Fluorescence Probes for the Evaluation of Diffusion of Ionic Reagents through Network Polymers. Chemical Quenching of the Fluorescence Emission of the Dansyl Probe in Macroporous Styrene–Divinylbenzene and Styrene–Diisopropenylbenzene Copolymers

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ABSTRACT: Dansyl probe 1 reacts with strong protic acids and electrophiles such as $Et_3O^+BF_4^-$ and $Ph_3C^+BF_4^-$. The site of attack has been determined to be at the dimethylamino nitrogen. These reactions convert the fluorescent dansyl probe to a nonfluorescent specie. The reaction is in equilibrium, and the position of equilibrium is dependent upon medium effects. The dansyl probe has been covalently incorporated into a variety of polymeric networks. When suspensions of polymer particles are treated with an excess of electrophile, the fluorescence intensity diminishes with a characteristic intensity–time profile. Factors that contribute to the quenching rate are diffusion of electrophile into the polymer particle and the equilibrium between probe and electrophile. Within a related series of materials, the final position of equilibrium and the rate of approach to equilibrium are a useful diagnostic to compare the gel-phase penetrability. These studies have revealed the influence of cross-linking, macroporosity, and the nature of the porogen on the facility with which electrophilic reagents penetrate the gel phase of complex amorphous network materials. The diffusion-quenching results are entirely consistent with earlier solvatochromic shift results, which reveal solvent penetrability of the gel phase *and* the facility with which ketal groups, covalently incorporated into the gel phase, are hydrolyzed.

Introduction

The diffusion of ionic reagents in network materials is a process of considerable fundamental and practical importance.[1] We have recently reported that an analysis of the solvatochromic shift of the fluorescence emission of dansyl probe **1a**, covalently incorporated into network polymers, permits a qualitative comparison of solvent penetrability of the gel phase of complex amorphous materials.[2,3] In the present study, we show that the fluorescence emission intensity of this same dansyl probe may also be used to evaluate the ability of ionic reagents to penetrate the gel phase of network polymers.[4] The analysis is based upon the reaction of electrophilic reagents with the dansyl probe to produce chemically modified species that are nonfluorescent.

Experimental Section

Probe and Polymer Synthesis. Detailed procedures for the synthesis of dansyl probes **1a** and **1b**, doped linear polystyrene, and gel and macroporous styrene–divinylbenzene and styrene–diisopropenylbenzene copolymers are reported in an earlier paper.[2] The formulation of each polymer and the identifying descriptor are given in Tables I and II.

Determination of the Site of Protonation of Probe 2 upon Quenching with Trifluoroacetic Acid. Into an NMR tube (5 mm × 7 in.) was placed 10.0 mg (29.3 μmol) of **1b** and 0.50 mL of $CDCl_3$. Trifluoroacetic acid (15 μL, 195 μmol) was added to extinguish the fluorescence emission to less than 1% of its original intensity. ^1H and ^{13}C NMR spectra were then recorded at 300 MHz on a GE QE 300 NMR spectrometer. For comparison, identical experiments were carried out with *N,N*-dimethylaniline (**3**). ^1H assignments of **1b** were made by a combination of decoupling experiments and comparison with data on related compounds[5] and by correlation with spectra in benzene-d_6. The chemical shift differences observed upon protonation are recorded in Figure 1.

Fluorescence-Quenching Studies. Triphenylcarbenium tetrafluoroborate ($Ph_3C^+BF_4^-$) was obtained from Aldrich and used without further purification. Triethyloxonium tetrafluoroborate was prepared according to a literature procedure.[6] Stock solutions of these electrophiles were prepared in a glovebox to a concentration of 0.020 M in CH_2Cl_2. A typical fluorescence-quenching experiment is described below.

Into a glass fluorescence cuvette (10 mm × 10 mm × 4 cm) equipped with a small stir bar was placed approximately 26 mg of polymer (2.0×10^{-8} mol of probe) and 2.0 mL of CH_2Cl_2–hexane (13:4 v/v). The cuvette was placed on a small stirrer in a Hitachi Perkin-Elmer MPF-2A fluorescence spectrophotometer and stirred for 30 min. The emission (460–490 nm) and excitation (350–360 nm) wavelengths were set to their maximum values for each polymer. The emission intensity was arbitrarily set at 100%. At this time, 10 μL of a 0.02 M stock solution of electrophile (2.0×10^{-7} mol, 10-fold molar excess of electrophile to probe) was added via syringe, and the emission intensity was continuously monitored. In some cases, if complete quenching was not observed, an additional 10 μL of aliquot of electrophile was added.

