Photopolymerization of Polyfunctional Acrylates and Methacrylate Mixtures: Characterization of Polymeric Networks by a Combination of Fluorescence Spectroscopy and Solid State Nuclear Magnetic Resonance[1]

Wolter F. Jager, Adrian Lungu, D. Y. Chen, and Douglas C. Neckers*

Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio 43403

Received October 2, 1996; Revised Manuscript Received December 17, 1996[⊗]

ABSTRACT: Fluorescence spectroscopy and solid state NMR methods were used to elucidate the detailed molecular structure of poly(meth)acrylate networks. Both techniques can be employed on identical samples and give complementary information. In this study a series of diacrylates, a series of dimethacrylates, and 1:1 mixtures of the triacrylate TMPTA with diacrylates (DA's) or dimethacrylates (DMA's), respectively, was investigated. Fluorescence spectroscopy was performed, using the shift in the fluorescence maximum of 4-(dimethylamino)-4′-nitrostilbene (**1**), a charge transfer probe. This probe monitors both the rigidity *and* the polarity of the medium in which it is incorporated. CPMAS ^{13}C NMR spectroscopy was employed monitoring the relaxation times, T_1, of carbon atoms from the main chains and pendant groups, determining cross-link densities, and measuring $T_{1\rho}(^1H)$ values. With these techniques information about the mobility of individual atoms and the homogeneity of the polymeric networks is obtained.

Introduction

Polyacrylate Networks. Multifunctional acrylates or acrylated oligomers are widely used as photopolymerizable resins employed in information storage systems, in rapid cure coatings, as restorative materials,[2] and in stereolithography.[3] Though their radical polymerizations are quenched by oxygen, acrylates form hard glassy polymeric networks, and for practical applications complex mixtures of multifunctional monomers, photoinitiators, and other additives are employed.[4] Though the use of multifunctional acrylates for the formation of thin films by photopolymerization is rather old and numerous studies concerning these systems have appeared in the literature,[5] many questions concerning the detailed molecular structure of the networks obtained and the exact mechanism by which they are formed remain.

The complex structures of acrylate networks are, in part, a consequence of the radical chain reactions by which they are formed.[6,7] One particularly complicating factor, not specific for networks formed by a chain reaction, is that topological factors and vitrification limit final double-bond conversion to well below 100%. Fully cured networks only form with oligomers that have relatively long and flexible spacers between acrylate functionalities.[8] As a result, pendant double-bonds or even unreacted monomers[9] are present in most polymeric networks. Such unreacted groups are unevenly distributed throughout the network. For diacrylates it has been shown that the first stages of photopolymerization form a polymeric network that is inhomogeneous in nature and best described by a random walk percolation model.[9] On the basis of this observation, the final polymer is also expected to be inhomogeneous on a molecular scale. Another factor that determines the structure of acrylate networks is that there seems to be no regularity as to which main chains are connected by which side chains. Main chains in poly(meth)acrylates formed by free radical polymerizations are atactic, a factor that further diminishes order in the system.

If mixtures of multifunctional monomers are used, the situation becomes even more complicated. The reactivity of the monomeric units, which apart from the chemical nature of these units[10] is influenced by steric factors that govern accessibility of the reactive sites and diffusion rates of free monomers, plays an important role. Another important factor determining network structure is solubility of the monomers and oligomers in one another. For binary mixtures of multifunctional monomers different scenarios can be anticipated.

In the simplest, most straightforward case, both resins are completely miscible at all stages of the polymerization process and the reactivities of the reactive groups in both are equal throughout the polymerization process. In this case a homogeneous network (at the NMR scale, <20 nm) is formed in which both monomers are incorporated in a statistical manner. If the corresponding linear polymers are not compatible, either due to differences in reactivity or to a limited solubility of one species in the other, a homogeneous network will not form. Discrete segments of networks of different compositions will form.

Finally, it should be noted that the structure of photoformed polymers depends on the photopolymerization conditions.[11] Therefore, to obtain identical polymeric networks, photopolymerizations need to be conducted using exactly the same conditions in terms of photoinitiator composition and concentration, light intensity, duration of irradiation, and so on. Also, analysis needs to be carried out promptly because a thermal aftercure[12] and physical aging alter the structure of the network.

