

Fluorescence Studies of Ionomers

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Ionomers are nonpolar chain molecules carrying, on a small portion of their monomer residues (2-6%), ionized substituents with their counterions. Typical of such polymers are slightly sulfonated polystyrenes with univalent or divalent counterions. Extensive studies of ionomers in bulk or in solution have been summarized in a number of reviews.¹⁻⁴ They reflect the high stability of ion pairs in media of low dielectric constant and the large driving force toward ion-pair aggregation. This leads in bulk ionomers to the segregation of ion pairs in a microphase exhibiting sharp X-ray diffraction peaks and a dramatic change in the viscoelastic properties when compared to a similar polymer without ion-pair substituents. When ionomers are dissolved in nonpolar solvents, two characteristic phenomena are observed: In highly dilute systems, when the polymer chains are isolated from each other, the ion-pair association is predominantly intramolecular, producing a contraction of the chains and a reduced solution viscosity, whereas at higher concentrations, where the association involves ion pairs carried by different macromolecules, a sharp increase in viscosity is observed.^{5,6}

In this Account I hope to show how fluorescence of ionomer systems can be used to illuminate a number of problems, such as the dependence of the kinetics of interpolymer reactions on the polymer chain length, the rate of counterion exchange in dilute ionomer solutions, the extent of ion-pair aggregation, and the diffusion of counterions in bulk ionomers.

Kinetic Excluded Volume Effect

More than a half-century ago, Flory demonstrated⁷ that in a polyesterification the reactivity of the functional groups is independent of the length of the chains to which they are attached. Yet, in his classical 1953 monograph *Principles of Polymer Chemistry* Flory conceded that^{8a} "the reactivity may decrease with an increasing polymer chain length when the terminal group of a very large polymer molecule will be shielded by the coiling of the chain . . . in very dilute solutions where sufficient space is available to permit the polymer molecules to exist more or less independently of one another". Since the osmotic pressure of polymers in good solvent media exhibits a large positive deviation from ideal solution behavior, reflecting an excluded volume effect showing that the coiled chains of flexible macromolecules resist strongly mutual interpenetration,^{8b} the polymers will "exist more or less inde-

pendently of one another" only at dilutions beyond the "critical overlap concentration" c^* at which the molecular coils occupy all available space without overlap.⁹ It is generally accepted that c^* is proportional to the reciprocal to the intrinsic viscosity, $1/[\eta]$ ($[\eta] = \lim_{c \rightarrow 0} (\eta - \eta_0)/c$, where η is the viscosity of a solution of concentration c and η_0 is the viscosity of the solvent), although different proportionality constants, close to unity, have been used by different investigators.¹⁰

The effect conjectured by Flory, which I have called "the kinetic excluded volume effect",¹¹ has been studied for diffusion-controlled processes such as the radical-radical recombination in free radical polymerizations^{12,13} and the interaction of polymer chains terminated by a phosphorescent group with polymer chains terminated by a phosphorescence quencher.¹⁴ As first shown by North and his collaborators,¹² such processes depend not only on the diffusion of the macromolecules toward each other but also on the rate of diffusion of the reactive residues to the surface of the molecular coils where they are accessible for reaction.

Much less is known about the kinetic excluded volume effect for polymer reactions involving an appreciable activation energy. In solutions of long-chain polymers at concentrations below c^* , the concentration of reactive groups is extremely low (on the order of 10^{-5} M), if the polymers carry a single such group. This presents experimental problems which probably account for the fact that some investigators did and others did not find an excluded volume effect.^{15,16} If more than one reactive group is attached to the macromolecules, then the kinetic data cannot be reliably interpreted if the interpolymer reaction leads to the formation of covalent bonds between the macromolecular chains, since the

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Herbert Morawetz, born in Prague in 1915, obtained his doctorate at the Polytechnic Institute of Brooklyn (now Polytechnic University) in 1951 and joined its Department of Chemistry. He served as Director of its Institute of Polymer Research from 1971 to 1981, when he was named Institute Professor. Since 1986 he has been Institute Professor Emeritus. In 1985 he received the Polymer Chemistry Award from the American Chemical Society. He is the author of *Macromolecules in Solution* (1965, second edition 1975) and *Polymers: The Origin and Growth of Sciences* (1985).

