# Solvatochromic Fluorescent Probes for Monitoring the Photopolymerization of Dimethacrylates

**Wolter F. Jager, Andries A. Volkers, and D. C. Neckers***

*Center for Photochemical Sciences,[1] Bowling Green State University, Bowling Green, Ohio 43402*

*Received June 20, 1995; Revised Manuscript Received September 13, 1995*[⊗]

ABSTRACT: The fluorescent probes 7-(dimethylamino)-4-(trifluoromethyl)coumarin (**1**), *N*,*N*-di-*n*-butyl-5-(dimethylamino)-1-naphthalenesulfonamide (**2**), 4-(dimethylamino)-4′-(methylsulfonyl)stilbene (**3**), 4-(dimethylamino)-4′-(methylsulfonyl)diphenylbutadiene (**4**), and 4-(dimethylamino)-4′-nitrostilbene (**5**) (Figure 2) were incorporated in polymeric networks formed by photopolymerization of dimethacrylates of different molecular sizes and polarities (Figure 3). The response of the probe's emission to changes in its environment during photopolymerization was determined and compared with the emissions in solvents of low viscosity of differing polarities (solvatochromism). A comparison between these data reveals that the blue shifts observed during polymerization are roughly proportional to the solvatochromism of each probe.

## Introduction

Monitoring the molecular environment of a small molecule by means of its fluorescence has been widely employed in chemistry.[2] Such small molecules are usually designed to examine specific properties of their immediate environment or microenvironment by means of a shift in the maximum of their emission or changes in their emission intensity and are referred to as fluorescent probes. Probes which monitor the polarity[3] as well as those which monitor the rigidity[4] of the matrix in which they reside are well-known.

In the design of fluorescent probes that monitor polymerization processes, the approach has been to find compounds the fluorescence of which monitors the rigidity of the medium. Polymerization, going from a liquid monomer of low viscosity to a solid polymer or a polymeric network, causes large changes in the mobility of the molecules or molecular fragments that comprise the medium.

One way to monitor a polymerization process is to investigate the degree of polarization in the emission of a probe that has been excited with linearly polarized light. The anisotropy of the probe's fluorescence gives information about the mobility, in particular the rotational mobility of the probe molecules, in the surrounding matrix.

Another option is the use of probes that form excimers. Excimer formation is a viscosity dependent process, because migration of the probe to a second molecule like it is required for it to be observed. Because a high concentration of the probe is needed in order to observe excimer formation, this limits the use of excimers for probing the molecular environment.[5]

In our research group[6] we have devoted considerable effort to fluorescent probes that exhibit dual fluorescence ascribed to the formation of a fluorescent twisted intramolecular charge transfer state (TICT).[7] During polymerization the red-shifted strongly solvatochromic emission, ascribed to the TICT state, is quenched and a strong blue shift is observed. However, since the fluorescence quantum yield of compounds such as 4-(dimethylamino)benzonitrile is low (typically 0.01–0.05), their utility as fluorescent probes is somewhat limited.

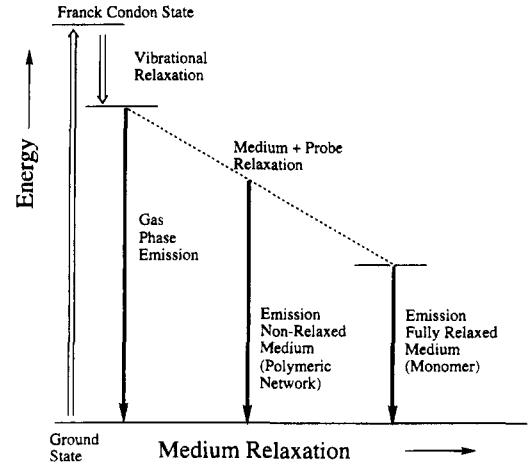


**Figure 1.** Schematic representation of the probe's emission in different media.

Recent publications have reported that the strongly solvatochromic D-$\sigma$-A compound "Fluoroprobe" is sensitive not only to the polarity of its environment but also to the morphology of the matrix in which it resides.[8] It was demonstrated that this compound can be used to follow the thermal polymerization of methyl methacrylate (MMA).[9]

Solvatochromism[3,10] is the response in the absorption or emission spectrum of a molecule upon changing the solvent polarity, and we have theorized that strongly solvatochromic D-$\pi$-A molecules should be sensitive probes, in the emission mode, for monitoring polymerization processes. In general these molecules have relatively low dipole moments in the ground state and large dipole moments in the excited state due to considerable intramolecular charge separation (ICT). The emission maxima of these molecules shift to longer wavelengths as the polarity of the solvent is increased because the stabilization of the dipolar excited state is larger in polar solvents. In solvents of low viscosity, the mobility of the solvent molecules compared to the lifetime of the emitting species is such that emission occurs from a fully relaxed state. A schematic representation of this process is presented in Figure 1.