CPMAS NMR. Cross-polarization magic angle spinning (CPMAS) ^{13}C NMR provides information about the detailed molecular structure of polymeric networks and

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1997.

S0024-9297(96)01468-4 CCC: $14.00

the dynamics of atomic motion in these networks.[13,14] Resolved isotropic chemical shifts identify chemical environments, and these may be unique to the solid state. Relaxation experiments exploit the high resolution that can be obtained by magic angle spinning, so that ^{13}C T_1's can be used to characterize individual main- and side-chain motions and $T_{1\rho}$'s[15] can be used to determine the homogeneity of networks.[16]

The influence of spin diffusion on proton relaxation times can be quite useful for investigating networks composed of different monomers.[13] High-resolution magic angle techniques used to obtain ^{13}C NMR spectra in solids can be employed to monitor the proton spin diffusion between the fragments originating from the different monomers incorporated in the polymer. For example, in a polymer network formed from two components, the protons may or may not all average to a common relaxation time. If the rate of spin diffusion (determined by the domain size and the spin diffusion constant) is large compared with the difference of that of the component monomers, only one $T_{1\rho}$ value is obtained for all protons. In such a case the components are all incorporated in *one* homogeneous network (on the scale of spin diffusion, $<15-20$ nm).[17] If the rate of spin diffusion is small compared to the difference in the relaxation rates (large domains/small diffusion constant), the components of the network retain their relaxation behavior. Different $T_{1\rho}$ values are determined for the components of the network, and it is concluded that a phase separation between the components of the network has occurred.[18] So, by determining the rates of spin diffusion of all components that are incorporated in a photoformed polymer, one can determine whether the network is homogeneous or whether a phase separation has occurred and monomers are incorporated in spatially separated networks. In fact, if the resolution allows one to distinguish ^{13}C absorptions from different monomers, one can determine which monomers are incorporated in which phase.[18]

The mobility of a specific carbon atom in a polymeric network can be determined by monitoring carbon spin−lattice relaxation times T_1 at different stages of the photopolymerization process.[18,19] However, a fair comparison between different polymers, components in a polymer blend or a heteropolymer, can be made only between similar types of carbon atoms, for instance, the methyl group of a methacrylate. Unfortunately, due to a limited resolution in solid state spectra, similar carbon atoms can not be resolved in blends or networks containing different components.

An interesting property of the polyacrylates under investigation is the cross-link density and the relative contributions of both components to the total cross-link density. Cross-link densities relate to the molecular architecture of the networks, which in turn determine the physical properties of acrylate networks. During the photopolymerization process of polyfunctional acrylates, ^{13}C T_1 measurements demonstrate that the mobility of the main chain carbons *specifically* decreases with an increase in the double-bond conversion. Based on these observations, cross-link densities in networks can be determined and even attributed to the individual components in the mixture, using the method developed by Rawland and Labun.[20]

Fluorescence Spectroscopy. 1. Introduction. Another method we have pioneered for monitoring polymerization processes is employing fluorescent probes. Polymerization processes, going from a liquid monomer to a solid glass, cause large changes in the mobility of the components that comprise the medium. Probes for monitoring polymerization progress fluoresce in a process that is directed by the rigidity or microviscosity of the medium.[21]

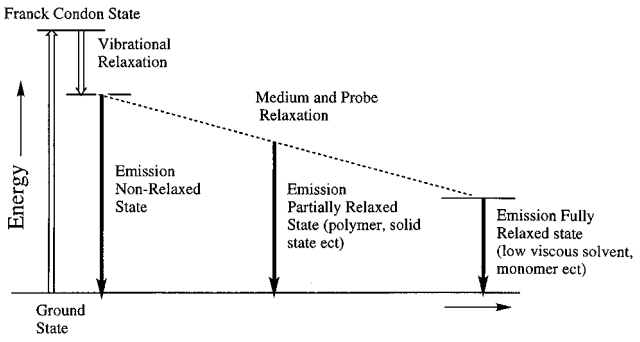

Figure 1. Schematic representation of the emission of **1** as a function of the medium relaxation.