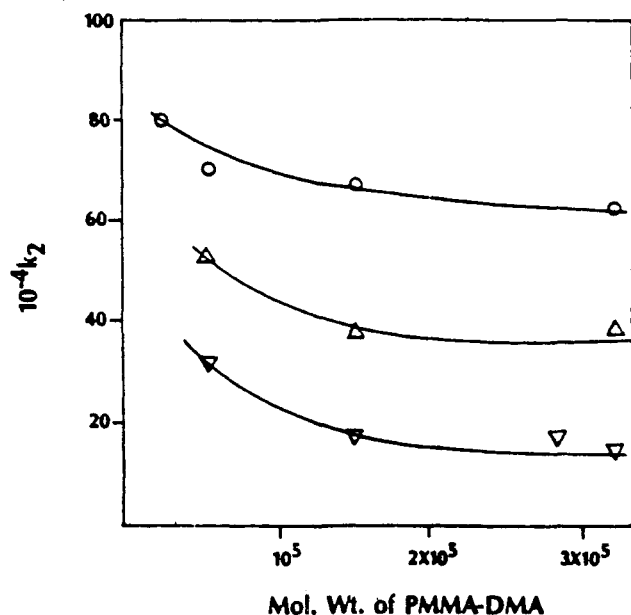
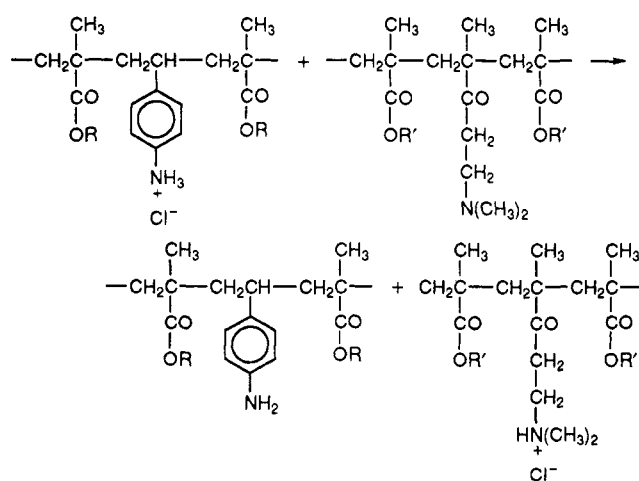


Figure 1. Kinetics of proton transfer from PMMA-AS to PMMA-DMA in toluene solution at 7 °C as function of the molecular weight of the interacting polymers. Molecular weight of PMMA-AS: (O) 21 000; (▽) 41 000; (Δ) 280 000.

first such bond alters profoundly the rate at which the two chains will be linked by additional bonds. We have tried to surmount this problem by following the reaction of a polymer carrying reactive substituents with polymers to which catalytic groups were attached, so that only a transient link of short duration would be formed between the two polymeric species.^{11,17} In these studies no kinetic excluded volume effect was observed.

Reliable data on the dependence of the rate of interpolymer reactions on the length of the interacting chains have now been obtained for the proton transfer in toluene solution from a copolymer of methyl methacrylate with ~1% of *p*-aminostyrene (PMMA-AS) to a methyl methacrylate copolymer carrying 1–2% of aliphatic tertiary amine substituents (PMMA-DMA).¹⁸



Since the fluorescence of the aminostyrene residues is quenched on protonation, the proton transfer to the aliphatic amine could be followed in a stopped-flow apparatus with fluorescence detection. As shown in Figure 1, for any molecular weight of PMMA-AS, the rate constant for the proton transfer decreases with an

