Fluorescence Study of the Kinetics of Alkali Counterion Transfer from a Carboxylic Ionomer to a Polymer Carrying Sulfonic Acid Substituents

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ABSTRACT: Copolymers of butyl methacrylate (BMA) with 3-(methacryloylamino)-2-naphthoic acid (MANA) were neutralized with lithium methoxide, sodium methoxide, and cesium hydroxide. The counterion transfer from these copolymers to a BMA copolymer with [(2-(acryloylamino)prop-2-yl]methanesulfonic acid (APMS) was monitored by the fluorescence change in a stopped-flow apparatus in which solutions with equivalent concentrations of MANA and APMS residues were mixed. The half-life of this transport was 17 times smaller in dioxane than in toluene and increased with a decreasing size of the counterion. The apparent rate constant increased with the progress of the ion transfer, which was interpreted as due to a decreasing ion-pair dimerization. The half-life of the process decreased much more rapidly with an increasing concentration of the interacting copolymers than expected for second-order kinetics. Addition of poly(butyl methacrylate) had no significant effect on the rate of counterion transfer from BMA/MANA to the BMA/APMS copolymer.

Introduction

Ionomers, nonpolar polymers carrying a small number of ionized (usually acid) substituents and their counterions, have been extensively studied in recent years both in bulk and in solution.[1-3] When dissolved in nonpolar solvents, the polymer-bound ionic groups and their counterions are expected to form ion pairs with a very small dissociation constant.[4] In very dilute solutions ion pairs carried by the same chain tend to associate as evidenced by the lowered solution viscosity reflecting a chain contraction.[5,6]

In a previous study in this laboratory the kinetics of the counterion interchange between ionomer chains was explored.[7] For this purpose, solutions of slightly sulfonated polystyrene with (ammoniomethyl)naphthalene and (ammoniomethyl)anthracene counterions, respectively, were mixed in a stopped-flow apparatus with fluorescence detection. As long as the two kinds of fluorescent counterions were associated with different polymer chains, nonradiative energy transfer[8] from the excited naphthalene donor to the anthracene acceptor was very small, but it became increasingly efficient as the counterion interchange progressed so that the donor and acceptor came to lie close to each other in the same polymer domain. Thus, the progress of this process could be followed by irradiating the naphthalene donor and monitoring the increase in the emission intensity of the anthracene acceptor.

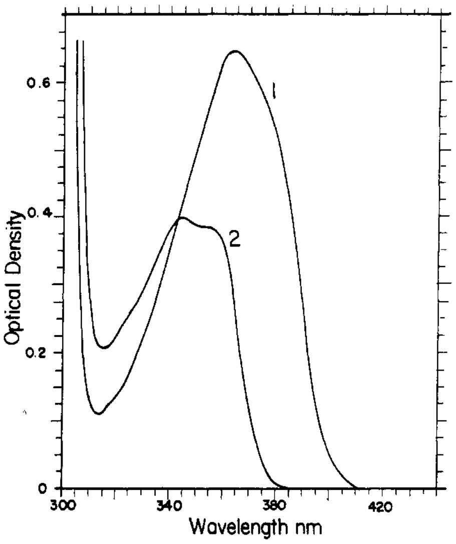
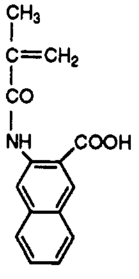
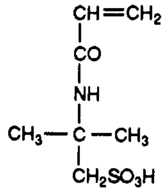


Figure 1. Absorption spectra of toluene solutions of 1.76 g/L BMA/MANA-2 (1) and its Na$^+$ salt (2).



MANA



APMS

Since most interest attaches to the behavior of ionomers with alkali counterions, we searched for a system where the alkali counterion interchange in an ionomer solution would be accompanied by a fluorescence change. We found that the absorption spectra of butyl methacrylate copolymers with 3-(methacryloylamino)-2-naphthoic acid (MANA) are blue-shifted when the carboxyl group is ionized (Figure 1), and we could, therefore, follow the transfer of alkali counterions from the MANA copolymer to a butyl methacrylate copolymer with [2-(acryloylamino)-prop-2-yl]methanesulfonic acid (APMS) by mixing solutions of the neutralized MANA copolymer with that of the APMS copolymer in a stopped-flow apparatus, irradiating at a wavelength where only the acid form of MANA absorbs and following the increase in the MANA emission intensity. In this report we present data of this process for different counterions at varying temperatures, different compositions of the MANA copolymers, and different concentrations of the interacting copolymers. We investigated also the effect of the addition

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Table 1. Polymer and Copolymers Used in This Study

	comonomer content (mol %)		
polymer desig	in feed	in copolymer	conv (%)
PMBA	0	0	93
BMA/MANA-0.1	0.1	0.09	70
BMA/MANA-2	2.5	3.34	77
BMA/MANA-4	5.0	4.0	88
BMA/APMS	7.2	1.95	67

of poly(butyl methacrylate) on the counterion exchange between the two copolymers.

