Organic Donor−π-Acceptor Salts: A New Type of Probe for Monitoring Photopolymerization Processes[1]

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ABSTRACT: Organic salts consisting of an organic cation, composed of an alkylated pyridinium ion linked to a dimethylamino group by a π-system, and an inorganic anion were incorporated in polymeric networks formed by photopolymerization of dimethacrylates of different size and polarity. The response of the probe's emission to changes in its environment during photopolymerization was determined and compared with the response of 4-(dimethylamino)-4′-nitrostilbene, a typical charge transfer probe. Emissions in solvents of low viscosity but with different polarities are also reported. A mechanism to explain the probe's response is presented.

Introduction

Fluorescent probes are widely used in chemistry for monitoring specific properties of the medium in which they are incorporated. An important application of fluorescent probes in polymer chemistry is in monitoring a polymerization process. During such a process, a significant increase in medium viscosity is observed; therefore probes whose emission is sensitive to the rigidity of their environment are specifically fit for this purpose. Probes whose intensity increases upon polymerization[2] or during other rigidification processes such as physical aging[3] and probes whose emission wavelength shifts to shorter wavelengths during a polymerization process are well known.

Thus far, all probes shown to exhibit blue shifts in emission wavelength during polymerization processes are solvatochromic probes of the charge transfer type. Both D−π-A[4] and D−σ-A[5] probes have been reported. In this paper, we introduce a new type of fluorescent probe for monitoring the degree of cure of polymerization reactions; organic salts of the D−π-A$^+$X$^-$ type. Structurally, such probes resemble the charge transfer probes of the D−π-A type. Though both kinds of probes are used as laser dyes[6] and have been extensively studied for second-order NLO applications,[7] their photophysical behavior is quite different. The organic salts described in this paper are found to be specifically sensitive to the rigidity of their environment. They do not monitor temperature or solvent polarity!

In this report, we describe the change in the emission spectra of the charge resonance probes **1**−**4** (Figure 1) during photopolymerization of dimethacrylates (Figure 2). The results are compared to those obtained with **5**, a typical charge transfer probe. We also report studies of the absorption and emission of such probes in solvents of low viscosity. A mechanism will be presented to explain these observations. Other experiments that support this mechanism will be briefly mentioned.

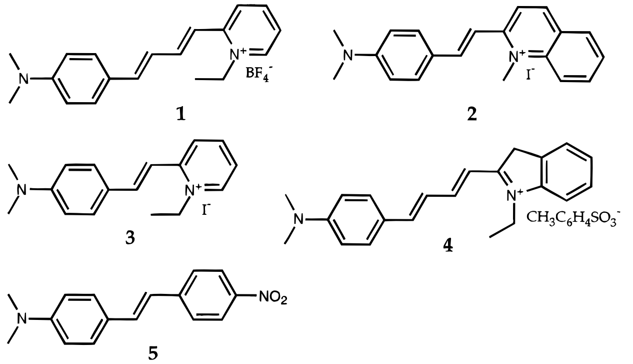

Figure 1. Fluorescent probes used for monitoring the degree of cure of a (photo)polymerization process.

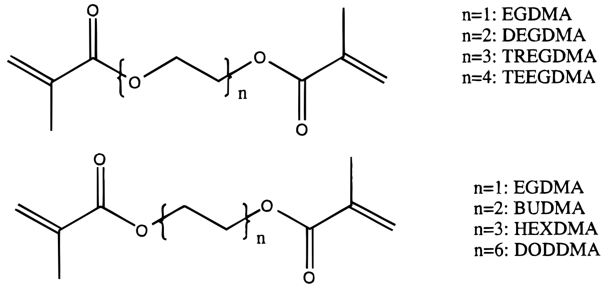

Figure 2. Different poly(ethylene glycol) and diol based dimethacrylates.

