Interfacial Electron Transfer Induced by Light in Methylene Blue Incorporated in Nafion Membranes. Laser Kinetic Spectroscopy

J. Kiwi,[†] N. Denisov,[‡] and V. Nadtochenko*[,‡]

EPFL, Institute of Physical Chemistry II, Lausanne 1015, Switzerland, and Institute of Chemical Physics Research RAS, Chernogolovka, Moscow 142432, Russia

Received: February 22, 1999; In Final Form: August 2, 1999

Quenching of excited states of methylene blue was studied in Nafion−H^+, Nafion−Na^+ and Nafion−Fe^{2+} membranes. Protonated, not protonated, and dimer forms of methylene blue in Nafion showed different fluorescence properties. Fe^{2+} is observed to quench the fluorescence of methylene blue embedded in the Nafion membrane. The excitation of monomer of methylene blue molecules induces the triplet excited state of the dye as revealed by laser spectroscopy. Methylene blue radical generation involved excitation of the dye dimeric species or excimers. Nafion−Fe^{2+} membrane quenched the excited methylene blue, leading to the formation of Fe^{3+} and the semiquinone of the methylene blue radical. The back reaction between Fe^{3+} and the semiquinone of the methylene blue radical occurred in the millisecond range and was seen to proceed by second-order kinetics. The latter process involves a dynamic mechanism of reaction including motion of one of the reactants or both. The mechanism of the photoreduction of MB incorporated in the Nafion by the Fe^{2+} ions of the double layer ionic aqueous phase is described in detail.

Introduction

Nafion is a widely used perfluorosulfonate polymer marketed by Du Pont.[1] The Nafion membranes have been shown to be able to act as a separate phase during chemical reactions.[2−4] Nafion membranes in the dry protonated form have been extensively used because of its superacid properties or as a catalyst for organic reactions.[5−8] Luminescent molecules such as a pyrene,[9,10] $Ru(bpy)_3^{2+}$,[11−13] $Ru(bpy)_2dppz^{2+}$ (dppz = dipyrido[3,2-*a*:2,3-*c*]phenazine)[14] have been used as probes for the excited-state interactions of polymers and to characterize specific sites in the polymer cluster. Also, the effects of the Nafion acidic environment on the exited triplet of xanthone,-(2,4-dibenzopyrone), benzophenone,[15] and the laser dye 7-amino-4 methylcoumarin have been reported.[16]

Nafion swollen membranes have been shown to be useful during photoisomerization of cyclic hydrocarbon[17,18] and in singlet oxygen generation.[19] They have also been useful as a support material during photocatalysis mediated by nanosized semiconductors.[20−22] The effect of polymer structure on the electrochemistry of phenothiazine dyes incorporated into Nafion films has been recently reported.[23] Methylene blue (MB from now on) sensitized the photooxidation of anthracene by O_2 contained in the Nafion, as recently reported.[24] The photoreduction of MB to its leuco form was seen to occur in Nafion under steady-state illumination.[24,25] Nafion is a unique medium to test the interaction of MB, a charged ionic organic compound with the Nafion interface containing hydrophobic and hydrophilic functional groups. On the other hand Fe^{2+}, which does not interact with the hydrophobic part of Nafion, has been used in this study as a hydrophilic quencher. At the same time Fe^{2+} interacts with MB* within hydrophilic surroundings. But it is not possible to claim a priori that Fe^{2+} interacts with the pending $-SO_3-$ end group of Nafion only because electrostatic reasons, since complex formation may also take place. Therefore, the interaction of the excited probe (MB*) and a quencher is investigated in this study in a complex organized media. Recently, Gopidas and Kamat[26] have reported the kinetics of electron transfer between a phenothiazine type dye (phenosafranine) and triethylamine.

MB is a widely used compound because of its photochemical, electrochemical, and disinfectant properties.[27] In the present study we will describe (a) the quenching of the photoexcited dye by Fe^{2+} ions exchanged at the Nafion surface and (b) the interfacial electron transfer in a system where the MB is located on the internal hydrophobic fluorocarbon Nafion surface and Fe^{2+} ions on the outside of the Nafion membrane. The Nafion ionic $-SO_3-$ groups compensate the negative charge by the positively charged ions found on the hydrophilic side (regions) of the Nafion. The interaction between ions is nonspecific, and this model has the restriction in the Nafion case for specific interactions between the ionic species in the aqueous media and the hydrophobic (fluorocarbon) part of the matrix.

During the present study the MB transients due to the electron transfer between MB* and Fe^{2+} in Nafion membranes are investigated by spectrophotometric methods and laser kinetic spectroscopy. Not much information is available on these processes which are important in some applications of polymeric thin films.

Experimental Section

Materials and Reagents. The cationic exchange transfer membrane Nafion 117 was obtained from Aldrich (no. 27,467-4, 177 μm thick). Fe(II)SO_4, Fluka p.a., was used as the source of the Fe^{2+} ions. Other organic and inorganic reagents were Fluka p.a. and used as received.

Samples Preparation. The Nafion film was sonicated for 1 h in a solution of distilled water and methanol (50%:50%). The Nafion film was subsequently washed repeatedly in distilled water. The Nafion−H^+ membrane was prepared by boiling the samples in $HClO_4$ (1 M) for 1 h. Alternatively, the last operation

10.1021/jp990626f CCC: $18.00
Published on Web 09/01/1999

could be substituted by sonication in $HClO_4$ (1 M) for 1 h. Sonication accelerates the time to attain equilibrium and allowed us to obtain a cleaner Nafion film. Both methods rendered Nafion$-H^+$ with the same properties. The Nafion$-Na^+$ films were obtained by washing Nafion in NaOH (1 M) solutions. Nafion$-Fe^{2+}$ membranes were prepared by equilibrating for 24 h Nafion$-H^+$ with $FeSO_4$ (1 M) aqueous solutions.

MB was incorporated into the Nafion film by suspending the film in the MB solution for 12 h. Nafion films 3 cm^2 in size were prepared from one batch of MB for all subsequent experiments. The exchange of H^+ by Fe^{2+} or Na^+ did not lead to MB loss in the Nafion by diffusion into the bulk solution. A blue Nafion material was obtained, and the blue color was maintained as long as the Nafion membrane was not allowed to dry. The Nafion$-$MB turned yellowish-green after it had been dried in a vacuum or in an Ar stream.

The reproducibility achieved after the preparation and ion exchange of the Nafion membranes can be inferred from the fact that the observed results from subsequent kinetic measurements did not vary more than 10% from experiment to experiment in the Fe(II)$-$MB$-$Nafion system. The quantitative results indicated that equilibrium between Nafion and the bulk solution was achieved after 12 h of stirring in solution, as indicated by the reagents concentration followed spectrophotometrically and by solution pH values. But more reproducible kinetic results were observed after 24 h of equilibration. Nafion$-$MB$-Fe^{2+}$ loaded materials were prepared by equilibrating Nafion$-$MB with a solution of Fe(II)SO_4 (1 M) for a period of 24 h. The aqueous solution was purged with Ar to avoid the oxidation of Fe(II) by air.