In our research group we have spent considerable effort developing new fluorescent probes for which the position of the emission maximum changes as a function of the rigidity of the surrounding matrix. Different types of probes have been investigated specifically for following photopolymerization processes.[22] These include excimer forming probes,[23] TICT (twisted intramolecular charge transfer) probes,[24] charge transfer probes,[25] and organic salts.[26] All of the probes exhibit pronounced blue shifts when a resin is polymerized, but the underlying mechanisms are fundamentally different.

2. The DMANS Probe. In this research we will employ 4-(dimethylamino)-4′-nitrostilbene (DMANS, **1**) as the fluorescent probe. This molecule is a typical charge transfer probe and the most sensitive we have encountered.[25a,27] The photophysics of this molecule are well established.[28] In the ground state it has a relatively low dipole moment of 9 D that, due to an almost complete charge transfer, increases to 38 D in the excited state. In emission, the molecule is highly solvatochromic. An increase in solvent polarity results in a red shift in the fluorescence due to an increased stabilization of the excited state.[29] This probe is also sensitive to changes in the rigidity of the medium, and large blue shifts in its emission are observed upon rigidification.[30] In a highly viscous environment such as a polymeric glass where the mobility of molecules or molecular fragments is decreased, the reorientation of the medium needed to stabilize the excited state cannot be completed within its lifetime.[31] Emission takes place from the probe in a partially relaxed medium at wavelengths shorter than that observed when the medium is fully relaxed (see Figure 1).

With dimethacrylates large blue shifts, well over 100 nm for **1**, have been observed upon polymerization. Our research has shown that the sensitivity for monitoring photopolymerization processes and the sensitivity toward solvent polarity are roughly proportional for charge transfer probes.[25a]

To the first approximation, immobilization of monomer fragments during the polymerization process is responsible for this blue shift in fluorescence. This is supported by temperature dependent emission of **1** in dimethacrylates[30] that form solid glasses at low temperatures. Changes in chemical composition, notably the disappearance of the acrylate double-bond, are of limited interest, especially in large systems in which the acrylate functionality represents only a small fraction of the monomer molecule. In a series of dimethacry-

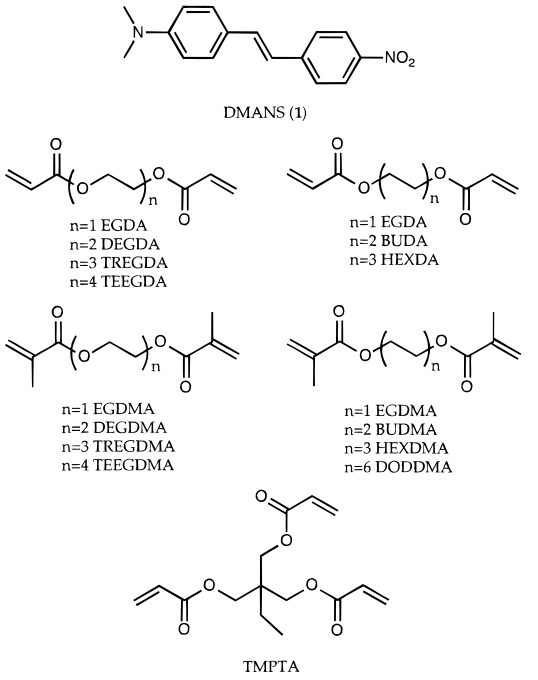

Figure 2. Fluorescent probe (**1**) and resins used in this research.

lates we observed larger blue shifts upon polymerization if monomers with shorter spacers between the polymerizable units are employed.[25a] Presumably the networks formed with these monomers are more rigid.[32] Forming a more rigid network will further retard and reduce the relaxation of the medium and lead to emission at shorter wavelengths.

Networks Composed of Different Monomers. When networks are generated from monomers of differing structures, the interpretation of the probe's emission can be complicated. In the simplest case, homogeneous networks form and emission in the network is the average in terms of the intensity, the position of its maximum, and the peak width of the probe's emission in the components.

