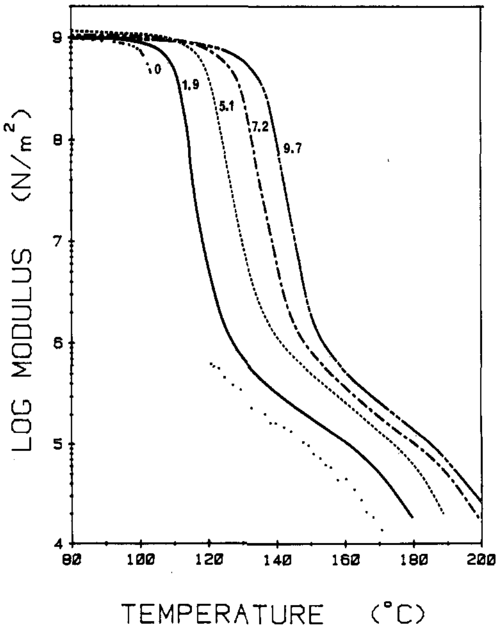

Figure 8. Variation of the storage modulus with temperature for styrene–4-vinylpyridinium ionomers of various ion contents.

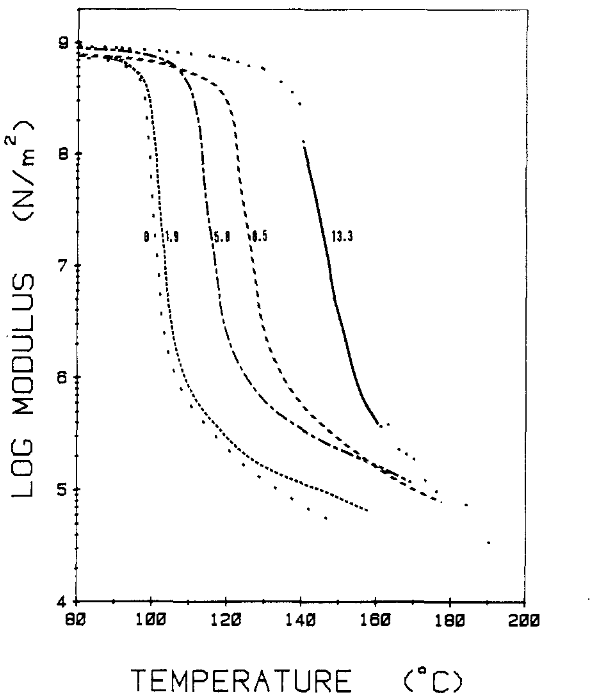

Figure 9. Variation of the storage modulus with temperature for styrene–2-methyl-5-vinylpyridinium ionomers of various ion contents.

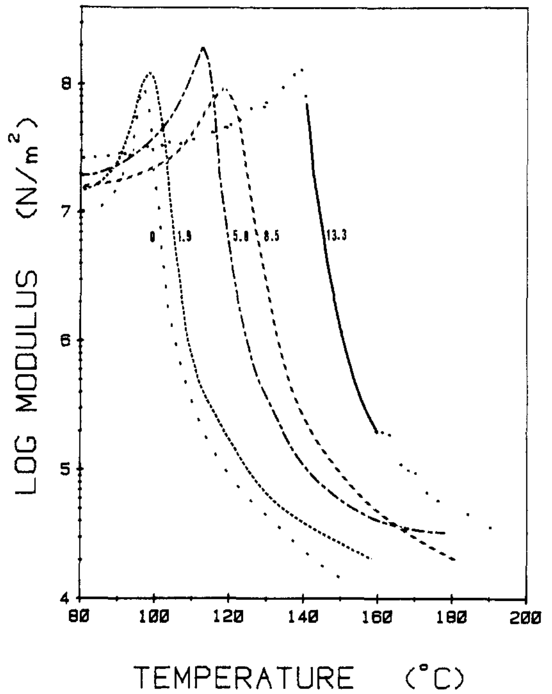

Figure 11. Variation of the loss modulus with temperature for styrene–2-methyl-5-vinylpyridinium ionomers of various ion contents.