Optical Measurements. The absorption spectra were recorded using a Hewlett-Packard 8452 diode array spectrophotometer. The fluorescence was monitored with a SPEX-2 photon-counting fluorescence spectrophotometer provided with a MX-2 correction unit.

Laser Flash Photolysis. The second harmonic of a ruby laser $\lambda = 347$ nm (10 mJ pulse energy, pulse width 30 ns), or the second harmonic of a Nd^{3+}:YAG laser at 532 nm ($\sim$12 ns pulse width, 5 mJ pulse energy) was used as the excitation wavelength. An Osram 450 W Ar$-$Xe arc lamp was used as the monitoring light source. The excitation of the solution in the optical quartz cell was carried perpendicular to the Ar$-$Xe monitoring light. To minimize the contribution of the irreversible transients produced in solution after the laser pulse, fresh solutions were used in successive measurements. Experiments were carried out either under (a) anaerobic conditions by purging the solution with Ar for 2 h or (b) in air-saturated solution. Residual amounts of O_2 showed negligible effects on the intermediate lifetimes because of the short lifetimes of the MB triplet excited-state incorporated in the Nafion.

Estimation of the Average Number of Fe^{2+} Ions and MB Units in the Cluster. The equation for H_{max} gives an estimate of the number of headgroups in a single cluster by considering the *average parameters* like density, E_w, Bragg d spacing, and adsorbed water volume. The number of headgroups in one cluster H_{max} is calculated by

$$H_{max} = \frac{N_0 \rho}{E_w} \frac{\nu}{1+V}$$

where $\rho = 1.98$ g/cm^3 is the Nafion density, $E_w = 1100$ is the equivalent weight, and $\nu = 4\pi R^3/3$ ($R = d/2$) refers to the collision cluster volume. The Bragg d spacing used was 47 Å,[11] and V, the water volume absorbed by 1 cm^3 of Nafion, was 0.56 cm^3. Taking into account all these data and $H_{max} = 73$, a maximum of $73/n$ M^{n+} ions could be loaded into a single cluster. The concentration of clusters c (in units of mol/cm^3) is calculated according to $c = \rho/E_w H_{max}$ and turns out to be $\sim 2.5 \times 10^{-5}$ mol/cm^3. The average number of ions in a cluster (the occupation number) $\langle \mu \rangle = ([\text{ions}]/1000)c$. [ions] refers to the concentration of ions in the membrane.

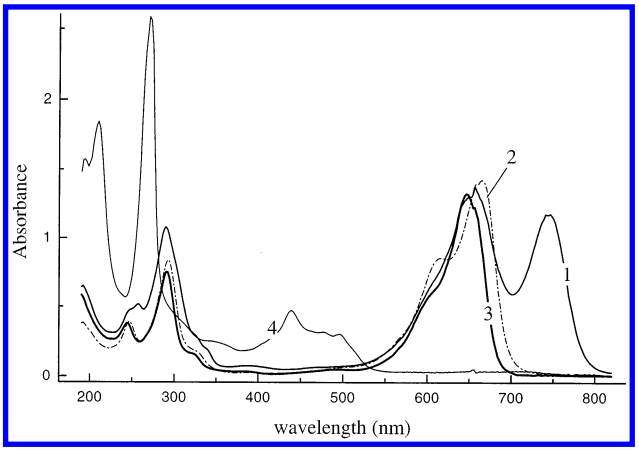

Figure 1. Absorption spectra of the following membranes: (1) Nafion$-H^+$ membrane with $[MB^+] = 1.16 \times 10^{-3}$ M, $[MBH^{2+}] = 1.08 \times 10^{-3}$ M; (2) aqueous solution, pH = 5, $[MB^+] = 1.5 \times 10^{-5}$ M; (3) Nafion$-Na^+$ membrane with $[MB^+] = 1.13 \times 10^{-3}$ M; (4) Nafion$-H^+$ membrane vacuum-dried, MB concentration as in trace 1.

Results and Discussion

Absorption and Fluorescent Characteristics of Methylene Blue in Nafion Film. The absorption spectra of MB monomers and dimers in aqueous solution have been reported.[28,29] The equilibrium constants for the protonation reaction 1 for monomer and dimers in aqueous media have been reported as

$$MBH^{2+} \leftrightarrow MB^+ + H^+ \qquad K_p = 1.4\ M^{-1}\ ^{29} \qquad (1)$$

$$\epsilon_{664}^{MB+} = 9.5 \times 10^4\ (M\ cm)^{-1},$$

$$\epsilon_{754}^{MBH2+} = 7.2 \times 10^4\ (M\ cm)^{-1}$$

$$[MB^+ \cdots MB^+] \leftrightarrow MB^+ + MB^+$$

$$K_2 = 1.7 \times 10^{-4}\ M^{-1} \qquad (2)$$

$$\epsilon_{605}^{[MB+\cdots MB+]} = 6.1 \times 10^4\ (M\ cm)^{-1}$$

$$[MB^+ \cdots MBH^{2+}] \leftrightarrow MB^+ + MBH^{2+} \qquad (3)$$

MB^+ shows an absorption maximum in Nafion at $\lambda = 651$ nm and $\epsilon_{651}^{MB+} = 6.77 \times 10^4\ (M\ cm)^{-1}$. MBH^{2+} has the band at $\lambda = 752$ nm, $\epsilon_{752}^{MBH2+} = 6.39 \times 10^4\ (M\ cm)^{-1}$. A shoulder band at $\lambda = 590$ nm for the MB^+ dimer has been observed.[23−25] Figure 1 presents the absorbance of MB in aqueous solution in Nafion$-H^+$ and Nafion$-Na^+$ and also for vacuum-dried Nafion$-H^+$. These results can be summarized: (a) the peak of MBH^{2+} at $\lambda = 744$ nm is observed in Nafion$-H^+$; (b) peaks of MB^+ are observed at $\lambda = 642$ and 653 nm in Nafion$-H^+$ and $\lambda = 648$ and 663 nm in Nafion$-Na^+$. Dimer peaks were observed at $\lambda = 597$ nm in Nafion$-H^+$ and at $\lambda = 611$ nm in Nafion$-Na^+$ membranes. The positions of these peaks were obtained by Gaussian resolution of the spectral region between 12500−20000 cm^{-1} (500−800 nm). The MB spectrum in a vacuum dried for the Nafion$-H^+$ membranes is seen to differ significantly from the spectrum observed in humidified films. It resembles the spectrum of MB in concentrated H_2SO_4

TABLE 1: Positions of the MB Fluorescence Spectral Bands in Nafion Membranes

	Nafion−H^+		Nafion−Na^+		Nafion−Fe^{2+}	
band	ν_{max} cm^{-1} (nm)	width cm^{-1}	ν_{max} cm^{-1} (nm)	width cm^{-1}	ν_{max} cm^{-1} (nm)	width cm^{-1}
I	12 983 (770)	863	13 232 (756)	2198	13 000 (769)	4259
II	14 180 (705)	705	14 370 (696)	1633	14 180 (705)	1315
III	15 200 (657)	889	14 782 (676)	649	14 587 (686)	693
IV	15 537 (644)	405				

