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Vinylpyridinium Ionomers. 2. Styrene-Based ABA Block Copolymers

Sylvie Gauthier[†] **and Adi Eisenberg***

Department of Chemistry, McGill University, Montreal, Quebec, Canada H3A 2K6.

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ABSTRACT: The thermal and dynamic mechanical behavior of styrene–4-vinylpyridinium ABA block ionomers was investigated as a function of ion content and method of preparation. Only one T_g, associated with the glass transition of the polystyrene phase, was observed in DSC experiments. The glass transition of the ionic domains was detected by dynamic mechanical measurements as a shoulder on the low-temperature side of the polystyrene. This unexpectedly low value for the T_g of the ionic domains was attributed to plasticization by water. The presence of water in these ionomers was related to the method of preparation of the materials.

Introduction

The field of ionomers has received increasing attention in the past few decades, from academic as well as industrial researchers.[1,2] The unique properties generally displayed by ionomers have been related to the presence of ionic aggregates within the organic polymer matrix. Numerous investigations have been conducted in an attempt to characterize these aggregates and determine the factors influencing their formation. While the exact structure of the aggregates has not yet been fully elucidated, evidence for the occurrence of aggregation, whatever the structure of the aggregates, is plentiful. The increase in glass transition temperature of most 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 ion content may be attributed to ionic interactions between the chains which persist even at temperatures far above the glass transition temperature of these systems. Selective plasticization of the ionic groups with polar plasticizers has been very effective in lowering the melt viscosity of certain ionomers, e.g., sulfonated styrene ionomers,[3] confirming the above assumption. The rate of stress relaxation has also been found to decrease with the ion content, and, above a certain proportion of ions, the breakdown in time–temperature superposition suggests the occurrence of a second relaxation mechanism associated with the presence of larger aggregates. The dynamic mechanical behavior of most ionomers also displays features that may be attributed to the presence of ionic aggregates: there is usually an additional, high-temperature peak in the tan δ curves and a decrease in the slope of the storage modulus curves with ion content. The styrene–vinylpyridinium systems described in the preceding article of this issue are notable exceptions in this respect.

All of the fundamental studies on the aggregation phenomenon in ionomers have been conducted on random copolymers. The introduction of ions in these systems has generally been achieved by one of two methods. The technique that is probably the most widely used is copolymerization with an ionizable comonomer; this is usually done by free-radical polymerization of two comonomers possessing reactivity ratios permitting the more or less random distribution of the ionizable groups along the chain. After isolation, these copolymers are transformed into ionomers using appropriate reactions. The second technique is by a postpolymerization reaction on the homopolymer. This method is especially useful in the preparation of a family of ionomers possessing identical backbones but different pendant ionic groups. Sulfonated and carboxylated styrene ionomers,[4] for example, have been synthesized from polystyrene; a family of polypentenamers[5–8] has also been produced in this way.

The ionomers produced by the techniques described above, however, will present a random distribution of ionic groups along the polymeric chain. A different type of ionomers, halatotelechelic polymers, has been produced and studied extensively in Teyssie's laboratory. Their study centered primarily on telechelic polybutadiene and polyisoprene prepolymers of relatively low molecular weight, capped with carboxylic acids. Quantitative neutralization with alkaline earth methoxides produced higher molecular polymeric materials, halatotelechelics, through linkage of the chains by the divalent cations. The ion content was varied by the use of telechelic prepolymers of different chain lengths. Thermal,[9,10] dilute solution,[11–13] morphological,[14] and viscoelastic,[9,15,16] studies revealed that the presence of ions in these systems sometimes manifests itself in a different fashion than in random ionomers.

Telechelic three-arm-star polyisobutylene polymers terminated with a sulfonic acid group have been prepared and studied by Kennedy, Wilkes, and co-workers.[17,18] The sulfonated polymers were neutralized with various metal hydroxides to produce the ionomers. While the acidic forms of these polymers are liquids at room temperature, the salts are rubbery materials with very unusual properties. Mechanical and structural studies[19,20] suggested the occurrence of network formation in the salts. Melt viscosity[21] and stress–strain[22] measurements demonstrated the marked improvement in the properties of these materials upon neutralization. Solution viscosity results[23] were in agreement with the findings of Teyssie's group.[11,12]

In an attempt to characterize the effect of ion placement on the state of aggregation in ionomers, styrene–4-vinylpyridinium ionomers of different architectures were prepared and studied in this laboratory. Two architectures were investigated, random and ABA (A, vinylpyridinium; B, styrene) block copolymers. The styrene–vinylpyridinium system was chosen because of the possibility of producing well-characterized materials of both architectures and also because relatively little work had been done to date on random ionomers bearing a positive charge. The study of the random copolymers has been described in the first publication of this series.[24] The investigation of the ABA block ionomers is the subject of the present article. It is expected that the block ionomers will present properties that are very different from those of the random ionomers, on the one hand, and from those of the telechelic ionomers, on the other.

Nonionic block copolymers have been known for a long time and have been studied extensively. Their most in-

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[†] Present address: Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 9B4.

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teresting properties are a consequence of the general incompatibility of the two, or more, types of polymeric segments present in the copolymer. Because the segments are chemically linked, however, phase separation may only occur on a relatively small scale, and these systems are usually described as microphase separated. The morphology of these materials is influenced by factors such as the chemical nature of the segments, their respective lengths, the architecture of the copolymer (AB, ABA or $(AB)_n$), and the solvent from which the material was cast. The effect of microphase separation on the thermal and dynamic mechanical properties of block copolymers is discussed briefly in the Results and Discussion.