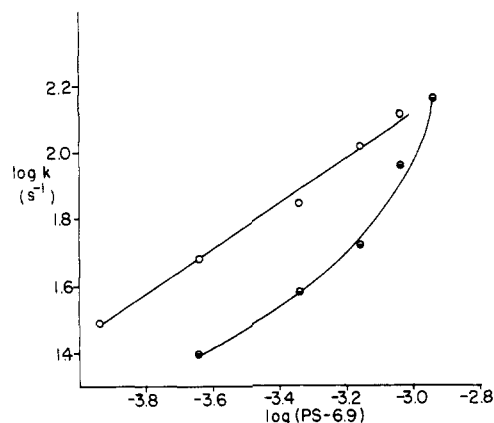


Figure 2. Kinetics of counterion interchange between polystyrene sulfonated in 6.9% of its styrene residues (PS-6.9), with 32% of the sulfonic acid groups neutralized with (aminomethyl)naphthalene or (aminomethyl)anthracene, respectively. Temperature: 17 °C. Solvent: (O) dioxane; (●) mixture of equal volumes of dioxane and cyclohexane.

increase in the molecular weight of the PMMA-DMA. Thus the kinetic excluded effect has been clearly established. The use of this system has the advantage not only of the high fluorescence sensitivity but also of the absence of any covalent bond formation between the interacting polymers, so that the analysis of kinetic data involving polymers carrying a number of reactive substituents presents no difficulty.

Counterion Exchange in Ionomer Solution

Whereas numerous studies have been concerned with ion-pair formation in media of low dielectric constant,¹⁹ I am unaware of any investigation of the rate at which ion pairs exchange their partners. The use of ionomers, where different chains carry different ion pairs, presents special advantages for the study of this problem. In our initial investigation²⁰ we mixed dilute solutions of two slightly sulfonated polystyrenes partially neutralized with (aminomethyl)naphthalene and (aminomethyl)anthracene, respectively, in a stopped-flow apparatus, taking advantage of the fact that nonradiative energy transfer is negligible below the critical overlap concentration⁹ of the ionomer as long as the two fluorophores are associated with different polymer chains, so that the distance between donor and acceptor fluorophores is large, but becomes increasingly efficient as the counterions interchange, so that they are both located in the same macromolecular domain. Thus, when irradiating the naphthalene donor, the increasing intensity of the anthracene acceptor emission allows us to monitor the counterion exchange.

Figure 2 represents the dependence of the first-order rate constant of this process as a function of the polymer concentration in two solvent media. In principle, the counterion exchange could take place by two mechanisms, involving either the interaction of two ion pairs or the attack of a free counterion on an ion pair. The first mechanism would lead to a slope of unity in the doubly logarithmic plot, whereas the very small dissociation constant of ion pairs¹⁹ would lead to a free counterion concentration proportional to the square root of the ionomer concentration and thus to a 0.5

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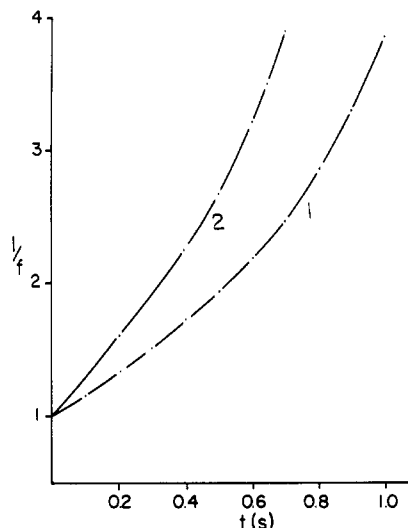
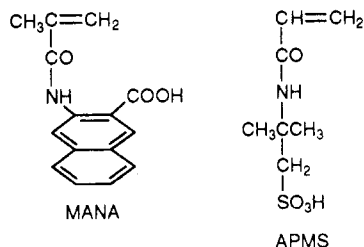


Figure 3. Kinetics of the Na^+ transfer from BMA/MANA copolymer with 2.2 mol % MANA to BMA/APMS copolymer in toluene solution with MANA and APMS residue concentrations of 4×10^{-5} M (f is the fraction of Na^+ associated with MANA at time t). Temperature: (1) 20 °C; (2) 30 °C.

slope in the doubly logarithmic plot. In dioxane solution we observed a slope of 0.7, suggesting that under our experimental conditions the two mechanisms make comparable contributions to the counterion interchange. In the less polar mixture of equal volumes of dioxane and cyclohexane, the counterion interchange at high ionomer dilution is, as expected, substantially slower. At higher concentrations a rapid acceleration of the process is observed, which I believe to be due to polymer association as the solubility limit is approached.