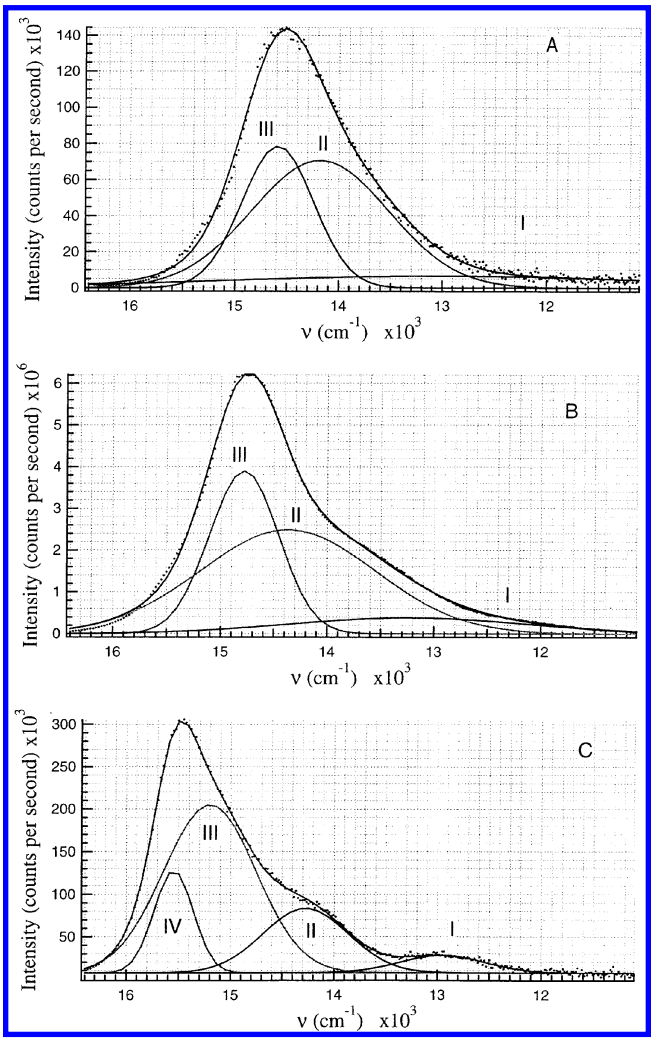

Figure 2. Fluorescence spectra of methylene blue showing the spectral bands obtained by Gaussian resolution: (A) in Nafion−Fe^{2+} membrane, concentration of Fe^{2+} in solution 51 mM, pH = 2.1; (B) in Nafion−Na^+ membrane; (C) in Nafion−H^+ membrane. Concentration of MB in all membranes is 1.0×10^{-3} M.

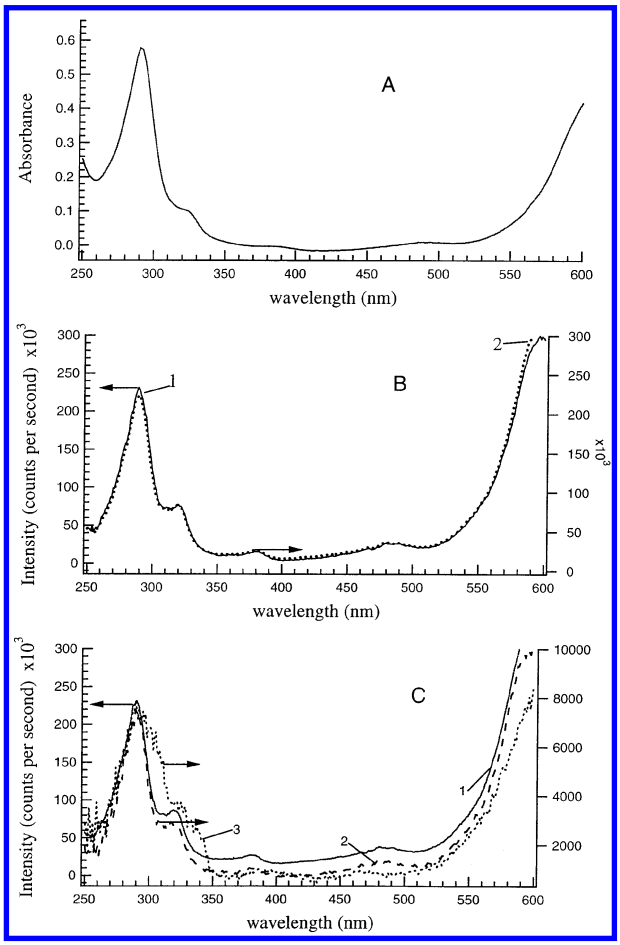

Figure 3. (A) Absorbance spectrum of MB in Nafion-Na membrane. (B) Fluorescence excitation spectra of MB with excitation at $\lambda = 590$ nm: (1) (solid line) Nafion−H^+ membrane emission at $\lambda = 657$ nm (band III); (2) (dots) Nafion−Na^+ membrane emission at $\lambda = 670$ nm (near the maximum of band III). (C) Fluorescence excitation spectra of MB in Nafion−H^+ membrane: (1) (solid line) emission at $\lambda = 657$ nm (band III); (2) (dashed line) emission at $\lambda = 705$ nm (band II); (3) (dots) the emission at $\lambda = 770$ nm (band I). Concentration of MB in all membranes is 1.0×10^{-3} M.

solutions. This agrees with the superacid properties reported for Nafion−H^+ in acidic media.[5−8] MB in the vacuum-dried membranes regained the original blue color after immersion in aqueous media or after equilibrating with air-saturated water vapor.

Parts A, B, and C of Figure 2 show the fluorescence spectra of MB in the Nafion−H^+, −Na^+, and −Fe^+ forms, respectively. The positions of the fluorescence bands are summarized in Table 1. Figure 2 shows that (a) the emission spectra of MB in parts A and B do not differ between themselves but they are quite different from the emission spectrum found for Nafion−H^+ and (b) the intensity of the MB fluorescence in Nafion−Na^+ is ∼40 times higher than in Nafion−Fe^{2+}. The Nafion−H^+ shows a band at $\lambda = 644$ nm (band IV) and a second band at 770 nm (band I) that is more intense than in the case of Nafion−Fe^{2+} and Nafion−Na^+. Bands II and III near $\lambda = 700$ nm and $\lambda =$ 660 nm are observed for the three Nafion membranes under investigation. The dimer formation seems to be more pronounced in Nafion−Na^+ films than in Nafion−H^+ films.