To facilitate a comparative study of materials, a narrow particle size range (125–150 μm) was used, and the probe to monomer ratio (10^{-4}) in all polymers was held constant. Furthermore, the ratio of polymer-bound probe **1a** to added electrophile was also held constant at 1:10. These ratios were chosen to yield convenient fluorescence quenching times while revealing the differences in penetrability of related polymeric materials.

Results and Discussion

Reaction of Dansyl Probe 1b with Electrophiles. The fluorescence intensity of the dansyl probe is diminished in protic solvents.[7,8] When present in excess, strong electrophiles (CF_3CO_2H, $Et_3O^+BF_4^-$, $Ph_3C^+BF_4^-$) can completely surpress the fluorescence.

The mechanism of the fluorescence surpression is assumed to involve reaction of the electrophile at the dimethylamino nitrogen (eq 1).[9] To verify this, solutions of **1b** in $CDCl_3$ or C_6D_6 were treated with CF_3CO_2H (6.7 equiv). Under these conditions, the fluorescence is completely supressed. The ^1H and ^{13}C spectral changes are given in Figure 1. The ^1H NMR data in the dimethylamino region were not particularly useful in identifying the site of protonation, considering the protons in a model compound, *N,N*-dimethylaniline (**3**), were shifted *upfield* upon protonation in C_6D_6 (Figure 1). However, although protonation at the dimethylamino nitrogen or the sulfonamide group remained a possibility, ring protonation can be ruled out as a result of the absence of sp^3 C–H hydrogens, characteristic of a benzenium ion.[10]

^{13}C NMR data proved to be more useful. The *N,N*-dimethyl carbons in aniline, upon treatment with CF_3CO_2H, are shifted downfield +6.9 and +6.1 ppm in $CDCl_3$ and C_6D_6, respectively. In probe **1b**, analogous downfield

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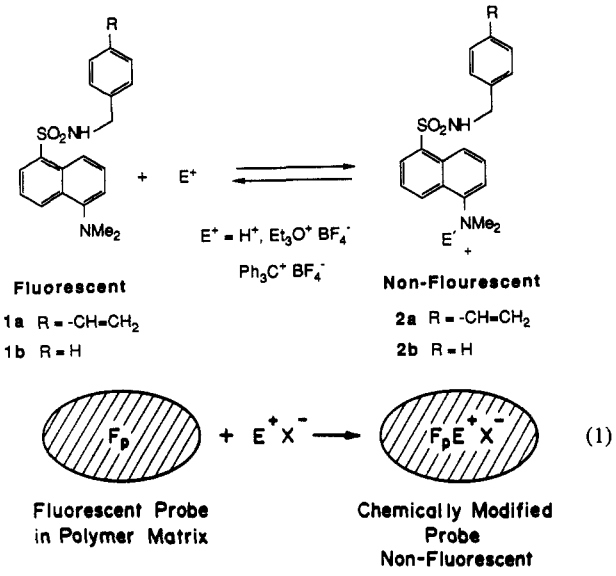

shifts of +1.40 and +1.64 ppm were recorded. The benzylic carbon, C-2, on the other hand, experiences a modest *upfield* shift (−0.92 ppm) in $CDCl_3$ and a downfield shift (+0.24 ppm) in C_6D_6. On the basis of these results, it is possible to assign the site of protonation of dansyl probe **1b** at the dimethylamino nitrogen. With electrophiles other than H^+, the NMR spectrum is complicated by the presence of signals arising from excess unreacted electrophile and other unidentified species. Despite this complication, all available data are consistent with electrophilic attack at the dimethylamino nitrogen rather than attack at a ring position or the sulfonamide group.[11] The origin of fluorescence quenching arises from quaternization of the dimethylamino nitrogen to produce a species that does not fluoresce upon excitation at 340 nm. The cause of this is a blue shift in the absorption spectra of protonated or alkylated probe; the protonated or alkylated ammonium ions **2a** and **2b** do not absorb at 340–360 nm, the absorption maximum of **1a** or **1b**.[9]

It should be noted that suppression of fluorescence emission requires an excess of electrophile, indicating an equilibrium between the weakly basic dimethylamino group in **1**[12] and electrophile. The equilibrium between protonated and nonprotonated probe **1b** is dependent upon both the acidity of the electrophile and the reaction medium. For example, the fluorescence intensity of a solution of **1b** in CH_2Cl_2 (10^{-7} M) is reduced 83% when treated with a 1000-fold excess of HCl. In ethylbenzene, the intensity is reduced only 35%. Upon further addition of HCl (1000 equiv), the intensity drops to 7% of the initial value in CH_2Cl_2 but to only 35% in ethylbenzene. Polar solvents (CH_2Cl_2) favor formation of the protonated probe in comparison with nonpolar solvents (ethylbenzene).