If heterogeneous networks are formed and a phase separation occurs, this is no longer the case. If the probe is evenly distributed over multiple phases, a multiple fluorescence can occur. In practice it is more likely that these emissions will merge to one broad emission.[33] The emission wavelength in the polymer will be positioned between those of both components but does not need to be the exact average. Differences in quantum yields or an uneven distribution over both phases are obvious reasons.

If preferential solution in one of the components occurs, an interpretation solely in terms of an increase in rigidity of the probe's environment is no longer valid. A net migration of the probe between environments of different polarity, i.e., a homogeneous mixture of monomers and a homopolymeric network, has occurred. In this case the position, the intensity, and the peak width of the emission should closely resemble that of the probe in the resin to which it has migrated.

In this paper we report the use of CPMAS ^{13}C NMR and fluorescence spectroscopy[34] to characterize photoformed polymeric networks prepared from binary mixtures of the triacrylate TMPTA and a diacrylate (DA) or a dimethacrylate (DMA).

The structures of the dimethacrylates, diacrylates, and TMPTA are shown in Figure 2. It should be noted

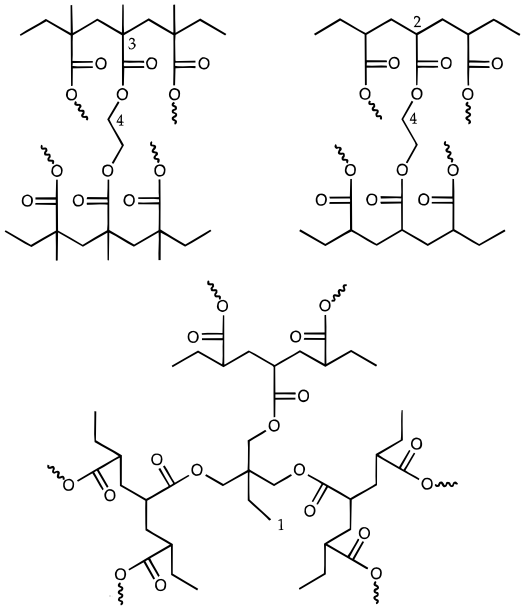

Figure 3. Schematic representation of polymeric networks formed with EGDMA, EGDA, and TMPTA. Carbons used for T_1 and $T_{1\rho}$ measurements are numbered.

that the di(meth)acrylates are selected so that a systematic variation of the length and the composition of the spacer that connects the (meth)acrylate units can be achieved. When the length of the side chain is increased, the dimensions of the "cages" formed in the polymeric networks (Figure 3) are expected to increase while the rigidity of the network will decrease. By the use of ethylene glycol spacer units, an increase in the length of the side chain will be accompanied by an increase in polarity, while increasing the length of an apolar diol side chain will decrease the polarity of the network. So the polarity and the length of the spacer can be varied independently.

The techniques, NMR and emission spectroscopy, are complementary. NMR is an elaborate, time-consuming technique giving detailed structural information on a molecular scale. Emission spectroscopy is fast, is versatile, and can be applied to objects of any size and shape but gives little detailed information. We will employ solid state NMR and emission spectroscopy on identical samples, analyze the results, and, by combining them, elucidate the detailed molecular structure of the polymeric networks.

Our long range goal is to obtain detailed information on the molecular level of complex polymeric systems by means of the faster technique fluorescence spectroscopy. In order to do this we need to obtain a large portion of this information by NMR spectroscopy first. Translating the detailed information obtained by NMR to the emission spectra will be the big challenge!