In a highly viscous medium in which the mobility of the molecules or molecular fragments is strongly decreased, the situation is fundamentally changed and the

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1995.

0024-9297/95/2228-8153$09.00/0 

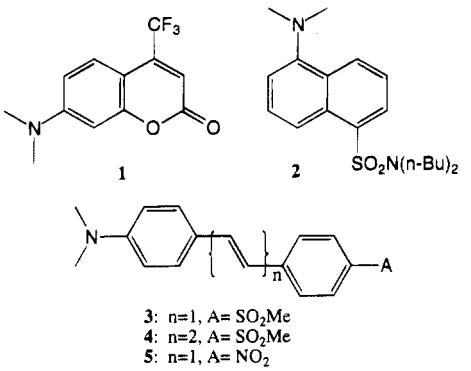


**Figure 2.** Fluorescent probes used for monitoring the degree of cure of a (photo)polymerization process.

reorientation of the medium cannot be completed within the lifetime of the excited state. Emission takes place from a partially relaxed medium at wavelengths shorter than observed when the medium is fully relaxed; see Figure 1.

The photopolymerization of multifunctional acrylates can be regarded as a process in which monomer units are immobilized by linking them together in a polymeric network. To the first approximation, immobilization of the monomers is the primary process and the response of a solvatochromic probe upon polymerization will be a blue shift. The changes in chemical composition of the medium, specifically the disappearance of double bonds, are neglected.

In this approximation the magnitude of the shift of a certain probe–monomer combination will mainly depend on two factors; the degree of immobilization of molecular fragments in the network and the sensitivity of the probe toward solvent polarity. A stronger immobilization will further reduce the relaxation of the medium and will lead to emission at shorter wavelengths.

The solvatochromism of the probe molecule will also determine the shift in emission during polymerization. If the stabilization that a certain polymeric network achieves during the probe's excited state lifetime is constant for a series of probes, the wavelength shift is proportional to the probe's sensitivity for solvent polarity. This process can also be visualized using Figure 1. For a stronger solvatochromic probe the slope of the line that connects gas phase emission and emission in the monomer will increase and, as can easily be seen, so will the blue shift.

On the basis of these considerations we expect blue shifts in emission for solvatochromic probes upon polymerization of their environment. The magnitudes of these blue shifts are expected to be proportional to the solvatochromism of the probe and will also increase if more rigid polymers are formed.

In this paper we describe the emission of the D-$\pi$-A[11] probes depicted in Figure 2 during photopolymerization of the dimethacrylates depicted in Figure 3. We will investigate the relation between the solvatochromism in emission of the probes and their behavior as probes during photopolymerization in different resins.

## Experimental Section

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

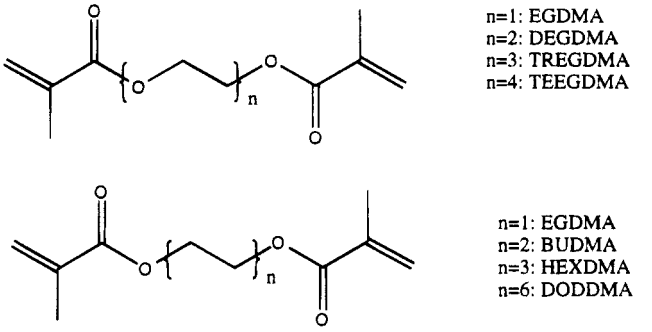


**Figure 3.** Different (poly)(ethylene glycol) and diol based dimethacrylates.

purchased from Monomer and Polymer and Dajac Laboratories. According to the manufacturers, the chemical purity of these monomers was between 90 and 98%. All monomers contained radical inhibitors, 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. 7-(Dimethylamino)-4-(trifluoromethyl)coumarin (coumarin 152, **1**), laser grade, and 4-(dimethylamino)-4′-nitrostilbene (**5**) were purchased from Kodak. *N*,*N*-Di-*n*-butyl-5-(dimethylamino)-1-naphthalenesulfonamide (**2**) was prepared by the reaction of *N*,*N*-di-*n*-butyl-5-(dimethylamino)-1-naphthalenesulfonyl chloride with dibutylamine.[12] 4-(Dimethylamino)-4′-(methylsulfonyl)stilbene (**3**) and 4-(dimethylamino)-4′-(methylsulfonyl)diphenylbutadiene (**4**) were prepared by the Wittig–Horner reaction of diethyl 4-(methylsulfonyl)benzyl phosphonate with (*N*,*N*-dimethylamino)benzaldehyde and (*N*,*N*-dimethylamino)cinnamaldehyde, respectively.[13]

Fluorescence measurements were recorded on a Spex Fluorolog 2 recording fluorometer, in the front face configuration for monomeric and polymeric films and at right angles for solutions. The solvatochromism of the emission of different probes was characterized by plotting the emission maxima of the probes as a function of the solvent polarity. The $\Delta f$ values for different solvents were taken from the literature, using eqs 1 and 2.[14] Fluorescence quantum yields were determined relative to 9,10-diphenylanthracene ($\Phi_f = 0.83$ in cyclohexane).