Quite interestingly, when linear polystyrene containing bound probe **1a** (DP = 372) is dissolved in CH_2Cl_2, the addition of HCl (1000 equiv) produces *no fluorescence intensity dimunition*. This same phenomenon is observed when "free" probe **1b** was added to a CH_2Cl_2 solution of linear polystyrene; that is, HCl addition did not diminish the fluorescence intensity. In these experiments, the microenvironment of both the covalently bound and absorbed probe is dominated by the polystyrene. To distinguish if this observed effect is due to a solvent effect or adsorption to the polymer, ethylbenzene was added to a CH_2Cl_2 solution of probe **1b** in an amount equivalent to the monomer units of polystyrene from the previous experiments. The original fluorescence intensity was diminished to 85% upon addition of HCl (1000 equiv). This

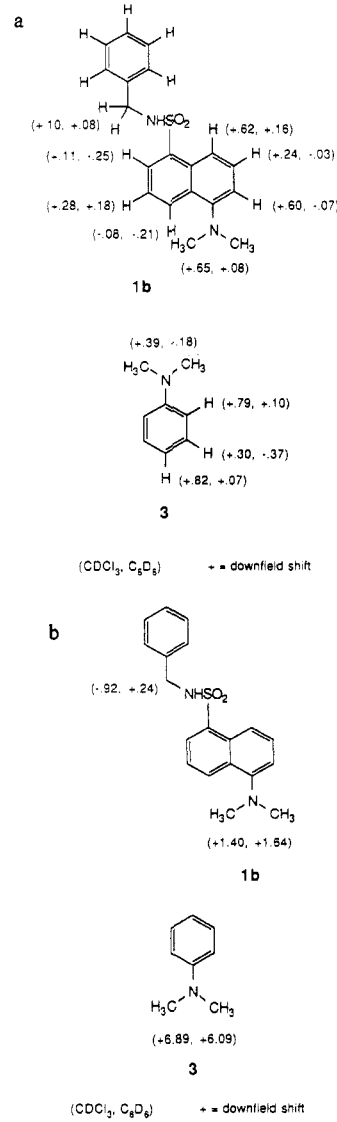

Figure 1. (a) Chemical shift changes of selected proton resonances of dansyl probe **1b** and *N,N*-dimethylanaline (**3**) upon treatment with 6.7 equiv of CF_3CO_2H in $CDCl_3$ and C_6D_6. (b) Chemical shift changes of selected ^{13}C resonances of **1b** and **3**.

mixed solvent result is similar to what one finds in *pure* CH_2Cl_2; that is, the addition of small amounts of ethylbenzene does not produce a noticeable effect on the intensity of the fluorescence emission.

The preceding results reveal the microenvironment effect that the polymer can exert on either bound or adsorbed probe. The probe spends more time in the polystyrene microdomain than in bulk solution. As a result, the effective basicity and/or reaction equilibrium of the probe is significantly diminished by the hydrophobic microenvironment provided by the polymer.[13] However, with stronger protic acids, such as trifluoroacetic acid, complete quenching of fluorescence emission of polystyrene-bound probe **1a** can be achieved. Furthermore, more powerful electrophiles, such as triethyloxonium tetrafluoroborate ($Et_3O^+BF_4^-$) and triphenylcarbenium ion ($Ph_3C^+BF_4^-$), when present in excess, will also react with polymer-bound probe **1a** to completely suppress the fluorescence emission with excitation at 350 nm. These two electrophiles were chosen for our studies of the penetrability of the gel phase of polymeric materials containing probe **1a** covalently bound in the network.[14]

Fluorescence-Quenching Results. Suspensions of polymers containing probe were treated with solutions of