Experimental Section

The dimethacrylates, ethylene glycol dimethacrylate (EGDMA), diethylene glycol dimethacrylate (DEGDMA), triethylene glycol dimethacrylate (TREGDMA), tetraethylene glycol dimethacrylate (TEEGDMA), and 1,4-butanediol dimethacrylate (BUDMA) were purchased from Aldrich. 1,6-Hexanediol dimethacrylate (HEXDMA) and 1,12-dodecanediol dimethacrylate (DODDMA) were purchased from Monomer-Polymer and Dajac Laborotories. The chemical purity of the monomers was between 90 and 98%. All monomers contained radical inhibitor, typically 100 ppm 1,4-dimethoxybenzene, and were used without further purification. Irgacure 907 (2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropanone-1) was a gift from Ciba-Geigy and was used as the photoinitator. 2-[4-(4-(Dimethylamino)phenyl)-1,3-butadienyl]-1-ethylpyridinium tetrafluoroborate ("pyridine 1", **1**),[8] 2-[4-(4-(dimethylamino)phenyl)-1,3-butadienyl]-3-ethylbenzothiazolium *p*-toluenesulfonate ("styryl 7", **4**), both laser grade, and 4-(dimethylamino)-4′-nitrostilbene (**5**) were purchased from Kodak. 2-[4-(Dimethylamino)styryl]-1-methylquinolinium iodide (**2**) and 2-[4-(dimethylamino)styryl]-1-ethylpyridinium iodide (**3**) were purchased from Aldrich.

Fluorescence measurements were recorded on a Spex Fluorolog 2 recording fluorometer in the front-phase mode for monomeric and polymeric films and at right angles for solutions. Absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. IR spectra were recorded on a Mattson Instruments 6020 Galaxy Series FT-IR.

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Table 1. Absorption Maxima of 1−5 in Selected Solvents

solvent	Δf	λ_{max} absorption (nm) 1	2	3	4	5
cyclohexane	0.100					419
di-*n*-butyl ether	0.194					421
diethyl ether	0.251					420
chloroform	0.251	498	554	478	598	438
ethyl acetate	0.292	465		452	540	426
tetrahydrofuran	0.308	476		462	552	432
1,2-dimethoxyethane	0.309	484	528	463	568	430
dichloromethane	0.319	530	556	500	622	439
acetonitrile	0.398	472	518	456	555	430

Table 2. Emission Maxima of 1−5 in Selected Solvents

solvent	Δf	λ_{max} emission (nm) 1	2	3	4	5
cyclohexane	0.100					498[a]
di-*n*-butyl ether	0.194					564
diethyl ether	0.251					601
chloroform	0.251	683	645	569	695	731
ethyl acetate	0.292	678		591	703	668
tetrahydrofuran	0.308	685		604	709	672
1,2-dimethoxyethane	0.309	684	673	597	709	694
dichloromethane	0.319	674	660	590	700	n.e.[b]
acetonitrile	0.398	690	n.e.[b]	608	707	n.e.[b]

[a] Vibrational structure in spectrum. [b] n.e., no emission.

Table 3. Fluorescence Maxima in Networks Formed with Different Dimethacrylates before and after Complete Photopolymerization

resin	phase	probe 1	2	3	4	5
DODDMA	monomer	659				639
	polymer	589				555
	difference	70				84
HEXDMA	monomer	660				664
	polymer	600				570
	difference	60				84
BUDMA	monomer	664	635	576	706	677
	polymer	607	598	544	66	576
	difference	57	37	32	43	101
EGDMA	monomer	668	635	569	705	691
	polymer	611	602	557	669[a]	585
	difference	57	33	12	36[a]	106
DEGDMA	monomer	672	628	570	705	697
	polymer	614	597	545	660	595
	difference	58	31	25	45	102
TREGDMA	monomer	673	625	576	703	695
	polymer	618	599	548	658	601
	difference	55	26	28	45	94
TEEGDMA	monomer	674	629	576	705	704
	polymer	621	603	554	*b*	613
	difference	53	26	22	*b*	91

[a] Weak emission due to photobleaching of the probe. [b] Not determined due to rapid photobleaching of the probe.

Photochemical Polymerizations. Polymeric networks were made by exposing 15 μm films of the target dimethacrylates to UV light in a Colight M218 lightbath (using two 400 W medium-pressure Hg lamps). Irgacure 907 (1% by weight) was used as the photoinitiator, and the fluorescent probes were added in amounts 0.02% by weight. Films were made by squeezing a drop of monomer between NaCl or glass plates divided by a 15 μm Teflon spacer. The emission spectra of various probes (Figure 1) in various dimethacrylates (Figure 2) were measured after subsequent irradiations, until no spectral shift was observed in the emission spectra (usually 15−20 min). Double-bond conversions were determined by FT-IR, focusing on the 810 cm^{-1} bending vibration of the acrylic CH group.

Results and Discussion

Spectroscopic Characterization. In this section, we discuss the spectroscopic properties of probes **1**−**4** in solvents of different polarity. Our studies were limited by the fact that **1**−**4**, which are actually organic salts, are not soluble in solvents with a polarity lower than that of ethyl acetate. Absorption and emission spectra of probes **1**−**4** are summarized in Tables 1 and 2. Data for the charge transfer compound **5** are included in these tables for comparison.

