of surface, tetrahedral, and octahedral sites of the spinel structure.

Conclusion

Nickel–cobalt hydroxide carbonate obtained by coprecipitation with Na_2CO_3 at pH 9 is an appropriate precursor in the synthesis of nickel cobaltite. The thermal decomposition is performed at low temperatures, and as a result spinel products of high dispersity are obtained, with no impurities being found in the IR spectra and X-ray diffractograms. Cobaltites with a preset stoichiometry are obtained, possessing a thermal stability over a considerably wide temperature interval (up to 870 K).

Acknowledgment. Special thanks are due to Dr. L. Minchev from the Institute of Kinetics and Catalysis for the temperature-programmed reduction experiment.

Registry No. $NiCoO_4$, 12017-35-5; $NiCo_2(OH)_3(CO_3)_{1.5}\cdot 1.74H_2O$, 136826-96-5; $Ni(NO_3)_2$, 13138-45-9; $Co(NO_3)_2$, 10141-05-6; Na_2CO_3, 497-19-8; $Ni_{0.2}Co_{2.8}O_4$, 136826-94-3; $Ni_{0.4}Co_{2.6}O_4$, 136826-93-2; $Ni_{0.6}Co_{2.6}O_4$, 136826-92-1; $Ni_{0.8}Co_{2.2}O_4$, 136826-91-0; $Ni_{0.9}Co_{2.1}O_4$, 136826-90-9; nickel–cobalt hydroxide carbonate, 136826-89-6.

Effect of Isomeric Ions on the Contact Charge of Polymers

D. Wollmann, D. Dreblow, and A. Diaz*

IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120

A. Eisenberg

Department of Chemistry, McGill University, 801 Sherbrooke St. W.,
Montreal, PQ, Canada H3A 2K6

Received May 16, 1991. Revised Manuscript Received August 9, 1991

The contact charge of styrene-*co*-butyl methacrylate powder containing a small fraction of a styrene-*co*-*N*-methylvinylpyridinium toluenesulfonate is found to depend on whether the nitrogen in the vinylpyridinium cation is ortho or para to the polymer chain. This is a particularly interesting result because the contact charge is proposed to develop from the transfer of the toluenesulfonate anion (OTs^-) to the second surface, thus, giving it a negative charge while the powder develops a positive charge. The cation is not involved in the transfer, yet it clearly affects the mobility and transfer of the anion. These results are explained in terms of differences in ion aggregation in this highly nonpolar medium.

Introduction

When two dissimilar materials are contacted and then separated, opposite sign charges are often generated on the two surfaces. This phenomenon has been widely observed, and in the specific case of two metals, it is generally accepted that contact charging occurs by electron transfer, where the direction of the transfer is determined by the relative Fermi levels.[1] In polymers, charge transfer is often attributed to electron transfer;[2-8] however, in the case with polymer blends containing a minor amount of *N*-methylpyridinium toluenesulfonate ions where the cation is "anchored" to the polymer by covalent bonding and the anion is mobile, the charging behavior is more readily explained by ion transfer.[9-11] The conclusion was based on the observation of a sulfur signal for the toluenesulfonate anion (OTs^-) on the surface of the second surface by XPS after the contact, and the correspondence between the sign of the charge and of the ion (negative). Thus, the polymer blend acquires the charge of the "anchored" cation (positive), and the second surface acquires the charge of the mobile ion (negative). This result is not limited to polymer-bound ions (ionomers). Similar results were observed with a polymer containing cetylpyridinium bromide.[12] This polymer charged positively against indium while the indium acquired a negative charge. SIMS analysis of the indium surface after the contact revealed the presence of both the cation and the anion (both mobile); however, the anion content was much greater. These results were explained by ion transfer where the sign reflected the higher mobility of the Br^- ion. In contrast with these studies, earlier reports with organic materials (molecular and polymer) explained the charging in terms of electron transfer because of the correlation between the charge and a substituent parameter for a series of substituted structures.[3,13] Even the charging results with ionomers containing methyltriphenylphosphonium arylsulfonate ions were explained by electron transfer because the charge correlated with a substituent parameter and because of the mismatch between the sign of the charge

---

(1) Harper, W. R. *Contact and Frictional Electrification*; Oxford University Press: Oxford, 1967.

(2) Nanya, T.; Tsubuko, K. *Japan Hardcopy '88, The Society of Electrophotography of Japan, 30th Conference*, 1988, 9.