Fluorescence excitation spectra for MB in Na^+ and H^+ are shown in the Figure 3. The absorption spectrum of MB in Nafion−Na^+ is shown in Figure 3A. The excitation spectra presented in Figure 3 show that (1) band III is due to the fluorescence of MB^+ monomer because the excitation spectra for band III (657 nm) of MB in Nafion−H^+ and in Nafion−Na^+ are identical in Figure 3B. The two latter spectra are also seen to coincide with the absorption spectrum observed for MB in Nafion−Na^+. Figure 3C shows that the excitation spectra for bands II and III in Nafion−H^+ are very close to the former ones. Band I can be assigned to MBH^{2+} fluorescence, since the excitation spectrum of band I is seen to be different from the excitation spectra of bands II and III. The band at 644 nm

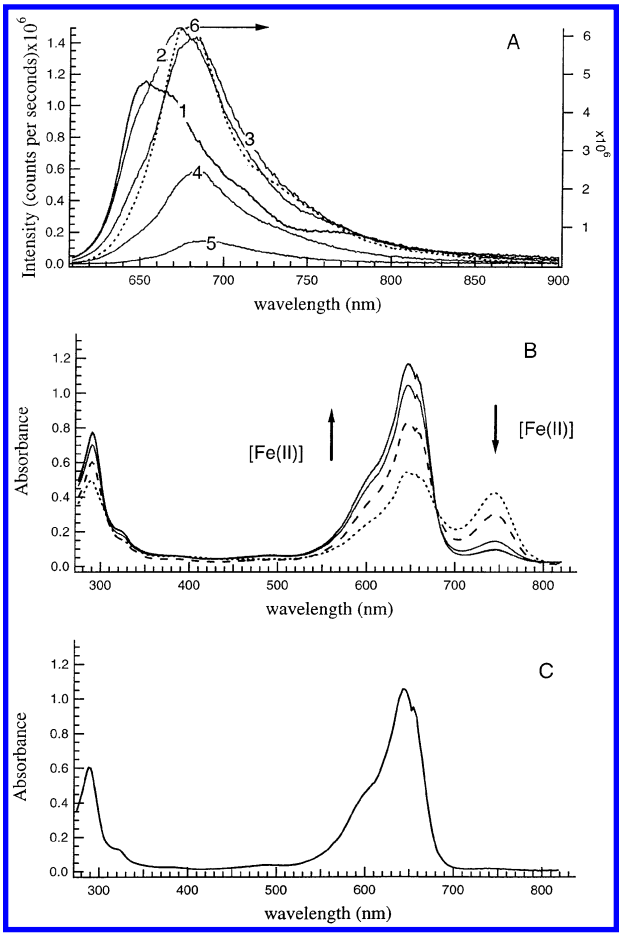

Figure 4. (A) Fluorescence emission spectra of MB in Nafion−H^+ when the Fe^{2+} concentration in solution is (1) $[Fe^{2+}] = 0$, (2) $[Fe^{2+}] = 3.19$ mM, (3) $[Fe^{2+}] = 9.56$ mM, (4) $[Fe^{2+}] = 29$ mM, (5) $[Fe^{2+}] = 51$ mM, (6) MB in Nafion−Na^+. Excitation at $\lambda = 590$ nm. (B) Absorption spectra MB in Nafion−H^+ when Fe^{2+} concentration in the solution is increased: (1) no Fe^{2+} added; (2) Fe^{2+} 9.56 mM; (3) 3.29 Fe^{2+} mM; and (4) Fe^{2+} 51 mM. (C) Absorption spectrum of MB in Nafion−Na^+. Concentration of MB in all membranes is 1.0×10^{-3} M.

(band IV) has the same maximum as observed for the absorption bands of the MB monomer at $\lambda = 642$ nm. The position of the maximum of the latter peak differs from that of the absorption maximum of the dimer at $\lambda = 597$ nm. Taking into consideration the Stokes shift, band IV is attributed to the MB dimer.

MB Fluorescence Changes Due to H^+ Substitution by Fe^{2+} in Nafion Membranes. Figure 4A shows the fluorescence and absorption spectra for MB in Nafion when H^+ is substituted by Fe^{2+} under constant MB concentration. Figure B shows the effect of the increase in concentration of Fe^{2+} as noted in the caption of Figure 4B. The increase in Fe^{2+} concentration leads to a decrease in the MBH^{2+} absorption peak at $\lambda = 744$ nm and a concomitant increase of the absorption MB^+ at $\lambda = 648$ nm. An isosbestic point is observed in Figure 4B at $\lambda = 680$ nm, suggesting that the increase in Fe^{2+} leads to equilibrium changes in the reaction $MBH^{2+} \leftrightarrow MB^+$. The absorption spectrum of MB in Nafion−Na^+ (Figure 4C) is similar to the Nafion−Fe^{2+}spectrum. The changes observed in the MB spectra in Figure 4 allow us to estimate the H^+ and Fe^{2+} concentrations in the membrane at different concentrations of added Fe^{2+}, taking into consideration that $K_p = 0.58$ M^{-1} for MB in Nafion.[25] It follows that $[H^+]_0 = [MBH^{2+}]/(K_p[MB^+]) = 1.41$ M in the membrane when $[Fe^{2+}] = 0$ at the maximum H^+ concentration, which is 1.67 M. At pH 2 when $[Fe^{2+}] = 51$ mM, $[H^+] = 0.14$ M. Fe^{2+} concentration in the membrane was

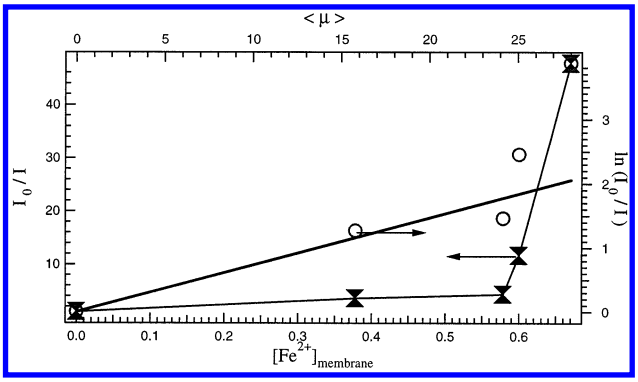

Figure 5. Dependence of fluorescent intensity of MB at $\lambda = 670$ nm vs Fe^{2+} concentration in Nafion membranes. Excitation at $\lambda = 590$ nm. Concentration of MBe in all membranes is 1.0×10^{-3} M.

determined as $[Fe^{2+}]_{membrane} = ([H^+]_0 - [H^+]_{Fe})/2$ and was ~0.63 M for an occupation number of $\langle\mu\rangle = 25.2$ (for the last calculation see experimental part).

Figure 4A shows spectral changes for the MB fluorescence when Fe^{2+} was added to the solution. Two effects were observed owing to Fe^{2+} addition. First, the decrease of H^+ concentration in the membrane leads to the disappearance of MBH^{2+} fluorescence due to deprotonation along with a concomitant increase in MB^+ concentration. Second, the effect of the MB^+ fluorescence quenching by Fe^{2+} in solution was observed.