Investigations of ionic block copolymers, i.e., block copolymers comprising at least one segment made of ionic repeating units, are relatively few. Extensive work on the solution properties of styrene–4-vinylpyridinium AB block copolymers has been done by Gallot's group. The emulsifying properties of graft and block copolymers containing a hydrophobic segment and a hydrophilic one, poly(2-vinylpyridinium chloride), were examined.[25-28] The investigation of the micellization behavior of such systems has centered mainly on the study of styrene–vinylpyridine block copolymers fully quaternized with ethyl bromide, although graft copolymers possessing a styrene backbone and vinylpyridinium grafts have also been examined.[29] A summary of the results and conclusions reached by these investigators on the behavior of these two systems has been published.[30] A more detailed description of the investigation of the micellization behavior of the block copolymers as a function of the quality of the solvent,[31] the molecular characteristics of the copolymers,[32] the temperature, and the salt concentration[33] has been published in a series of three articles. A review on ionic block copolymers has been published recently by Gallot.[34] It should be noted that the majority of the systems described in this article were characterized by a large ionic segment length and, therefore, were not true ionomers.

Aside from this thorough investigation, very little work relevant to this publication has been conducted on block copolymers containing vinylpyridinium segments. A study of some optical and mechanical properties of a styrene–butadiene–2-vinylpyridine block copolymer quaternized with hydrochloric acid[35] showed a marked increase (of about 1 order of magnitude) in the height of the rubbery plateau upon quaternization, which was attributed to an "ionomeric behavior". Aside from the latter study, vinylpyridinium block copolymers do not seem to have ever been examined as ionomers; most of the studies have been oriented toward applications of these systems.

Finally, a preliminary study on AB block ionomers containing carboxylic acid salts has been conducted in McGrath's laboratory.[36,37] Copolymers consisting of a styrene block and an alkyl methacrylate block were synthesized by anionic polymerization. Subsequent hydrolysis produces the ionomers; different ion contents were obtained by varying the extent of hydrolysis. Thermomechanical analysis of one of the block ionomers showed that the rubbery plateau was much higher than that of the nonionic material. Styrene–methoxypoly(ethylene glycol methacrylate) ABA ionomers have been prepared recently by Khan and co-workers[38] and displayed physical properties superior to those of the corresponding homopolymers.

The ABA block copolymers studied in our investigation were also prepared by living anionic polymerization of styrene and 4-vinylpyridine. The 4-vinylpyridine end blocks were quaternized with methyl iodide to produce the ionomers. As it seemed desirable to study materials possessing fully ionized end blocks, i.e., materials for which every unit of the end blocks is ionic, polymers of different ion contents were prepared by producing copolymers of different 4-vinylpyridine end block lengths but having an identical styrene middle block size. The synthesis of these materials was conducted on an elaborate polymerization line constructed in this laboratory. A brief description of the line as well as of the procedure followed to prepare the block copolymers has been presented before[39] and will be the subject of a more extensive future publication. The present article describes the thermal and dynamic mechanical behavior of the styrene–4-vinylpyridinium ABA block ionomers.

Table I
Sample Compositions[a]

sample	4VP content, mol %	no. of 4VP units/end block
1	2.4	12
2	4.7	24
3	7.0	35
4	9.1	46

[a] Molecular weight of styrene block is 10^5.

Experimental Section

Preparation of the Block Copolymers. The block copolymers were synthesized by living anionic polymerization performed on a polymerization line constructed in this laboratory.[39] The polymerization of styrene was initiated with sodium naphthalene to produce chains possessing two living ends; enough styrene was added to yield styrene chains of a molecular weight of about 10^5. Each living end was capped with one molecule of 1,1-diphenylethylene to reduce the reactivity of the anions and prevent side reactions with the pyridine moiety of the vinylpyridine monomer.[40] Enough 4-vinylpyridine (4VP) was then added (as a 1% solution of 4VP in dry THF[39]) to obtain a sample containing about 2.5 mol % of 4VP or end blocks of about 12 units of 4VP. A certain amount of the polymerization mixture was withdrawn, using the transferring apparatus,[39] and deactivated with a few drops of methanol. About 20 g of polymer containing 2.4 mol % 4VP was eventually recovered from that solution. Enough 4VP monomer was then added to the remainder of the active polymerization solution to produce a polymer containing about 5 mol % 4VP or end blocks of about 25 units of 4VP. Again a predetermined amount of the polymerization mixture was withdrawn to yield about 20 g of polymer of this composition. Two subsequent additions of 4VP, each followed by transfer of a certain volume of polymerization solution, produced polymers containing about 7.5 and 10 mol % 4VP or about 32 and 50 units of 4VP per end block, respectively.

A series of copolymers possessing absolutely identical styrene middle blocks (i.e., styrene blocks of identical molecular weight and polydispersity) and various 4VP end block lengths was thus produced. The 4VP contents of the materials were determined by FTIR[24] and are listed in Table I.

Quaternization. Attempts to quaternize the styrene–4-vinylpyridine ABA block copolymers following the procedure employed for the random materials (by refluxing with excess methyl iodide in dry THF[24]) proved to be unsuccessful, as gelation occurred minutes after reflux had started. Although it had been shown that gelation does not prevent quantitative quaternization,[30] it was decided to develop an alternate method that would yield quaternized samples of a more practical texture. The alternative involved soaking of a molded sample of the nonionic block copolymer into a 80/20 (v/v) absolute ethanol/methyl iodide solution for 3 days, at the reflux temperature.