(3) Gibson, H. W. *J. Am. Chem. Soc.* **1975**, *97*, 3832.

(4) Gruber, R. J. *SID 87 Digest* **1987**, 272.

(5) Matsui, N.; Oka, K.; Inaba, Y., *The Sixth International Congress on Advances in Non-Impact Printing Technologies Black and White and Color* **1990**, 45.

(6) Duke, C. B.; Salaneck, W. R.; Fabish, T. J.; Ritsko, J. J.; Thomas, H. R.; Paton, A. *Phys. Rev. B* **1978**, *28*, 5717.

(7) Duke, C. B.; Fabish, T. J. *J. Appl. Phys.* **1978**, *49*, 315.

(8) Gibson, H. W. *Polymer* **1984**, *25*, 3.

(9) Diaz, A.; Fenzel-Alexander, D.; Miller, D. C.; Wollmann, D.; Eisenberg, A. *J. Polym. Sci., Polym. Lett. Ed.* **1990**, *28*, 75.

(10) Diaz, A.; Fenzel-Alexander, D.; Wollmann, D.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.*, in press.

(11) Unpublished results from this laboratory.

(12) Mizes, H. A.; Conwell, E. M.; Salamida, D. P. *Appl. Phys. Lett.* **1990**, *56*, 1597.

(13) Cressman, P. J.; Hartmann, G. C.; Kuder, J. E.; Saeva, F. D.; Wychick, D. *J. Chem. Phys.* **1974**, *61*, 2740.

0897-4756/91/2803-1063$02.50/0 © 1991 American Chemical Society

and of the mobile ion.[14,15] The second surface acquired a negative charge regardless of whether the polymer had an "anchored" cation and mobile anion or an "anchored" anion and a mobile cation. However, the latter appears to be a result from having the methyltriphenylphosphonium cation as the free ion. It is large and has very low mobility even if it is not "anchored" to the polymer. This is certainly borne out with the molecular analogue, methyltriphenylphosphonium toluenesulfonate, which transfers a negative charge, suggesting the greater mobility of the OTs^- anion.[14] Therefore, the charge developed by the ionomer with the methyltriphenylphosphonium cation may result from the transfer of small ions from moisture or impurities.

Aside from the mobility differences between an "anchored" and a free ion, changes in the surface–bulk ion distribution will affect the charge since charging is a surface phenomenon and it depends on the surface ion content. Thus, it was previously shown that the magnitude of the charge developed in ionomer blends containing styrene-*co*-*N*-methylpyridinium toluenesulfonate was sensitive not only to the overall ion concentration in the blend but also to the ion content of the pure ionomer.[10] It was also shown that the ionomer and the host styrene-*co*-butyl methacrylate polymer were not completely miscible. The lack of complete miscibility was proposed to lead to differences in the extent of ion aggregation in the blends which in turn affected the amount of OTs^- transferred and the charging levels but not the sign. This conclusion was based on the fact that the strengths of the Coulombic interactions experienced by an isolated ion and an ion in an aggregate are very different and will affect the amount of ion transfer and charge.

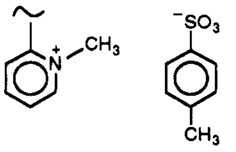
As an extension of the previous work, we proceeded to study blends of isomeric salts that have different levels of ion association to measure the effect on contact charge. While a mobile toluenesulfonate anion and a polymer "anchored" *N*-methylpyridinium cation produce a negative charge on the contacted surface,[9,10] it seemed likely that structural changes in the cation (which does not transfer) can affect the environment of the anion (e.g., ion aggregation) and the amount of ion transfer. Thus, the styrenic ionomers with the isomeric ions, *N*-methyl-2-vinylpyridinium toluenesulfonate and *N*-methyl-4-vinylpyridinium toluenesulfonate were used to probe the effect of Coulombic interactions on ion transfer. With these isomeric cations the distance of closest approach between the cation and the anion should respond to steric constraints while keeping other factors nearly constant. We report here the charging results for these two ionomer ions. We detect differences in the contact charges and explain them in terms of variations in the amount of ion transfer and of ion pair aggregation.