Quenching of MB Fluorescence by Fe^{2+} in Nafion Membranes. Figure 4 has shown that Fe^{2+} quenches the fluorescence of MB in Nafion. Figure 5 presents the dependency of MB fluorescence intensity at $\lambda = 660$ nm as a function of the Fe^{2+} concentration in the Nafion membrane and the occupied number $\langle\mu\rangle$ in Stern−Volmer coordinates (left y axis) and on the logarithmic scale, $\ln(I_0/I)$ vs $[Fe^{2+}]$ in t, Figure 5 (right y axis). It is readily seen that the Stern−Volmer dependence is not obeyed in Figure 5. The lifetime of MB in Nafion has been determined to be $\tau_S = 0.45$ ns by fluorescence measurements.[33] Thomas and co-workers[34] have shown from ^1H and ^{23}Na magnetic resonance and absorption−fluorescence studies that the dipole−dipole and ion−dipole interactions between the water molecules and between the water and charged headgroups are similar to those in bulk solution when the radius of the water clusters in reverse micelles approach ~23 Å. Since the radius of water clusters in Nafion is about 21 Å, the structure and mobility of these clusters and the spectroscopic properties of inorganic cations on the Nafion resemble those obtained in aqueous solution. Assuming a diffusion limit rate constant of Fe^{2+} in the Nafion cluster and in the water solution with a value of $k_{dif} = 6 \times 10^9$ $(M\ s)^{-1}$, it is possible to estimate the occupation number μ of Fe^{2+} when the collision frequency of Fe^{2+} with MB equals the reciprocal lifetime of the singlet excited MB in Nafion. The estimated value from the relation $k_{dif}\mu/(1000N_A\nu) = 1/\tau_S$ renders a value close to $\mu \approx 1$. Therefore, fluorescence quenching of MB can be expected for clusters with $\mu > 1$. For nonhomogeneous systems (micellar systems), when the chromophore and the quencher are soluble in the micelle, deviations in the Stern−Volmer dependence have been frequently reported as presented in Figure 5.[34,35] The statistics of the quencher occupation of clusters can be described by the Poisson distribution $P_i = (\langle\mu\rangle^i/i!)\exp(-\langle\mu\rangle)$. The probability of an empty cluster is given by $P_0 = \exp(-\langle\mu\rangle)$. Assuming zero emission from the empty clusters, the dependence of the fluorescence intensity vs quencher concentration should be linear in a plot of $\ln(I_0/I)$ vs $[Fe^{2+}]$.[34,35] This was not the case in Figure 5. When the concentration of Fe^{2+} in the Nafion is close to the limiting value of the Fe^{2+} concentration in the cluster of

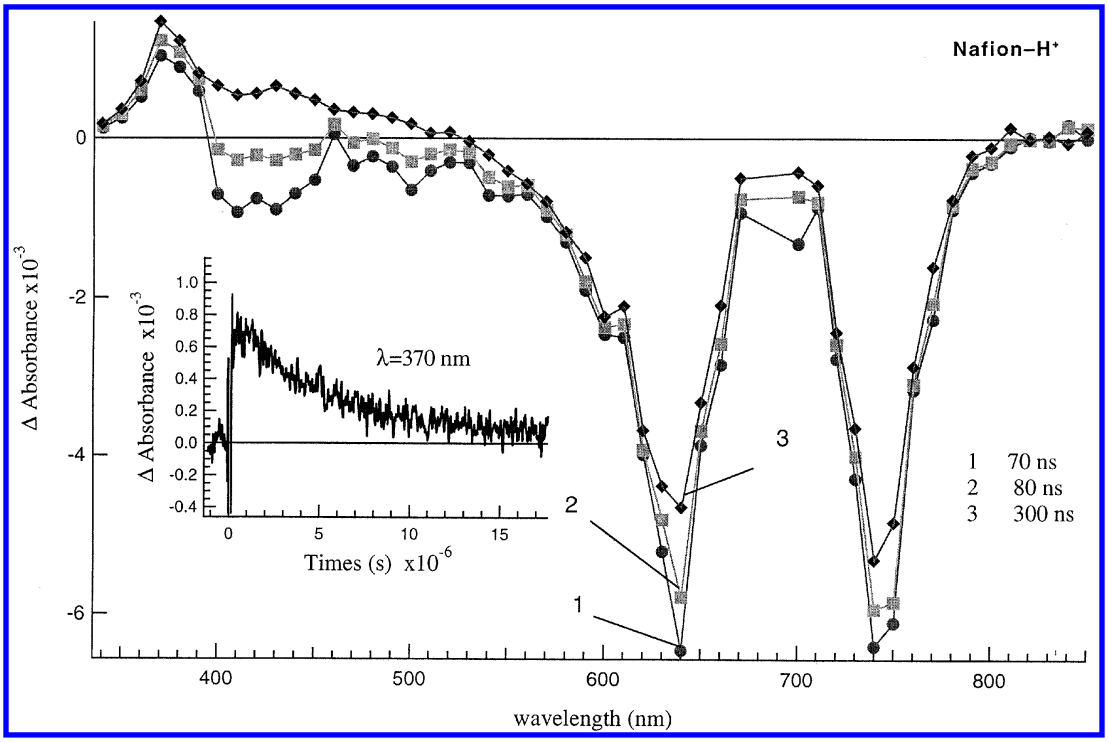

Figure 6. Transient absorption spectra of MB in Nafion−H^+. Excitation at $\lambda = 347$ nm. Concentration of MB in the membranes is 0.5×10^{-3} M. Time delay: (1) 70 ns; (2) 80 ns; (3) 300 ns. Inset: transients at $\lambda = 370$ nm.