(a) Materials. Absolute ethanol was used without further purification. Methyl iodide was distilled under nitrogen at 42–43 °C, a few hours before use.

(b) Procedure. The desired amount material (0.8–1.0 g) was compression molded into a rectangular slab at a temperature of about 140 °C and removed from the mold at about 90 °C. The molded sample was then dried in a vacuum oven at 70 °C overnight.

All the glassware used was dried in an oven for a few hours, at about 120 °C. A condenser was connected to a 125-mL Erlenmeyer flask equipped with a standard tapered neck, while still hot. The assembly was kept under a positive pressure of nitrogen. Absolute ethanol (40 mL) and methyl iodide (10 mL) were added, and the molded sample was dropped in. The mixture was then refluxed under nitrogen for 3 days, producing a yellowish sample. After cooling, the sample was removed, soaked in fresh absolute ethanol for a few minutes, and transferred to a heating pistol. The pistol was evacuated overnight at room temperature and then heated to about 80 °C for 3 days to effect complete removal of the solvent and reactant.

(c) Analysis. A small piece of quaternized material was broken off after the final molding of each sample and remolded into a thin film in order to determine the degree of quaternization by FTIR analysis.[24] Quantitative quaternization was achieved for all samples.

Thermal Properties. The thermal properties of the ionic and nonionic block copolymers were determined on a Perkin-Elmer DSC II. The samples were dried under vacuum at 80 °C for 3 days prior to measurements. The samples were heated on the DSC head at a temperature of 150 °C for about 5 min, quenched to 50 °C, and scanned at a rate of 20 °C/min. Duplicate determinations were made for each sample.

Dynamic Mechanical Properties. The dynamic mechanical measurements were made on a torsion pendulum.

(a) Sample Preparation. Rectangular slabs of the nonionic materials were obtained by compression molding at about 140 °C.

The quaternized samples were also compression molded by slipping the quaternized slabs into a slightly bigger mold and heating at about 130 °C. The samples were dried for 3 days at 80 °C under vacuum prior to the torsion pendulum measurements. The unexpected dynamic mechanical behavior (described in detail in the Results and Discussion) of these samples, however, suggested the desirability of developing a second method for the preparation of the quaternized materials, in order to break the ionic interactions prior to remolding. This was achieved by dissolving the quaternized samples and reprecipitating them in a nonsolvent.

Different solvents and mixed solvents were tested. It was found that the common styrene ionomer solvents such as toluene/methanol, THF/methanol, or Me_2SO did not dissolve these materials; however, both dimethylformamide and a Me_2SO/methanol mixtures proved to be effective. Because of the greater reproducibility in experimental conditions expected from a pure solvent, dimethylformamide (DMF) was chosen. Two slabs of quaternized material (1.5–2.0 g total) were dissolved in 30 mL of DMF to make a 5% solution; the polymer was precipitated in acetone. It was dried under vacuum at room temperature overnight and then further at about 80 °C for 3 days. It was compression molded at the same temperature as the undissolved, quaternized samples. The remolded samples were dried at 80 °C under vacuum for 3 days before the dynamic mechanical experiments.

(b) Plasticization with Me_2SO. About 0.8 g of material containing 9.1 mol % of 4-vinylpyridine was quaternized and molded as described before (first method, without reprecipitation). It was dried for 3 days at 80 °C under vacuum in a heating pistol. The pistol was then allowed to cool and filled with dry nitrogen, and the sample was quickly transferred to an Erlenmeyer containing 100 mL of Me_2SO. The flask was stoppered and the sample left to soak for a few days. It was then removed, the surface dried, and the sample placed under vacuum, at room temperature, for about 1 h.

Results and Discussion

Block copolymers generally display physical properties that are very different from their random counterparts; while random systems exhibit properties that are a weighed average of the properties of the two components, block copolymers will usually retain the characteristics of each component. The reason for this difference in behavior is related to the occurrence of phase separation in most block copolymer systems. Because of the frequent incompatibility of the two types of segments present, block copolymers generally exhibit two distinct glass transitions at temperatures very close to those of the corresponding homopolymers. This is in marked contrast to the behavior of random copolymers, which display a single T_g, at a temperature intermediate between the T_g of the two homopolymers and dependent upon the composition of the material.

The dynamic mechanical properties of block copolymers also reflect the microphase separation encountered in these systems. As expected, the variation of the loss tangent (tan δ) with temperature exhibits two peaks corresponding to the two distinct glass transitions of the sample, the magnitude of each peak being related to the amount of each component present in the material. If phase separation is incomplete, as in the case of a sample cast from a mutual solvent, a peak at an intermediate temperature may also be present, reflecting the presence of a certain degree of mixing of the two types of segments. The variation of the storage modulus with temperature also displays unique features, drastically different from the behavior of random copolymers and, in fact, much closer to that of immiscible polymer blends, because of the occurrence of phase separation in both blends and blocks. A variation in the composition of a random copolymer does not alter the shape of the storage modulus curve but simply shifts the whole curve on the temperature axis, reflecting the change in the glass transition temperature of the material with composition. A change in the composition of a block copolymer, however, is reflected by a shift in the height of the rubbery plateau. Two inflection points are also observed, as expected, reflecting the two distinct glass transitions of the materials.

