11b). The simulated result was analyzed by eq 11 and $D_0 = (4.18 \pm 0.01) \times 10^{-8}$ cm^2/s and $(D_3 - D_1)/D_0 = 0.48 \pm 0.02$ were obtained for a given value of $\Theta = 320$ s^{-1}. From the above results, his experimental data are considered to suggest $(D_3 - D_1)/D_0 \simeq 0.3$ at least.

If previous results were reanalyzed by the new method, most of them would show nonzero anisotropy ratios. In all cases,[8,9,17] however, the incident beam from a low-power He–Ne laser and an analog spectral method prevent us from obtaining a very quantitative result on anisotropy.

Appendix B. Eigenvalues of the Matrix M in Eq 3

With the eigenvalue and the column eigenvector of **M** as $\lambda_p = \lambda_p^{(0)} + \epsilon\lambda_p^{(1)} + \epsilon^2\lambda_p^{(2)} + ...$ and $\mathbf{U}_p = \mathbf{U}_p^{(0)} + \epsilon\mathbf{U}_p^{(1)} + ...$, respectively, we have

$$\lambda_p^{(0)} = p(p+1) + \mu^2 L_0(p)$$

and

$$\mathbf{U}_p^{(0)} = [0, ..., 0, 1, 0, ..., 0]^t \qquad (\mathrm{B1})^{23}$$

Define $H_{k,p} = [\mathbf{U}_k^{(0)}]^t\mathbf{M}^{(1)}\mathbf{U}_p^{(0)}$. We have only four kinds of $H_{k,p}$'s:

$$H_{p,p-2} = \mu^2 L_1(p)$$

$$H_{p,p+2} = \mu^2 L_2(p)$$

$$H_{p-2,p} = \mu^2 L_2(p-2)$$

and

$$H_{p+2,p} = \mu^2 L_1(p+2) \qquad (\mathrm{B2})^{23}$$

Since $H_{p,p} = 0$, we have $\lambda_p^{(1)} = 0$. The $\lambda_p^{(2)}$ is given by a formula

$$\lambda_p^{(2)} = \sum_{m \neq p} H_{p,m}H_{m,p}/[\lambda_p^{(0)} - \lambda_m^{(0)}] = [A_{p-2}(\mu^2) - A_p(\mu^2)]\mu^4 \qquad (\mathrm{B3})$$

where

$$A_p(\mu^2) = [(p+1)^2(p+2)^2(2p-1)(2p+7)]/\{2(2p+1) \times (2p+3)(2p+5)[(2p-1)(2p+3)^2(2p+7) - 2\mu^2]\} \qquad (\mathrm{B4})$$

These results were used to express Γ_0 and Γ_2 in eq 12c,d and to draw the dotted lines in Figure 8.

