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An Ionomer with a Fluorescence Sensitivity to the Nature of the Counterion and the Degree of Ion-Pair Association

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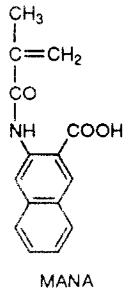
ABSTRACT: Butyl methacrylate copolymers with 3-(methacryloylamino)-2-naphthoic acid (MANA) carrying alkali counterions exhibit in highly dilute dioxane or toluene solution two emission bands, one (α) with a maximum at 405–415 nm, the other (β) with a maximum at 490–500 nm. In copolymers containing 2.23% MANA residues the β emission is very weak with Li^+ counterions, and the α emission is very weak with Cs^+ counterions, whereas the ionomer with Na^+ counterions has similar emission intensities in the α and β bands. Varying the MANA content of the copolymers with Na^+ counterions increases the relative intensity of the α emission with an increasing density of MANA residues in the ionomer chain, and in chains containing only 0.1% MANA residues only the β emission is seen. This suggests that the α emission is due to associated and the β emission to unassociated ion pairs. This interpretation is supported by solution viscosity data, where an increasing viscosity with a counterion change in the order $Cs^+ < Na^+ < Li^+$ is the same as the order of increasing intensity of the α emission. Addition of methanol to the toluene solution of the copolymer with Na^+ counterions reduces both the α and β emission with little change in their relative intensities, whereas a solution of this copolymer with Na^+ or Li^+ counterions in dioxane, 1,2-dimethoxyethane, or 2-propanol reduces the ratio of the α to the β emission intensities.

Introduction

Ionomers are nonpolar polymers carrying on a small portion of their monomer residues (typically 2–6%) ionizable (usually acidic) substituents which have been neutralized. In bulk ionomers and in ionomer solutions in nonpolar solvents the polymer-bound anions and their counterions form stable ion pairs which tend to associate with each other. This leads to characteristic phenomena which have been the subject of several reviews.[1-3]

Previous reports from this laboratory dealt with initial studies of the kinetics of counterion transfer between ionomer chains in dilute solution[4] and in bulk.[5] In these studies fluorescent organic counterions were employed. However, since the main interest of ionomer investigations concerns systems containing alkali cations, we searched for a system in which the transfer of the alkali counterion from a carboxylic ionomer to an ionomer carrying more acidic substituents could be monitored by a change of fluorescence. We found that the absorption of copolymers of 3-(methacryloylamino)-2-naphthoic acid (MANA) with butyl methacrylate is blue-shifted when the carboxyl is neutralized, and we could, therefore, follow the transfer of the counterions to a polymer carrying sulfonic acid groups by the increasing fluorescence when exciting at a wavelength at which only the acidic form of the MANA residues absorbed.[6] In the course of this study we discovered that the neutralized MANA copolymer exhibits a most unusual fluorescence behavior, which is the subject of this report.



MANA

Experimental Section

Solvents. Toluene (Fisher Scientific) was dried by boiling over sodium for 24 h and distilled. Dioxane (Fisher Scientific) was refluxed with $NaBH_4$, then refluxed over sodium for 48 h, and distilled under nitrogen. 1,2-Dimethoxyethane (DME) (Aldrich, HPLC grade) was refluxed with CaH_2 and distilled.

Monomers. Butyl methacrylate was vacuum distilled. 3-(Methacryloylamino)-2-naphthoic acid (MANA) was obtained by Schotten-Baumann acylation of 3-amino-2-naphthoic acid (Fluka) with methacryloyl chloride. After acidification the crude product was filtered off, dissolved in methanol, treated with activated charcoal, and recrystallized twice from methanol. Anal. Calc for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.36; H, 5.14; N, 5.37. Mp: 219–220 °C. Molar extinction coefficient in dioxane: 2560 L·mol^{-1}·cm^{-1} at 354 nm.

Polymerization. Free radical initiated copolymerization of butyl methacrylate and MANA was carried out in 30% dioxane solution using 0.2 wt % AIBN at 60 °C. The composition of the copolymers was obtained from the absorption of dioxane solutions using the extinction coefficient for the monomer in the same solvent. Table I lists the monomer and polymer compositions and the conversion. The intrinsic viscosity of the butyl methacrylate homopolymer was 0.42 dL/g in butanone at 23 °C, corresponding to M_v = 290 000,[10] and a similar chain length was assumed for the copolymers prepared under the same conditions.