Experimental Section

The purification of solvent and butyl methacrylate (BMS), the synthesis of MANA, the preparation of BMA copolymers with MANA, the spectroscopic determination of their composition, and their conversion into the lithium, sodium, and cesium salts have been described in a previous publication.[9] The APMS (Scientific Polymer Products, Ontario, NY) was used as received. Copolymerization of BMA and APMS was carried out in 2-propanol containing 10 vol % methanol and sufficient diisobutylamine to neutralize the APMS. The copolymer was precipitated into 25 vol % aqueous methanol containing 0.3 wt % HCl, and reprecipitated from dioxane into 25 vol % aqueous methanol. The composition of BMA/APMS was determined by titration of a dioxane solution of the copolymer with 0.1 M sodium methoxide in methanol to the phenolphthalein end point.

Static fluorescence spectra were recorded on a Perkin-Elmer LS 50B luminescence spectrometer at room temperature. The transfer of counterions from BMA/MANA to BMA/APMS was monitored by mixing solutions with an equivalent concentration of MANA and APMS residues in a DX 17MW stopped-flow spectrometer interfaced with an Archimedes 420/I computer purchased from Applied Photophysics, Leatherhead, England, irradiating at 380 nm (a wavelength at which only the acid from of MANA absorbs) and recording the emission intensity above 400 nm as a function of time.

Results

Table 1 lists the monomer compositions, the designation and composition of the copolymers, and the polymerization conversion of the materials used in this study. Since the copolymerization was carried to high conversion, the possible dispersion of the copolymer composition should be considered. The copolymerization of methyl methacrylate with methacrylamide is characterized by reactivity ratios of $r_1 = 1.5$ and $r_2 = 0.7$,[13] and a similar behavior might be expected for the copolymerization of BMA with MANA. Actually, the similarity of the monomer and copolymer compositions for BMA/MANA-0.1 and BMA/MANA-2 at conversions of 70 and 77%, respectively, suggests that the dispersion of the copolymer compositions was narrower than expected on that basis and without any appreciable effect on the kinetics of counterion transfer. As for the copolymerization of BMA with APMS, the copolymer contained only a very small fraction of APMS residues, and any dispersion of the copolymer composition would have been without influence on the reaction kinetics which are the subject of this study.

The kinetics of a second-order reaction involving equal concentrations of two reagents is represented by

$$(c^0/c) - 1 = k_2c^0t \qquad (1)$$

where c^0 and c are the reagent concentrations at $t = 0$ and at time t, with k_2 the second-order rate constant. In our case, where the fluorescence intensity I increases from 0 at $t = 0$ to I_∞ at the completion of the process, the decay of the concentration of counterions associated with MANA residues would be expected to be related to the fluorescence intensity by

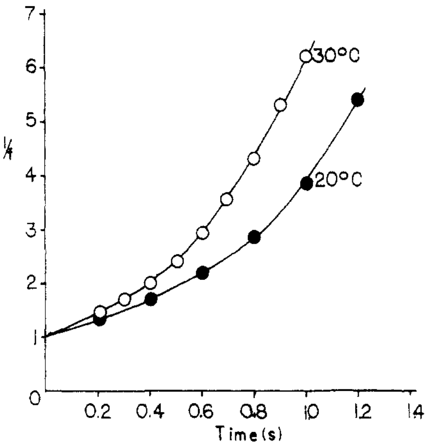

Figure 2. Kinetics of the Na$^+$ transfer from BMA/MANA-2 to BMA/AMPS ([MANA] = [AMPS] = 40 μM).

$$(I_\infty)/(I_\infty - I) - 1 = (1/f) - 1 = k_2c^0t \qquad (2)$$

where f is the fraction of counterions which remain associated with MANA at time t.

Typical runs in which Na$^+$ was transferred from BMA/MANA-2 to the BMA/APMS copolymer in toluene solution are plotted according to eq 2 in Figure 2. These plots exhibit an upward curvature indicating that the apparent rate constant increases with the extent of the counterion transfer.

Because of this anomaly, the various kinetic runs were characterized (Table 2) by two parameters, the half-life $t_{1/2}$ and the ratio $R = t_{3/4}/t_{1/4}$ of the times required for 3/4 and 1/4 of the counterion transfer from MANA to AMPS residues. For strict adherence to second-order kinetics $R = 9$, and the lower the values observed for this parameter, the more pronounced is the increase of the apparent rate constant as the process proceeds ($R > 9$ would be expected for a second-order reaction with a distribution of rate constants independent of conversion).