Absorption spectra were recorded on a Hewlett Packard 8452A diode array spectrophotometer.

**Photochemical Polymerizations.** Polymeric networks were made by exposing 15 $\mu$m films of the target dimethacrylates to UV light in a Colight M218 light bath (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 0.02% amounts by weight. Films were made by squeezing a drop of monomer between NaCl or glass plates divided by a 15 $\mu$m Teflon spacer. The emission spectra of various probes (Figure 2) in various dimethacrylates (Figure 3) were measured in the front face configuration before irradiation and after subsequent irradiations, until no spectral shift was observed in the emission spectra (usually 15–20 min).

Using 4-(dimethylamino)-4′-nitrostilbene (**5**) as the fluorescent probe, the photopolymerization process was followed by FT-IR, focusing on the 810 $cm^{-1}$ bending vibration of the acrylic CH group. The emission wavelengths and emission intensities were determined as a function of the double bond conversion.

## Results and Discussion

**Probe Characterization.** In this research we have investigated a wide range of fluorescent probes having a strong electron donor (dimethylamine) and a strong electron acceptor attached to an aromatic moiety. Commonly, these compounds are used as laser dyes or as second-order NLO materials.[15] The coumarin (**1**)[16] is a strongly fluorescent laser dye. *N*,*N*-Di-*n*-butyl-5-(dimethylamino)-1-naphthalenesulfonamide (**2**) is a fluores-

**Table 1. Emission Maxima of 1–5 in Selected Solvents**

| solvent | $\Delta f$ | $\lambda_{max}$ emission (nm) 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| cyclohexane | 0.100 | 426 | 450 | 439[a] | 470[a] | 498[a] |
| di-*n*-butyl ether | 0.194 | 449 | 471 | 450 | 496 | 564 |
| diethyl ether | 0.251 | 452 | 480 | 465 | 515 | 601 |
| ethyl acetate | 0.292 | 478 | 501 | 491 | 545 | 668 |
| tetrahydrofuran | 0.308 | 478 | 500 | 496 | 552 | 672 |
| 1,2-dimethoxyethane | 0.309 | 485 | 506 | 502 | 552 | 694 |
| dichloromethane | 0.319 | 476 | 502 | 506 | 556 | n.e.[b] |
| acetonitrile | 0.398 | 501 | 524 | 522 | 587 | n.e. |

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

**Table 2. Fluorescence Quantum Yields of 1–5 in Solution**

| solvent | $\Phi_f$ 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| cyclohexane | 1.0 | 0.64 | 0.03 | 0.08 | 0.24 |
| tetrahydrofuran | 1.0 | 0.61 | 0.03 | 0.08 | 0.007 |
| acetonitrile | 0.37 | 0.46 | 0.06 | 0.07 | 0 |

**Table 3. Linear Relationship between $\nu_{CT}$ and $\Delta f$**

| | | |
|---|---|---|
| **1** | $\nu_{CT} = 24651 - 11332\Delta f$ | $R = 0.942\ 13$ |
| **2** | $\nu_{CT} = 23237 - 10568\Delta f$ | $R = 0.987\ 19$ |
| **3** | $\nu_{CT} = 24470 - 13838\Delta f$ | $R = 0.963\ 00$ |
| **4** | $\nu_{CT} = 22906 - 15103\Delta f$ | $R = 0.991\ 48$ |
| **5** | $\nu_{CT} = 22816 - 26245\Delta f$ | $R = 0.993\ 24$ |

cent probe developed in our group.[17] The stilbenes (**3**[13,18] and **5**[19]) are known to have strong dipole moments in their excited state and are extensively studied as promising materials for second-order nonlinear optics applications. The 1,4-diphenylbutadiene (**4**), bears the same donor and acceptor groups as stilbene **3** and is included to determine if its larger size influences its sensitivity as a probe. Each of these molecules have comparatively low dipole moments in the ground state but have high dipole moments in the excited state due to intramolecular charge transfer (ICT) from the donor to the acceptor group.

The strongly dipolar excited states can be stabilized due to electrostatic interactions with the solvent and their fluorescence undergoes a red shift when the polarity of the solvent is increased.

$$\nu_{CT} = \nu_{CT(0)} - (2[\mu_e - \mu_g]^2/\rho^3 hc)\Delta f \quad (1)$$

$$\Delta f = (\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(4n^2 + 2) \quad (2)$$

Equation 1 states that the emission wavenumber in a solvent of low viscosity ($\nu_{CT}$) equals the emission wavenumber in the gas phase ($\nu_{CT(0)}$) minus a stabilization term in which $\mu_g$ and $\mu_e$ are the dipole moments in the ground and excited states, respectively, $\rho$ is the radius of the cavity in which the molecule fits, $h$ is Planck's constant, $c$ is the speed of light, and $\Delta f$ is the solvent parameter. The solvent parameter $\Delta f$ is defined by eq 2, in which $\epsilon$ is the dielectric constant and $n$ is the optical refractive index of the solvent.