Experimental Section

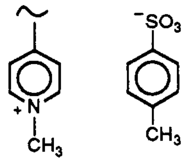
General Sample Preparation. Styrene-*co*-*N*-methyl-2-vinylpyridinium toluenesulfonate [S-*co*-2MVP OTs] and styrene-*co*-*N*-methyl-4-vinylpyridinium toluenesulfonate [S-*co*-4MVP OTs] ionomers were prepared from the unquaternized random styrene–vinylpyridine copolymers. The preparation of these copolymers has been described before[16] but is summarized here for clarity. The 2- and 4-vinylpyridine monomers (2VP, Aldrich, 97%; 4VP, Aldrich, 95%) were purified by distillation under reduced pressure (2VP, 72 °C 29 mmHg; 4VP, 62–3 °C 15 mmHg) before use. Styrene monomer (Aldrich, 99%) was first washed with 5% aqueous NaOH solution to remove inhibitor, dried over CaH_2 and finally distilled under reduced pressure (47–8 °C 19–21 mmHg). All monomers were stored at −12 °C until needed.

Polymerization was carried out in the bulk using benzoyl peroxide initiator. The relative proportions of vinylpyridine to styrene for the desired VP content were calculated from known r_1 and r_2 values.[17] The initiator concentration was adjusted to produce a polymer of approximately 30000–40000 number average molecular weight. The solutions of monomers and initiator were degassed by three freeze–thaw cycles, and then the ampule was sealed. If necessary, they were then stored at −12 °C. Polymerization was carried out at 60 °C in a water bath for just over 6 h to obtain 30% conversion. For example, 7.06 g of benzoyl peroxide was added to a flask containing 290 g of styrene and 10.6 g of 4-vinylpyridine. After degassing and sealing, the solution was heated to 60 °C in a water bath for 6 h. The polymer solutions were diluted with toluene to 5% solids and then the polymer recovered by precipitation into 10 volumes of methanol. The polymers were filtered from the nonsolvent, then redissolved, and reprecipitated. Finally, they were dried to constant weight under vacuum at 60 °C. The vinylpyridine contents of the copolymers were determined by titration in chlorobenzene solution using 0.030 N perchloric acid in glacial acetic acid as titrant and methyl violet indicator. Triplicate titrations of 0.3 g of the polymer in 50 mL of chlorobenzene (bubbled with N_2) were run to the aquamarine endpoint, and the appropriate blank was applied. Thus, for the above example, 0.290 g of polymer was neutralized with 5.63 mL of titrant, resulting in a calculated 4-vinylpyridine mole fraction of 0.059. The vinylpyridine contents of the copolymers, in mole percent, are as follows: 2VP, 1.8, 5.3; 4VP, 2.0, 6.0, and 11. The typical error in the titrations was ±1.5%. The molecular weights of the copolymers were determined by GPC analysis in THF solutions, and calibrated with polystyrene standards. The M_N of the copolymers was in the range (3–4) × 10^4 g/mol and the M_W was in the range (6–7) × 10^4 g/mol. The polydispersity of the copolymers varied from 1.8 to 1.9.

A procedure for the quaternization of styrene–vinylpyridine copolymers with iodomethane[16] was modified to prepare the methyl toluenesulfonate containing ionomers. The procedure described below is for the preparation of the S-*co*-4MVP OTs ionomers, and changes to the procedure for the preparation of S-*co*-2MVP OTs are given in parentheses. A known amount of the copolymer was dissolved in THF to make a 5% solution. The number of moles of vinylpyridnine present was calculated, and a 25-fold (10-fold) molar excess of methyl toluenesulfonate was added. The solution was refluxed under nitrogen for 24 h (4 days), and then the ionomer was isolated by precipitation into 10 volumes of rapidly stirred methanol (warm hexanes). The white powdery solid was recovered by filtration and then purified by reprecipitation. The ionomer was finally freeze-dried from a benzene/methanol (90/10 v/v) solution. Completion of the quaternization was verified by the disappearance of the pyridine peak in the infrared at 1414 cm^{-1} for the S-*co*-4VP samples and at 1472 cm^{-1} for the *S*-*co*-2VP polymers. XPS analysis of the quaternized S-*co*-4MVP OTs ionomer (520 μmol 4MVP OTs/g) indicated the following composition (calculated values in parentheses): C, 95.9 (96.6); N, 0.50 (0.69); S, 0.99 (0.69; O, 2.7 (2.1):[9]



S–*co*-2MVP OTs



S–*co*-4MVP OTs

2-Ethyl-*N*-methylpyridinium toluenesulfonate [2EtMP OTs] and 4-ethyl-*N*-methylpyridinium toluenesulfonate [4EtMP OTs] were prepared from the reaction of methyl toluenesulfonate with the appropriate ethylpyridine isomer in hexanes solution. The

---

(14) Bugner, D. E.; Anderson, J. H. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, *29*, 463.