The following characteristics of the results should be noted: (a) The counterion transfer is much faster in dioxane, the more polar solvent, than in toluene. (b) The speed of the reaction increases with the size of the counterion. (c) The rate constant for the Na$^+$ transfer is a little slower with BMA/MANA-2 than with BMA/MANA-0.1, but it is reduced much more when the concentration of MANA residues is further increased in BMA/MANA-4. (d) The deviation from second-order kinetics, as characterized by the R parameter, is largest with the Li$^+$ counterion. When Na$^+$ is transferred from the copolymer containing only 0.09% MANA residues, R increases with the reaction temperature, reaching values close to those expected for a second-order process with a well-defined rate constant.

The temperature dependence of the half-time t_2 for the transfer of Li$^+$, Na$^+$, and Cs$^+$ from BMA/MANA-2 to BMA/APMS is illustrated in Figure 3. It corresponds to activation energies of 29, 23, and 40 kJ/mol, respectively. It is surprising that the transfer of Cs$^+$, which is fastest, should have the highest activation energy.

An unexpected result was obtained when following the Na$^+$ transfer from BMA/MANA to BMA/APMS using a stoichiometric equivalence of MANA and APMS residues and varying their concentration from $c = 10$ μM to $c = 80$ μM. Instead of a half-life for the process inversely proportional to the reagent concentration, as expected for

Table 2. Kinetic Data for the Counterion Transfer from BMA/MANA to BMA/AMPS Copolymers[a]

solvent	copolymer	counterion	temp (°C) 20	25	30	35	40
dioxane	BMA/MANA-2	Na$^+$	0.025				
toluene	BMA/MANA-0.1	Na$^+$	0.42 (6.7)	0.25 (8.4)	0.27 (9.1)	0.31 (10.3)	0.23 (11.3)
toluene	BMA/MANA-2	Na$^+$	0.53 (5.0)	0.46 (4.6)	0.39 (5.1)	0.34 (5.3)	
toluene	BMA/MANA-2	Li$^+$	0.78 (3.4)	0.48 (3.9)	0.64 (3.4)	0.45 (2.9)	0.31 (3.4)
toluene	BMA/MANA-2	Cs$^+$	0.14 (6.5)	0.16 (6.2)	0.090 (6.1)	0.070 (5.5)	0.057 (6.3)
toluene	BMA/MANA-4	Na$^+$	1.00 (3.1)	0.75 (3.2)	0.60 (6.1)	0.53 (6.7)	0.41 (7.2)

[a] Half-lives in seconds, R values in parentheses; concentration of MANA residues 40 μM.

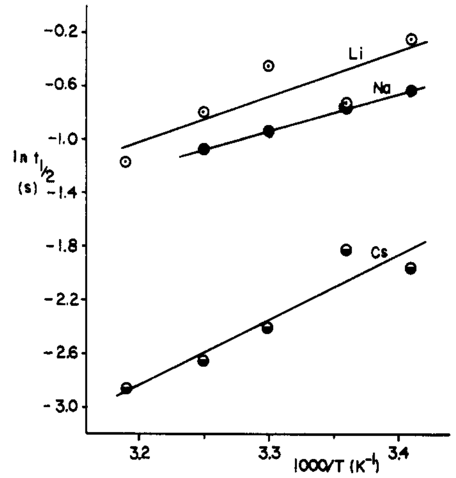

Figure 3. Temperature dependence of the half-life for the transfer of counterions from BMA/MANA-2 to BMA/APMS ([MANA] = [APMS] = 40 μM).

second-order kinetics, we found a much steeper dependence on the concentration of the interacting species (Figure 4) with $t_{1/2}$ decreasing by a factor of 44 as the reagent concentration was increased eightfold. At the same time, the increase in the apparent rate constant during the progress of the counterion transfer became more prominent, with $t_{3/4}/t_{1/2}$ decreasing gradually from 7.3 for c = 10 μM to 5.2 for c = 80 μM.

We investigated also the effect of additions of poly(butyl methacrylate) (PBMA) on the rate of Na$^+$ transfer from BMA/MANA-2 to BMA/AMPS. The results are listed in Table 3. The rate of the process changed little on addition of the homopolymer.

Discussion

The most striking feature of the kinetic data in Table 2 is the much higher rate of counterion transfer from MANA to APMS residues when the solvent is changed from toluene to the more highly solvating dioxane and the increase of this rate as the radius of the alkali ion is increased. Both these features are to be expected since an increase in the anion–cation spacing and a more strongly solvating medium should destabilize the ion pairs.