Experimental Section

General Information. 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. Ethylene glycol diacrylate (EGDA), diethylene glycol diacrylate (DEGDA), triethylene glycol diacrylate (TREGDA), tetraethylene glycol diacrylate (TEEGDA), 1,4-butanediol diacrylate (BUDA), 1,6-hexanediol diacrylate (HEXDA), 1,6-hexanediol dimethacrylate (HEXDMA), and 1,12-dodecanediol dimethacrylate (DODDMA) were purchased from Monomer-Polymer and Dajac Laboratories. Trimethylpropane triacrylate (TMPTA) was

Table 1. Double-Bond Conversion in Fully Cured, Photochemically Prepared Networks as Determined by CPMAS ^{13}C NMR Spectroscopy

	DMA	DA	TMPTA/DMA	TMPTA/DA
EG	78	84	75	83
DEG	82	91	79	88
TREG	86	94	79	90
TEEG	92	96	83	91
EG	78	84	75	83
BUD	81	88	80	86
HEX	86	92	88	88
DOD	91		89	

purchased from Sartomer Co. Manufacturers claims indicated chemical purity to be between 90% and 98%. The amount of inhibitor present in all samples was between 100 and 275 ppm. The fluorescent probe 4-(dimethylamino)-4′-nitrostilbene (DMANS, **1**) was purchased from Kodak. Irgacure 907 (2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one) was a gift from Ciba-Geigy. The structures for all monomers and the fluorescent probe are presented in Figure 2.

Sample Preparation. The mixtures of TMPTA and each of the diacrylic and dimethacrylic monomers were 1:1 by weight. Irgacure 907, used as photoinitiator, was added in 1% by weight. The fluorescent probe was present in 0.02% by weight. Polymeric networks were prepared by exposing films of the monomers and their mixtures to UV light (from both sides) in a Colight M218 light bath (using two 400 W medium-pressure Hg lamps). Films were made by squeezing a drop of the monomer between NaCl plates or glass slides divided by a 15 μm Teflon spacer. The emission spectra of the DMANS probe were measured using a front face configuration before irradiation and after subsequent irradiations, until no spectral shift was observed in the emission spectra (usually 15−20 min). FT-IR spectra could be obtained from the same samples, if NaCl plates were used.

Samples for NMR spectroscopy, which contained 0.001% of the probe, were prepared using 0.5 mm Teflon spacers. The degree of cure of these samples was measured using fluorescence spectroscopy in front phase. After the irradiation was complete, the 0.5 mm films were crushed and used for NMR.

CPMAS NMR. Solid state CPMAS ^{13}C NMR spectra were recorded at 100.56 MHz using a Varian Unity Plus 400 spectrometer equipped with a high-power amplifier and a Varian CPMAS probe. Samples were packed as powders in silicon nitride rotors with Kel-f endcaps and spun at the magic angle with a spinning rate of 6.5 kHz at 290 K. Cross-polarization was performed at 33 kHz (7.5 μs 90° pulses for both ^{13}C and ^{1}H), the proton-decoupling strength was approximately 63 kHz, and the delay between successive acquisitions was 5 s. The mixing time was varied between 0.1 and 25 ms.

Fluorescence Spectroscopy. Fluorescence measurements were recorded on a Spex Fluorolog 2 recording fluorimeter in the front face configuration. Using Teflon spacers, 15 μm or 0.5 mm films were prepared between NaCl plates or glass slides.

FT-IR Measurements. The photopolymerization process was followed by FT-IR, using the 810 cm^{-1} bending vibration of the acrylic CH. The CH stretching vibrations at 2800−3100 cm^{-1} were used as a reference signal to compensate for differences in sample thickness. No difference was observed in the IR spectrum of the crushed samples and of the films.

Results and Discussion

Double-Bond Conversions. We have determined double-bond conversions in our resins, using either NMR spectroscopy (Table 1) or FT-IR spectroscopy (Table 2). For the NMR measurements 0.5 mm samples, containing 1% photoinitiator and 0.001% probe, were irradiated between glass plates for 15 min. Double-bond conversions were determined by integration of the carbonyl signals of the pending and the incorporated

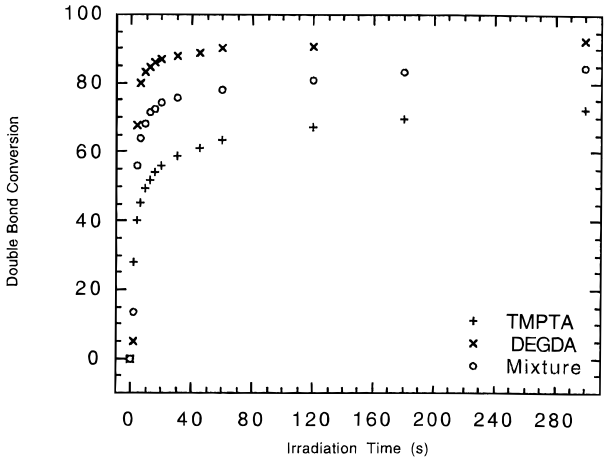

Figure 4. Double-bond conversion of DEGDA, TMPTA, and a 1:1 DEGDA/TMPTA mixture, measured by FT-IR as a function of the irradiation time.