Thermal Properties of Styrene–4-Vinylpyridine Block Copolymers. (a) Nonionic Blocks. As mentioned above, block copolymers generally display two glass transition temperatures characteristic of each type of segment. DSC traces of the unquaternized blocks of different 4VP contents show only one transition, however, which is associated with the glass transition of the polystyrene segments. This is not surprising in view of the relatively small amount of 4VP present in these samples, which may be below the detection limit of the instrument. The absence of a transition around the glass transition temperature of poly(4-vinylpyridine) may also be related to their architecture. Because these polymers are of the ABA type, the length of each 4VP end block is only half of the total percentage of 4VP in the copolymer. For the sample containing 9 mol % 4VP, for example, each end block has a molecular weight of only about 4500 (based on a middle block length of 10^5) which will be characterized by a glass transition temperature lower than that of poly(4-vinylpyridine) and probably close to the T_g of polystyrene. Thus, if the variation of T_g with molecular weight for poly(4-vinylpyridine) is approximately the same as for polystyrene, a poly(4VP) chain of molecular weight 4500 should have a T_g of about 115 °C.[41]

(b) Ionic Blocks. Because the T_g of the poly(vinylpyridinium) segments should be well above 200 °C and the maximum temperature to which the samples may be heated is around 150 °C due to the occurrence of dequaternization above this temperature,[24] the ionic blocks studied here were expected to show only one transition at around 106 °C, related to the T_g of the polystyrene domains. The DSC traces confirm this hypothesis. A slight increase in the temperature of this transition with ion

Table II
Variation of T_g with Ion Content for Ionic Block and Random Copolymers

ion content, mol %	glass transition temp, °C block nonionic	block ionic	random[a] ionic
0.0	104	104	104
2.4	105	105	110
4.7	106	106	118
6.7	105	108	124
9.1	105	108	131

[a] Values interpolated from Figure 1, ref 24.

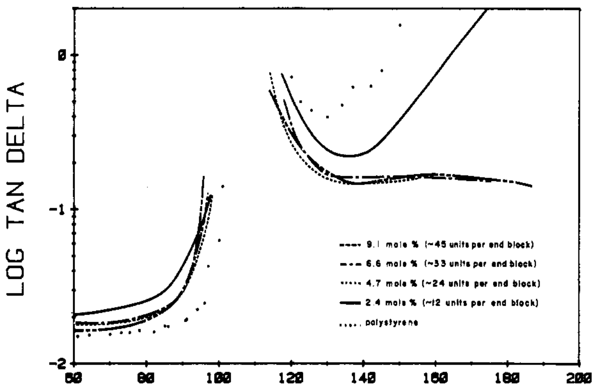

Figure 1. Variation of tan δ with temperature for nonionic block copolymers of various 4VP contents.

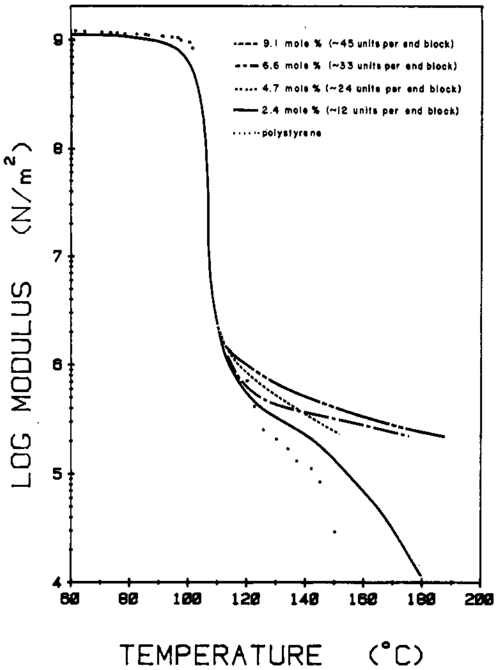

Figure 2. Variation of the storage modulus with temperature for nonionic block copolymers of various 4VP contents.

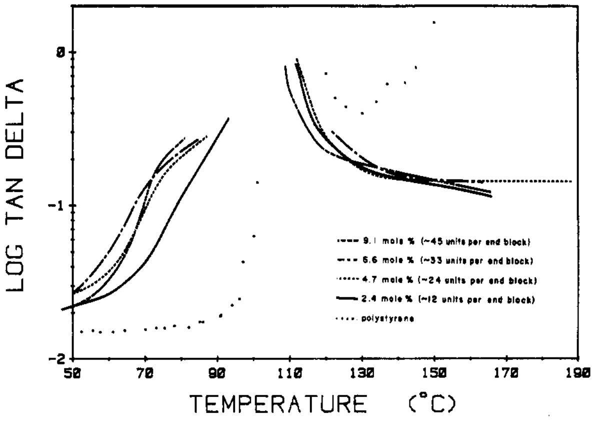

Figure 3. Variation of tan δ with temperature for ionic block copolymers of various ion contents.

content is observed (Table II), probably reflecting a small decrease in mobility due to the dispersion of rigid ionic domains within the styrene phase or possibly to a small extent of mixing of the two types of segments at the interface. This effect is equivalent to that expected for a reinforcing filler. The thermal properties of random and block copolymers are contrasted in Table II. As mentioned above, the T_gs of block copolymers are relatively unaffected by the composition of the sample, aside from molecular weight effects.