References and Notes

(1) Berne, B.; Pecora, R. "Dynamic Light Scattering"; Interscience: New York, 1975.
(2) Chu, B. "Laser Light Scattering"; Academic Press: New York, 1974.
(3) de Gennes, P.-G. "Scaling Concepts in Polymer Physics"; Cornell University Press: London, 1979.
(4) Maeda, T.; Fujime, S. *Macromolecules* **1981**, *14*, 809.
(5) Dubin, S. B.; Lunacek, J. H.; Benedek, G. B. *Proc. Natl. Acad. Sci. U.S.A.* **1967**, *57*, 1164.
(6) Cummins, H. Z.; Carlson, F. D.; Herbert, T. J.; Woods, G. *Biophys. J.* **1969**, *9*, 518.
(7) Wada, A.; Suda, N.; Tsuda, T.; Soda, K. *J. Chem. Phys.* **1969**, *50*, 31.
(8) Fujime, S. *J. Phys. Soc. Jpn.* **1970**, *29*, 416.
(9) Schaefer, W. D.; Benedek, G. B.; Schofield, P.; Bradford, E. *J. Chem. Phys.* **1971**, *55*, 3884.
(10) Loh, E.; Ralston, E.; Schumaker, V. N. *Biopolymers* **1979**, *18*, 2549.
(11) Wilcoxon, J.; Schurr, J. M. *Biopolymers* **1983**, *22*, 849.
(12) Boedtker, H.; Simmons, N. *J. Am. Chem. Soc.* **1958**, *80*, 2550.
(13) Broersma, S. *J. J. Chem. Phys.* **1960**, *32*, 1626.
(14) Tirado, M.; Garcia de la Torre, J. *J. Chem. Phys.* **1979**, *71*, 2581.
(15) Quoted in: Newman, J.; Swinney, H. L. *Biopolymers* **1976**, *15*, 301.
(16) Maeda, H.; Saito, N. *J. Phys. Soc. Jpn.* **1969**, *27*, 984.
(17) Hartford, S. L. Ph.D. Thesis, University of Illinois, 1975.
(18) Rallison, J. M.; Leal, L. G. *J. Chem. Phys.* **1981**, *74*, 4819.
(19) Wada, A.; Ford, N. C., Jr.; Karasz, F. E. *J. Chem. Phys.* **1971**, *55*, 1798.
(20) Pecora, R. *J. Chem. Phys.* **1968**, *49*, 4126.
(21) Gierke, T. D. Ph.D. Thesis, University of Illinois, 1973.
(22) Loh, E. *Biopolymers* **1979**, *18*, 2569.
(23) Maeda, T.; Fujime, S. *Macromolecules* **1984**, *17*, 1157, where D_3 in eq 38a and $(2n - 5)$ in eq B2 should read $D_3/3$ and $(2n + 5)$, respectively.
(24) C.M.I./A.A.B. Description of Plant Viruses, 1975.
(25) Ohbayashi, K.; Kohno, T.; Utiyama, H. *Phys. Rev. A* **1983**, *27*, 2632.
(26) Koppel, D. E. *J. Chem. Phys.* **1972**, *57*, 4814.
(27) Koene, R. S.; Mandel, M. *Macromolecules* **1983**, *16*, 220.
(28) Broersma's revised equations in ref 15 and in Newman et al. (Newman, J.; Swinney, H. L.; Day, L. A. *J. Mol. Biol.* **1977**, *116*, 593) are used.

Electron Spin Resonance Studies of Ionic Interactions in Sulfonated Polystyrene Ionomers: Manganese(II) Salts

Hirokazu Toriumi and R. A. Weiss*

Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06268

Harry A. Frank

Department of Chemistry, University of Connecticut, Storrs, Connecticut 06268.

Received December 5, 1983

ABSTRACT: Ionic interactions in sulfonated polystyrene manganese(II) salts were studied by electron spin resonance spectroscopy. It is shown by comparison with earlier small-angle X-ray scattering observations that the aggregation of ionic groups in unheated samples develops from isolated ions through multiplets into clusters as the ionic group concentration is increased, while in samples once heated above their glass transition temperature multiplets predominate. The formation and decomposition of higher order ionic aggregates are discussed in terms of a competition between attractive interactions of ionic groups and elastic constraints associated with the segmental motions of backbone chains. The observed ESR spectra are satisfactorily reproduced by a combination of two reference spectra representing an isolated Mn^{2+} ion and coupled Mn^{2+}- - -Mn^{2+} ions, from which the proportion of ions participating in the aggregation may be estimated.

Introduction

Self-organization or clustering of ionic groups influences the morphology and physical properties of ion-containing organic polymers (ionomers).[1] The most striking observation in the study of ionomers is a small-angle X-ray scattering (SAXS) peak that commonly appears for all ionomers in the salt form. The scattering entity responsible for this peak is believed to be aggregated ionic groups

0024-9297/84/2217-2104$01.50/0

which are spatially distributed, though it is unclear as to whether the Bragg spacing of several tens of angstroms calculated from the SAXS data results from inter- or intraparticle distances. This structure is now referred to as an "ionic cluster" according to the nomenclature of Eisenberg.[2] In recent papers,[3,4] we have reported that for zinc(II) salts of lightly sulfonated polystyrenes (SPS) the SAXS peak appears when the concentration of ionic groups C is increased beyond a certain minimum value, and its intensity decreases when samples are annealed above their glass transition temperatures.