As Table 1 shows, all probes are strongly solvatochromic in their emission. The emission wavelengths of the probes in a selected number of solvents are displayed in Table 1.

The solvatochromism in fluorescence of **1–5** is quantified by plotting the emission wavenumbers [$\nu_{max}$ (in $cm^{-1}$)] as a function of the solvent parameter $\Delta f$. Linear correlations are obtained for all probes (Table 3) and the slope of the line determines the sensitivity of the probe toward solvent polarity. For all probes slopes between 10 000 and 27 000 $cm^{-1}$ are obtained. These data indicate that **5** shows the strongest solvatochromism in its fluorescence.[20]

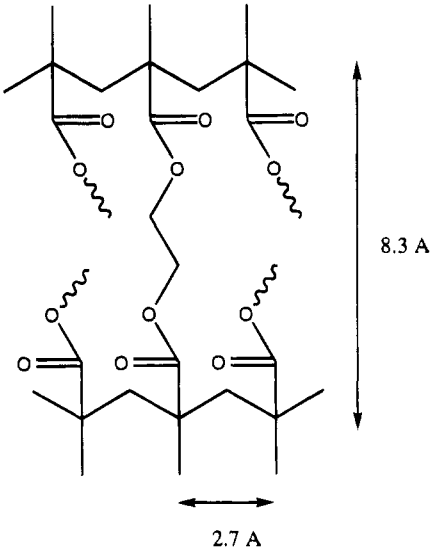


**Figure 4.** Schematic representation of the polymeric network formed with EGDMA.

The fluorescence quantum yields ($\Phi_f$) of the probes were determined and are shown in Table 2. For **1** the fluorescent quantum yield approaches unity in most solvents. Compound **2** has a high quantum yield (0.5–0.6) that is fairly insensitive to the solvent. The quantum yields of compounds **3** and **4** are lower by 1–2 orders of magnitude in all solvents. For the stilbene **5** a strong fluorescence in cyclohexane, which strongly decreases with increasing solvent polarity, is observed.[19] In polar solvents such as dichloromethane and acetonitrile no fluorescence was observed for **5**.

**Photopolymerization of Dimethacrylates.** For most practical purposes photocurable resins consist of a combination of multifunctional acrylates that form very complex polymeric networks. As an example, the standard resin used in our group for stereolithography consists of a mixture of di-, tri-, and pentaacrylates.[21] For this work we used pure dimethacrylates that form homogeneous polymeric networks with a simpler, more predictable structure.

As monomers a series of dimethacrylates of which the length and the composition of the spacer connecting the methacrylate units can be varied systematically were employed. Upon polymerization these monomers form polymeric networks in which the spacers act as side chains that connect rigid polymethacrylate main chains. A schematic representation of a polymeric network is displayed in Figure 4. The distance between the side chains is 2.7 Å for all polymers presented in this work, while the side chain length can be varied between 8 and 21 Å.[22]

As side chains (poly)glycols and aliphatic diols were used. When the length of the side chain is increased, the dimensions of the cages formed in the polymeric networks are increased while the rigidity of the network will decrease. By use of ethylene glycol units the decrease of the rigidity of the network will be accompanied by an increase in the polarity, while increasing the length of an apolar diol side chain will decrease both the rigidity and the polarity of the network.

It should be emphasized that these dimethacrylates are selected for distinguishing effects caused by the polarity and effects caused by the length of the side

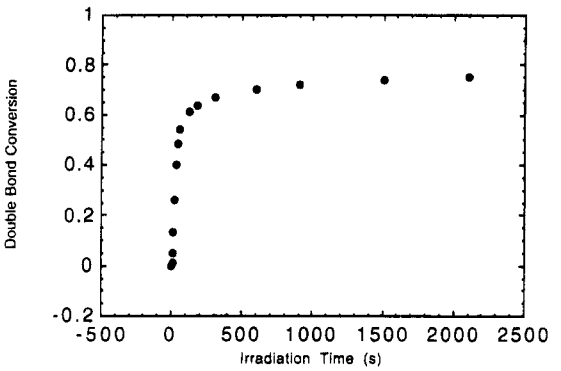


**Figure 5.** Double bond conversion of EGDMA, measured by FT-IR, as a function of the irradiation time.

**Table 4. Degree of Polymerization of Dimethacrylates Obtained after a 20 min UV Irradiation Period**

| monomer | deg of polym (%) | side chain length[a] (Å) |
|---|---|---|
| EGDMA | 76 | 8.3 |
| DEGDMA | 80 | 11.7 |
| TREGDMA | 87 | 15.3 |
| TEEGDMA | 92 | 18.8 |
| EGDMA | 76 | 8.3 |
| BUDMA | 78 | 10.8 |
| HEXDMA | 83 | 13.3 |
| DODDMA | 90 | 20.9 |