The data presented in Table 1 clearly indicate that **1**−**4** are nonsolvatochromic in absorption, and no correlation was found between the absorption maxima and the solvent parameter Δf.[5b] In dichloromethane a strong red shift is observed for all probes. Similar shifts also occur in chloroform. These red shifts are likely caused by stabilization of the excited state by solvents whose highly polarizable electrons rearrange rapidly enough to influence the absorption spectra.[9]

No solvatochromism is observed in the emission spectra of **1**−**4** (see Table 2). For **1** a slight red shift upon increasing the polarity of the solvent is observed, but this is negligible compared to the shift that is observed for **5**. For all probes **1**−**4**, a slight blue shift in dichloromethane and chloroform is observed, but this shift is much smaller that the red shift in absorption. An explanation for this blue shift is similar to the explanation for the red shift in absorption. A stabilization of the ground state due to polarizable electrons in the solvent molecules is fast enough to be observed in emission.[9]

The quantum yields of fluorescence for all the organic salts are low. For **1**, a compound that is used as a laser dye, the quantum yield of emission in THF is 0.05, while a quantum yield of 0.02 is determined in acetonitrile. These values are similar to those of solvatochromic stilbene- or 1,4-diphenylbutadiene-based probes.[4b] For **3** and **4** the quantum yields are lower, and **2** is virtually nonfluorescent in most solvents of low viscosity, including monomers. Only in polymers can a reasonably intense emission be obtained from **2**.

Photopolymerization of Dimethacrylates. Position of Fluorescence Maxima before and after Curing. The emission maxima for different probes in different dimethacrylates were measured as a function of the irradiation time. Emission spectra were taken every 5 min and, after 15−20 min, no spectral shifts were observed upon further irradiation. These results are in accord with FT-IR measurements, which indicate that double-bond conversions do not increase significantly after a 15−20 min irradiation period.[4b] The degree of cure obtained in these polymers is the same as those reported in ref 4b. Addition of 0.02% probe has not influenced the rate of the photopolymerization process or the final double-bond conversion. The emission wavelengths of **1**−**5** in monomeric phases and after photopolymerization are summarized in Table 3. Normalized emission spectra of **1** in EGDMA are displayed in Figure 4, and the probe's emission plotted against the double-bond conversion is shown in Figure 5.

Not all probe−resin combinations are included in Table 3, due to the limited solubility of the probes in the apolar resins HEXDMA and DODDMA. Due to the lack of solvatochromism, the emission of probes **1**−**4** is observed to be at similar wavelengths regardless of the monomer.

All probes exhibit significant blue shifts upon the formation of a photopolymer in their presence. Values range from 70 nm for **1** in DODDMA to 12 nm for **3** in EGDMA.[10] The data in Table 3 clearly indicate that

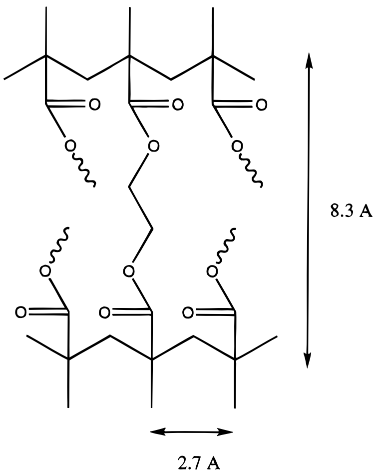

Figure 3. Schematic representation of the polymeric network formed with EGDMA.

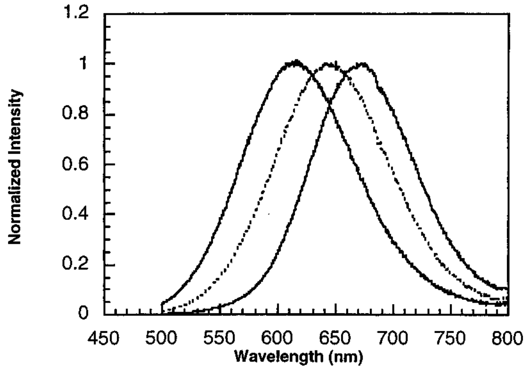

Figure 4. Normalized emission of **1** in EGDMA before irradiation (right spectrum), after 2 min irradiation (middle spectrum), and after 20 min irradiation (left spectrum). Double-bond conversions, determined by FT-IR, are 0, 38, and 76%, respectively.