Table I
Reaction Mixtures for Suspension Polymerization[a]

polymer code[a]	DVB, %	tech DVB, g	styrene, g	H_2O, mL	AIBN, mg	toluene, mL	probe **1a**, 10^3 g	methocel, mg
DVB-50-S-T	50	20.0	0	200	200	20.0	5.66	100
DVB-50-S-N	50	20.0	0	200	200	0	5.66	90
DVB-20-S-T	20	9.00	11.0	200	200	20.0	6.45	100
DVB-20-S-N	20	9.00	11.0	200	200	0	6.45	70
DVB-5-S-T	5	2.40	17.6	200	200	20.0	6.88	100
DVB-5-S-N	5	2.40	17.6	200	200	0	6.88	80

[a] Polymer code refers to cross-linking monomer (DIB = diisopropenylbenzene, DVB = divinylbenzene)-% cross-linker in monomer mixture-type of polymerization (B = bulk, S = suspension)-porogen (T = toluene, A = acetonitril), N = no porogen).

Table II
Reaction Mixtures for Bulk Polymerization[a]

polymer code[a]	DVB, %	tech DVB, g	styrene, g	DIB, g	AIBN, mg	toluene, mL	CH_3CN, mL	probe **1a**, 10^3 g
DVB-50-B-T	50	8.00	0	0	80	8	0	2.27
DVB-50-B-A	50	8.00	0	0	80	0	8	2.27
DIB-50-B-T	50	0	3.20	4.80	80	8	0	2.24
DIB-50-B-A	50	0	3.20	4.80	80	0	8	2.24

[a] Polymer code refers to cross-linking monomer (DIB = diisopropenylbenzene, DVB = divinylbenzene)-% cross-linker in monomer mixture-type of polymerization (B = bulk, S = suspension)-porogen (T = toluene, A = acetonitrile, N = no porogen).

electrophile ($Ph_3C^+BF_4^-$ or $Et_3O^+BF_4^-$) as described in the Experimental Section. A trace of the dimunition of fluorescence intensity over time reflects the overall rate of diffusion of reagent into the polymer domain *and* the rate of reaction with the fluorescence probe. In control experiments, the fluorescence emission of **1b** was found to be quenched "instantaneously" when excess electrophile was added to a homogeneous solution of **1b**. Since quenching in homogeneous solution occurs "instantaneously", factors that contribute to the intensity–time curve in polymer-bound systems are (1) the extent that the polymer impedes transport of electrophile through the network and (2) the microenvironment influence on the position of equilibrium between electrophile and probe. In these heterogeneous cross-linked polymers, the *average* microenvironment will be a characteristic of the material, resulting in a characteristic equilibrium for each polymer.

A typical fluorescence intensity–time plot is given in Figure 2. It shows a quenching-recovery study of probe **1a** in DVB-50-S-T with $Ph_3C^+BF_4^-$ as electrophile. The intensity–time trace reveals that virtually all fluorescence is quenched after 6 min upon addition of 10 equiv of $Ph_3C^+BF_4^-$ to the polymer. If quenching occurs by the mechanism proposed in eq 1, the reaction should be reversible. Two successive additions of diethylamine (10 equiv each) restores the original fluorescence intensity consistent with a *reversible* attack of electrophile on the dimethylamino group of the dansyl probe. We note that the stoichiometry of this reaction requires 2 equiv of amine for complete recovery of fluorescence intensity.[15] It is interesting to note that fluorescence recovery is dependent upon diffusion of a *neutral* species (diethylamine), the rate of which is *qualitatively* faster than the diffusion of the ionic electrophile in the quenching reaction.

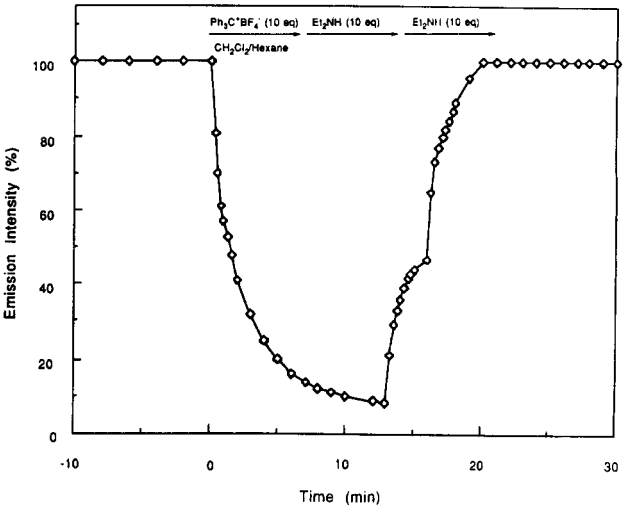

Figure 2. Plot of fluorescence emission intensity (λ_{em}^{max} = 480 nm) vs time for a stirred suspension of macroporous DVB-50-S-T in CH_2Cl_2/hexane (13:4) after treatment with $Ph_3C^+BF_4^-$ (10 equiv). Following quenching (ca. 13 min), the suspension was treated with $HNEt_2$ (20 equiv) in two 10-equiv portions.