Dynamic Mechanical Properties of Styrene–4-Vinylpyridine Block Copolymers. (a) Nonionic Blocks. Curves showing the variation of tan δ with temperature for the styrene–4-vinylpyridine block copolymers are collected in Figure 1. Each curve displays only one peak, related to the glass transition of the polystyrene segments which suggests the coincidence of the 4VP peak with that of polystyrene, due to the small size of the end blocks. These results parallel the DSC findings. The shape of the curve for the 2 mol % sample is very similar to that of polystyrene, while the samples of higher 4VP contents display a flat region at temperatures above the transition.

The absence of a second transition associated with the 4VP segments is also evident in the curves relating the variation of the storage modulus, G', with temperature (Figure 2), which exhibit only one drop in the modulus around the T_g of polystyrene. Only the 2 mol % sample shows a second drop which, in this case, is associated with liquid flow. The development of a rubbery plateau in the curves obtained for the samples of higher 4VP contents may be attributed to the incompatibility of the two different types of segments. Because of this incompatibility, it is more difficult for the chains to flow, even at temperatures well above their T_g, as flow requires each type of segment to pass through regions that are composed primarily of segments of the other type. The high melt viscosity of block copolymers, compared to their random counterparts, has been observed for numerous materials.[42] As seen in Figure 2, the rubbery plateau becomes more pronounced with increasing 4VP content, in agreement with this concept. The variations of the loss modulus, G'', with temperature do not present any unusual features.

(b) Ionic Blocks. Plots of the variation of tan δ with temperature for samples molded directly from the slabs used for quaternization (without reprecipitation in acetone, see Experimental Section) are collected in Figure 3 and show an unexpected shoulder at temperatures just below that of the transition. The intensity as well as the breadth of this shoulder increase with increasing ion content, suggesting that it is probably associated with the presence of ionic domains. The temperature at which the shoulder occurs is also seen to decrease slightly with ion content. These characteristics are, in fact, more apparent in the loss modulus curves (Figure 4), where the shift of the maxima toward lower temperatures with increasing ion content is evident.

The G' curves (Figure 5) also reflect this unexpected behavior: there is a slight shift of the curves toward lower

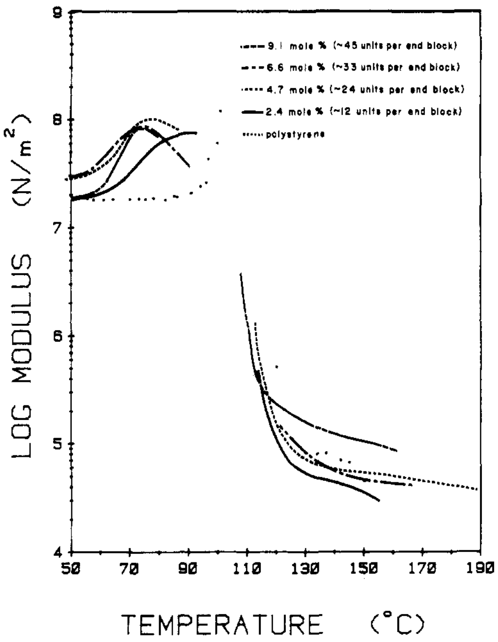

Figure 4. Variation of the loss modulus with temperature for ionic block copolymers of various ion contents.

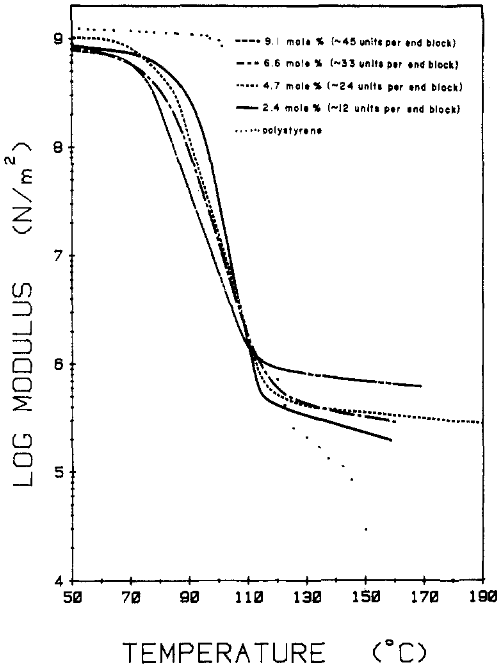

Figure 5. Variation of the storage modulus with temperature for ionic block copolymers of various ion contents.

temperatures with increasing ion content as well as a decrease in the slope in the transition region. At temperatures above the transition, however, the samples display the behavior expected from phase-separated block copolymers; i.e., all samples (even the 2 mol % material) show a rubbery plateau, the modulus corresponding to this plateau increasing slightly with 4-vinylpyridinium content. The interphase region is not expected to be very large in the ionic block copolymers.

In order to confirm the relation between the sub-T_g shoulder and the presence of ions in these materials, a sample plasticized with Me_2SO, a selective plasticizer for the ionic domains, was investigated. The tan δ curve for this sample is contrasted with the one obtained for the unplasticized material in Figure 6: a shift of about 10 °C of the shoulder toward lower temperatures is observed, in agreement with this hypothesis. The height of the rubbery plateau in the G' curve (Figure 6) is, not surprisingly, slightly lower for the plasticized sample.