Despite a number of SAXS studies, relatively little work has been done to examine actual changes in the local environments of each ionic group during the cluster formation. Electron spin resonance (ESR)[5-7] has been recently employed as a useful technique to approach this problem. Yano et al.[6,7] showed that for ethylene–acrylic acid copolymers neutralized with magnetically active manganese(II) ions, the spectral shape changes as C is increased to high values and insisted that the ESR technique directly confirms the existence of ionic clusters. In a preliminary study on the Mn-SPS system, however, we found that a similar spectral change occurs when the sample is heated to temperatures where the decomposition of clusters has been evidenced by a decrease in the SAXS peak intensity.[4] For a consistent explanation of SAXS and ESR results one may have to assume an intermediate structure of ionic aggregates between the isolated singlet and the cluster. (The terms singlet and multiplet refer in this article to the degree of ionic association and should not be confused with spin multiplicities.)

In the present study we examine the temperature dependence of the ESR spectrum of Mn-SPS ionomers and discuss a possible structural model for the evolution of ionic group aggregates. Also demonstrated is a potential applicability of the ESR technique for an estimation of the relative amount of ions participating in the ionic aggregation in the system.

Experimental Section

The preparation of SPS samples with various concentrations of sulfonic acid groups (C in mol %) has been described elsewhere.[3,4] The manganese(II) salts were prepared by titrating SPS dissolved in a toluene–methanol mixture (90/10 (v/v)) with excess amounts of manganese acetate in methanol. The Mn-SPS ionomers were then precipitated and washed with methanol and dried for several days under vacuum at room temperature. In order to minimize water adsorption, the samples were stored in a desiccator prior to use. For the purpose of this study we considered a sample dry when we achieved constant mass during vacuum-drying. As pointed out by one reviewer, it is difficult to remove all traces of water from sulfonate ionomers, and water influences the ionic aggregation. It is possible, in fact probable, that some water is bound sufficiently by the sulfonate group so that it is not removed by our drying operation. Better drying may have been achieved by using elevated temperatures, but this in turn has a tremendous influence on the microstructure.[14] Although we cannot state unequivocally that our results are not unduly influenced by the presence of trace amounts of water, other studies in our laboratory (not yet reported) when water was purposely introduced into the system indicate that the influence of residual water on the ESR spectra reported here is negligible.

The glass transition temperatures T_g of Mn-SPS samples were measured by a Perkin-Elmer DSC-2 differential scanning calorimeter and are given in Figure 1 as a function of sulfonate concentration. The magnitude of the increase in T_g with increasing sulfonate concentration is less than has been previously observed for the sodium(I) and zinc(II) salts of SPS. These samples were thermally cycled in the DSC to elevated temperatures and the measured T_g remained invariant. This indicates that residual moisture or solvent is probably not responsible for the lower T_g. Although the reason for the difference in the T_g's of the Mn(II) and Zn(II) salts is not known, it is known from small-angle X-ray scattering studies that isomers based on both counterions exhibit cluster morphologies.

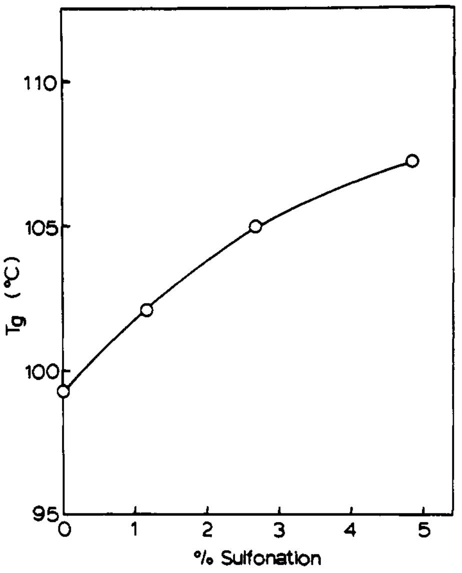

Figure 1. Glass transition temperatures vs. sulfonate concentration (mol %) for Mn-SPS ionomers.