Samples for fluorescence measurements were prepared as follows: A weighed amount of MANA was dissolved in methanol and titrated with $LiOCH_3$, $NaOCH_3$, or CsOH to the phenolphthalein end point. A MANA solution was then neutralized with the same proportion of the base (in the absence of

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Table I. Preparation of Butyl Methacrylate Polymer and MANA Copolymers

polymer designation	MANA mol % in feed	MANA mol % in copolymer	% conversion
PBMA	0	0	92.7
BMA/MANA-0.1	0.10	0.090	70.5
BMA/MANA-0.5	0.50	0.44	71.5
BMA/MANA-2	2.50	2.23	76.8
BMA/MANA-4	5.00	4.00	88.0
BMA/MANA-6	7.50	6.10	87.0

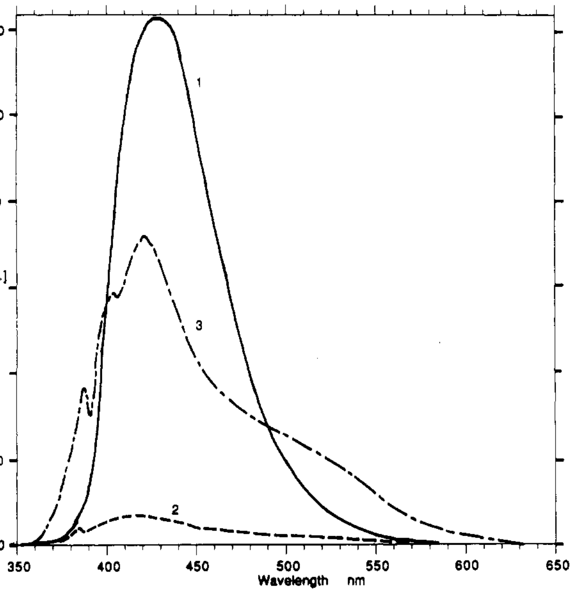

Figure 1. Emission spectra of MANA monomer (1) and its Cs^+ salt (2) in dioxane. Spectrum 3 corresponds to (2) magnified 10×.

phenolphthalein) and crystallized. The amount of base required for the neutralization of MANA copolymers was determined by titrating aliquots of the copolymer in dioxane solution either to the phenolphthalein end point or (in the case of BMA/MANA-0.5 and BMA/MANA-0.1) by the sharp break in the plot of the absorption at 362 nm against the amount of titrant added. Solutions of neutralized copolymers were film cast on a Teflon sheet and dried for 24 h at ambient temperature and for 48 h under vacuum at 60 °C.

Static fluorescence spectra were recorded on a Perkin-Elmer luminescence spectrometer LS 50B at room temperature using solutions with an optical density of 0.19 and excitation at 344 nm. Fluorescence lifetimes were measured using Edinburgh Analytical Instruments FL 900CDT in the T-format method with excitation at 344 nm.

Results

Although the MANA monomer fluoresces strongly, the emission is almost completely quenched when the carboxyl group is neutralized (Figure 1).[7] Yet, the butyl methacrylate copolymer containing 2.23% of MANA residues (BMA/MANA-2) fluoresces strongly when the carboxyl groups are neutralized. This in itself would not be surprising, since it has been known for a long time that the restricted mobility in a polymer domain may lead to a greatly enhanced fluorescence quantum yield of fluorophores subject to internal quenching in fluid media.[8] However, the observation which seems to be unprecedented is the nature of the dependence of the emission spectrum on the counterion. Figure 2 shows the emission spectra of BMA/MANA-2 solutions in toluene at a concentration of 0.80 g/L with Li^+, Na^+, and Cs^+ counterions. They have two emission bands with maxima at 405–415 nm and 490–500 nm, respectively (to be referred to below as the α and β bands), but the *relative intensities of the two bands change dramatically as the counterion is changed.* Whereas both emission maxima may be observed with Na^+ counterions, with the Li^+ counterion the β emission is merely a shoulder and with the Cs^+ counterion only a shoulder is seen for the α emission. It should be noted that the absorption spectrum of the neutralized BMA/MANA-2 is the same for all three counterions (Figure 3) and that excitation spectra for both the α and β emissions (at 400 nm and 491 nm, respectively) match the absorption spectrum.