Since most interest in ionomer studies concerns ionomers with alkali counterions, we searched for a system in which the counterion transfer could be followed by fluorescence. This was accomplished²¹ by following the transfer of alkali ions from neutralized copolymers of butyl methacrylate (BMA) with 3-(methacryloylamino)-2-naphthoic acid (MANA) to a BMA copolymer with [2-(acryloylamino)prop-2-yl]methanesulfonic acid (APMS). Irradiating at a wavelength



where only the unneutralized MANA residues absorb, we again followed the process by the increasing fluorescence intensity in a stopped-flow apparatus. When we plotted $1/f$, the inverse of the fraction of counterions which remain associated with MANA, against time for kinetic runs in which solutions of copolymers containing equivalent amounts of MANA and APMS were mixed, an upward curvature, as illustrated in Figure 3, was invariably observed. Thus, the apparent second-order rate constant for the counterion transfer increased as the process proceeded. This unusual effect is tentatively interpreted as follows: It will be shown below that the ion pairs formed by the

ionization of MANA residues dimerize to an extent which diminishes as the spacing of these ion pairs along the polymer chain increases, so that the fraction of ion pairs dimerized should decrease as the alkali ions are transferred from the MANA to the APMS residues. If we then make the plausible assumption that the rate constant is smaller for ion transfer from dimerized than from isolated ion pairs, then the average rate constant for this process will increase with an increasing transfer of the cation from MANA to APMS.

As expected, the rate of counterion transfer becomes faster with an increasing counterion size, i.e., a decreasing ion-pair stability. With a copolymer containing 2.2 mol % of MANA residues in toluene solution containing 4×10^{-5} M MANA at 20 °C, the half-times for counterion transfer were 0.78 s for Li^+ , 0.53 s for Na^+ , and 0.14 s for Cs^+ . When using the more polar dioxane as the solvent, the rate for the Na^+ transfer was increased 20-fold.

Yet, in processes involving counterion transfer between two ionomers, this transfer is not necessarily the rate-determining step. Dowling and Thomas²² reported experiments in which they used toluene solutions of a slightly sulfonated polystyrene ionomer doped with the doubly charged $\text{Ru}(\text{bpy})_3^{2+}$ fluorophore and similar ionomer solutions containing the fluorescence quencher Cu^{2+} . A sufficient amount of the inert Ca^{2+} was added to keep the concentration of divalent counterions equivalent to 85% of the polymer-bound sulfonate groups. When the two solutions were mixed, the kinetics of the fluorescence decay was found to be independent of the ionomer concentration. This was interpreted as showing that the rate-determining step is not the transfer of the Cu^{2+} quencher to the ionomer doped with the fluorophore, but a slow Cu^{2+} diffusion from the "shell" to the "core" of the ionomer which contains most of the ionized species, including the fluorescent probe.

Determination of the Degree of Ion-Pair Association

When we irradiated the neutralized BMA/MANA copolymer solutions carrying Na^+ counterions at a wavelength where the neutralized MANA residues absorb, two emission bands were observed: one, α , with an emission maximum at 405–415 nm, the other, β , with a maximum at 490–500 nm. The significance of these bands was clarified by recording the fluorescence of copolymers with a varying MANA content. As shown in Figure 4, the intensity of the α band decreased with decreasing MANA content and almost disappeared in solutions of a copolymer containing only one MANA in 1000 monomer residues. This result was interpreted as showing that the α band is due to associated ion pairs. The extent of this association is strongly dependent on the nature of the counterion. Figure 5 shows emission spectra of a copolymer containing 2.2 mol % of MANA residues with different alkali counterions. While the Na^+ salt exhibits comparable emission intensities in the α and β bands, the Li^+ salt emits almost exclusively in the α band and the Cs^+ salt almost exclusively in the β band. The conclusion that