[a] Side chain lengths were calculated using MM2 for fully stretched, all-trans chains.

chains in the polymeric networks. For effects where polarity plays a major role, a monotonic change going from DODDMA to TEEGDMA via EGDMA is expected because the polarity of the monomers increases in this order. However, if the length of the side chains plays a decisive role, similar monotonic changes are expected going from EGDMA to TEEGDMA and going from EGDMA to DODDMA.

The double bond conversion for the diacrylates was monitored as a function of the irradiation time by monitoring the decrease of the 810 $cm^{-1}$ bending vibration of the acrylic CH. Figure 5, which is typical for the photopolymerization of all dimethacrylates used in this investigation,[23] shows the double bond conversion of EGDMA as a function of the irradiation time. As shown, the initial double bond conversion is fast and during the first 100 s a 65% double bond conversion is obtained. Subsequently, the double bond conversion is much slower, and after a 15–20 min irradiation no increase in double bond conversion is observed by FT-IR spectroscopy. We think that during the first stages of the photopolymerization, polymers with a low degree of cross-linking are formed. During the latter stages, presumably after the glass transition temperature, $T_g$, has risen above the reaction temperature, formation of rigid polymeric networks through extensive cross-linking takes place at a much lower rate.[24] $C^{13}$ CPMAS NMR experiments are in progress to verify this assumption. The double bond conversions obtained after 20 min irradiation periods are displayed in Table 4. These data reveal that when monomers with longer side chains are employed, higher degrees of polymerization result. This is observed in both the (poly)(ethylene glycol) and the alkanediol series. Also, for monomers with longer side chains, the rate of polymerization is higher. It should be emphasized that the double bond conversions summarized in Table 4 are by no means the maximum double bond conversion that can be obtained with these monomers. Preliminary experiments have shown that higher conversions are obtained by thermal polymerization (benzoyl peroxide, 100 °C).

**Table 5. Fluorescence Maxima in Networks Formed with Different Dimethacrylates before and after Complete Photopolymerization**

| | | probe | | | | |
|---|---|---|---|---|---|---|
| resin | phase | **1** | **2** | **3** | **4** | **5** |
| DODDMA | monomer | 473 | | 477 | | 639 |
| | polymer | 449 | | 448 | | 555 |
| | difference | 24 | | 29 | | 84 |
| HEXDMA | monomer | 480 | 498 | 487 | 541 | 664 |
| | polymer | 455 | 478 | 453 | 488 | 570 |
| | difference | 25 | 20 | 34 | 53 | 94 |
| BUDMA | monomer | 482 | 502 | 489 | 544 | 677 |
| | polymer | 455 | 484 | 456 | 491 | 576 |
| | difference | 27 | 18 | 33 | 53 | 101 |
| EGDMA | monomer | 484 | 502 | 493 | 547 | 691 |
| | polymer | 458 | 485 | 459 | 496 | 585 |
| | difference | 26 | 17 | 34 | 51 | 106 |
| DEGDMA | monomer | 487 | 506 | 498 | 552 | 697 |
| | polymer | 462 | 485 | 460 | 497 | 595 |
| | difference | 25 | 21 | 38 | 55 | 102 |
| TREGDMA | monomer | 487 | 508 | 497 | 552 | 695 |
| | polymer | 464 | 488 | 463 | 503 | 601 |
| | difference | 23 | 20 | 34 | 49 | 94 |
| TEEGDMA | monomer | 491 | 510 | 503 | 554 | 704 |
| | polymer | 464 | 490 | 467 | 508 | 613 |
| | difference | 27 | 20 | 36 | 46 | 91 |

**Position of Fluorescence Maxima before and after Polymerization.** 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. After 15–20 min no spectral shifts were observed upon further irradiation. These results are in accordance with FT-IR measurements, which indicate that the double bond conversion does not increase significantly after a 15–20 min irradiation period. The emission wavelengths of **1**–**5** in monomeric phases and after photopolymerization are summarized in Table 5. The degrees of polymerization obtained for these polymers are the same as those reported in Table 4.

After the photopolymerization process, samples were stored in the dark and reexamined regularly. We observed significant blue shifts for most probes. For instance when using **5** in EGDMA, emission wavelengths of 585, 573, and 563 nm are observed directly after a 20 min irradiation, after 2 days in the dark, and after 2 months in the dark, respectively. FT-IR studies indicate that the double bond conversion increases slowly upon standing in the dark and an 85% cure was observed for EGDMA after 2 months. (For thermally cured EGDMA [benzoyl peroxide, 100 °C] double bond conversions of 85% are observed also). However, besides an increase of the double bond conversion (aftercure), a decrease of the free volume in the network (physical aging) is also expected to occur upon standing.[25] In order not to confuse these two processes, the emissions obtained after physical aging of the polymer are omitted. Instead, the emissions obtained directly after irradiation are discussed in this paper.