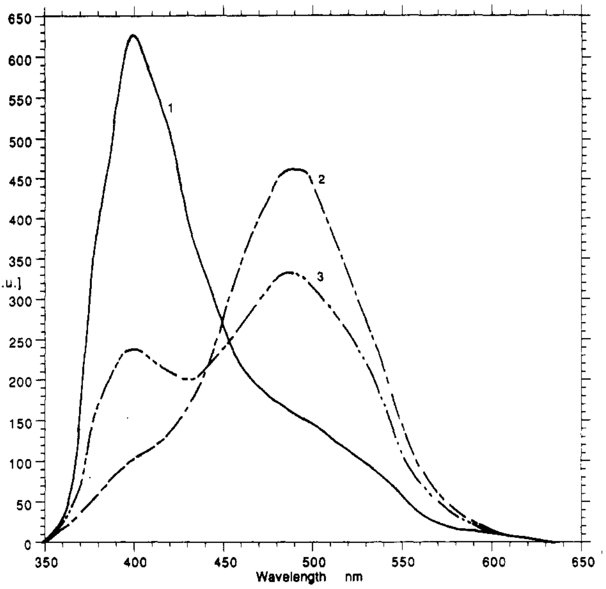

Figure 2. Emission spectra of BMA/MANA-2 in toluene solution with (1) Li^+, (2) Cs^+, and (3) Na^+ counterions.

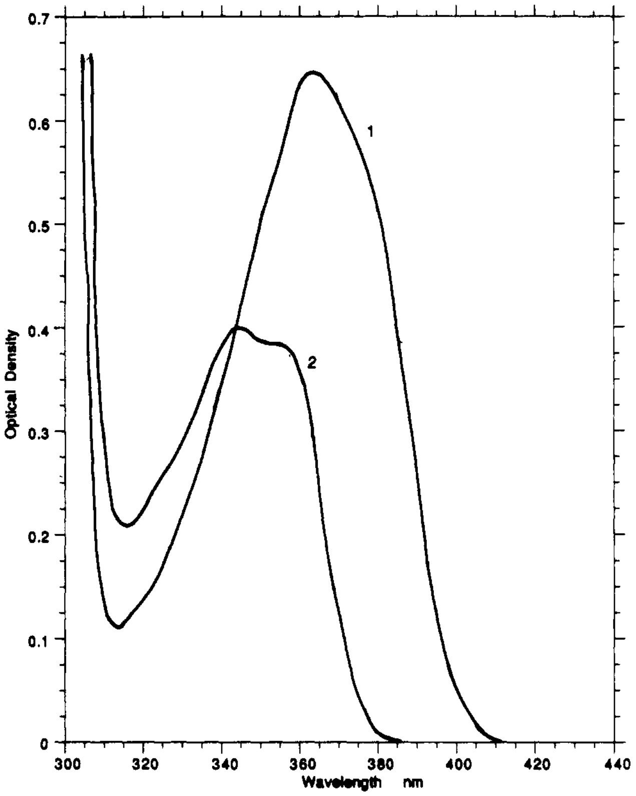

Figure 3. Absorption spectra of toluene solutions of BMA/MANA-2 (1.76 g/L) (1) and of its Na^+ salt (2).

All fluorescence decays, in both the α and the β emission band, followed closely biphasic kinetics,

$$I = I_0[A_1 \exp(-t/\tau_1) + (1 - A_1) \exp(-t/\tau_2)] \qquad (1)$$

Table II. Fluorescence Lifetimes of BMA/MANA-2 with Different Counterions in Toluene Solution at 25 °C

	α-emission				β-emission			
counterion	λ_{em} (nm)	A_1	τ_1 (ns)	τ_2 (ns)	λ_{em} (nm)	A_1	τ_1 (ns)	τ_2 (ns)
Li^+	400	0.34	2.7	6.1	520	0.65	4.0	6.7
Na^+	380	0.29	2.7	6.4	500	0.62	5.1	7.8
Cs^+	390	0.33	2.9	6.5	500	0.50	4.4	7.4