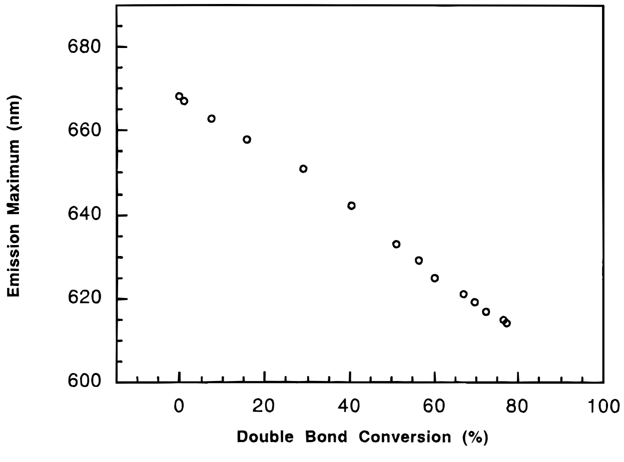

Figure 5. Emission maximum of **1** in EGDMA as a function of the double-bond conversion (15 μm samples between NaCl plates).

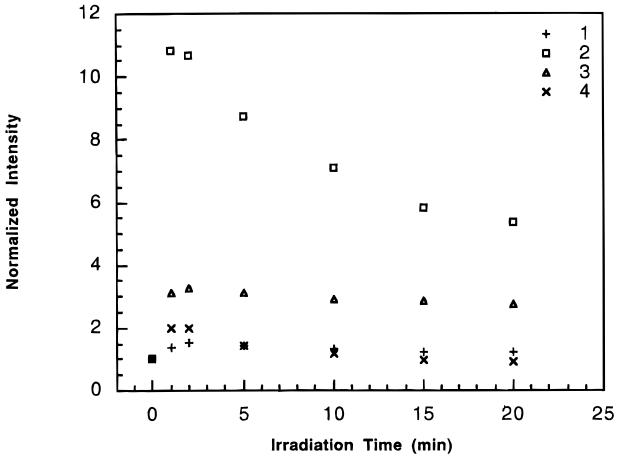

Figure 6. Normalized emission intensity of **1**−**4** in TREGDMA as a function of the irradiation time (15 μm samples between glass plates). The emission in the monomer, before irradiation, is set to 1 for all probes.

the magnitude of the blue shift, which is primary determined by the probe, is larger for the 1,4-diphenylbutadiene probes **1** and **4** than for the stilbene type probes **2** and **3**. It can also be seen that the shifts observed for **1** are significantly larger than those for **4**.

The exact value of the blue shift that a probe exhibits is determined by the type of resin used. It is clear that the magnitude of the shift increases with a decrease in resin polarity, especially for probe **1**. This is mainly caused by differences in the probe's emission in polymeric phases. Upon decreasing the medium polarity, as in going from TEEGDMA to DODDMA, the emission wavelength of **1** in the monomer decreases 15 nm, while the emission wavelength in the polymer decreases 32 nm.

Intensity of the Emission. A direct comparison between the performance of **1**−**4** in different resins in terms of the intensity of emission during the photopolymerization process cannot be made, since even 0.02% of these probes cannot be dissolved in all resins.

The best solubility for **1**−**4** is reported in TREGDMA and surprisingly BUDMA. This indicates that a simple correlation between the polarity of the resin and the solubility of the probe in the resin does not exist. However, with the exception of **1** that has a better solubility, none of the probes could be dissolved in HEXDMA and DODDMA in satisfactory quantities.[11]

For all probes the photopolymerization of their environment results in a blue shift in emission and an increase of the emission intensity. The increase in emission intensity in polymers compared to that in solvents of low viscosity is a fairly general phenomenon. Emission intensities for the probes **1**−**4** in TREGDMA, which are normalized to 1 in the monomer, are plotted as a function of the irradiation time in Figure 6. Clearly, the biggest increase in emission is observed for **2**—roughly a factor of 12—while probes **1** and **4** show only a twofold intensity increase upon polymerization. It should be noted that the spectacular increase in emission intensity for **2**, as much as 20-fold in BUDMA, is merely a consequence of the fact that the emission quantum yields of **2** in nonviscous solvents are extremely low. The emission maxima of all probes reach a maximum after an irradiation period of 1−2 min. Further irradiation causes photochemical bleaching of the probes, which results in a decrease in emission intensity, especially for **2** and **4**. Probes **1** and **3** are fairly stable under prolonged irradiation.

