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Kinetics of Ion-Pair Interchange in Ionomer Solution

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ABSTRACT: Solutions of polystyrene in which 3.4 and 6.9 mol % of the monomer residues were sulfonated were partially neutralized with 2-(aminomethyl)naphthalene and 9-(aminomethyl)anthracene, respectively. The solutions were mixed in a stopped-flow apparatus and the interchange of the two counterions was followed by the increase in the anthracene emission intensity, when the solution was irradiated in the naphthalene absorption band, due to an increasing efficiency of nonradiative energy transfer. The kinetics of the process were studied as a function of the polymer concentration in dioxane and a 1:1 mixture of dioxane and cyclohexane, as a function of the excess of unneutralized sulfonic acid groups, and as a function of temperature.

Introduction

Although factors affecting the equilibrium of ion-pair formation in media of low dielectric constant have been explored in great detail,[1] no studies of the kinetics of such processes seem to have been reported. Rate constants for the complexation of monovalent cations with crown ethers have been determined with the use of NMR[2] and ultrasonic relaxation techniques,[3] and corresponding rates for the Na^+ complexation with the cyclic polypeptide Gramicidin A have also been measured.[4] As would be expected, the exchange of alkali cations with their cryptates[5] is much slower than with the less stable crown ether complexes. All these complexes involve several ligand groups so that the kinetics of their formation and dissociation involves different considerations than the formation of an ion pair, depending only on the interaction of a cation and an anion.

The kinetics of ion-pair interchange in organic solvents is not only of general physicochemical interest but concerns the polymer chemist for two specific reasons: (a) In the anionic polymerization of vinyl compounds, the rate constant for chain propagation is different for chains terminated by "contact ion pairs" and "solvent-separated ion pairs", leading to a bimodal molecular weight distribution if ion-pair interchange is slow.[6] (b) The interaction between ion pairs in ionomers leads to a sharp increase in viscosity both in bulk and in solution.[7,8] It has been suggested[9] that such effects on the rheology of the system should be sensitive to the rate of ion-pair interchange.

The present investigation is based on the following idea: In a dilute ionomer solution in which half of the anionic chains carry donor and half carry acceptor fluorophores, the donor-acceptor distances are too large for a significant nonradiative energy transfer ("Förster transfer"[10]). However, as the counterions are interchanged, so that donor and acceptor fluorophores come to be associated with the same polymer chain, their spacing becomes sufficiently short so that the efficiency of energy transfer from the donor to the acceptor fluorophore is substantially increased. The emission intensity of the acceptor, when the solution is irradiated in the donor absorption band, is then a measure of the extent of counterion exchange. This paper reports initial results in which this principle is used by mixing solutions of slightly sulfonated polystyrene with fluorescent counterions in a stopped-flow apparatus.

Experimental Section

Materials. Polystyrene (number-average molecular weight 105 000) with 3.4% and 6.9% of the monomer residues converted to the sulfonic acid was donated to us by Dr. R. D. Lundberg of the Exxon Chemical Co., Linden, NJ. 9-(Hydroxymethyl)-anthracene (Aldrich) was converted to 9-(chloromethyl)anthracene and the method of Hezowski et al.[11] was used for the preparation of 9-(anthrylmethyl)phthalimide and its hydrazenolysis to 9-(aminomethyl)anthracene (AMA) (mp 105-110 °C). The same procedure was used to convert 2-(chloromethyl)naphthalene (Aldrich to 2-(aminomethyl)naphthalene (AMN) (bp 114-118 °C at 0.1 Torr).

Kinetics. Solutions of partially sulfonated polystyrene containing AMA or AMN counterions were mixed in the stopped-flow apparatus with fluorescence detection previously described.[12] The solutions were irradiated at 282 nm, the absorption maximum for AMN. At this wavelength the molar extinction coefficients

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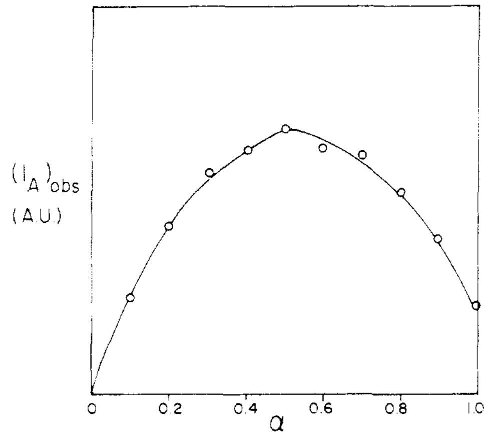

Figure 1. Emission intensity of AMA at 415 nm from dioxane solutions of PS-6.9 (1.38×10^{-3} base M) neutralized with a 4.05×10^{-5} M mixture of AMN and AMA as a function of the fraction of AMA in the mixed amines.

were 2500 for AMA and 7000 M^{-1} cm^{-1} for AMN. A clear glass filter (Optics Technology Co., Palo Alto, CA) with a cutoff at 360 nm was used to isolate the emission from the AMA. Each kinetic run was repeated 20 times and the data were averaged by a dedicated computer. A Perkin-Elmer MPF-44B fluorescence spectrophotometer was used for static fluorescence measurements.