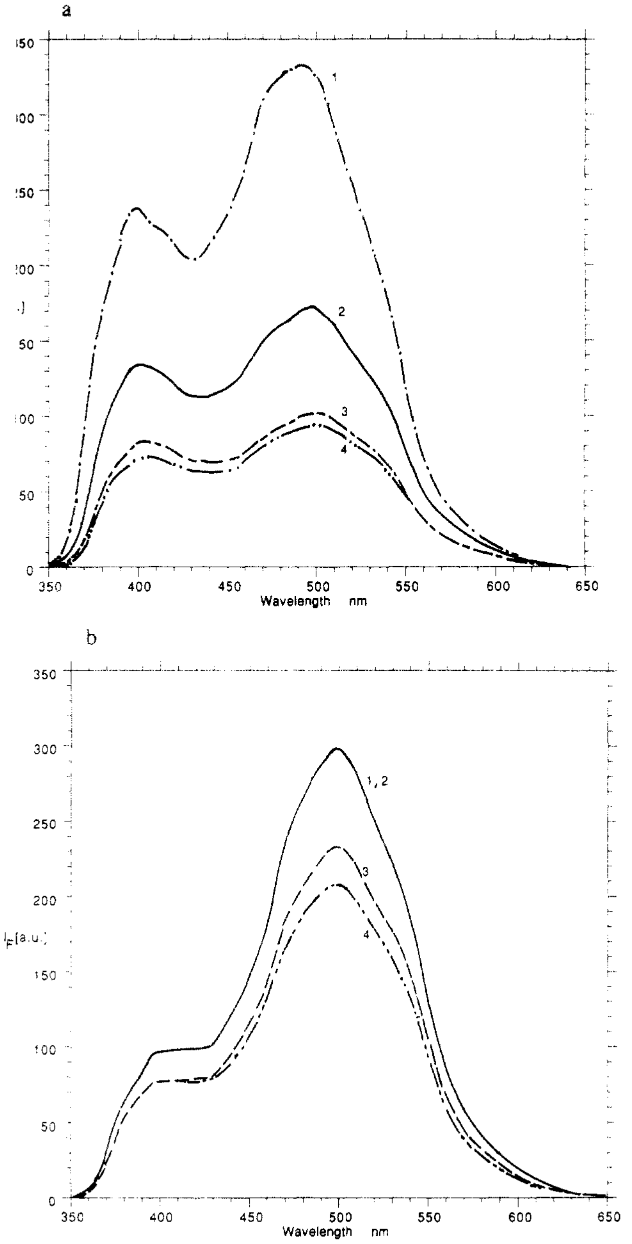

Figure 4. Effect of methanol addition on fluorescence of BMA/MANA-2 sodium salt in toluene (a) and dioxane (b) solution. Volume % methanol: (1) 0; (2) 1; (3) 5; (4) 8.