(15) (a) Anderson, J. H.; Bugner, D. E. US Patent 4,837,391, June 6, 1989. (b) Anderson, J. H.; Bugner, D. E.; DeMejo, L. P.; Sutton, R. C.; Wilson, J. C. US Patent 4,837,392, June 6, 1989.

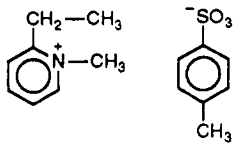
(16) Gauthier, S.; Duchesne, D.; Eisenberg, A. *Macromolecules* **1987**, *20*, 753.

(17) Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 2nd ed.; Wiley-Interscience: New York, 1975.

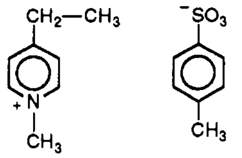
salt precipitated upon formation and was recovered by filtration. It was purified by recrystallization from ethyl acetate. The melting points were 2EtMP OTs, 71.7–73.6 °C and 4EtMP OTs, 107.4–109.9 °C and were not previously mentioned in the literature. Infrared spectra were used to determine the extent of quaternization by the disappearance of the peak associated with unquaternized pyridine, 2EtMP OTs, 1472 cm^{-1}; 4EtMP OTs, 1414 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$) δ 2EtMP OTs, 9.16 ppm (d, 1 H, EtMP), 8.26 (t, 1 H, EtMP), 7.79 (t, 1 H, EtMP), 7.67 (d, 1 H, EtMP), 7.64 (d, 2 H, OTs), 7.08 (d, 2 H, OTs), 4.36 (s, 3 H, EtMP), 3.02 (q, 2 H, EtMP), 2.30 (s, 3 H, OTs), 1.31 (t, 3 H, EtMP). ^{1}H NMR (250 MHz, $CDCl_3$) δ 4EtMP OTs, 8.98 (d, 2 H, EtMP), 7.70 (d, 2 H, EtMP), 7.63 (d, 2 H, OTs), 7.11 (d, 2 H, OTs), 4.43 (s, 3 H, EtMP), 2.79 (q, 2 H, EtMP), 2.31 (s, 3 H, OTs), 1.24 (t, 3 H, EtMP).

Anal. Calcd for $C_{15}H_{19}NO_3S$: C, 61.41; H, 6.53; N, 4.77; O, 16.36; S, 10.93. Found: 2EtMP OTs, C, 60.96; H, 6.71; N, 4.73; O, 16.05; S, 11.50. Found: 4EtMP OTs, C, 60.96; H, 6.88; N, 4.72; O, 16.57; S, 10.86.



2EtMP OTs



4EtMP OTs·

Experimental Methods

Solid blends of the ionomers or of the salts with a styrene-*co*-butyl methacrylate, S-*co*-BMA, nonionic polymer were prepared for contact charging studies. A small amount of the ion-containing sample was first dry blended with a styrene–butyl methacrylate copolymer for the desired final ion content, typically less than 50 μmol/g. This mixture was then melt blended at 160 °C, ground, and size classified, yielding irregularly shaped particles typically 10 μm in diameter. In the charging experiments, 2.5% by weight of the powder was added to 140 μm, irregular metal beads (sponge iron), and the mixture was rolled in a tin can for 30 min to ensure equilibration of the charge. The ambient temperature was 69–70 °F, and the relative humidity varied from 49 to 53%. In triplicate runs, 3.0 ± 0.2 g of the mixture was carefully weighed into a Faraday cage having 44-μm screens at each end. The charge on the cage was brought to zero, and most (>97%) of the powder was blown off from the beads with forced air at 60 psi for 2 min. The net charge was recorded on a Keithley 616 Electrometer and was typically of the order of 40×10^{-7} C. The weight of powder blown off from the beads was determined, and the charge to weight ratio, $\Delta Q/\Delta M$, was calculated for the powder. The values given in Table I are the average of four determinations measured on two different days and the error in the $\Delta Q/\Delta M$ values are 2–4% within the same day and up to 15% from day to day.