In our preceding study of the fluorescence of BMA/MANA copolymers,[9] we found that emission bands at 405–415 nm and at 490–500 nm were due to associated and unassociated ion pairs, respectively. In toluene solutions of BMA/MANA-0.1 with either Na$^+$ or Li$^+$ counterions, only unassociated ion pairs were observed, whereas the degree of ion-pair association in salts of BMA/MANA-2 exhibited a striking dependence on the nature of the counterion: With Li$^+$ almost all ion pairs were associated, with Cs$^+$ almost all ion pairs were unassociated, and with Na$^+$ there were about equal concentrations of associated and unassociated ion pairs. We should emphasize that these results were obtained well below the critical overlap concentration c^* of the ionomers. If we use I/[η] as a rough measure of c^*,[10] we obtain for these salts of BMA/MANA-2 values of c^* in the range of 1.9–2.2 g/dL, while the BMA/MANA-2 concentration at which fluorescence was recorded was only 0.08 g/dL. Thus, the ion-pair association inferred from the emission spectra was due to the interaction of ion pairs appended to the same polymer chain. Similarly, BMA/MANA-2 with a counterion concentration of 4×10^{-5} M used in experiments on the kinetics of counterion transfer corresponded to a polymer concentration of 0.054 g/dL, again far below c^*.

The question then arises whether rates of counterion transfer from MANA to AMPS residues reflect in any way the influence of ion-pair association. This question can best be addressed by considering the kinetics of the Na$^+$ counterion exchange from: BMA/MANA-2, in which the concentration of associated and unassociated ion pairs is similar. If these two species had lifetimes long compared to the counterion transfer experiment and if they were

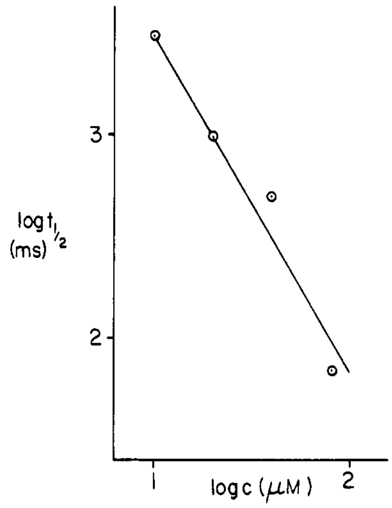

Figure 4. Dependence of the half-life for the Na$^+$ transfer from BMA/MANA-2 to BMA/APMS on the Na$^+$ concentration.

Table 3. Effect of the Addition of PBMA on the Kinetics of Na$^+$ Transfer from BMA/MANA-2 to BMA/AMPS in Toluene Solution at 20 °C ([Na$^+$] = 40 μM)

PMBA concn (g/dL)	half-life (s)	R
0	0.48	5.4
0.5	0.56	5.3
1.0	0.45	5.1
1.5	0.40	6.1
2.0	0.31	5.8

characterized by substantially different transfer rate constants, the kinetics should reflect a dispersion of the k_2 constants with the parameter $R > 9$. This is not observed. On the other hand, if the intramolecular exchange between associated and unassociated ion pairs is much faster than the counterion transfer from MANA to AMPS residues, a weighted average of the k_2 characterizing the two species should be observed at any one time. If we then assume that the counterion transfer is slower from associated ion pairs, the observed increase in the apparent rate constant during the progress of the counterion transfer can be tentatively interpreted as due to the gradual decrease of the fraction of associated MANA ion pairs. This interpretation is supported by two features of the results: (a) The half-life of the Na^+ transfer at constant Na^+ concentration increases with the density of MANA residues in the BMA/MANA copolymers. (b) The values of the R parameter are largest with the Cs^+ counterion (where ion-pair association is least) and smallest with Li^+ (where ion-pair association is most pronounced). On the other hand, in the case of the Na^+ salt of BA/MANA-0.1, where the fluorescence spectrum indicates no ion-pair association, conventional second-order kinetics of the counterion transfer are approached ($R \rightarrow 9$) only as the temperature is gradually raised from 20 to 40 °C.

The anomalously rapid increase in the rate of counterion transfer from the MANA to the APMS residues as the concentration of the interacting copolymers is increased may be related to the observation of Lantman et al.[11] (based on neutron scattering) that ionomers associate to some extent even in solutions below the critical overlap concentration. At any rate, this is an effect for which we know of no precedent.

The failure of the interaction of the two copolymers to be slowed down by the presence of the butyl methacrylate homopolymer seemed at first surprising. However, it is but another demonstration of the principle, first explained by Flory,[12] that interpolymer reactions characterized by substantial activation energies have rate constants independent of polymer mobility, since a reduced mobility will reduce equally the diffusion of interacting functions toward and away from each other.

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