In EGDMA the emission of all probes lies between those reported for ethyl acetate and for 1,2-dimethoxyethane, molecules whose polarities are roughly comparable to those of a methyl methacrylate and an ethylene glycol unit. The probe emissions in our monomers, which apart from TREGDMA are all solvents of low viscosity, shift to the red as the polarity of the monomers increases. For all probes a steady increase of emission wavelength in the series HEXDMA–EGDMA–TEEG-

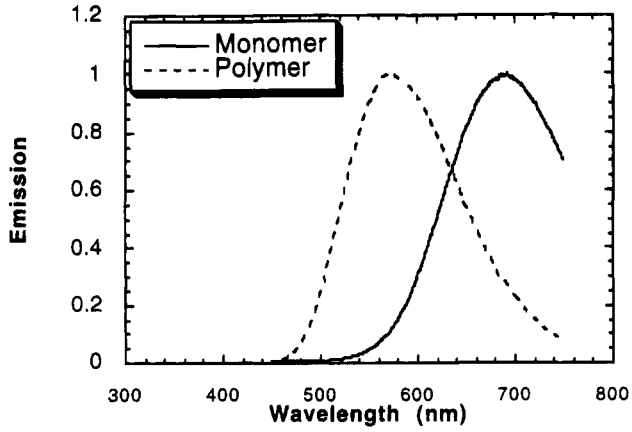


**Figure 6.** Normalized emission spectra of **5** in EGDMA before and after photopolymerization.

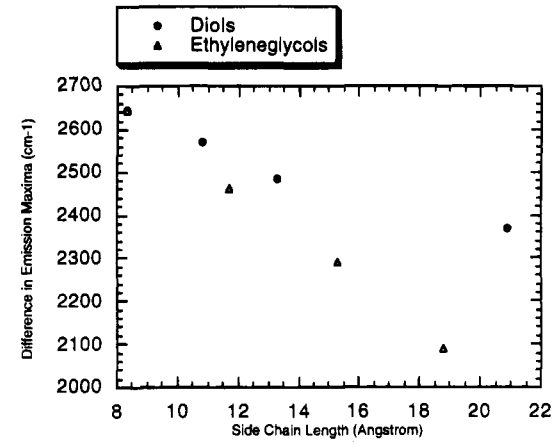


**Figure 7.** Shift in the emission maxima of **5** (in $cm^{-1}$) plotted against the length of the side chain (in Å).

DMA is observed. This indicates that the overall polarity of the dimethacrylate directs the response of the probes. As expected, this shift is larger for **5** which is clearly the most solvatochromic probe.

For all probes the emission wavelengths shift toward shorter wavelengths upon polymerization. This implies that the strongly dipolar excited states of the probe molecules are clearly less stabilized in the polymeric networks than in the corresponding monomeric phases.

Trends similar with regard to the emission wavelengths of the probes in the corresponding monomers are observed in polymeric networks. Despite variations in the length of the side chain, emission wavelengths increase monotonically in the HEXDMA–EGDMA–TEEGDMA series. Even the magnitude of these shifts are roughly the same as that of the corresponding shifts in the monomeric phases. Again this indicates that the polarity of the monomer, which is determined by the length and the composition of the spacer, and not the lengths of the side chains in the polymeric network, controls the emission wavelength of the probe.

A large variation of the shift in emission wavelengths upon photopolymerization is found for probes **1**–**5**. For **1** and **2** small shifts of 26 and 19 nm, respectively, are observed. The blue shifts for **3** and **4** are increased to values of 34 and 51 nm, respectively, while the **5** blue shifts up to 106 nm are found, Figure 6. Comparison of the data in Tables 3 and 5 reveals a fair correlation between the shift of emission upon polymerization of the dimethacrylate and the solvatochromism of the fluorescent probes.

For all probes we observed that a stronger sensitivity toward solvent polarity results in a larger blue shift upon polymerization. This implies that the assumption that the sensitivity toward solvent polarity and the sensitivity as probe for monitoring polymerization reactions are related is correct. The reason for this correlation is that both phenomena depend *upon the capability of the probe's strongly dipolar excited state to be stabilized by its environment by means of electrostatic interactions.*

Probes **3**–**5** undergo cis–trans isomerization in solvents of low viscosity, such as cyclohexane, when irradiated by our light source. This was checked by UV–vis measurements. For **4** and **5** isobestic points and a regular decrease of the long wavelength absorption are observed, indicating that only trans–cis isomerizations are occurring. Since the cis isomers do not absorb at the excitation wavelength we use (420 nm for **4** and **5**) and are not fluorescent, trans–cis isomerization can diminish the intensity but not change the shape of the emission spectrum. UV measurements of **5** in monomer and polymer show that the degree of trans–cis isomerization is low. The decrease in absorption at 420 nm is below 5% in the first stages of the polymerization process.