Solid samples were prepared for the UV–visible studies by melting a small amount of the blend between two glass slides. Solution samples of the ionomers and the model compounds were prepared in spectrograde chloroform, methanol or distilled water as appropriate. The ion concentration in the solutions ranged from 10^{-5} to 10^{-2} M. Spectra were taken on a HP 8452A diode array spectrophotometer. The XPS analyses were performed on the particles supported on indium foil using an SSX-100 Model 05 XPS spectrophotometer and a 300-μm spot size. Low-energy electrons were supplied to the sample as required to neutralize surface charging, and the binding energies were referenced to the main carbon peak, taken as 285.6 eV. Solutions for the NMR studies were prepared from the ionomers and the small salts in the appropriate deuterated solvent, with ion concentrations ranging from 10^{-4} to 10^{-2} M. Spectra were collected on a Bruker 250 FT-NMR. The number of transients needed ranged from 16 to 160 depending on the solution concentrations.

Results and Discussion

Two types of ion-containing materials, i.e., styrene-*co*-*N*-methylvinylpyridinium toluenesulfonate ionomers and their analogous small salts, ethyl-*N*-methylpyridinium toluenesulfonate, were used in this study. These materials have the same toluenesulfonate anion, while the *N*-methylpyridinium cations are isomeric. Styrene-based ionomers containing either *N*-methyl-2-vinylpyridinium toluenesulfonate (S-*co*-2MVP OTs) or *N*-methyl-4-vinylpyridinium toluenesulfonate (S-*co*-4MVP OTs) were blended with a S-*co*-BMA copolymer for final ion contents of 2.6, 5.2, and 26 μmol/g. Powders of these blends were then charge activated by can rolling with irregular metal beads for 30 min, a length of time sufficient for the charge to equilibrate. The charge observed increases with increasing final ion content in the powder as shown in Table I. While both materials develop a positive charge, powders prepared with 2MVP OTs ionomers typically charge more positively than the corresponding samples prepared with 4MVP OTs ionomers. A positive charge is consistent with transfer OTs$^-$ to the bead surface. Previous results showed the OTs$^-$ transfer is not accompanied by transfer of the pyridium cation.[9,10] The different charge levels suggest that more anion transfers with the 2MVP OTs blends. For comparison, charging studies with the analogous small salts, 2EtMP OTs and 4EtMP OTs, were also performed. The charging behavior of these blends is much more difficult to interpret because the surface ion concentrations do not resemble the bulk and can be 3–4 times greater.[9] Therefore, the lack of control of the surface ion concentration will undoubtedly produce unexpected variations in the charge. Furthermore, both the cation and the anion are mobile and can transfer to produce a compromised charge level, as was observed with tetraethylammonium toluenesulfonate blends.[9] Since the distinction in the cation–anion mobility, characteristic of ionomers, is absent in the molecular salts, further study of the latter was not pursued.

Table I. Charge Data for the Ionomer Blends

MVP OTs content, μmol/g		$\Delta Q/\Delta M$,[a] μC/g	
ionomer	blend	2MVP OTs	4MVP OTs
		−2.1	−2.1
200	2.6	+28	+30
	5.2	+52	+45
	26	+99	+68
500	2.6	+28	+19
	5.2	+40	+38
	26	+78	+50

[a] Values from total blowoff of a lightly rolled 2.5% powder/97.5% 140 μm bead mixture.

The difference in charging between the 2- and 4-MVP OTs ionomer blends could reflect a higher OTs$^-$ content on the surface of 2MVP OTs blends. The surfaces of five different blends, each containing 26 μmol/g 2MVP OTs and 4MVP OTs were examined by XPS (300-μm spot size), and the experimentally determined surface compositions all resemble the calculated bulk compositions, as seen in Table II. There is no evidence of 2-MVP OTs fractionating to the surface. Therefore, there is no gross difference in the surface ion concentration to account for the difference in charge.

Pressed pellets of the ionomer blends have a turbid appearance, indicating some immiscibility where the size of the phase-separated polymer domains are of the order of the wavelength of visible light (500 nm).[10] While microscopic differences in the ion concentration may result from the presence of these domains, these differences are averaged out by the larger (300 μm) spot size of the XPS beam. Nevertheless, the presence of ion-rich domains whose ion enrichment varies with the level of immiscibility could account for the charge difference. The relative

Table II. Surface Composition of Blends Containing 26 μmol/g of MVP OTs

[MVP OTs] in S-co-MVP OTs, μmol/g	ionomer in blend, wt %	atom %^{a}			
		C	O	S	N
		4MVP OTs^b			
185	14	94.30	5.66	0.04	nd^c
		(94.18)	(5.75)	(0.034)	(0.034)
520	5	93.61	6.35	0.04	nd
		(93.54)	(6.38)	(0.034)	(0.034)
875	3	93.70	6.25	0.04	nd
		(93.45)	(6.48)	(0.034)	(0.034)
		2MVP OTs			
163	16	94.45	5.53	0.02	nd
		(94.31)	(5.62)	(0.034)	(0.034)
461	6	93.65	6.33	0.02	nd
		(93.63)	(6.30)	(0.034)	(0.034)

^{a} Calculated values in parentheses. ^{b} Data reported in ref 7. ^{c} Not detected.