Discussion. The results show that the organic salts **1**−**4** are suitable probes for monitoring photopolymerization processes *in situ*. The blue shifts observed upon polymerization are comparable to those observed for most charge transfer probes.[4b] However, the shift that these probes exhibit upon polymerization must be explained by another mechanism.

The largest blue shifts are observed for probes **1** and **4**, suggesting that increasing the size of the π-system that separates the cation and the dimethylamino group

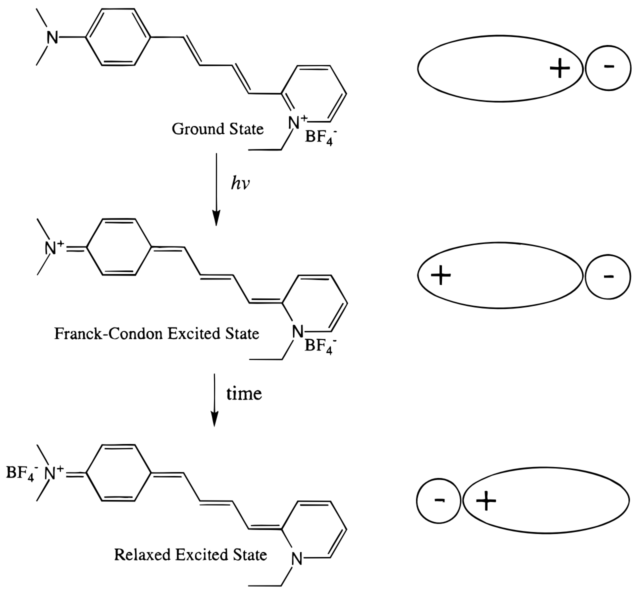

Figure 7. Schematic representation of the ground state, Frank Condon excited state, and fully relaxed excited state proposed for **1**.

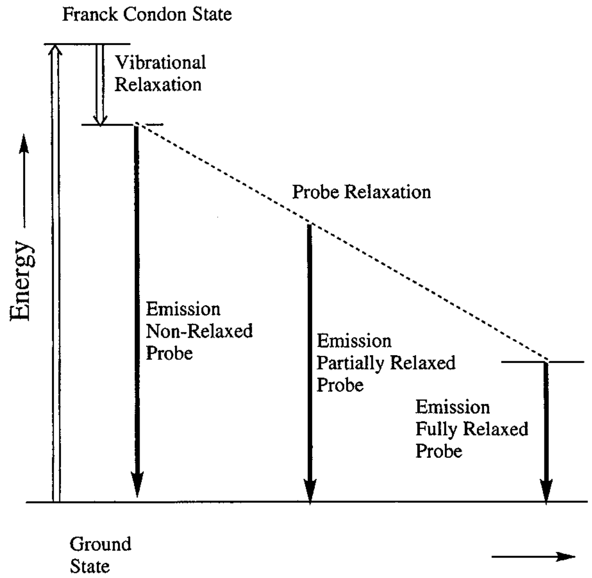

Figure 8. Schematic representation of the probe's emission in different media.

results in an increase of this shift. Another observation is that the shift of **1** is significantly larger than the shift that **4** exhibits.

In order to explain the photophysical behavior of **1**−**4**, in particular the lack of solvatochromism and the blue shift in emission upon photopolymerization, we propose the mechanism presented in Figures 7 and 8. We discuss the mechanism in detail, presenting additional observations for **1** that support this mechanism. We propose that the positive charge in the cation is localized on the pyridinium ion in the ground state, but that it changes its locus in the excited state (see Figure 7). For the 4-[4-(dimethylamino)styryl]-1-methylpyridinium ion, calculation of the HOMO and the LUMO indicates that positive charge is transferred from the pyridinium ion to the (dimethylamino)phenyl group.[12] For simplicity, we assume that the positive charge is at the dimethylamino group after excitation. We also assume that this positive charge will be stabilized *primarily* by the counterion. Stabilization by the solvent does occur, but plays a less significant role.