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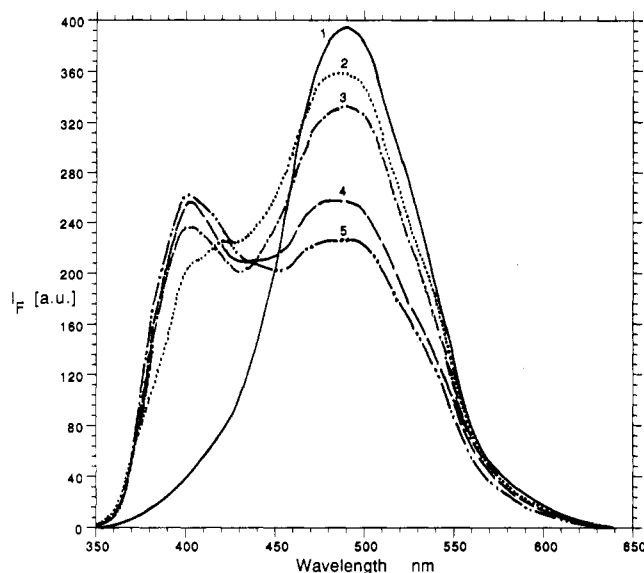


Figure 4. Emission spectra of Na^+ salts of BMA/MANA copolymers in toluene. Mole percent MANA in copolymers: (1) 0.09; (2) 0.44; (3) 2.2; (4) 4.0; (5) 6.1.

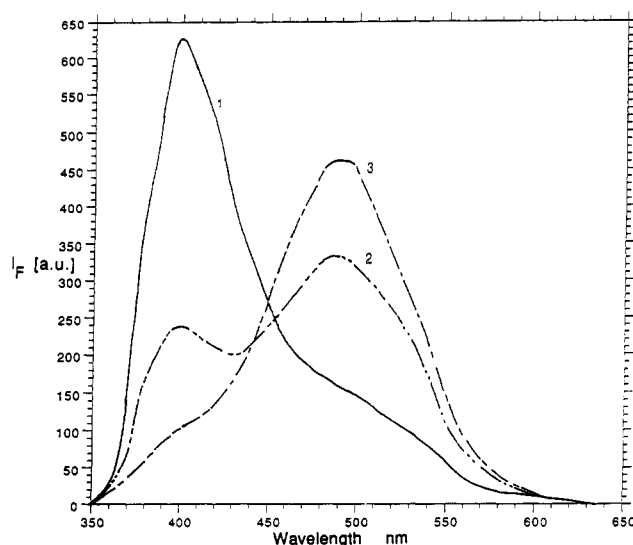


Figure 5. Emission spectra of BMA/MANA containing 2.2 mol % MANA carrying (1) Li^+ , (2) Na^+ , and (3) Cs^+ counterions.

the extent of ion-pair association increases in the order $\text{Cs}^+ < \text{Na}^+ < \text{Li}^+$ is confirmed by solution viscosity data.

For all these counterions, the decrease in the β emission intensity of an ionized MANA residue, reflecting the decreasing fraction of unassociated ion pairs, is proportional to the density of MANA residues in the copolymer. Our data lead then to an estimated fraction of 0.037, 0.14, and 0.37 associated ion pairs for a copolymer with 2.2 mol % MANA residues with Cs^+ , Na^+ , and Li^+ counterions, respectively, in toluene solution. Since our fluorescence spectra were recorded below the critical overlap concentration⁹ of the polymer, this characterizes the intramolecular association of ion pairs attached to the same polymer chain.