Table 2. Double-Bond Conversion in Fully Cured, Photochemically Prepared Networks as Determined by FT-IR Spectroscopy

DEGDMA	DEGDA	TMPTA	TMPTA/ DEGDMA	TMPTA/ DEGDA	DEGDA/ DEGDMA
84	94	78	78	88	92

acrylate, respectively. For the FT-IR measurements 15 μm samples, containing 1% photoinitiator and 0.02% probe, were irradiated between glass or NaCl plates for successive periods, being 20 min in total. Double-bond conversions were followed by the disappearance of the CH bending vibration at 820 cm^{-1}. The double-bond conversions in Tables 1 and 2 are identical, indicating that both methods yield comparable results.

For all difunctional monomers a clear correlation between the double-bond conversion and the length of the spacer, regardless of the composition, is observed. This result indicates that topological factors governing steric crowding, accessibility of reactive sites and pending double-bonds, are reasonable explanations for the measured final degrees of cure. Significantly higher conversions are observed for diacrylates than for the corresponding dimethacrylates. The increased reactivity of the acrylate group, about 5 times that of a methacrylate[10] (Appendix), the higher flexibility of the acrylate backbone, and the smaller size of the acrylate moiety may explain this observation. Moreover, tertiary hydrogen abstraction mobilizes the radical sites in polyacrylates more efficiently than in the polymethacrylates.

For the mixtures of TMPTA and difunctional monomers (with the exception of the HEXDMA/TMPTA mixture), double-bond conversions lower than those of the corresponding difunctional monomers are reported in all cases. As for the pure difunctional monomers, a correlation between the spacer length in the difunctional component and the double-bond conversion is observed. For a few selected resins the double-bond conversions were determined as a function of the accumulated irradiation time, and Figures 4−6 show the results. Figure 4, which compares the double-bond conversion in TMPTA, DEGDA, and the TMPTA/DEGDA mixture as a function of the (accumulated) irradiation time, clearly demonstrates that, due to topological factors only, DEGDA reacts much faster than TMPTA. While the photopolymerization of DEGDA is virtually completed after 3 min, TMPTA is still reacting after a 15

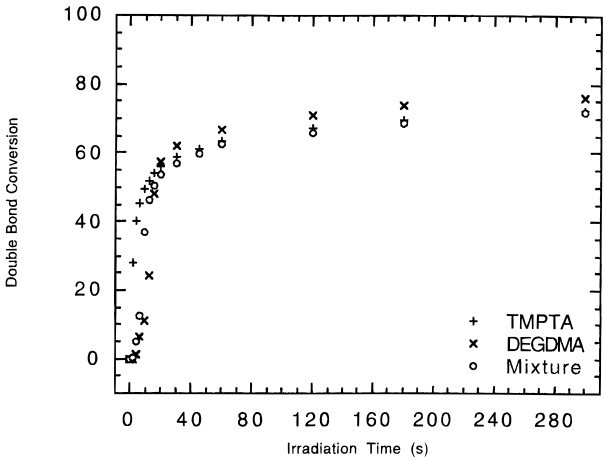

Figure 5. Double-bond conversion of DEGDMA, TMPTA, and a 1:1 DEGDMA/TMPTA mixture, measured by FT-IR as a function of the irradiation time.