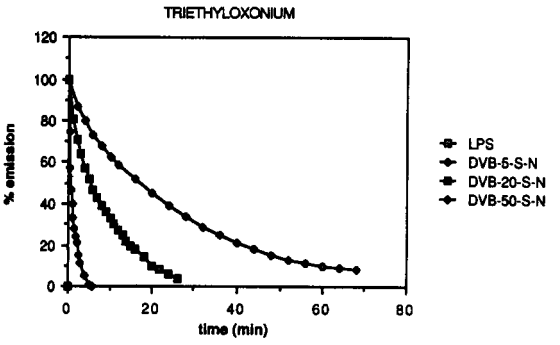

Figure 3. Plot of fluorescence emission intensity (λ_{em}^{max} = 480 nm) vs time for a solution of LPS and suspensions of nonporous gel polymers DVB-5,20,50-S-N in CH_2Cl_2/hexane (13:4) after treatment with $Et_3O^+BF_4^-$ (1:10 ratio of probe to electrophile).

Relationship of Polymer Properties to Diffusion Quenching

Influence of Cross-Linking. Figure 3 contains the fluorescence-quenching traces ($Et_3O^+BF_4^-$ electrophile) of four materials. These include a linear polystyrene (LPS, DP = 372) and three nonporous styrene–divinylbenzene bead copolymers prepared by suspension polymerization. The copolymers differ with respect to the extent of cross-linking and include samples of 5%, 20%, and 50% divinylbenzene (DVB-5,20,50-S-N). A 125–150-μm particle size is used for all measurements. The fluorescence emission of a homogeneous solution of linear PS is completely quenched upon mixing with electrophile (<30 s). By comparison, the fluorescence emission of solvent-swollen 5% cross-linked gel beads is completely quenched within 6 min. Under identical conditions, the 20% cross-linked material (DVB-20-S-N) is quenched after 30 min while the fluorescence emission of 50% cross-linked material (DVB-50-S-N) is only 90% quenched after 1 h.

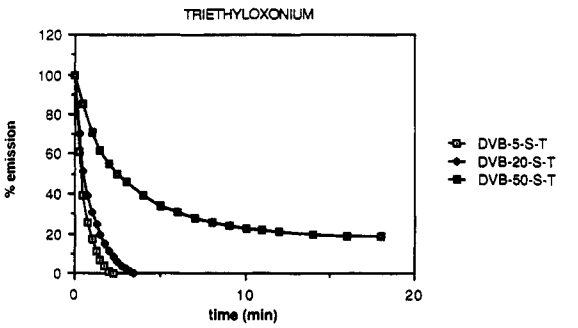

Figure 4. Plot of fluorescence emission intensity (λ_{em}^{max} = 480 nm) vs time for suspensions of macroporous polymers DVB-5,20,50-S-T in CH_2Cl_2/hexane (13:4) after treatment with $Et_3O^+BF_4^-$ (1:10 ratio of probe to electrophile).

The rate of fluorescence quenching is inversely related to the nominal cross-linking percent. Not surprisingly, increasing the cross-link density impedes the rate of transport of ionic electrophilic reagents through the network. In the time scale of these experiments (minutes), diffusion of reagent into the polymer bead is the limiting factor. These trends may also be correlated with polymer swelling, which shows a similar inverse relationship with cross-link density.[16]

Influence of Macroporosity. The fluorescence-quenching traces of materials of a more complex morphology are plotted in Figure 4. These network materials are styrene–divinylbenzene bead-type copolymers prepared by suspension polymerization in the presence of toluene (1:1, v/v) as porogen[17] (DVB-5,20,50-S-T). Copolymerization in the presence of diluents such as toluene results in formation of macroporous materials with a permanent internal pore structure and a high internal surface area.[18] The influence of the porous nature of all three materials is readily apparent upon comparison with the corresponding nonporous materials (prepared without diluent) of comparable nominal cross-link percentage (Figure 3). In all cases, the time necessary to achieve almost complete fluorescence quenching by $Et_3O^+BF_4^-$ is dramatically reduced. The relative order of penetrability, however, is the same; that is, the inverse relationship of diffusion rate to the percent cross-linking is maintained in these porous materials. Macroporosity attenuates the influence of cross-linking; thus, the fluorescence emission of both 5% and 20% cross-linked materials is completely suppressed in less than 4 min, and 80% quenching is observed in DVB-50-S-T after only 15 min. Despite similar particle size in the two groups of materials, the greater surface area to volume ratio in the macroporous materials accounts for their different behavior.