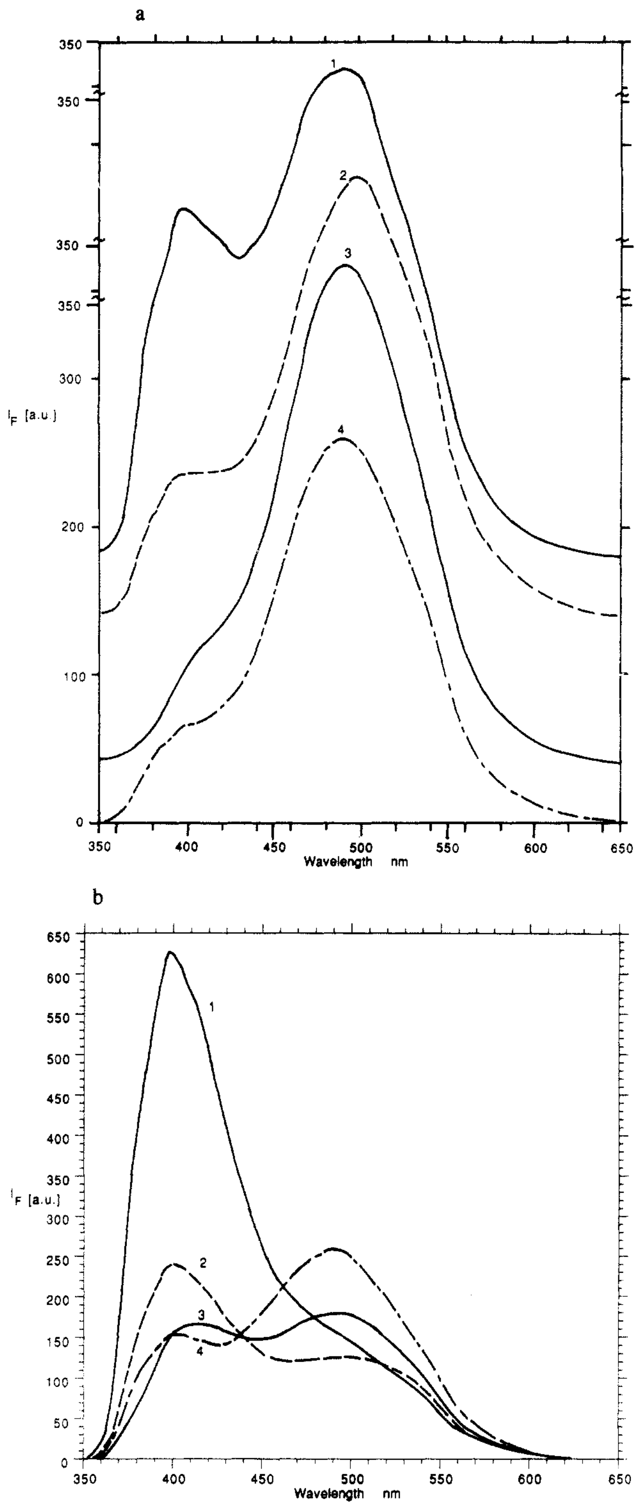

Figure 5. Dependence of the emission spectrum of the Na^+ (a) and Li^+ (b) salt of BMA/MANA-2 on the solvent: (1) toluene; (2) dioxane; (3) DME; (4) 2-propanol.

and the results for the Li^+, Na^+, and Cs^+ salts of BMA/MANA-2 are summarized in Table II.

Addition of methanol to the ionomer solutions, to solvate the ion pairs and reduce their stability, resulted in a reduced fluorescence intensity with no significant change in the ratio of the α and β emissions. This effect is much more pronounced for toluene solutions, where an addition of 2 vol % methanol reduced the fluorescence by 61%, whereas a similar addition of methanol to a dioxane solution reduced the emission intensity by only 15% (Figure 4). This is not surprising, since dioxane, a hydrogen bond acceptor, competes with the ion pairs in binding methanol. On the other hand, as the solvent medium is changed from toluene to the more strongly solvating dioxane, 1,2-dimethoxyethane (DME), and 2-propanol, the ratio of the α to the β emission intensities diminishes for BMA/MANA-2 with both the Na^+ and Li^+ counterions (Figure 5).

The nature of the two emission bands was clarified by spectra of butyl methacrylate copolymers with various MANA contents. As seen in Figure 6, in spectra recorded for solutions with a constant MANA-Na^+ concentration, the α emission becomes weaker with a diminishing MANA content of the copolymer. It disappears completely in BMA/MANA-0.1 which carries on the

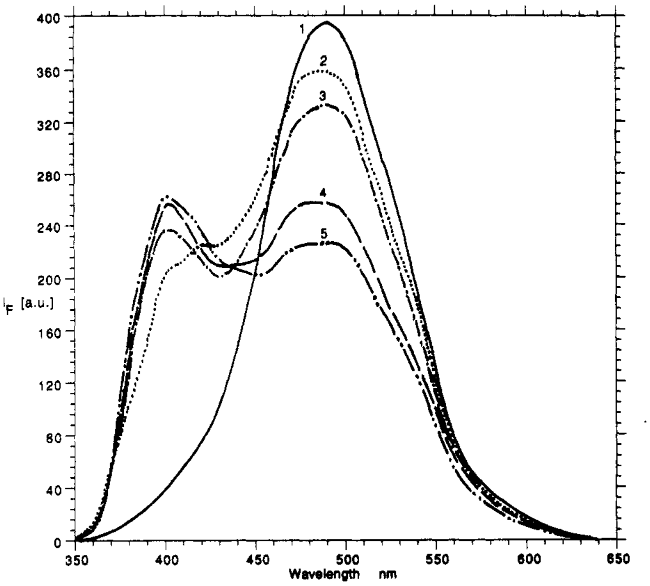

Figure 6. Fluorescence spectra of Na^+ salts of (1) BMA/MANA-0.1, (2) BMA/MANA-0.5, (3) BMA/MANA-2, (4) BMA/MANA-4, and (5) BMA/MANA-6 in toluene solution.

average only one ion pair for 1100 monomer residues. This proves that the α emission is related to an intramolecular interaction of ion pairs.

Discussion

The association of polymer-bound ion pairs when ionomers are dissolved in nonpolar solvents was first described by Lundberg and his collaborators.[9] They showed that this phenomenon leads to a decreased viscosity due to a shrinkage of the ionomer chains in highly dilute solution where the association involves mostly ion pairs carried by the same macromolecule, while at higher concentrations, with ion pairs of different chains associating, a large viscosity increase is seen. More recently, Bakeev and MacKnight[11] used 1,3,6,8-pyrenetetrasulfonic acid tetrasodium salt as a probe to study ion-pair associations in slightly sulfonated polystyrene with Na^+ and Zn^{2+} counterions in tetrahydrofuran, arguing that the excimer emission of the probe "can be considered to result from a solubilization and concentration of the probe inside a spacially restricted polar medium composed of aggregates of ionomer salt groups". While this approach demonstrates differences in ion-pair association under different conditions, the authors did not claim to deduce from their data a quantitative measure of the extent of such association.