It is instructive to compare these results with those obtained in studies of the intramolecular association of low molecular weight ion pairs. An equilibrium constant for such a process was first reported by Fuoss and Kraus,²⁴ who estimated from cryoscopic data $K_d = 10$

M^{-1} for the dimerization of the triamylammonium picrate ion pair in benzene. In recent years a variety of methods have been used to study ion-pair association in media of low dielectric constant.²⁵ Although both dimer and tetramer formation has been observed, the latter is easily inhibited by steric hindrance,²⁶ so that we can confidently assume that association of the bulky neutralized MANA residues in solutions of MANA copolymers does not proceed beyond the dimer. Infrared spectroscopy has been demonstrated to be a powerful tool for the study of alkali thiocyanates, since the frequency of the CN stretching vibration is reduced when the salt dimerizes.^{27,28} In a careful study by Firman et al.²⁸ a dimerization constant of 32 M^{-1} was obtained for NaSCN in THF at 25°C , while an earlier study by Chabanel and Wang²⁷ led to dimerization constants of 0.24, 45, and 60 M^{-1} for the Li, Na, and K thiocyanates. It is striking that here the stability of the ion-pair dimer increases with the increasing size of the cation, i.e., in an order opposite to that we have observed in the association of alkali salts of MANA residues. Chabanel and Wang explain their results by pointing out that in the THF solution the ion pairs have to be largely desolvated to form the dimer, a process which becomes more difficult as the size of the cation is reduced. By contrast, our results with the salts of MANA copolymers were obtained in toluene solution where no solvation of ion pairs has to be considered and the stability of the ion-pair dimer should then increase with decreasing distance between the ion pairs, i.e., decreasing ion size.

I should like to propose a method by which data on the intermolecular interaction of groups attached to polymer chains can be interpreted in terms of the intermolecular interaction of low molecular weight analogs of these groups. Many years ago, Kuhn pointed out²⁹ that the probability distribution $F(h)$ (eq 1) for

$$F(h) dh = (2\pi h^2/3)^{-3/2} \exp(-3h^2/2\langle h^2 \rangle) 4\pi h^2 dh \quad (1)$$

the end-to-end displacement h of flexible chain molecules has $F(h) dh/4\pi h^2$ approach a limit as $h \rightarrow 0$, which may be viewed as the effective concentration c_{eff}° of one end of the chain end in the neighborhood of the other. Expressing c_{eff}° as a molarity,

$$c_{\text{eff}}^\circ = (1000/N)(3/2\pi\langle h^2 \rangle)^{3/2} \quad (2)$$

where N is Avogadro's number.

We have generalized this result to a chain with many interacting groups attached at random along the chain backbone. We used for the mean square displacement of groups separated by n backbone atoms $\langle h^2 \rangle_n = Cnb^2$ where b is the length of the bond between backbone atoms and C is Flory's "characteristic ratio"³⁰ characterizing the flexibility of the chain. Assuming that cyclic structures containing fewer than n' atoms have a negligible probability and neglecting chain end effects, we have then an effective concentration c_{eff}° of all interacting groups in the vicinity of one of them,

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$$c_{\text{eff}} = K \int_n^{\infty} n^{-3/2} dn = 2K(n')^{-1/2}$$

$$K = (1000/N)(3/2\pi Cb^2)^{3/2} p \quad (3)$$

where p is the probability that a given backbone atom carries one of the interacting groups. With this approach we estimated for a methacrylate copolymer with 2.2 mol % MANA $c_{\text{eff}} = 0.03$ M and equilibrium constants for the intermolecular dimerization of MANA salts in toluene solution of 0.7, 3.2, and 16 M⁻¹ with Cs⁺, Na⁺, and Li⁺ cations, respectively. In view of the various assumptions used in deriving these values, they may be only approximations, though their relative magnitudes should be more reliable. Since ion pairs such as MANA salts are too insoluble in nonsolvating media such as toluene to study their dimerization, the attachment of such residues to polymers, which allows them to be brought into solution, provides an indirect method to estimate the dimerization equilibrium.

Counterion Diffusion in Bulk Ionomers

To study the diffusion of counterions in a bulk ionomer, we attached films of alkyl methacrylate copolymers with a small porportion of APMS, partially neutralized with benzylamine (BA) or *N,N*-dimethylbenzylamine (DBA), to a pellet of a similar unneutralized copolymer carrying a fluorescence quencher.³¹ The assembly was heated above the glass transition temperature of the copolymer and periodically cooled to room temperature to measure by reflectance fluorescence the amount of base which had diffused from the film into the pellet. Similar experiments were carried out with the base incorporated into a poly(alkyl methacrylate) containing no sulfonic acid groups.