Influence of Porogen. The nature of the porogen used for formation of macroporous materials can exert a profound effect on many aspects of the materials morphology.[19] Conventional dry techniques for evaluating surface area, pore size, and pore distribution of DVB-50-B-T and DVB-50-B-A are not always helpful in providing a distinction between these materials with regard to penetrability of the network.[2] Figure 5 shows the fluorescence-quenching curves by $Et_3O^+BF_4^-$ for two macroporous materials of the same nominal cross-linking (50%). The two materials differ only with respect to the porogen used during polymerization: in the first example, a solvating porogen, toluene, was used (DVB-50-B-T); in the second, a nonsolvating porogen, acetonitrile (DVB-50-B-A), was used.

There is a very dramatic difference between the rate of quenching of these two materials. Polymer prepared with toluene as porogen has a large fraction of probes quenched

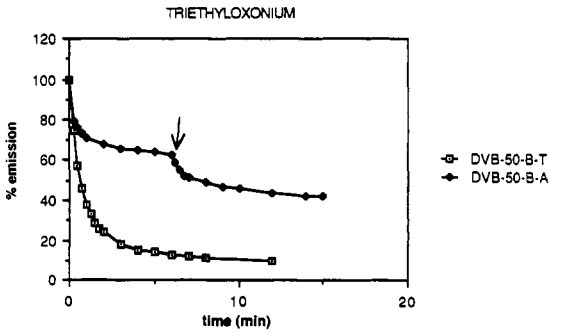

Figure 5. Plot of fluorescence emission intensity (λ_{em}^{max} = 480 nm) vs time for stirred suspensions of macroporous DVB-50-B-T and DVB-50-B-A in CH_2Cl_2/hexane (13:4) after treatment with $Et_3O^+BF_4^-$ (1:10 ratio probe to electrophile). After 6 min, an additional 25 equiv of $Et_3O^+BF_4^-$ (arrow) was added to the latter.

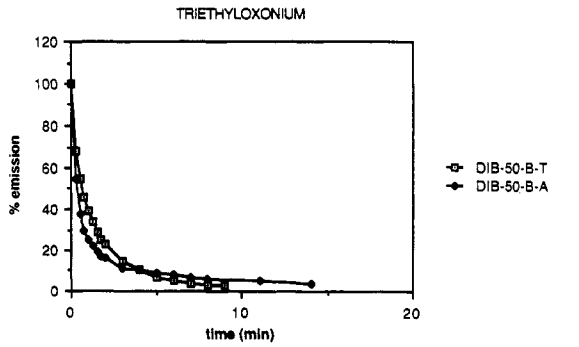

Figure 6. Plot of fluorescence emission intensity (λ_{em}^{max} = 480 nm) vs time for stirred suspensions of macroporous DIB-50-B-T and DIB-50-B-A in CH_2Cl_2/hexane (13:4) after treatment with $Et_3O^+BF_4^-$ (1:10 ratio probe to electrophile).

within 5 min (Figure 5). The small residual fluorescence that persists after this time indicates attainment of an equilibrium under the conditions of the experiment since further suppression of fluorescence can be achieved by addition of more electrophile. In contrast, materials prepared with CH_3CN as diluent (DVB-50-B-A) show a fast burst of quenching (~35% within 4 min) and then relatively little quenching thereafter. Again, the equilibrium can be modified by additional electrophile (25 equiv), Figure 5. This finding is consistent with the view that in nonsolvating porogens such as CH_3CN, a macroporous material is produced which has a dense, relatively impenetrable gel phase in contrast to materials prepared with solvating porogens.[2,20] This can be attributed to phase separation of a collapsed, nonsolvated network in CH_3CN compared with phase separation of a solvated, expanded toluene network. The difference between the two networks is maintained *after* removal of porogen. In the preceding study, the two materials may be characterized by both the rate of quenching and by the final residual fluorescence intensity (equilibrium).