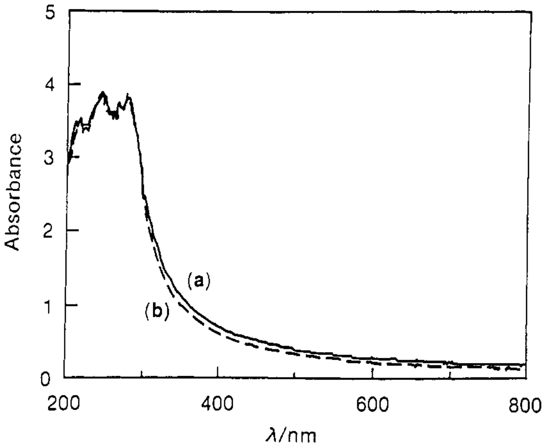


Figure 1. UV-visible absorption spectra of (a) S-*co*-2MVP OTs and (b) S-*co*-4MVP OTs blends (200 μmol/g of MVP OTs in ionomer; 26 μmol/g of MVP OTs in blend).

amounts of phase separation can be compared using light scattering in the UV-visible spectra as was previously used to determine the presence of phase separation in a series of styrene-*co*-4-methylvinylpyridinium OTs blends.[10] It was found that the spectra of blends containing 2MVP OTs and 4MVP OTs indicate typical light-scattering behavior, that is, a variation in absorbance with $\lambda^{1/4}$. The spectra are shown in Figure 1. The UV-visible spectra of blends with comparable amounts of 2MVP OTs and 4MVP OTs are very similar, although the blend containing 2MVP OTs shows a slightly higher absorption, which may be due to different sample thicknesses. More relevant to this study is the difference in sensitivity between the two samples to $\lambda^{1/4}$. The blend prepared with 4MVP OTs ionomer is much more sensitive, which may be related to a difference in the size or number of phase-separated regions. If this difference changes the surface-bulk OTs$^-$ content it may account for the higher charge in the blends containing 2MVP OTs, even though XPS does not detect a gross difference in the ion content at the surface.

The higher charge observed with the blends containing 2MVP OTs may also reflect a difference in the amount of OTs$^-$ transferred resulting from differences in the strengths of the Coulombic interactions between the MVP$^+$ and OTs$^-$ ions. These interactions are particularly important when the ions are highly associated into pairs and aggregates of ion pairs,[18] and they will affect the extent of ion separation and transfer. To test this proposal, evidence of ion aggregation was sought spectroscopically (UV-visible) using 2-ethyl-*N*-methylpyridinium toluenesulfonate (2EtMP OTs) and 4-ethyl-*N*-methylpyridinium toluenesulfonate (4EtMP OTs) as model compounds for this class of salts. Unfortunately, the ionomers could not be studied directly because the blends scatter light and the dilute solution of the pure ionomers had too much interference from the styrene groups at shorter wavelengths. In addition, ionomer solubility became an added concern. On the other hand, the salts 2EtMP OTs and 4EtMP OTs are soluble in a wide range of solvents from chloroform (dielectric constant 4.81 at 20 °C) to water (dielectric constant 80.4 at 20 °C).[19] Spectra in each solvent at ca. 10^{-5} M are shown in Figure 2. Both isomers showed a similar dependence on the solvent and salt concentration. In

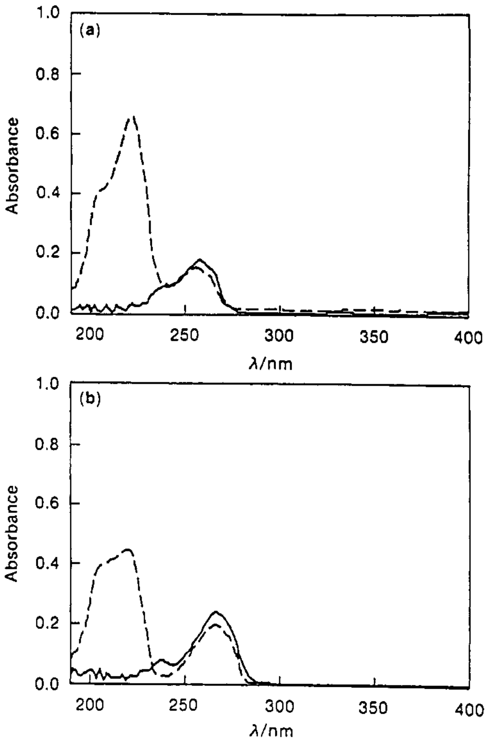


Figure 2. UV-visible absorption spectra for 10^{-5} M solutions of 4EtMP OTs (a) and 2EtMP OTs (b) in chloroform (—) and methanol (- - -).