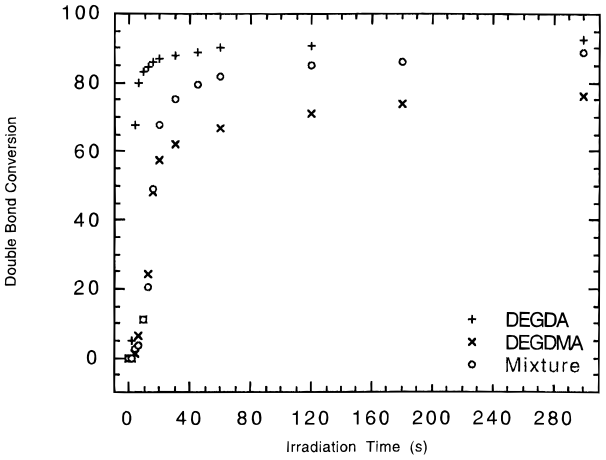

Figure 6. Double-bond conversion of DEGDA, DEGDMA, and a 1:1 DEGDA/DEGDMA mixture, measured by FT-IR as a function of the irradiation time.

min irradiation period. For the TMPTA/DEGDA mixture the double-bond conversion is between those of both components during *all* stages of the photopolymerization process. The fact that both the rate of polymerization and the final double-bond conversion are perfect averages strongly suggests the formation of a homogeneous network in which both monomers are incorporated according to the feed ratio in all stages of the photopolymerization process.

Figure 5 compares the double-bond conversion in TMPTA, DEGDMA, and the TMPTA/DEGDMA mixture as a function of the (accumulated) irradiation time. It shows that the photopolymerization of DEGDMA is inhibited during the first seconds of the irradiation and starts at a lower rate than that of TMPTA but that for DEGDMA a higher final conversions is obtained. For both resins a steady increase in double-bond conversion is observed, even after a 15 min irradiation period. The double-bond conversion for the mixture is between those of its components during the first stages of the photopolymerization, but after 50% conversion it trails the conversion of both components, and finally it slowly approaches that of TMPTA.

In order to understand the significance of the inherent differences in reactivity between acrylate and methacrylate functionalities, we have photopolymerized a DEGDA/DEGDMA mixture (see Figure 6). In this case the topology of both monomers is identical, the only difference being the increased size of the methacrylate moiety. This will decrease the mobility of the methacrylate in viscous media and is expected to play a significant role in the later stages of the polymerization only. During the first stages of the polymerization, up to 50% cure, the double-bond conversion of the mixture is virtually identical with that of pure DEGDMA, but in later stages the double-bond conversion approaches that of pure DEGDA. Qualitatively this behavior is as expected on the basis of the rates of propagation and the reactivity coefficients of methylacrylate and methyl methacrylate[10] (Appendix).

On the basis of the data from Figure 4 and similar results obtained for TMPTA/BUDA and TMPTA/HEXDA mixtures, we assume a similar behavior for all TMPTA/DA mixtures. Double-bond conversions are expected precisely between those of the components at all times, and both components are incorporated in the network in amounts according to the feed ratio during the photopolymerization process. Homogeneous networks are formed. The final double-bond conversions, determined by topological factors, are expected to be exactly between those of the parent compounds. The data in Table 1 confirm this is indeed the case.

On the basis of the data presented in Figures 5 and 6 and similar results obtained for TMPTA/HEXDMA and TMPTA/BUDMA mixtures, we expect a different kinetic profile for the TMPTA/DMA mixtures. In the first instance double-bond conversions close to those of the methacrylates, indicating a disproportional incorporation of this monomer in the network, are expected. In the last stages of the photopolymerization process mainly acrylate is incorporated. This means that heterogeneous networks are formed. It appears that final double-bond conversions are determined by the topology of the acrylate to a large extent. The data presented in Table 1 suggest that this assumption, predicting a final double-bond conversion of TMPTA/DMA mixtures close to that of TMPTA, does hold in most cases. For mixtures with the larger dimethacrylates, however, this is no longer the case, and significantly higher double-bond conversions are obtained.