Influence of Monomer Composition. An objective of this study is to identify highly permeable and yet highly cross-linked polymer networks. One such material is a styrene–diisopropenylbenzene copolymer (50:50) prepared by bulk polymerization with toluene or acetonitrile as porogen (DIB-50-B-T, DIB-50-B-A). The quenching traces are shown in Figure 6. Despite the fact that these materials contain the same nominal percent of cross-linking (50%) as the DVB materials in Figure 5, 95% of all fluorescence emission intensity is quenched within 10 min by $Et_3O^+BF_4^-$. Although these materials exhibit certain differences in the dry state with regard to the pore size and distribution when compared with the DVB materials,[2] these properties alone do not provide insight regarding

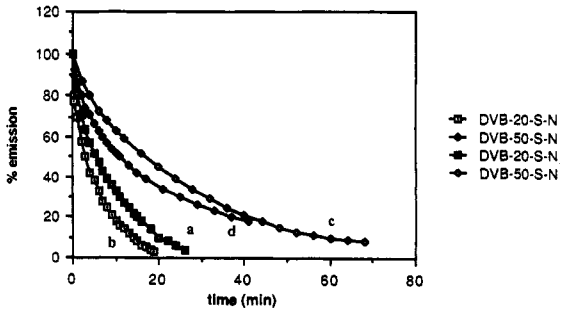

Figure 7. Plots of fluorescence emission intensity (λ_{em}^{max} = 480 nm) vs time for stirred suspensions of nonporous gel polymers DVB-20-S-N and DVB-50-S-N. Curves A and B correspond to treatment of DVB-20-S-N with $Et_3O^+BF_4^-$ and $Ph_3C^+BF_4^-$ (10 equiv), respectively, and curves C and D correspond to treatment of DVB-50-S-N with $Et_3O^+BF_4^-$ and $Ph_3C^+Bf_4^-$, respectively.

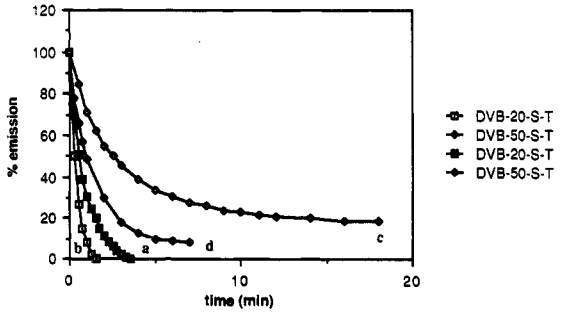

Figure 8. Plots of fluorescence emission intensity vs time for stirred suspensions of macroporous DVB-20-S-T and DVB-50-S-T. Curves A and B correspond to treatment of DVB-20-S-T with $Et_3O^+BF_4^-$ and $Ph_3C^+BF_4^-$, respectively, while C and D correspond to treatment of DVB-50-S-T with $Et_3O^+BF_4^-$ and $Ph_3C^+BF_4^-$, respectively.

their significant differences in penetrability. The striking difference in penetrability between DIB and DVB networks can be attributed in part to the lower degree of double-bond incorporation into the network, as determined by independent chemical methods.[2,21]

Influence of Electrophile on Quenching Rate. Figures 7 and 8 permit evaluation of the relative quenching rates of $Et_3O^+BF_4^-$ and $Ph_3C^+BF_4^-$ for the gel DVB-20,50-S-N (Figure 7) and macroporous DVB-20,50-S-T (Figure 8). The results show a marked similarity between the two electrophiles, but in all cases examined, a slightly *faster* rate of quenching is noted for the "larger" $(Ph_3C)^+$ electrophile. The origin of this difference may be due to a number of factors, including the difference in the effective size of the *solvated* electrophile,[22] their relative hydrophobicities, and any differences in the intrinsic reactivity of the two electrophiles that might exist. It is not possible at present to attribute a specific cause to the observed difference in rate or to assign the importance of electrophile size on the relative rates of diffusion of these two reagents.