By contrast, we believe that in our system the α and β emissions are proportional to the concentration of associated and unassociated ion pairs, respectively. This conclusion is supported by several lines of evidence: (a) In the ionomer with Na^+ counterions the β emission

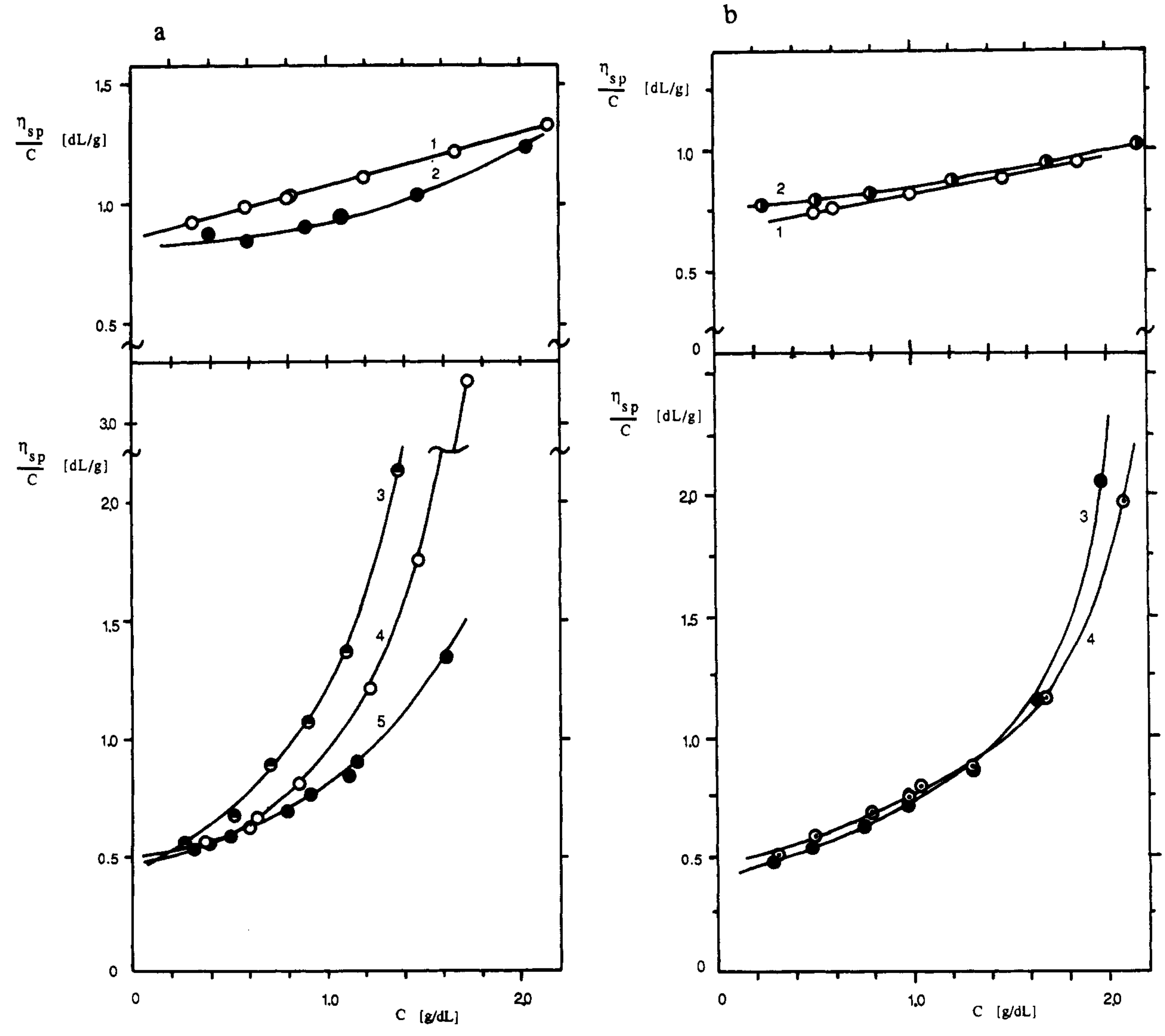

Figure 7. Solution viscosities in (a) toluene and (b) dioxane at 25 °C of (1) PBMA, (2) BMA/MANA-2, and BMA/MANA-2 with (3) Li^+, (4) Na^+, and (5) Cs^+ counterions.