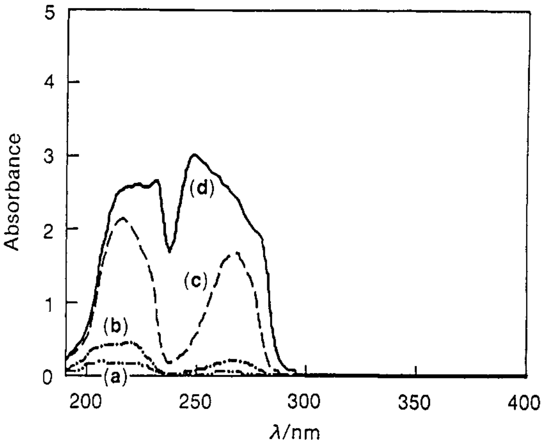


Figure 3. UV-visible absorption spectra of methanol solutions of 2EtMP OTs as a function of concentration: (a) 10^{-6}, (b) 10^{-5}, (c) 10^{-4}, and (d) 10^{-3} M.

---

(18) Eisenberg, A. *Macromolecules* **1970**, *3*, 147.

(19) Weast, R. C., Ed. *Handbook of Chemistry and Physics*, 53rd ed.; CRC Press: Cleveland, 1970.

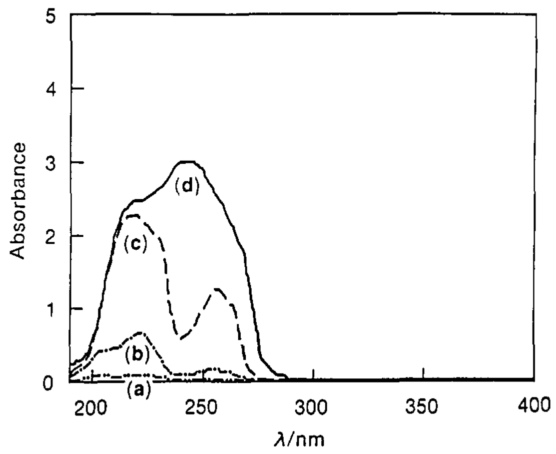


Figure 4. UV-visible absorption spectra of methanol solutions of 4EtMP OTs as a function of concentration: (a) 10^{-6}, (b) 10^{-5}, (c) 10^{-4}, and (d) 10^{-3} M.

methanol and in water, the spectra of the more dilute solutions, e.g., 10^{-5} M, exhibit two peaks, at 220 and 256 nm, due to absorption by OTs^-. This assignment is based on the fact that the same spectrum is produced by 1 mM Et_4N OTs in methanol with the peaks at 224 and 256 nm. The 256-nm peak increased proportionally with the salt concentration, and there is an isobestic point at 230 nm. This can be seen in Figures 3 and 4. The spectra of the methanol and water (not shown) solutions are virtually identical. The spectra indicate a mixture of two species, one more dissociated than the other. The longer wavelength absorption, 256 nm, is assigned to the larger ion aggregate form. In these polar solvents, the important equilibrium is probably the dissociation of ion pairs as in eq 1. In chloroform, only the 256-nm peak appears for

$$[EtMP^+OTs^-] \rightleftarrows EtMP^+ + OTs^- \qquad (1)$$

$$[EtMP^+OTs^-]_2 \rightleftarrows 2[EtMP^+OTs^-] \qquad (2)$$

$$[EtMP^+OTs^-]_n \rightleftarrows n[EtMP^+OTs^-] \qquad (3)$$

all the concentrations indicating that all the ions are associated. The level of ion association remains to be determined and may be primarily ion pairs and pair dimers as in eq 2. On the other hand, higher levels of association as in eq 3 may also be present. Beer's law ($A = \epsilon bc$) is obeyed for the total absorption at low concentrations in all solvents; the peak saturates at ca. 1 mM in chloroform and ca. 0.1 mM in methanol. Even at these concentrations, the 220-nm peak is still the major peak. As expected, the distribution of absorbing species (dissociated ions, ion pairs, or aggregates of pairs) varies with the salt concentration and change in solvent polarity (from hydroxylic to aprotic solvents). Solution NMR spectra of the unblended ionomers and small salts, were not helpful in determining ion association because ionic association does not appear to affect the spectra.