Kinetic Model of Diffusion. The simplest description of the diffusion process may be approximated by an approach to equilibrium (eq 2). A quantitative analysis of the fluorescence trace may be expressed by the following relationship.

$$P + E \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PE \qquad (2)$$

$$[P] = \frac{k_1[E][P]_0}{k_{-1} + k_1[E]}\left(\frac{k_{-1}}{k_1[E]} + \exp[-(k_1[E] + k_{-1})t]\right)$$

$$[P]_\infty = \frac{k_1}{k_1[E] + k_{-1}}[P]_0$$

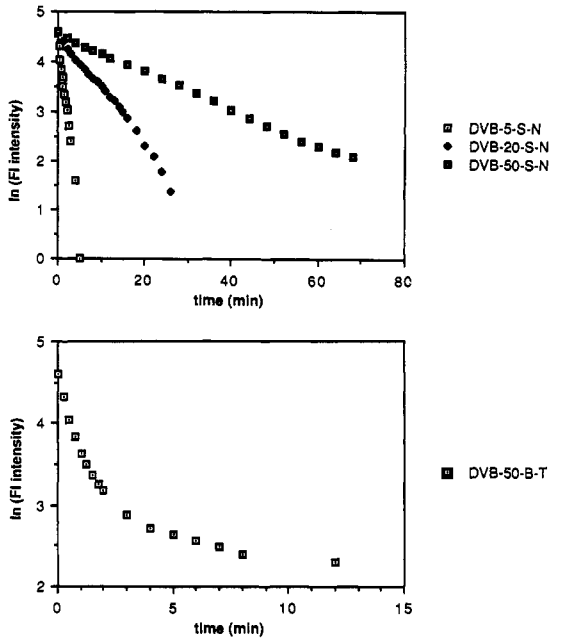

Figure 9. (a, Top) log plots of fluorescence intensity vs time for the quenching traces of DVB-5,20,50-S-N with $Et_3O^+BF_4^-$. (b, Bottom) log plot of fluorescence intensity vs time for the quenching trace of DVB-50-B-T with $Et_3O^+BF_4^-$.

This analysis predicts that log plots of fluorescence intensity vs time should be linear. In fact, this appears to be approximately correct for the simple, nonporous gel-type polymer beads (DVB-5,20,50-S-N, Figure 9a). A material of more complex morphology (i.e., DVB-50-B-T, Figure 9b) reveals at least bimodal behavior, indicating at least two kinetically distinct phenomena at the early and latter stages of the reaction. This situation perhaps corresponds to a fast initial reaction with probes at or near the surface followed by a slower diffusion into the interior of the gel. A more quantitative analysis aimed at extracting diffusion coefficients is currently under investigation. For the present time, a simple visual comparison of the decay traces provides the needed insight into the relative penetrabilities of these materials.

Conclusion

The fluorescent probe 1 offers a valuable handle for a detailed analysis of the solvation and penetrability of highly cross-linked polymers. A comparison between the present study involving diffusion of electrophiles and an earlier investigation of the solvatochromic shift of the fluorescence emission of probe 1 imbedded in these same materials[2] permits a link to be established between polymer chain solvation and the rate of transport of ionic reagents.

Furthermore, these findings are fully corroborated with chemical hydrolysis yields of ketal groups imbedded in these networks—a reaction that requires transport of solvent and ionic reagents in the gel phase.[2] The probe method can graphically reveal significant differences in the penetrability between highly cross-linked materials containing the same nominal cross-link percent, i.e., DVB-50-B-T and DVB-50-B-A. It also readily reveals differences in materials produced by changes in cross-linkers and the degree of cross-linking.

It is also noted that even in highly cross-linked materials suitable conditions can be found to permit the rapid and complete penetrability of even *ionic reagents*. The dansyl probe method should be of general utility in evaluating the influence of the polymer matrix on the accessibility of

functionality incorporated by copolymerization. We would also assume that the results of the probe-quenching technique provides information regarding the penetrability of simple electrolytes through these networks.

Several factors contribute to the rate of decay of fluorescence intensity. These include a reagent diffusion contribution and a contribution arising from the final equilibrium between polymer-bound probe and electrophile. In macroporous materials, the decay of fluorescence intensity is not modeled by a simple approach to equilibrium approximation.

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Registry No. **1a**, 105029-42-3; (**1a**)(styrene) (copolymer), 105186-78-5; (**1a**)(DVB)(styrene) (copolymer), 105186-79-6; (**1a**)(DIB)(styrene) (copolymer), 118018-24-9; **1b**, 34532-49-5; $Ph_3C^+BF_4^-$, 341-02-6; $Et_3O^+BF_4^-$, 368-39-8; CF_3CO_2H, 76-05-1.

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