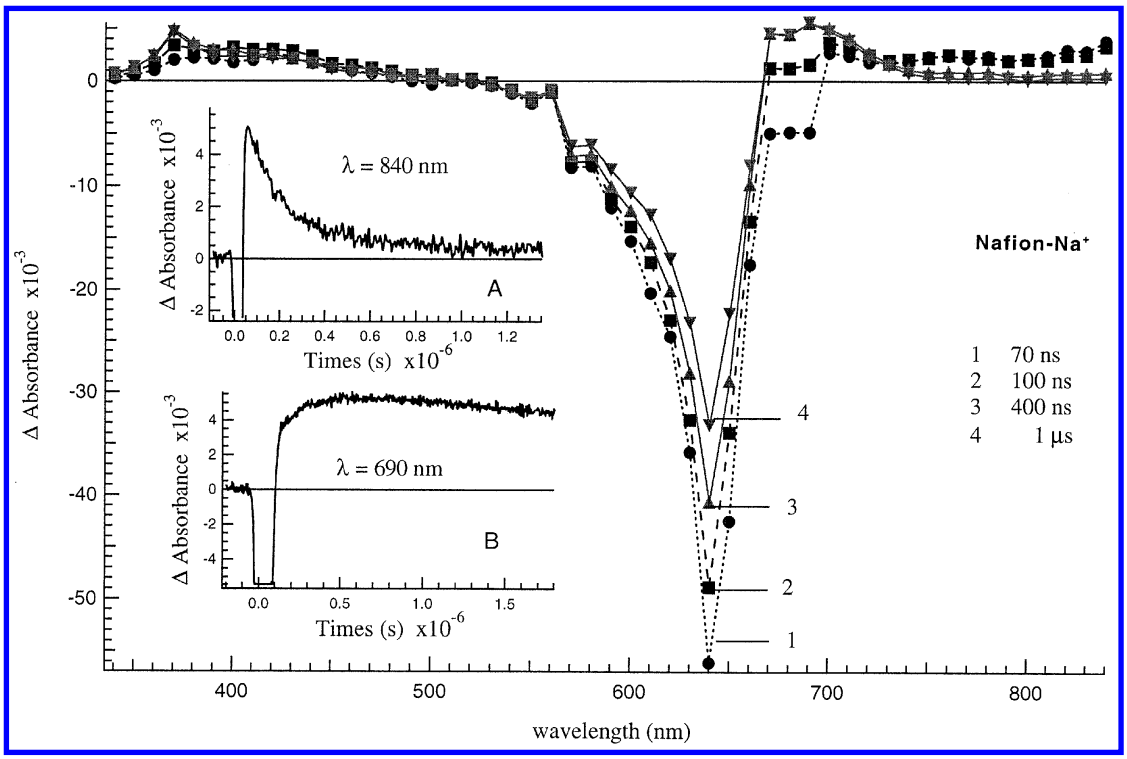

Figure 7. Transient absorption spectra of MB in Nafion−Na^+. Excitation at $\lambda = 347$ nm. Concentration of MB in the membranes is 0.5×10^{-3} M. Time delay: (1) 70 ns; (2) 100 ns; (3) 400 ns.; (4) 1 μs. Inset: (A) transients at $\lambda = 840$ nm. (B) transients at $\lambda = 690$ nm.

~20−25, the quenching efficiency of MB fluorescence exceeds the efficiency predicted by the Poisson distribution. This is seen in Figure 5. Therefore, a simple model to account for the statistical distribution of Fe^{2+} between clusters fails in the case of high Fe^{2+} concentrations.

Laser Photolysis of Methylene Blue in Nafion−H^+, −Na^+, and −Fe^{2+}. Figures 6, 7, and 8 present the transient absorptions of MB in Nafion−H^+, Nafion−Na^+, and Nafion−Fe^{2+} membranes, respectively.

Figure 6 shows the absorption and bleaching bands of MB^+ and MBH^{2+} monomer in Nafion−H. The transient absorption band at $\lambda = 370$ nm in water at acidic pH for MB shown in the inset of Figure 6 is ascribed to the protonated triplet−triplet absorption of the dye monomer $(MBH^{2+})^{T30}$ in the region between 420 and 820 nm. The inset in Figure 6 reveals that the absorption transient recovers to the baseline. This is also observed with the bleaching transients at 640 and 740 nm. The nature of the transient is assigned from the similarity of the

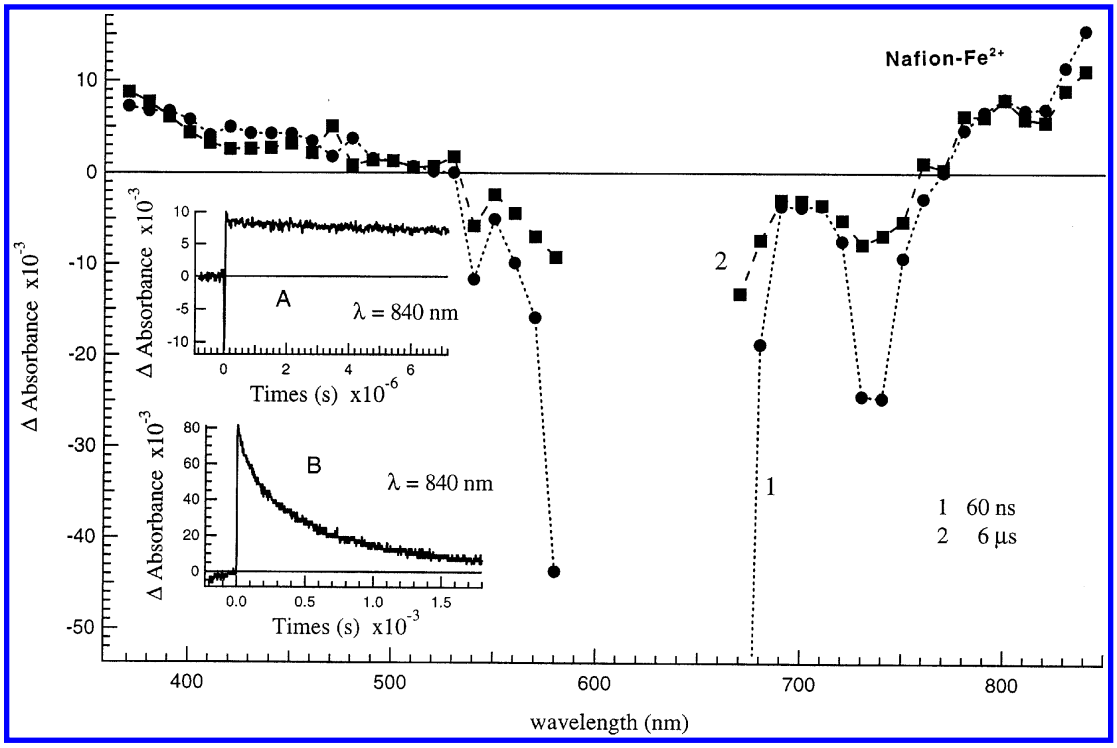

Figure 8. Transient absorption spectra of MB in Nafion−Fe^{2+}. Excitation at $\lambda = 347$ nm. Concentration of MB in the membranes is 0.5×10^{-3} M. Concentration of Fe^{2+} in solution is 42 mM, pH = 2.4. Time delay: (1) 60 ns; (2) 6 μs. Inset: (A) transients at $\lambda = 840$ nm, microsecond time scale; (B) transients at $\lambda = 840$ nm, millisecond time scale.

decay time of the absorption and bleaching transient found during the experiments presented in Figure 6. In both cases no product formation was observed. The spectral shift from 375 to 420 nm and the absorption band at $\lambda = 820$ nm is interpreted as due to the different protonation of the triplet state when going from acid to neutral and then to basic media. The pK_a of triplet MB has been estimated to be 6.7−7.5 in water.[30] The transients decaying more slowly than the triplet described above is suggested to be due to loosely bound semiquinone and $(MB^{2+}\cdots MB)$.[31,32]

The absorption in Nafion−Na^+ membrane around 660−700 nm for MB is presented in Figure 7, corresponding to the semiquinone and univalent charged MB dimer $(MB^{2+}\cdots MB)$. This is consistent with the assignment already mentioned in Figure 6. In the case of the Nafion−H^+, bleaching was observed with a maximum ~740 nm for the protonated forms and at 640 nm in the case of the nonprotonated form. Figure 7 shows for Nafion−Na^+ bleaching occurring at the position of the nonprotonated form. In both cases in Figures 6 and 7 bleaching is observed at the position of the dimer absorption band. This means that laser photolysis is able to excite protonated, nonprotonated, and dimer forms of Nafion−H^+. In Figure 7 the absorption at >700 nm is be ascribed to $(MB^+)^T$. As seen from the insets A and B (Figure 7) the transient decay at 840 nm occurs concomitantly with a rise in transient absorption at $\lambda = 690$ nm. The lifetime of the transients at $\lambda = 840$ nm is seen to be about 110 ns and the transient at $\lambda = 690$ nm shows a longer lifetime of about 6.7 μs. Therefore, the semiquinone and univalent-charged MB dimer $(MB^{2+}\cdots MB^{\bullet})$ formation seems to originate from the quenching of MB*.