For **3** a trans–cis isomerization is followed by the formation of a species, presumably a dihydrophenanthrene, that both fluoresces and absorbs at the excitation wavelength used (380 nm). This means that formation of this isomer, which can occur during the first stages of the photopolymerization, affects both the shape and the intensity of the emission spectra. Therefore **3** is not a suitable probe for monitoring photopolymerizations because its fluorescent response will be determined by both the probe's environment and the isomeric composition of the probe itself.

For most probes the shifts in emission upon polymerization are similar for each of the dimethacrylates. Differences in polarity, rigidity of the polymeric matrix, or the obtained double bond conversion apparently do not influence this shift.[26] For **5** a correlation between the shift and the length of the side chain was observed. Figure 7 displays the shift in fluorescence as a function of the side chain length in both the (poly)(ethylene glycol) and the diol based dimethacrylates. Clearly, the shift increases as the length of the side chain decreases, especially in the (poly)(ethylene glycol) series. These results indicate that in EGDMA the changes upon polymerization are larger than for the other dimethacrylates. Despite the fact that the double bond conversions are lower, this result suggests that more rigid networks are formed with monomers that have shorter spacers.

**Intensity of the Emission.** Upon polymerization the intensity of the emission, which is proportional to the fluorescence quantum yield, $\Phi_f$, changes as a function of irradiation time. For **1** and **2**, probes that have high fluorescence quantum yields in solution, a steady decrease of the emission intensity upon photopolymerization was observed. The most likely explanation is that a photochemical decomposition of the probe molecules occurs during the reaction. For **3**–**5** a sharp increase in intensity during the first stages of the polymerization is observed, followed by a slow decrease. The steep increase in emission intensity during the photopolymerization, which is similar to the effects reported by Loutfy,[4] can be ascribed to a decrease of the rate of internal conversion in viscous media.

The enhancement of the intensity of emission upon polymerization is especially pronounced for **5**. If one

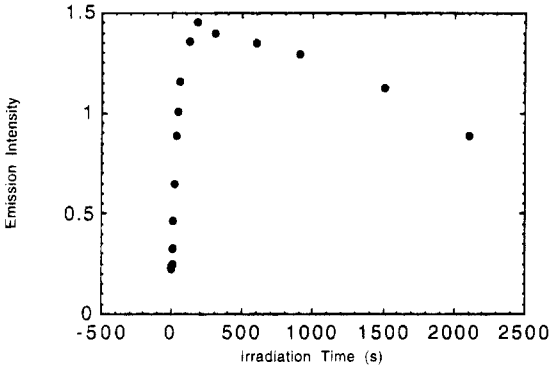


**Figure 8.** Emission intensity of **5** in EGDMA. The maximum value is reached after a 3 min irradiation, where a 64% double bond conversion is achieved.

follows emission intensity as a function of irradiation time (and the degree of polymerization), Figure 8 shows the result with EGDMA as the monomer. The large increase in emission intensity, a factor 6 in the case of EGDMA, depends strongly upon the polarity of the dimethacrylate. For the polar TEEGDMA a 9-fold increase in intensity is observed, while in DODDMA the increase was only 2-fold. In all cases **5** is strongly fluorescent in polymer films. As reported in the previous section, the fluorescence quantum yield of **5** sharply decreases with an increase of the solvent polarity in low-viscosity solvents. The fact that the strongest increase in intensity is observed in the most polar dimethacrylates suggests that the fluorescence quantum yield of **5** reaches the same value in all polymeric networks.

## Conclusions

Strongly solvatochromic fluorescent probes are excellent compounds for monitoring photopolymerization processes. We have demonstrated that for neutral D-$\pi$-A molecules the sensitivity toward solvent polarity and the sensitivity to act as a fluorescent probe for monitoring polymerization processes are correlated and roughly proportional.

In a series of dimethacrylates in which the length of the spacer that connects the methacrylate moieties and the polarity of the dimethacrylates was altered systematically, the shift of most probes appeared to be relatively insensitive to these changes. This indicates that these probe molecules experience similar changes in their environment.

For 4-(dimethylamino)-4′-nitrostilbene (**5**), however, the blue shift increased when monomers with shorter spacers are used, regardless of the composition of those spacers. This behavior is in accordance with our expectation that solvatochromic probes mainly monitor the changes in rigidity of the medium upon polymerization. Other fluorescent probes, such as those that undergo considerable changes in charge distribution upon excitation but which are not necessarily solvatochromic, are currently under investigation.