Results and Discussion

Interpretation of the anthracene emission intensity in terms of the extent of counterion exchange from first principles would have encountered great difficulties for two reasons: (a) The sulfonate groups with their fluorescent counterions were distributed at random along the contour of the polymer chain, leading to a corresponding dispersion of the donor–acceptor spacings and the efficiency of nonradiative energy transfer. (b) The dynamics of the chain molecules lead to a variation of the donor–acceptor spacing during the excited lifetime of the donor.[13] We used, therefore, the following procedure to arrive at an estimate of the relation between the emission intensity of AMA and the fraction β of the AMA counterions which have become associated with the polymer carrying originally only AMN counterions.

(1) Dioxane solutions were prepared containing 1.83×10^{-3} base M polystyrene carrying 6.9 mol % sulfonic acid groups (PS-6.9). These were neutralized with 4.05×10^{-5} M mixtures of AMN and AMA, varying the fraction α of AMA. Excitation at 282 nm led to anthracene emission intensities at 415 nm $(I_A)_{obsd,\alpha}$ plotted in Figure 1.

(2) If 1.83×10^{-3} base M PS-6.9 carrying 4.05×10^{-5} M AMN and AMA counterions are mixed, the solution will contain, after the exchange of a fraction β of the counterions, equal concentrations of polymer chains in which AMA constitutes a fraction α and $1 - \alpha$, respectively, of the counterions. To obtain the AMA emission intensity expected for the two kinds of chains, half of $(I_A)_{obsd,\alpha}$ and $(I_A)_{obsd,1-\alpha}$ have to be corrected by a factor f_α to account for the change in the average light intensity to which the fluorophores are exposed when half of the chains with a fraction α of AMA counterions are replaced with chains with a fraction $1 - \alpha$ of AMA counterions. This factor is given, for a cell with a 1-cm optical path length, by

$$f_\alpha = \int_0^1 \exp[(1 - 2\alpha)xr]\ dr = \frac{\exp[(1 - 2\alpha)x] - 1}{(1 - 2\alpha)x}$$

$$x = 2.3(c/2)(\epsilon_{AMN} - \epsilon_{AMA}) \qquad (1)$$

where c is the total counterion concentration and ϵ_{AMN} and ϵ_{AMA} are the molar extinction coefficients of the two counterions.

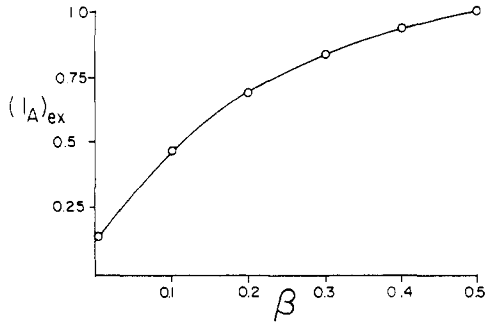

Figure 2. Dependence of the AMA emission intensity after an exchange of a fraction β of the counterions expected on the basis of the data in Figure 1.

(3) The AMA emission intensity after an exchange of a fraction β of the counterions, relative to its steady-state value, is then expected to be

$$(I_A)_{ex}(\beta) = [(I_A)_{obsd,\alpha} f_\alpha + (I_A)_{obsd,1-\alpha} f_{1-\alpha}]/2(I_A)_{obsd,\alpha} = 1/2 \qquad (2)$$

Figure 2 shows a plot of $(I_A)_{ex}$, and it may be seen that the AMA emission intensity is expected to become decreasingly sensitive to β with an increasing extent of counterion exchange.

In the stopped-flow experiments on the kinetics of counterion exchange we mixed solutions containing equal concentrations of polystyrene in which 3.4 or 6.9 mol % of the styrene residues had been sulfonated (PS-3.4 and PS-6.9) and which had been partially neutralized with AMN and AMA, respectively, with the ratio of amine to styrene residues held at 1/45. Unless stated otherwise, all kinetic runs were carried out at 17 °C.