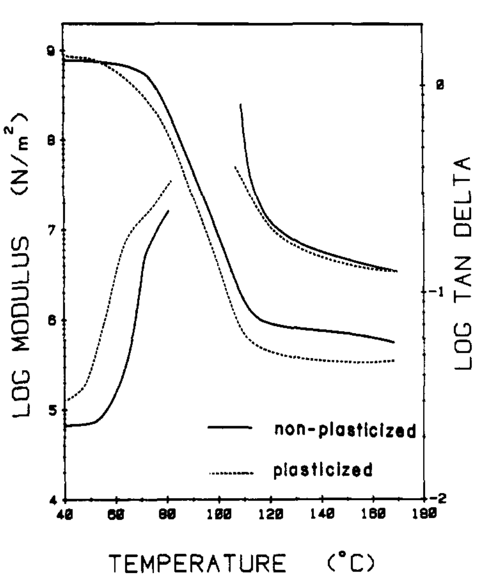

Figure 6. Variation of tan δ and storage modulus with temperature for plasticized and nonplasticized samples containing 9 mol ionic groups.

A 2-vinylpyridinium block ionomer was then investigated to determine if the occurrence of this shoulder was related to the position of the charge on the ring. This feature, however, was also present in the 2-vinylpyridinium system, eliminating this possibility.

Because the method used for the preparation of the ionic samples for torsion pendulum experiments involved quaternization in the solid state (or very slightly swollen state), the size and shape of the ionic domains in these samples are expected to be virtually the same as those of the domains formed in the nonionic polymers and possibly not those dictated by the new interactions between the polystyrene and poly(vinylpyridinium) chains. Breaking of the ionic interactions may only be accomplished by dissolution of the materials in a polar solvent; the materials could then be recovered by subsequent precipitation in a nonsolvent. As for solvent-cast samples, it is expected that the nature of the solvent and, in this case, the nonsolvent should affect the morphology of the ionomers to some extent. It is also important to note that the melt viscosity and solution properties of random sulfonated styrene ionomers have been found to vary to some extent with the concentration of the solution from which the polymers were isolated by freeze-drying.[43]

As described in the Experimental Section, the quaternized samples were dissolved in DMF, a better solvent for polystyrene than for poly(vinylpyridinium),[44] and precipitated in acetone, a poor solvent for polystyrene but a nonsolvent for poly(vinylpyridinium). The tan δ curve obtained for the sample containing 9 mol % of 4VP is shown in Figure 7, along with the curve shown before for the nonprecipitated material; the shoulder has disappeared and the material now exhibits the expected behavior: there is only one peak associated with the T_g of polystyrene. The storage modulus curve of the reprecipitated sample (Figure 8), however, exhibits an unusually high rubbery plateau for a copolymer of a 90/10 composition. An increase of the same magnitude in the height of the plateau in a butadiene–styrene block copolymer,[45] for example, is encountered for a copolymer containing twice that amount of high-T_g material, i.e., for a composition of 80/20 butadiene–styrene.

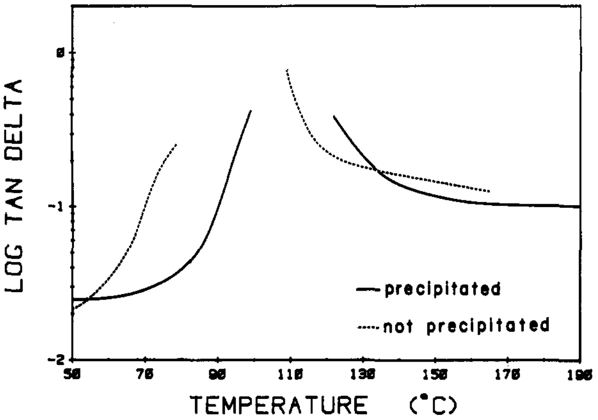

Figure 7. Variation of tan δ with temperature for precipitated and nonprecipitated samples containing 9 mol % ionic groups.

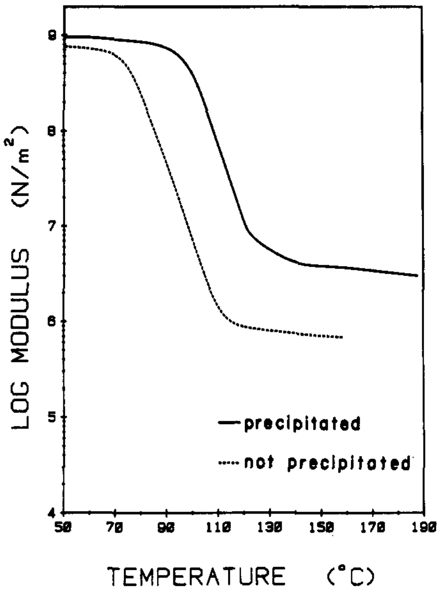

Figure 8. Variation of the storage modulus with temperature for precipitated and nonprecipitated samples containing 9 mol % ionic groups.

Elimination of the sub-T_g shoulder upon dissolution and reprecipitation was expected for samples of all ion contents. A sample containing 2 mol % of 4VP was thus quaternized, dissolved in DMF, and precipitated in acetone, and its dynamic mechanical properties were examined. Surprisingly, however, the shoulder was still present in the tan δ curve obtained for this reprecipitated sample. A 2-vinylpyridinium sample containing 5 mol % ions was then studied and displayed the same behavior.