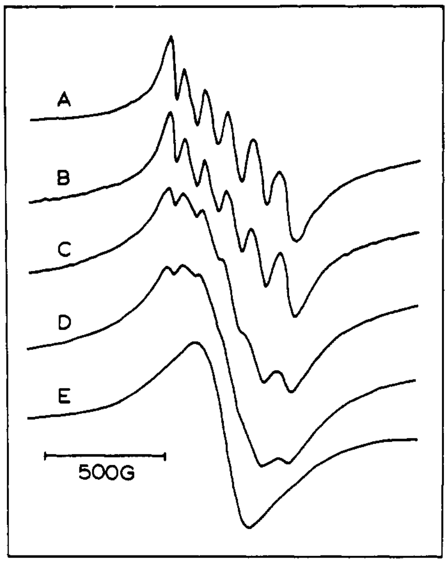

Figure 2. ESR spectra of Mn-SPS as a function of sulfonate concentration (mol %): (a) 0.26, (b) 0.92, (c) 3.24, (d) 5.53, and (e) 5.53 after annealing at 140 °C.

For the ESR measurements, the Mn-SPS ionomers were placed into 4-mm quartz tubes and the samples were degassed and hermetically sealed. The ESR measurements were performed with a Varian E-3 spectrometer operating at an X-band frequency of 9.1 GHz. The temperature was controlled by a Varian E-4540 temperature controller and monitored by a copper–constantan thermocouple before and after each measurement. The spectrum was recorded by both a Varian E-80 recorder and an Apple II microcomputer; the digitized data stored on the microcomputer were then transferred to an IBM 3081 computer for numerical analyses.

Results

Figure 2 shows the ESR spectra of unheated Mn-SPS ionomers as a function of C. The spectrum in the low-C region consists of six absorption lines associated with the $I = {}^5/_2$ nuclear spin of Mn^{2+} ions. With increasing C the individual absorption lines broaden and the six-line spectrum eventually coalesces into a single absorption line.

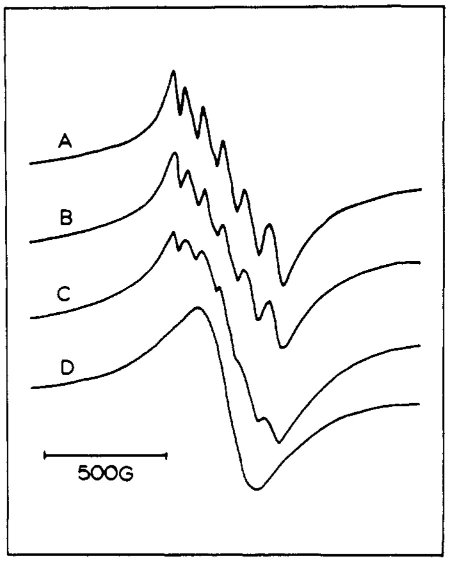

Figure 3. ESR spectra of Mn-SPS with 0.92% sulfonate as a function of temperature: (a) 22.5, (b) 60, (c) 100, and (d) 140 °C.

The influence of temperature on the spectrum shape is shown in Figure 3 for a Mn-SPS sample with $C = 0.92\%$. A gradual line broadening with temperature below 100 °C is followed by a rapid coalescence of the six-line spectrum into a single-line spectrum. It should be noted that the spectral change with temperature follows a similar process as that observed in Figure 2 with increasing C; e.g., the transformation from spectrum 3a to spectrum 3c with temperature corresponds to that from spectrum 2b to spectrum 2c with concentration. For every sample studied, the spectral change with temperature occurred in this manner, covering all intermediate states between its original spectrum in Figure 2 and the final spectrum d in Figure 3. No changes in the spectra were observed by heating above 140 °C. The temperature at which the spectrum became a single peak, between 100 and 140 °C, generally appeared to correspond to T_g for the ionomer.