Phase separation into ion-rich and ion-poor regions is known to occur in ionomers.[18,20,21] Although evidence for ion pairing cannot be obtained directly with these ionomer blends by techniques employed here for the small salts, such pairing is expected because the driving force for ionic aggregation (Coulombic interactions) is present in both systems. The styrene matrix of the ionomer has a low dielectric constant (2.55 at 25 °C)[19] and will not support a high concentration of dissociated ions. This is also the case with the ionomer–resin blends used in the charging studies, which are nonpolar and phase separated. Furthermore, the blends may contain ion-rich regions resembling those in unblended ionomer.[18,20] Therefore, very few ions are dissociated in the bulk. Not only do these ions preferentially aggregate in media of low dielectric constant, but they are likely to be associated even when the dielectric constant is high. This is in agreement with previous studies on ion association in solution.[22-24]

While the $\Delta Q/\Delta M$ values are often found to respond monotonically to the bulk compositions, the OTs content on the surface and the effects of resin immiscibility[10] and ion aggregation on ion transfer must be understood for proper interpretation of charging phenomena. Recognizing that ion aggregation can produce variations in the charge levels is not sufficient to properly interpret contact charging behavior, because the surfaces are often contaminated with ambient moisture. This can change the distribution of ion pair aggregate sizes and could possibly stabilize some dissociated ions. A further complication is the competing charge transfer due to the presence of H^+ [5,25] and other ionic impurities. The presence of undetected ions, such as H^+, further cautions us on the interpretation of charging results in which the materials are not well characterized.

Conclusions

Styrene-based ionomers containing either *N*-methyl-2-vinylpyridinium toluenesulfonate (2MVP OTs) or *N*-methyl-4-vinylpyridinium toluenesulfonate (4MVP OTs) were each blended with styrene-*co*-butyl methacrylate. The blends had a final ion content equal to 5.2 and 26 μmol of ions/g. Powders of these blends were rolled against metal beads to develop a charge, which is proposed to result from the transfer of OTs^- from the powder surface to the bead surface. The contact charge on the powder was positive, and it was higher for the samples containing the 2MVP OTs isomer. This is an interesting result since the cation is "anchored" and is not involved in the transfer process. Dilute solutions of the molecular counterparts *N*-methyl-2-ethylpyridinium and *N*-methyl-4-ethylpyridinium toluenesulfonate show the presence of extensive ion aggregation, and the 2-ethyl isomer shows a slightly higher ion aggregation level. Although the ionomers could not be studied directly, it is reasonable to expect them and the ionomer/polymer blends to also have a parallel level of ion aggregation. The molecular salts also charge positively, although the net charge is more difficult to interpret because each salt contains two mobile ions, both of which can transfer. The molecular salts did not show the charge variations like the ionomers.

Acknowledgment. It is a pleasure to acknowledge the contributions to this work by D. Fenzel-Alexander, D. Nguyen, and J. Zhu.

Registry No. S-*co*-2MVP OTs, 135975-07-4; S-*co*-4MVP OTs, 107039-54-3; S-*co*-BMA, 25213-39-2; 2EtMP OTs, 135975-13-2; 4EtMP OTs, 134470-00-1.

---

(20) Eisenberg, A.; Hird, B.; Moore, R. C. *Macromolecules* **1990**, *23*, 4098.

(21) MacKnight, W. J.; Taggart, W. P.; Stein, R. S. *J. Polym. Sci., Polym. Symp.* **1974**, *45*, 113.

(22) Satchell, D. P. N.; Satchell, R. S. *Trans. Faraday Soc.* **1965**, *61*, 1118.

(23) Satchell, D. P. N.; Satchell, R. S. *Chem. Rev.* **1969**, *69*, 251.

(24) Pettit, L. D.; Bruckenstein, S. *J. Am. Chem. Soc.* **1966**, *88*, 4783.

(25) Wollmann, D.; Diaz, A., *SPIE/SPSE Conference on Electronic Imaging Science and Technology*, 1991, San Jose.