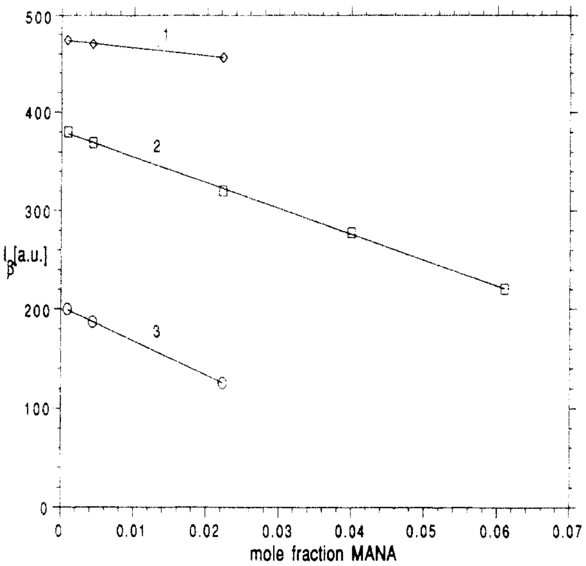

Figure 8. Dependence of the β emission intensity of MANA residues (1.28×10^{-4} M) in toluene solution on the composition of the BMA/MANA copolymer. Excitation at 344 nm. (1) Cs^+, (2) Na^+, (3) Li^+ counterions.

increases and the α emission decreases with a diminishing MANA content in the copolymer and the emission disappears when this content is very low. (b) Whereas α and β intensities of BMA/MANA-2 with Na^+ counterions are similar in toluene solution, the α emission is much weaker in dioxane and almost disappears in DME and 2-propanol, reflecting the smaller tendency of ion pairs to associate in a more polar medium. (c) The intensity of the α band increases with the counterion in the order $Cs^+ < Na^+ < Li^+$, the same order in which the solution viscosity increases, reflecting ion-pair association (Figure 7).

We should emphasize that our assignment of the α emission band, seen at shorter wavelengths, to associated ion pairs, implies that this association does not result in excimer formation. In view of the severe steric restraints involved in the approach of two MANA residues to each other, it is hardly surprising that the ion-pair association does not lead to the exactly defined overlap of the naphthalene chromophores required for excimer fluorescence.

The data listed in Table II show that the slower component of the biphasic fluorescence decay has a similar lifetime for the α and β emissions of BMA/MANA-2 with all three counterions. The intensity of the β emission of BMA/MANA copolymers, measured in toluene solutions with a constant concentration of MANA residues, decreased linearly with the mole fraction x of MANA residues in the copolymer (Figure 8), reflecting the increasing association of ion pairs. Denoting by I_β the β emission intensity of a given copolymer and by $I_\beta°$ its value extrapolated to $x = 0$, we may estimate the dependence of the fraction f of associated ion pairs on the copolymer composition from $1 - f = I_\beta/I_\beta°$. The data represented in Figure 8 lead then to $f = 1.7x$ for Cs^+, $f = 6.7x$ for Na^+, and $f = 17x$ for Li^+, demonstrating the increasing tendency of the ion pairs to associate as the size of the counterion decreases. Figure 8 also shows that the fluorescence intensity of the unassociated ion pairs decreases with decreasing counterion size.

An interesting feature of the results is the difference between the effect produced on the fluorescence when the ion pairs are solvated by either adding methanol to the toluene solution of the Na^+ salt of BMA/MANA-2 or by using as solvents the more polar dioxane, DME, and 2-propanol. In the first case both α and β emissions were reduced with little change in the ratio of their intensities, whereas in the second case the ratio of the α to the β fluorescence intensity decreased sharply as the polarity of the solvent was increased. This suggests that methanol partially dissociates the ion pair, whereas dioxane, DME, and 2-propanol bind to it, leaving it intact but inhibiting its association with other ion pairs.

Concluding Remarks

Absorption and emission spectra of ion pairs have been studied for many years, largely with the use of fluorenyl salts. The main emphasis in these investigations was on the distinction between contact and solvent-separated ion pairs which can be characterized by different absorption[12,13] and emission spectra.[14,15] In one study[16] the absorption spectrum of [9-(2-hexyl)fluorenyl]lithium in cyclohexane and other hydrocarbons was found to exhibit a maximum at 368 nm, intermediate between 357 nm observed for contact ion pairs in diethyl ether and 387 nm for solvent-separated ion pairs in THF, and since ebullioscopy indicated a stronger dimerization in cyclohexane than in THF, the spectral shift was interpreted, not too convincingly, as due to ion-pair dimerization.