Before an explanation is suggested for the different phenomena described above, it seems useful to summarize the experimental results obtained for the ionic blocks: (a) the tan δ curves of all nonprecipitated samples exhibited a sub-T_g shoulder; (b) this shoulder was not encountered in the nonionic blocks or in the ionic random copolymers;[24] (c) the transition was not detected in the DSC measurements; the T_g of all of the samples was around 107 °C; (d) plasticization with a polar plasticizer shifted the shoulder to lower temperatures; (e) reprecipitation eliminated the shoulder only for the 4VP sample of highest ion content; the shoulder was still present in the curves obtained for samples of lower ion content (2 mol % 4VP and 5 mol % 2VP).

The assignment of this sub-T_g shoulder to a particular transition or process is not trivial. The persistence of the shoulder after precipitation for the samples of low ionic contents seems to indicate that dissolution does not affect the structure responsible for it or, more likely, that this structure is formed again upon precipitation of these materials. The disappearance of the shoulder upon precipitation of the sample of highest ion content suggests that dissolution destroys this structure and that it is not formed again upon precipitation in this case.

As in most block copolymers, the 4VP domains in the nonionic materials are expected to be relatively well defined. The development of a rubbery plateau in the G' curves of the nonionic materials at temperatures above that of the transition and its persistence at higher temperatures are in agreement with the assumption that well-defined domains are present in these copolymers. As mentioned before, because the chains were not allowed to rearrange in the nonprecipitated materials, the ionic domains present in these ionomers are expected to be very similar to those in the nonionic polymers. The structure of the nonprecipitated ionic copolymers should then consist of an arrangement of tight ionic domains in a polystyrene matrix. Because the shoulder is present for nonprecipitated samples of all ion contents, it seems reasonable to relate its occurrence to the presence of these well-defined ionic domains. The reprecipitated samples of lower ion contents may be assumed to present a morphology that is not very different from the morphology of the nonprecipitated materials, as the sub-T_g shoulder is present in samples prepared by both methods.

In contrast with the samples of low ion contents, the disappearance of the shoulder upon reprecipitation of the sample of highest ionic content suggests that the precipitated and nonprecipitated samples of this material are characterized by a different morphology. As the mobility of the ionic end blocks is expected to decrease with increasing length, it seems reasonable to assume that it may be difficult to reform well-defined ionic domains upon reprecipitation of a sample of high ion content, because the chains will not have sufficient mobility. Instead, the arrangement of the chains will probably be more or less frozen-in upon precipitation, and loose aggregates consisting of a small number of end blocks may form. These small agglomerates are expected to be dispersed within the polystyrene matrix, and the structure of the resulting polymer might be somewhat looser than that formed for the materials of lower ionic content, in which tight, well-defined domains should be present.

Because the sub-T_g shoulder is present only for samples that are assumed to have well-defined ionic domains, it is tempting to assign this shoulder to the glass transition of the ionic domains. Quaternization, however, is expected to increase the T_g of the end blocks to temperatures well above the dequaternization temperature of 150 °C. The T_gs of polyelectrolytes are typically a few hundred degrees above those of the corresponding nonionic homopolymers.[46] The shoulder, therefore, cannot be the T_g of the pure ionic domains.

An inspection of the FTIR spectra (3300-cm^{-1} region) of the precipitated and nonprecipitated block copolymer containing 9 mol % of ionic groups suggests, in a very qualitative way, that the nonprecipitated sample is more hygroscopic than the precipitated material. It has been observed before[47] that the presence of water in ionomeric materials usually results in plasticization of the ionic regions and thus lowers the temperature at which the peak related to the ionic (cluster) transition appears in the tan δ curve. Because the samples could only be dried at a relatively low temperature (about 80 °C) to prevent dequaternization, it appears possible that the drying treatment to which the samples were subjected prior to the measurement of their dynamic mechanical properties may not have effected complete removal of the water absorbed by the materials possessing well-defined domains. It seems quite probable, therefore, that the sub-T_g shoulder so far associated with the presence of well-defined ionic regions is the glass transition of the water-plasticized ionic domains. Because well-defined domains are not formed in the precipitated 9 mol % sample, the structure of this material is expected to be much looser, and the water absorbed is probably more effectively removed during the drying treatment, since more of the vinylpyridinium segments would now be surrounded by polystyrene chains. The T_g of the dryer ionic segments in this sample (which is expected to be well above 200 °C) is thus not detected at the temperatures at which the experiments were conducted. Assignment of the shoulder to the T_g of the water-plasticized ionic domains is further substantiated by a shift of the shoulder to higher temperatures when the sample is dried at 120 °C for the same amount of time.

The results of studies performed by Krause and Wang on styrene block copolymers have been presented in a recent article.[48] A glass transition temperature considerably lower than that of corresponding polystyrene chains of the same lengths is observed. This lowering was attributed to the presence of a phase-separated region of considerably lower T_g than that of the polystyrene, which, because of the proximity of much of the polystyrene to these soft regions, lowers the overall T_g of the polystyrene. The same behavior is also seen to occur for the block ionomers studied here (Figure 3) but to a much smaller extent. Thus, the presence of phase-separated water-plasticized ionic domains seems to be responsible for the decrease in the T_g of the polystyrene matrix observed in dynamic mechanical measurements. The fact that the expected polystyrene glass transition temperature of about 106 °C was observed by DSC can be attributed to a more nearly complete dehydration of the samples due to their very small volume and to the preheating of the materials at 150 °C before the scans.