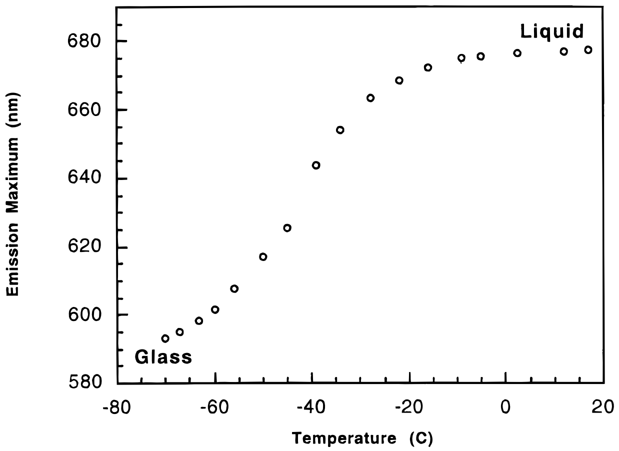

Figure 9. Emission maxima of **1** as a function of temperature in DEGDMA.

The lack of solvatochromism can be explained by observing that, from an electrostatic point of view, the ground state and the fully relaxed excited state are roughly equivalent (see Figure 7). Therefore the polarity of the solvent does not significantly influence the emission wavelength of the probe. The ability of these probes to monitor the rigidity of their environment is explained by the decreased mobility of the counterion. In systems of increased rigidity, the anion will not be able to follow the cation and the excited state is stabilized to a lesser extent (see Figure 8). It should be noted that in these cases the polarity of the solvent might play an important role.

A blue shift in emission after photopolymerization is observed for all probes (see Table 3). It turns out that one does observe a blue shift for these salts not only during polymerization reactions but also in other processes in which the rigidity of the probe's environment increases. When the emission spectra of **1** in DEGDMA as a function of temperature are recorded, for example, an 80 nm blue shift is observed upon cooling (see Figure 9).[13] (It should be noted that at 60 °C this monomer forms a solid glass though it is a liquid of low viscosity at room temperature.) This blue shift can be ascribed to rigidity changes in the medium only. The emission of **1** does not shift as a function of temperature; in THF, a solvent that has a low viscosity even at −80 °C, no changes in emission maxima are observed between −80 and +20 °C.

That the 1,4-diphenylbutadiene probes **1** and **4** are more sensitive probes can be explained by the fact that the charge will be displaced over a longer distance in these systems. The observation that **1** is more sensitive than **4** cannot be rationalized on the basis of this study. Finally, we can explain the increase of this shift upon decreasing the polarity of the monomer observed for **1** by assuming that in polymeric systems, in which the anion is immobilized, stabilization of the excited state by the solvent will play a significant role.

Conclusions

We have reported a new type of probe for monitoring photopolymerization reactions. Though structurally similar to charge transfer probes reported previously by our group, the photophysical behavior of these organic salts is rather different. In order to explain the blue shifts that occur upon photopolymerization, we propose a mechanism in which the position of the positive charge on the cation changes position. We postulate that the excited state is stabilized primarily by the (position of the) anion. Since the anion is more mobile in monomers than in polymers, a blue shift upon polymerization is expected. A similar blue shift in the same monomers is obtained by freezing monomers to a glass. The lack of solvatochromism can be explained by this mechanism. In photopolymerization reactions **1** is by far the most sensitive probe, and blue shifts up to 70 nm are observed. In the future, a systematic variation of the position of the pyridinium ion, the number of double bonds, and the anion needs be undertaken to deepen our understanding of the behavior of these types of probes. Attempts will be undertaken to make these probes more soluble in apolar resins, for instance by extending the alkyl chain attached to the pyridinium ion.

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(7) (a) For examples, see: *Polymers for Second-Order Nonlinear Optics*; Lindsay, G. A., Singer, K. D., Eds.; ACS Symposium Series 601; American Chemical Society: Washington, DC, 1994. (b) Marder, S. R.; Perry, J. W.; Yakymyshyn, C. P. *Chem. Mater.* **1994**, *6*, 1137.

(8) For pyridine **1** the structural formula, 3-[4-(4-(dimethylamino)phenyl)-1,3-butadienyl]-1-ethylpyridinium tetrafluoroborate, is given in the Kodak Optical Products catalog. Based on ^{1}H NMR spectra and U.S. Patent 3,833,863, we conclude that 2-[4-(4-(dimethylamino)phenyl)-1,3-butadienyl]-1-ethylpyridinium tetrafluoroborate is the correct structure.

(9) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH: Weinheim, 1988; Chapter 6.

(10) It should be noted that the 12 nm blue shift observed for **3** in EGDMA is exceptionally small and mainly due to emission in the polymer at an exceptionally long wavelength. We will exclude this result from further discussions.

(11) Actually, emission spectra from these very dilute solutions can be recorded but at these low concentration, fast photobleaching occurs.

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