Figure 8 shows transient absorption spectra after the pulse laser excitation of MB in the Nafion−Fe^{2+} membrane. Despite meaningful spectral overlap between MB* and the semiquinone radical forms it was found that the MB semiquinone radical was generated in solution because of electron transfer between Fe^{2+} and MB*. The observed decay in Figure 8 is different

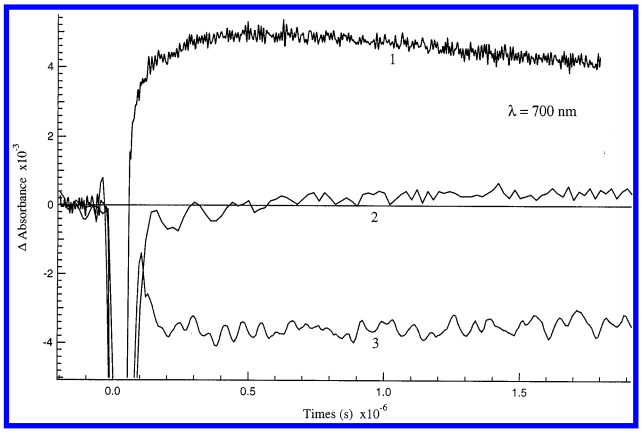

Figure 9. Transients of MB at $\lambda = 700$ nm in the three type of Nafion membranes: (1) Nafion−Na^+, (2) Nafion−H^+, and (3) Nafion-Fe^{2+}. Concentration of MB in the membranes is 0.5×10^{-3} M. Excitation is at $\lambda = 347$ nm.

from the decay reported in Figures 6 and 7. As seen from the insets A and B in Figure 8 the transient formation is very fast but the decay occurs in milliseconds, in the contrast to results for Nafion−Na^+. The transients had lifetimes of ~110 ns at $\lambda = 840$ nm. Two types of quenching processes, static and dynamic do occur simultaneously between excited MB and Nafion−Fe^{2+}. Analysis of the transient kinetics reported in Figure 8 allows us to differentiate between the two processes and will be shown next.

Figure 9 shows the transients at $\lambda = 700$ nm for Nafion−H^+, Nafion−Na^+, and Nafion−Fe^{2+} membranes. The absorptions due to MB* and MB^+ are responsible for the transient observed at $\lambda = 700$ nm in Figure 9, trace 1, in the case of Nafion−Na^+. No optical absorption is seen under the same experimental conditions in Nafion−H^+ as seen in Figure 9, trace 2. The bleaching seen in the case of Nafion−Fe^{2+} at 700 nm is due to the formation of the MB-reduced radical (Figure 9, trace

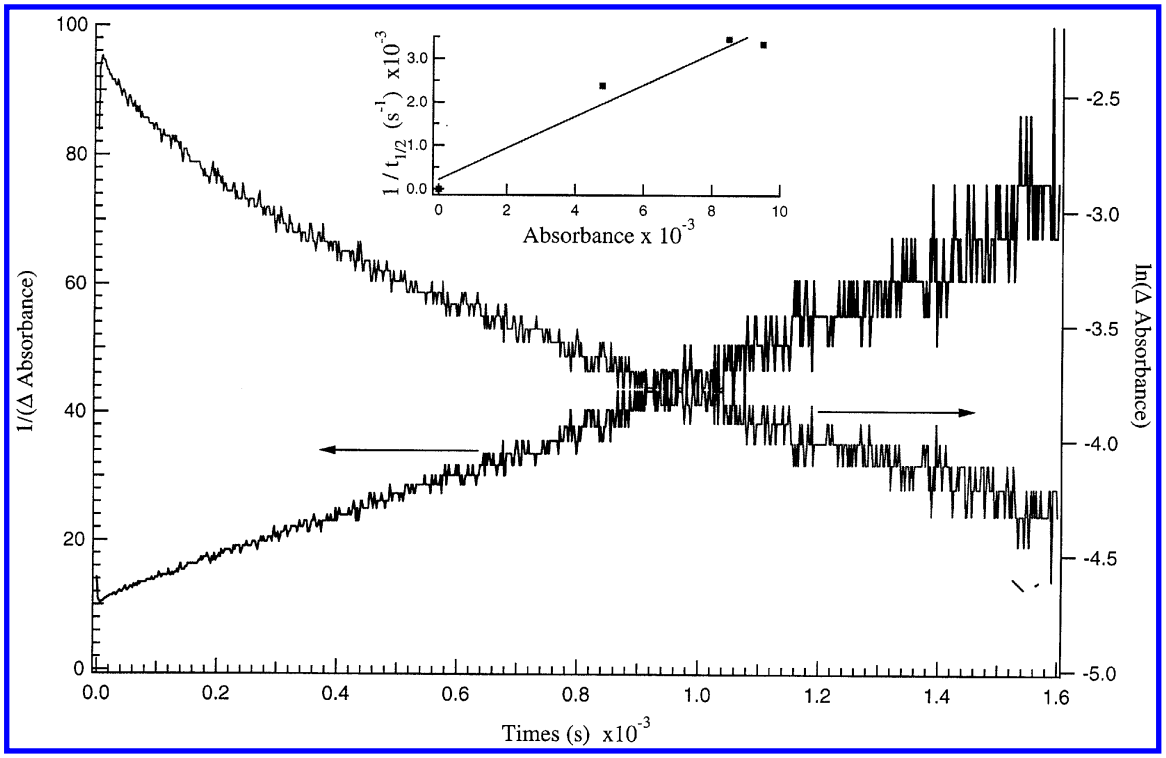

Figure 10. Transient decay at $\lambda = 830$ nm for MB in the Fe^{2+}−Nafion as 1/(Δabsorbance) vs time (left axis) and ln(Δabsorbance) vs time (right axis). Inset shows the dependence of reciprocal half-time of the decay vs the amplitude of the initial absorbance ($t = 0$) when the excitation energy is varied.