Discussion

A. Ionic Multiplets and Clusters. The transformation in the ESR spectrum from six lines to single line reflects the change in local environments of Mn^{2+} ions. The well-resolved six absorption lines in the low-C region are consistent with those observed in solution spectra of Mn^{2+} ions,[8-10] indicating that the ionic groups are dispersed in a polymer matrix essentially as isolated ion pairs (SO_3^----Mn^{2+}---^-O_3S). The formation of the single absorption line at high C values, however, indicates an appearance of short-range interactions between Mn^{2+} ions. Spectrum 2e having a symmetric line shape and a narrowing (compare the width with those in the low-C region) shows a close resemblance to an "exchange-coupled spectrum".[11,12] This interaction, arising from a coupling of unpaired electron spins on neighboring ions, is short range in nature and interionic. Therefore, Mn^{2+} ions displaying the exchange spectrum are expected to be close together and exist in the aggregated form (pair or higher order multiplet)[12] where each individual Mn^{2+} ion is kept conjugated with two SO_3^- ions. It is seen from a gradual transformation in the ESR spectrum in Figure 2 that the proportion of aggregated ionic groups x increases as the total ion concentration C is increased. This aggregation is due to the electrostatic attractive interaction between ionic groups, and the equilibrium value of x is a consequence of a competition of this attractive interaction and the elastic energy required to deform backbone chains in order to accomplish ion association.[2]

It should be noted that the SAXS ionic peak begins to appear around C = 1–2%,[3,4] where the ESR exchange interaction becomes obvious, suggesting that ionic multiplets develop into clusters at high ion concentrations. According to a model of MacKnight et al.,[13] multiplets comprise a central core of the cluster, which is surrounded by a shell of backbone chains. The characteristic size of scattering cores and their shell spacing were estimated for Zn-SPS from SAXS studies to be 7 and 37 Å, respectively.[3] The experimental classification of these different structures of ionic groups is in agreement with Eisenberg's theoretical predictions.[2]

High-temperature ESR experiments, in conjunction with SAXS studies, revealed different responses of ionic multiplets and clusters to a temperature increase. As seen in Figure 3, ionic groups that were originally dispersed as isolated ion pairs in a virgin sample readily aggregate into multiplets around 120 °C. The correspondence of this temperature with T_g in Figure 1 indicates that increased segmental motions of backbone chains are responsible for multiplet formation. These motions may provide the ionic groups with higher reorientational freedom and hence a higher probability of collisions for multiplet formation. Multiplets once formed remain stable at low and high temperatures whether they are formed in virgin samples or by heating. It is suggested, therefore, that the attractive interactions between ion pairs are strong enough to maintain the multiplet structure against a continuous agitation due to main-chain segmental motions. In fact, multiplets survive annealing at 300 °C, some 200 °C above T_g.[4]

If the interactions between multiplets are also strong, clusters will develop at high temperatures by a mechanism similar to that suggested above for multiplets. This is the situation in Na-SPS ionomers, for which we have observed an enhancement of the SAXS peak intensity after annealing.[4] In contrast, SPS neutralized by divalent zinc cations exhibits a decrease in the cluster concentration after annealing.[4] For as yet unknown reasons, the attractive interactions been multiplets in the latter system appear to be weaker than those in Na-SPS to the extent of being easily overcome by segmental motions. Lefelar and Weiss have recently tried to explain this result in terms of packing of the counterions in monovalent and divalent salt ionomers.[14]

B. Proportion of Mn^{2+} Ions Participating in Multiplet Formation. As shown in the previous section, Mn^{2+} multiplets distinguish themselves from isolated ion pairs by displaying the exchange-coupled ESR spectrum. This characteristic allows us to estimate the proportion of Mn^{2+} ions existing in multiplets x from a simulation of the observed spectrum. We have chosen two reference spectra: spectrum 2a, for which the ionic concentration is very low, was assumed to represent the case where only isolated ion pairs exist (x = 0) and spectrum 2e, for which the ionic concentration was higher and the sample had been annealed above T_g, was chosen to represent the case where all the ionic groups are aggregated (x = 1). Attempts were made to reproduce the experimental spectra by a linear combination of the reference spectra, i.e., varying x. Figure 4 compares the observed and simulated spectra for these different samples studied in Figure 2. The calculation satisfactorily reproduces the details of each spectrum and the general trend of the transformation with C as well. The optimum x values obtained were 0.16, 0.56, and 0.75 at C = 0.92, 3.24, and 5.53%, respectively. By the same method