**Acknowledgment.** This work has been supported by the Office of Naval Research (ONR-N00014-91-J-1921) and the National Science Foundation (DMR 90-13109). The authors are most grateful for this support. The authors also gratefully acknowledge the McMaster Endowment at Bowling Green State University for partial support. The Colight reactor was a gift of Conrad Hanovia Corp. (Mr. Len Perre) upon the occasion of the inauguration of the Center for Photochemical Sciences.

## References and Notes

(1) Contribution No. 238 from the Center for Photochemical Sciences.
(2) Rabek, J. F. *Mechanisms of Photophysical Processes and Photochemical Reactions in Polymers*; John Wiley & Sons: Chichester, U.K., 1987; Chapter 4.
(3) Reichardt, C. *Chem. Rev.* **1994** *94*, 2319. Paley, M. S.; McGill, R. A.; Howard, S. C.; Wallace, S. E.; Harris, J. M. *Macromolecules* **1990**, *23*, 4557.
(4) Loutfy, R. O. *Macromolecules* **1981**, *14*, 270. (b) Loufty, R. O.; Teegarden, D. M. *Macromolecules* **1983**, *16*, 452.
(5) Valdes-Aguilera, O.; Pathak, C. P.; Neckers, D. C. *Macromolecules* **1990**, *23*, 689.
(6) (a) Paczkowski, J.; Neckers, D. C. *Chemtracts: Macromol. Chem.* **1992**, *3*, 75. (b) Paczkowski, J.; Neckers, D. C. *Macromolecules* **1991**, *24*, 3013.
(7) (a) Rettig, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 971. (b) Al-Hassan, K. A. *J. Photochem. Photobiol. A: Chem.* **1994**, *84*, 207.
(8) Jenneskens, L. W.; Verhey, H. J.; van Ramesdonk, H. J.; Witteveen, A. J.; Verhoeven, J. W. *Macromolecules* **1991**, *24*, 4038.
(9) van Ramensdonk, H. J.; Vos, M.; Verhoeven, J. W.; Möhlmann, G. R.; Tissink, N. A.; Meesen, A. W. *Polymer* **1987**, *28*, 951.
(10) (a) Lippert, E. *Z. Electrochem.* **1957**, *61*, 962. (b) Liptay, W. *Z. Naturforsch.* **1965**, *20A*, 1441.
(11) The distinction of a D-$\pi$-A probe from a D-$\sigma$-A probe involves the structure of the carbon hydrogen skeleton by means of which the donor and acceptor are separated.
(12) Song, J. C.; Torres-Filho, A.; Neckers, D. C. *RadTech '94 North Am. UV/EB Conf. Exhib. Proc.* **1994**, *1*, 338.
(13) Ulman, A.; Willand, C. S.; Köhler, W.; Robello, D. R.; Williams, D. J.; Handley, L. *J. Am. Chem. Soc.* **1990**, *112*, 7083.
(14) Mes, G. F.; de Jong, B.; van Ramesdonk, H. J.; Verhoeven, J. W.; Warman, J. M.; de Haas, M. P.; Horsman van den Dool, L. E. W. *J. Am. Chem. Soc.* **1984**, *106*, 6524.
(15) (a) Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 690. (b) Kanis, P. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195.
(16) Jones, G., II; Jackson, W. R.; Choi, C.; Bergmark, W. R. *J. Phys. Chem.* **1985**, *89*, 294.
(17) Song, J. C.; Neckers, D. C. *Polym. Mater. Sci. Eng.* **1995**, *72*, 571.
(18) Yu, D.; Yu, L. *Macromolecules* **1994**, *27*, 6718.
(19) Shin, D. M.; Whitten, D. G. *J. Phys. Chem.* **1988**, *92*, 2945.
(20) To our knowledge the strongest gradient, 34 000 $cm^{-1}$, is reported for the D-$\sigma$-A compound "Fluoroprobe"; see ref 14.
(21) Torres-Filho, A.; Neckers, D. C. *J. Appl. Polym. Sci.* **1994**, *51*, 931.
(22) The chain lengths were calculated by molecular mechanics (MM2) from isolated, fully stretched "*all trans*" chains.
(23) Aseth, K. S.; Decker, C.; Bowman, C. N. *Macromolecules* **1995**, *28*, 4040.
(24) (a) Kloosterboer, J. G.; van de Hei, G. M. M.; Gossink, R. G.; Dortant, G. C. M. *Polym. Commun.* **1984**, *25*, 322. (b) Fitzgerald, J. J.; Landry, C. J. T. *J. Appl. Polym. Sci.* **1990**, *40*, 1727.
(25) Royal, J. S.; Torkelson, J. M. *Macromolecules* **1993**, *26*, 5331.
(26) The margin of error for each emission maximum is ±2 nm, and errors in differences in emission maxima are ±4 nm. Therefore no conclusions can be drawn from the small variations in shifts of probes **1**−**4**.

MA950873R