The counterion exchange, as followed by the increase in the AMA emission intensity, had two unexpected features: (a) The initial value of I_A was between 40% and 60% of its equilibrium value. If we compare this result with the $(I_A)_{ex}$ plot in Figure 2, we must conclude that the exchange of 10–15% of the counterions is too fast to be recorded by the stopped-flow technique which has a "dead-time" of about 1 ms. (b) Within experimental error, the I_A exhibited in all runs a simple exponential approach to its equilibrium value. Although Figure 2 shows that the expected AMA emission intensity is not expected to be linear in the extent of counterion exchange, so that such a simple behavior cannot be justified, the first-order rate constants, k, describing the results provide a useful parameter for their characterization.

In Figure 3 we have presented a double logarithmic plot of the rate constants against the PS-6.9 concentration in two solvent media, dioxane and a 1:1 mixture of dioxane and cyclohexane. In dioxane solution k was found to be proportional to the 0.7 power of the polymer concentration. If counterion exchange required the interaction of two ion pairs, k would be expected to be proportional to the first power of the polymer concentration. On the other hand, if the ion pairs are characterized by a dissociation constant small compared with the ion-pair concentration, then the concentration of free counterions is proportional to the square root of the polymer concentration. Then, if the counterion exchange involves the interaction of a free counterion with an ion pair, k should be proportional to the square root of the polymer concentration. This exchange mechanism was supported by the observation that for a given polymer concentration with the same number of ion pairs per polymer chain the rate of counterion exchange was sharply increased when the excess of unneutralized sulfonic acid groups was reduced, which would,

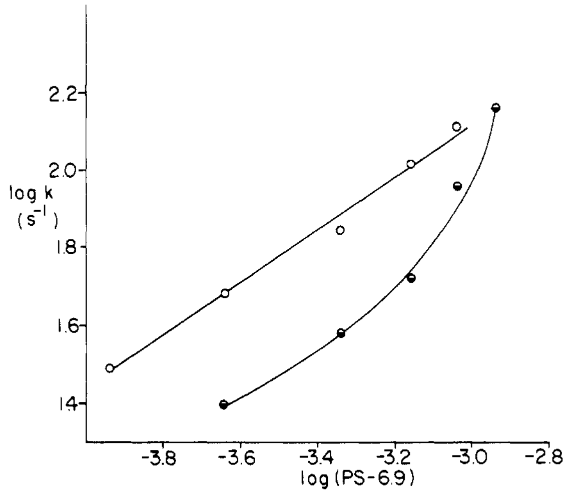

Figure 3. Dependence of the apparent rate constant for AMA emission enhancement on the concentration of PS-6.9 after the mixing of solutions neutralized with AMN and AMA.

presumably, favor the dissociation of the ion pairs. In experiments using 4.56×10^{-4} base M polymer, k was increased by a factor of 2.4 in dioxane and by a factor of 1.7 in a 1:1 mixture of dioxane and cyclohexane when PS-3.4 was substituted for PS-6.9. The finding that k was found to be proportional to the 0.7 power of the polymer concentration may then be interpreted in two ways: (a) Both binary ion-pair interactions and interactions of free counterions with ion pairs may be significant. (b) The ion-pair dissociation constant may not be small compared to the ion-pair concentration, so that the free counterion concentration may increase more rapidly than in proportion to the square root of the polymer concentration.

In 1:1 dioxane/cyclohexane solution, the dependence of k on polymer concentration follows a more complicated pattern. At polymer concentrations from 2.3×10^{-4} to 6.9×10^{-4} base M, the counterion exchange in the mixed solvent was half as fast as in pure dioxane and such a deceleration of the process was consistent with the increased stability of ion pairs to be expected in a medium of lower dielectric constant. However, at higher polymer concentrations k exhibited an anomalously rapid increase, so that it attained, at a polymer concentration of 1.14×10^{-3} M, a value to be expected in pure dioxane. This behavior may reflect an association of the ionomer, since phase separation was observed when the cyclohexane content of the mixed solvent was raised to 60%. Ionomer association is also indicated by the viscometric behavior of their solutions.[7,8]

Since dioxane freezes at 11.7 °C and rate constants much larger than 100 s^{-1} cannot be confidently determined in a stopped-flow apparatus, a study of the temperature dependence of the counterion exchange could be carried out only in the mixed solvent. In 4.56×10^{-4} base M PS-6.9, values of 15, 38, and 47 s^{-1} were found at 6, 17, and 21 °C, corresponding to an activation energy of 52 kJ/mol.

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