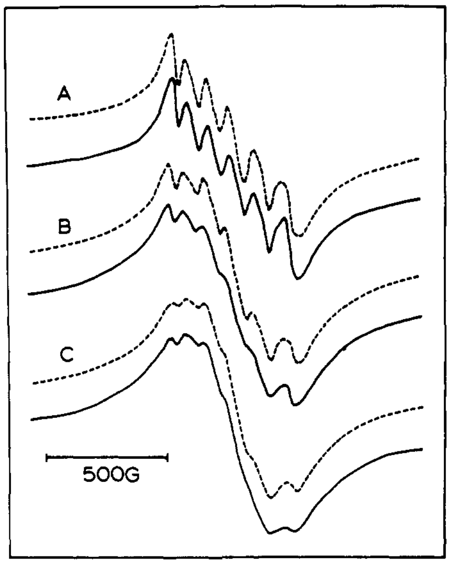

Figure 4. Comparison of the calculated (- - -) and observed (—) ESR spectra of Mn-SPS ionomers as a function of sulfonate concentration: (a) 0.92, (b) 3.24, and (c) 5.53 mol %.

the temperature dependence of the spectra in Figure 3 may also be explained.

The model used here involves a crude simplification of the actual structure of the multiplet. For example, the configuration and the number of simultaneously interacting Mn^{2+} ions are not known; instead we assume an aggregate of Mn^{2+} ions (two or more) as a model of the ionic association. The observations can be remarkably well represented by this scheme.

Conclusion

ESR experiments have revealed a new aspect of the ionic interaction in SPS ionomers neutralized by divalent cations. The presence of multiplets is a necessity for the cluster formation, but it does not always mean the presence of clusters. High temperatures promote the formation of multiplets, while clusters decompose. The difference in the temperature resistance of these two structures can be accounted for by a single mechanism. The increased segmental motions of the backbone favor the formation of multiplets rather than higher ordered, cluster structures. It is also shown that a simple two-phase model can reproduce the spectral transformations with ionic group concentration and temperature. This result is indicative of the potential applicability of the ESR technique for an estimation of the proportion of ionic groups participating in the multiplet formation.

Acknowledgment. Support for this work by the National Science Foundation, Polymers Program (DMR-8108333), is gratefully acknowledged.

References and Notes

(1) For recent reviews, see: Holliday, L., Ed. "Ionic Polymers"; Applied Science Publishers: London, 1975, Eisenberg, A.; King, M. "Ion-Containing Polymers"; Academic Press: New York, 1977, MacKnight, W. J.; Earnest, T. R. *J. Polym. Sci., Macromol. Rev.* **1981**, *16*, 41.
(2) Eisenberg, A. *Macromolecules* **1970**, *3*, 147.
(3) Peiffer, D. G.; Weiss, R. A.; Lundberg, R. D. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1503.
(4) Weiss, R. A.; Lefelar, J.; Toriumi, H. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 661.
(5) Pineri, M.; Meyer, C.; Levelut, A. M.; Lambert, M. *J. Polym. Sci., Polym. Phys. Ed.* **1974** *12*, 115.
(6) Yano, S.; Yamashita, H.; Matsushita, M.; Aoki, K.; Yamauchi, J. *Colloid Polym. Sci.* **1981**, *259*, 514.
(7) Yamauchi, J.; Yano, S. *Macromolecules* **1982**, *15*, 210.
(8) Garrett, B. B.; Morgan, L. O. *J. Chem. Phys.* **1966**, *44*, 890.
(9) Hinckey, C. C.; Morgan, L. O. *J. Chem. Phys.* **1966**, *44*, 898.
(10) Reed, G. H.; Leigh, J. S.; Pearson, J. E. *J. Chem. Phys.* **1971**, *55*, 3311.
(11) Pake, G. E.; Estle, T. L. "The Physical Principle of Electron Paramagnetic Resonance"; Benjamin: Reading, 1973.
(12) Owen, J.; Harris, E. A. In "Electron Paramagnetic Resonance"; Geschwind, S., Ed.; Plenum Press: New York, 1972.
(13) MacKnight, W. J.; Taggart, W. P.; Stein, R. S. *J. Polym. Sci., Polym. Symp.* **1974**, *No. 45*, 113.
(14) Lefelar, J.; Weiss, R. A. *Macromolecules*, in press.