Since the bulkier DBA diffused in an ethyl methacrylate-APMS copolymer twice as fast as BA (although BA diffused somewhat faster in poly(ethyl methacrylate) carrying no sulfonic acid groups), it was concluded that the diffusion rate in the ionomer reflects the concentration of *free* counterions, i.e., the larger degree of ion-pair dissociation with the bulky cationic group. Assuming that the mobility of DBA is not significantly altered by protonation, we can then obtain the degree of ion-pair dissociation α from the ratio of diffusion coefficients in polymers with and without sulfonic acid groups.

Using this approach, we studied the degree of ion-pair dissociation as a function of temperature and the polarity of the medium. Figure 6 represents an Arrhenius plot of the diffusion coefficient D for DBA in a butyl methacrylate-APMS copolymer and in poly(butyl methacrylate). The plot for poly(butyl methacrylate) is curved, as expected, since the temperature dependence of diffusion coefficients in rubbery polymers is governed by the distance from the glass transition temperature as expressed by the WLF equation.³² Data such as those shown in Figure 6 were used to obtain the temperature dependence of the ion-

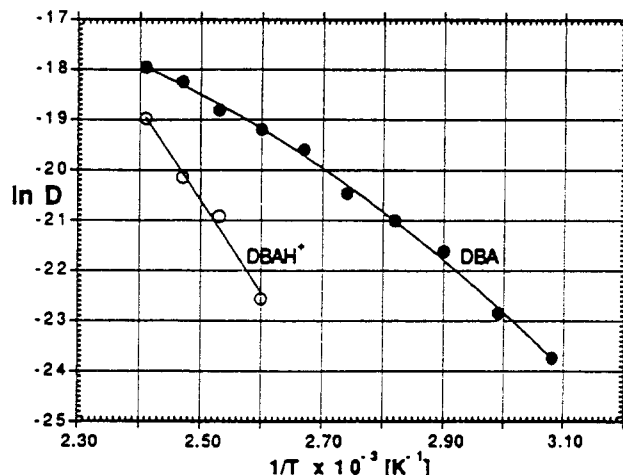


Figure 6. Diffusion coefficients of DBA in poly(butyl methacrylate) and DBAH⁺ counterions in BMA/APMS copolymer containing 2.5 mol % APMS neutralized 16%.

pair dissociation and the enthalpy ΔH_d of this process. This was found to decrease sharply with an increasing polarity of the medium. Diffusion coefficients of DBA in poly(butyl methacrylate), poly(ethyl methacrylate), a 1:1 copolymer of methyl acrylate and methyl methacrylate, and the corresponding copolymers with APMS yielded, in the temperature interval 120–140 °C, ΔH_d values of 101, 60, and 47 kJ/mol, respectively.

Conclusions

We have shown that fluorescence studies of ionomers may be used to clarify a number of properties of these interesting materials. This approach provided the first unambiguous proof that other than diffusion-controlled interpolymer reactions exhibit rate constants decreasing with an increasing length of the macromolecular chains. In this study it was crucial that we could study a process which did not lead to the formation of covalent bonds.

In studying counterion interchange and ion-pair dimerization in ionomer solution, we could take advantage of the fact that attachment of ion pairs to a polymer chain makes it possible to study their behavior in media in which they would otherwise not be sufficiently soluble for investigation. The results have, therefore, a significance beyond polymer chemistry, extending our understanding of the behavior of ion pairs. They provided, I believe, the first data on the kinetics with which ion pairs exchange their partners. They also allowed us to study, for the first time, the dimerization of a carboxylic acid salt as a function of the cation size in a medium where the process is not affected by cation solvation.

Finally, the study of counterion diffusion in bulk ionomers is of interest in view of the relation between cation diffusion and the electrical conductivity of solid polymer electrolytes, a class of materials of considerable technological interest.³³

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