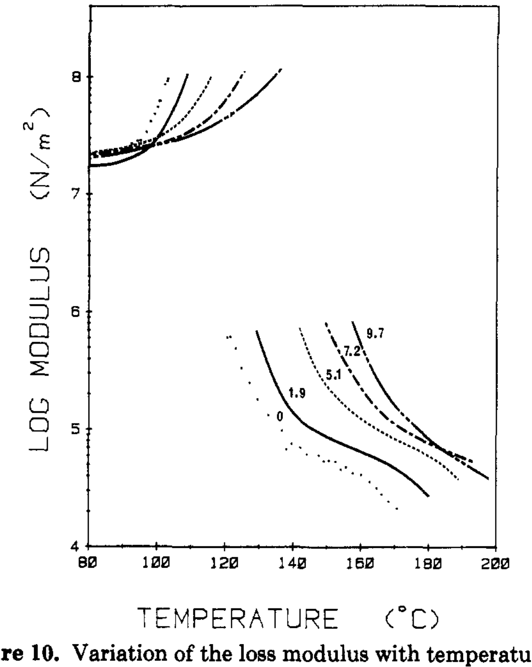

Figure 10. Variation of the loss modulus with temperature for styrene–4-vinylpyridinium ionomers of various ion contents.

observed for ionomers[16] is absent in the pyridinium systems; the curves are all very similar to that obtained for polystyrene, except for a shift to higher temperatures brought about by the increase in the glass transition temperature of the materials with ion content. The variations of the loss modulus, G'', with temperature for the quaternized 4VP and 2Me5VP ionomers are presented in Figures 10 and 11.

In amorphous materials, the occurrence of two major peaks in the loss tangent curve in the glass transition region is usually associated with phase separation, each peak being associated with a transition of one of the phases present in the material. As mentioned in the Introduction, in styrene as well as other amorphous ionomers, the lower temperature peak is generally associated with the glass transition of the matrix while the higher temperature one is attributed to a transition of the ion-rich phase-separated microdomains. The increase in the matrix T_g with ion content is the result of a decrease in the mobility of the chains brought about by the formation of ionic aggregates. This increase is also observed in the styrene–vinylpyridinium systems studied here. The absence of a second peak, however, seems to indicate that these systems are not phase-separated above T_g and therefore devoid of clusters.

As mentioned before, the formation of clusters will occur only if this process is energetically favorable.[7] Thus, if the amount of energy spent in the necessary stretching of some of the chain segments to form clusters is greater than that gained electrostatically by aggregation of the multiplets, clusters will not form. As the amount of energy spent in stretching styrene chain segments is the same whatever the ionic group involved, it seems that clusters are not formed in the vinylpyridinium systems because the electrostatic energy gained upon cluster formation would be smaller for these ionomers. The main reason for this is probably the smaller charge density of both the cation (pyridinium) and the anion (iodide) involved. Indeed, the interionic distance in 1-methylpyridinium iodide crystals has been found to be about 3.8 Å,[34] while a distance of 1.5 Å[7] was suggested for the carboxylate pair. The iodide counterion is also very polarizable. In addition, because the positive charge is carried by an atom (nitrogen) which is part of an aromatic ring, delocalization of the charge occurs to some extent. It thus seems quite likely that once the ions have aggregated into multiplets, (a process in which there is negligible chain stretching[7]), there would be no additional gain in energy in the formation of higher aggregates.

The presence of larger aggregates in the quaternized butadiene–2-methyl-5-vinylpyridine system seems clear from the data of Otocka and Eirich,[24,25] the increase of the Young's modulus with ion content being most easily explained by the presence of cross-linking by larger aggregates. This may probably be attributed, however, to the greater stability of the vinylpyridinium aggregates at the low temperatures at which these ionomers were examined. Thus, it can be assumed that the absence of clusters in the styrene–vinylpyridinium copolymers studied in the course of this investigation is due to the high glass transition temperature of the matrix, above which pyridinium clusters are thermally unstable.

More information about the kind of ionic interactions involved in these systems could have been obtained by stress-relaxation studies. However, the occurrence of dequaternization at temperatures fairly close to the T_g of these materials makes these types of measurements unfeasible.

Conclusions

The styrene–vinylpyridinium systems studied here can be regarded as single-phase materials. As is demonstrated by the variation of the storage modulus G' with temperature (Figure 8), which parallels that of polystyrene, the ionic interactions seem to be thermolabile and do not hold together very well at the temperatures above T_g. There seems to be enough interaction between the ion pairs, however, to decrease the mobility of the chain segments rather effectively up to T_g, as is demonstrated by the relatively large increase in the glass transition temperature of the copolymers with ion content. In fact, as mentioned previously, it seems that the ions are more efficient at raising the glass transition temperature of the copolymers if they are present exclusively in multiplets. This is to be expected, as each multiplet in the system can then act as a cross-link instead of being incorporated in ion-rich phase-separated microdomains, where some ion pairs may be less effective in raising the glass transition temperature.

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Registry No. ((Styrene)(4-vinylpyridine))·(methyl iodide) (copolymer), 84516-62-1; ((styrene)(2-vinylpyridine))·(methyl iodide) (copolymer), 60262-64-8; ((sytrene)(2-methyl-5-vinylpyridine))·(methyl iodide) (copolymer), 107054-30-8.

References and Notes

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