Finally, the higher rubbery modulus of the reprecipitated 9 mol % sample (Figure 8) may probably be attributed to a more effective filler effect. The loose aggregates of ionic segments present in this sample are expected to hinder the flow of the styrene middle blocks to a greater extent than would the well-defined domains.

Conclusion

As is apparent in this study, the effect of ion placement on the state of aggregation and the physical properties of styrene–4-vinylpyridinium ionomers is quite drastic. While large ionic aggregates are absent in the random ionomers,[24] the blocks seem to yield well-defined ionic domains containing a large number of ionic groups. The dynamic mechanical behavior of the styrene–4-vinylpyridinium ABA block ionomers seems to be related to the morphology of the materials. When the samples are quaternized in the solid state, no rearrangement of the chains is possible; the morphology of the nonreprecipitated materials should, therefore, closely resemble that of the nonionic polymers and consist of tight ionic domains dispersed in a polystyrene matrix. Most of these domains should contain a large number of ions and be surrounded by polystyrene chains, rendering the removal of water molecules associated with the ions relatively difficult. The heating treatment (vacuum at 80 °C for 3 days) to which these samples were subjected probably only effected partial drying: the glass transition of the water-plasticized ionic domains was thus detected at around 80 °C for nonreprecipitated samples of all ion contents.

Reprecipitation only affected the dynamic mechanical behavior of the 9 mol % sample. It is thus reasonable to assume that the well-defined domains were formed again upon reprecipitation of the samples of lower ion contents. The incapability of the 9 mol % sample to form well-defined domains upon reprecipitation may probably be attributed to the lower mobility of the longer end blocks in this sample. Even when well-defined ionic domains cannot be developed, however, it is expected that small aggregates consisting of a few chain ends may still form through ionic interactions. These aggregates should be distributed throughout the sample. Because of the small size of the aggregates and the looser, more disorganized structure of these materials, it is very likely that the water associated with these ions will be more easily removed, raising the glass transition temperature of the ionic domains or aggregates beyond the temperature at which these samples dequaternize. This would explain the disappearance of the shoulder associated with the ionic domains in the tan δ curve of the reprecipitated 9 mol % sample.

The formation of the ionic domains in the block ionomers thus appears to be dependent on the method of preparation of the samples only above a certain ion content. It is expected that this "critical" ion content, below which the morphology is unaffected by reprecipitation, should vary when different solvent–nonsolvent systems are used for reprecipitation. It would also be interesting to examine the behavior of AB block copolymers under the same conditions. These aspects are now being investigated and will be discussed in a future publication.

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Registry No. H_2O, 7732-18-5; ((styrene)(vinylpyridine))·(methyl iodide) (block copolymer), 107082-96-2.

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Heterocyclic Polymers as Catalysts in Organic Synthesis. Effect of Macromolecular Design and Microenvironment on the Catalytic Activity of Polymer-Supported (Dialkylamino)pyridine Catalysts

André Deratani, Graham D. Darling, Daniel Horak, and Jean M. J. Fréchet*

Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 9B4.

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ABSTRACT: Several new polystyrene-based resins containing (dialkylamino)pyridine pendant groups have been prepared by chemical modification of halogenated bead polymers or by suspension copolymerization of the corresponding monomers with divinylbenzene and styrene or 4-vinylpyridine. Kinetic studies on the polymeric catalysts and comparisons with low molecular weight analogues indicate that their efficiency as acylation catalysts depends on the microenvironment and the structure of the catalytic sites, the degree of functionalization, and the distance of the catalytic sites from the polymer aryl. Best results are obtained with gel-type polymers containing a three-carbon spacer group between the polystyrene rings and the catalytic site and functionalized to an extent of less than 50%, providing a hydrophobic local environment to the catalytic centers. Copolymers containing 4-vinylpyridine units in addition to the catalyst units, or high concentrations of the latter, show a strong microenvironment effect whereby activity is lowered drastically in a way that cannot be duplicated with other catalysts under homogeneous conditions.

Introduction

Polymers containing pyridine moieties have been widely studied in the preparation of polymer reagents and catalysts for general use in organic applications.[1] Some of these have found commercial applications[1,2] due to the availability of cross-linked poly(4-vinylpyridine) in various bead forms. Similarly, the emergence of commercial sources for other heterocyclic bead polymers such as poly(benzimidazole) suggests their application as simple heterogeneous hydrogenation catalysts[3] or in other types of supported chemistry.[4] Significant potential for a different kind of catalysis has recently drawn much attention to the possibilities of polymers containing 4-(dialkylamino)pyridine heterocycles as supported functional groups.[4-11]

(Dimethylamino)pyridine (DMAP, **1a**) is a material that has found numerous important applications since it became commercially available several years ago. It is an excellent catalyst for a variety of nucleophilic addition reactions, being most notably useful in difficult acylations and silylations of tertiary and other hindered hydroxyls.[12-14] DMAP is of particular interest to the research chemist and to the pharmaceutical and fine chemicals industry as its presence increases conversion yields while reducing side-product formation in such otherwise slow reactions. Current drawbacks to this soluble catalyst include its relatively high cost and the additional treatment that may be needed to remove it during product purification. In contrast, a polymer-bound catalyst possessing an activity comparable to DMAP would at once be easier to separate[15] from reaction media and repurified for later recycling, which may favorably counterbalance the somewhat higher initial cost of such a material.

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