3). The bleaching in trace 3 grew in with $\tau = 170$ ns when the concentration of Fe^{2+} in the membrane is $[Fe^{2+}] = 0.67$ M. This corresponds to a quenching rate constant $k_q = 8.78 \times 10^6$ $(M\ s)^{-1}$. The form of the bleaching trace suggests static quenching taking place between the singlet excited MB by Fe^{2+}, leading to the reduction of the excited MB by Fe^{2+}. This agrees with the fluorescence quenching of MB by Fe^{2+} in the Nafion membrane. Owing to the spectral overlap between triplet excited MB and the MB semiquinone radical, it is difficult to separate quantitatively the dynamic from the static leading to the reduced form of MB. After the reduced semiquinone radical formation of MB and Fe^{3+}, back electron transfer should be expected as stated in reaction 4. The kinetics of the back-electron-transfer reaction is described by the decay of the absorption at $\lambda = 840$ nm on the millisecond time scale (inset B, Figure 8).

$$MB^{\bullet} + Fe^{3+} \rightarrow MB^{+} + Fe^{2+} \qquad (4)$$

The kinetics of reaction 4 is shown in the Figure 10 in coordinates of first- and second-order decay. The inset in Figure 10 shows the dependence of the reciprocal half-time as a function of the initial laser pulse energy. Both, the dependence of the half-time in reaction 4 on the initial amplitude and of 1/(Δabsorbance) vs time in reaction 4, proceed with second-order kinetics. The dependence of the half-decay time on the transient initial amplitude at time zero indicated that a second-order decay process was also present as a second reaction channel. This result is not evident because Fe^{3+} and MB−semiqunione are formed in the cluster as ion pairs. Second-order recombination processes are possible in Nafion if the exchange of Fe^{3+} ions occurring between clusters proceeds faster than the reaction of the MB−semiquinone radical and Fe^{3+} in the particular cluster. The analysis of the bleaching trace of MB indicates that the MB−semiquinone radical recovered completely. The bleaching trace in the laser photolysis was seen to attain the zero level after completion of reaction 4. This indicates dismutation of MB radicals leading to the leuco form of MB, in agreement with the decoloration of MB observed in Nafion−Fe^{2+} under steady-state illumination.[25]

Acknowledgment. This work was supported by the European Communities Environmental Program ENV 95-0064 (OFES Contract No 96.350, Bern).

References and Notes

(1) Eisenberg, A., Yeager, H. L., Eds. *Perfluorinated Ionomer Membranes*; ACS Symposium Series 180; American Chemical Society: Washington, DC, 1982.
(2) Szentirmay, M. N.; Martin, C. R. *Anal. Chem.* **1984**, *56*, 1898.
(3) Cutler, S. G. In *Ions in Polymers*; Eisenberg, A., Ed.; Advances in Chemistry Series 187; American Chemical Society: Washington, DC, 1980; Chapter 9.
(4) Hsu, W. Y.; Gierke, T. D. *Macromolecules* **1982**, *15*, 101.
(5) Olah, G. A.; Meidar, D. *Nouv. J. Chim.* **1979**, *3*, 269.
(6) Olah, G.A.; Kaspi, J.; Bukala J. *J. Org. Chem.* **1977**, *42*, 4187.
(7) Olah, G. A.; Meidar, D.; Olah, J. A. *Nouv. J. Chem.* **1977**, *3*, 275.
(8) Olah, G. A.; Meidar, D.; Malhorta, D. R.; Olah, J. A. *J. Catal.* **1980**, *61*, 96.
(9) Lee, P. S.; Meisel, J. *Photochem. Photobiol.* **1985**, *41*, 21.
(10) Deng, Q.; Hu, Y.; Moore, R. B.; McCormick, C. L.; Mauritz, K. A. *Chem. Mater.* **1997**, *9*, 36.
(11) Lee, P. S.; Meisel, J. *J. Am. Chem. Soc.***1980**, *102*, 5477.
(12) Pietro, N. E.; Martin, C. R. *J. Electrochem. Soc.* **1984**, *131*, 751.
(13) Szentirmay, M. N.; Prietro, N. E.; Martin, C. R. *J. Phys. Chem.* **1985**, *89*, 3017.
(14) Sabatini, E.; Gray, H. B.; Anson, F. C. *J. Am. Chem. Soc.* **1996**, *118*, 1158.
(15) Weir, D.; Scaiano, J. C. *Tetrahedron* **1987**, *43*, 1617.
(16) Priyadarsini, K. I.; H.; Mittal, J. P. *J. Photochem. Photobiol. A* **1993**, *69*, 345.
(17) Childs, R.F.; Mika-Gibata, A. *J. Org. Chem.* **1982**, *47*, 4204.
(18) Tung, C.-H.; Guan, J.-Q. *J. Org. Chem.* **1996**, *61*, 9417.
(19) Lee, P. C.; Rodgers, M. A. J. *J. Phys. Chem.* **1984**, *88*, 4385.
(20) Kuczynski, J. P.; Ilosavljevic, B. H.; Thomas, J. K. *J. Phys. Chem.* **1984**, *88*, 980.
(21) Mua, A. W.; Kakuta, N.; Bard, A. J. *J. Am. Chem. Soc.* **1986**, *106*, 6537.

(22) Morrison, C.; Bandara, J.; Kiwi, J. *J. Adv. Oxid. Technol.* **1996**, *2*, 160.
(23) John, S. A.; Ramaraj, R. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1241.
(24) Niu, Er.-P.; Mau, A. W.-H.; Chiggino, K. P. *Aust. J. Chem.* **1991**, *44*, 695.
(25) Mika, A.; Lorenz, K.; Szczurek, A. *J. Membr.* Sci. **1989**, *41*, 163.
(26) Gopidas, K.; Kamat, P. V. *J. Phys. Chem.* **1990**, *94*, 4723.
(27) Gak, Y.; Nadtochenko, V.; Kiwi, J. *Photochem. Photobiol. A* **1998**, *57*, 116.
(28) Bergmann, K.; O'Konski, C. T. *J. Phys.Chem.* **1963**, *67*, 2169.
(29) Mujerkee, P.; Ghosh, A. K. *J. Am. Chem. Soc.* **1970**, *92*, 6403.
(30) Nilsson, R.; Merkel, P. B.; Kearns, D. R. *Photochem. Photobiol.* **1972**, *16*, 109.
(31) Kato, S.; Morita, M.; Koizumi, M. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 117.
(32) Danziger, R.; Bar-Eli, K.; Weiss, K. *J. Chem. Phys.* **1967**, *71*, 2633.
(33) Niu, E. P.; Chiggino, K. P.; Mau, A. W. H.; Sasse, W. H. E. *J. Lumin.* **1988**, *40*, 563.
(34) Infelta, P. P.; Gratzel, M.; Thomas, J. K. *J. Chem. Phys.* **1974**, *78*, 190.
(35) Nadtochenko, V. A.; Rubtsov, I.V.; Smirnov, V. A.; Dgabiev, T. S. *Chem. Phys.* **1986**, *5*, 209.