Only a few studies of spectral properties of ion pairs carried by polymers have been reported. Two reports[17,18] deal with the spectral change accompanying the conversion of poly(2-vinylfluorene) to its alkali-metal salts, interpreting the data as reflecting a gradual change in the equilibrium between loose and tight ion pairs as the degree of metalation is increased. A third paper, most closely resembling our study, dealt with styrene copolymers with (2-vinylfluorenyl)sodium.[19] The authors of this study found that neither the absorption nor the emission spectra of the fluorenylsodium moiety changed with the copolymer composition. However, whereas a copolymer containing only 2 mol % of vinylfluorene residues exhibited monoexponential decay with a lifetime of 34 ns, the appearance of a more rapidly decaying component ($\tau = 2.9 \pm 0.3$ ns) in copolymers with a higher fluorenylsodium content was interpreted as due to ion-pair aggregation.

In comparison of our results with these other reports on the spectral properties of ion pairs, some striking differences may be noted: (a) Our absorption spectra were independent of the counterion and the solvent. (b) Our emission spectra exhibited distinct bands for associated and unassociated ion pairs, but the location of these bands did not change significantly with the counterion or the solvent. (c) We did not observe the drastic reduction of lifetime accompanying ion-pair association which seems to be characteristic of fluorenyl salts.[15,19] It is reasonable to ascribe these diffeences between the behavior of fluorenyl salts and salts of MANA residues to the much less intimate contact of the cation with the naphthoic acid chromophore.

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References and Notes

(1) MacKnight, W. R.; Earnest, T., Jr. *J. Polym. Sci., Macromol. Rev.* **1981**, *16*, 41.

(2) Eisenberg, A., Bailey, F. E., Eds. *Coulumbic Interaction in Macromolecular Systems*; ACS Symposium Series 302; American Chemical Society: Washington, DC, 1986.

(3) Pineri, M., Eisenberg, A., Eds., *Structure and Properties of Ionomers*; NATO Advanced Study Institute Series 198; D. Reidel: Dordrecht, Holland, 1987.

(4) Morawetz, H.; Wang, Y., *Macromolecules* **1988**, *21*, 107.

(5) Vyprachticky, D.; Morawetz, H.; Fainzilberg, V. *Macromolecules* **1993**, *26*, 339.

(6) Mikeš, F.; Morawetz, H.; Bednář, B. Manuscript in preparation.

(7) The same behavior is exhibited by the saturated analog of MANA, 3-(acetylamino)-2-naphthoic acid.

(8) Oster, G. *J. Polym. Sci.* **1955**, *16*, 235. Oster, G., Nishijima, Y. *J. Am. Chem. Soc.* **1956**, *78*, 1481.

(9) Lundberg, R. D.; Makowski, H. S. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1821. Lundberg, R. D.; Phillips, R. R. Ibid. **1982**, *20*, 1142.

(10) Chinai, S. N.; Guzzi, R. A. *J. Polym. Sci.* **1956**, *21*, 417.

(11) Bakeev, K. N.; MacKnight, W. J. *Macromolecules* **1991**, *24*, 4578.

(12) Hogen-Esch, T. E.; Smid, J. *J. Am. Chem. Soc.* **1966**, *88*, 307.

(13) Smid, J. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 112.

(14) Plodinec, M. J.; Hogen-Esch, T. E. *J. Am. Chem. Soc.* **1974**, *96*, 5262 and studies cited therein.

(15) Hogen-Esch, T. E.; Plodinec, J. *J. Am. Chem. Soc.* **1978**, *100*, 7633.

(16) Exner, M. M.; Waack, R.; Steiner, E. C. *J. Am. Chem. Soc.* **1973**, *95*, 7009. See also: Takaki, Collins, and Smid *J. Organomet. Chem.* **1978**, *145*, 139.

(17) Wong, K. H.; Ambroz, L.; Smid, J. *Polym. Bull.* **1982**, *8*, 411.

(18) Watanabe, A.; Matsuda, M. *Br. Polym. J.* **1986**, *18*, 376.

(19) Wong, K. H.; Cho, K. C.; Ng, H. C.; Chan, C. K.; Choy, C. L. *Polym. Bull.* **1987**, *17*, 375.