CPMAS ^{13}C NMR. T_1 relaxation times of selected carbon atoms were measured for all TMPTA/DA and TMPTA/DMA combinations. Our choice was limited to monitoring the methyl carbon in TMPTA (1), the tertiary (2) and the quaternary (3) carbons in the main chains of the diacrylates and dimethacrylates, respectively, and the methylene carbon attached to the (meth)acrylate esther (4), since the resonances of all other carbons severely overlap (see Figure 3). For each TMPTA/D(M)A combination a series of networks with increasing double-bond conversions was prepared by varying irradiation times. Based on the fluorescence of **1** in the freshly prepared samples, and later confirmed by NMR spectroscopy, conversions of 25%, 40%, 45%, 60%, and 70% of the maximum attainable double-bond conversion were obtained. Results are presented in Tables 3 and 4 and Figures 7 and 8.

The data in Tables 3 and 4 clearly indicate a decrease in T_1 values for the main- and side-chain carbons in the di(meth)acrylates upon increasing double-bond conversions, indicating a decrease in mobility. No decrease in relaxation time was observed after the first 25% of cure for the carbons in the side chains. This might indicate that after the formation of a solid no decrease in mobility is monitored by these atoms. For the carbon atoms in the main chains, a continuous decrease in T_1

Table 3. T_1 Values (in s) at Different Stages of the Photopolymerization of DA/TMPTA Mixtures

		conversion[a]						
monomer	C atom	0%[b]	25%	40%	45%	60%	70%	aged[c]
HEXDA	CH_2O (4)	1.95	0.65	0.64	0.65	0.65	0.63	0.63
	CH (2)	1.1	0.92	0.83	0.75	0.59	0.43	
TMPTA	CH_3 (1)	1.11	1.19	1.19	1.22	1.23	1.22	1.23
BUDA	CH_2O (4)	1.21	0.78	0.80	0.78	0.78	0.79	0.78
	CH (2)	0.93	0.89	0.73	0.65	0.60	0.42	
TMPTA	CH_3 (1)	1.20						1.11
EGDA	CH_2O (4)	1.82	1.41	1.40	1.38	1.41	1.41	1.34
	CH (2)	0.87	0.80	0.76	0.71	0.63	0.48	
TMPTA	CH_3 (1)	1.24						1.08
DEGDA	CH_2O (4)	1.35	0.82	0.81	0.82	0.82	0.82	0.79
	CH (2)	0.90	0.79	0.68	0.59	0.53	0.45	
TMPTA	CH_3 (1)	1.06						0.93
TREGDA	CH_2O (4)	1.20	0.70	0.71	0.69	0.69	0.70	0.71
	CH (2)	0.81	0.69	0.60	0.54	0.49	0.40	
TMPTA	CH_3 (1)	0.94						0.99
TEEGDA	CH_2O (4)	0.91	0.60	0.60	0.60	0.60	0.62	0.62
	CH (2)	0.69	0.59	0.56	0.52	0.44	0.33	
TMPTA	CH_3 (1)	0.92						1.11

[a] Relative double-bond conversion based on the shift in emission maximum of the probe: 0 = monomer, 100 = fully cured polymer. Absolute double-bond conversions can be calculated using Table 1, assuming a linear relationship between the emission maximum of **1** and the double-bond conversion. [b] Measured in $CDCl_3$ solution, 50.3 MHz. [c] Samples of full cure after storage for for 60 days at room temperature.

Table 4. T_1 Values (in s) at Different Stages of the Photopolymerization of DMA/TMPTA Mixtures

		conversion[a]						
monomer	C atom	0%[b]	25%	40%	45%	60%	70%	aged[c]
DODDMA	CH_2O (4)	0.92	0.60	0.59	0.59	0.60	0.59	0.56
	quart C (3)		0.76	0.63	0.54	0.50	0.43	0.37
TMPTA	CH_3 (1)	1.13						1.24
HEXDMA	CH_2O (4)	1.22	0.68	0.69	0.69	0.68	0.68	0.67
	quart C (3)		0.80	0.68	0.60	0.54	0.51	0.42
TMPTA	CH_3 (1)	1.22						1.31
BUDMA	CH_2O (4)	1.37	0.85	0.84	0.80	0.84	0.84	0.80
	quart C (3)		0.92	0.80	0.71	0.66	0.62	0.57
TMPTA	CH_3 (1)	1.25						1.24
EGDMA	CH_2O (4)	2.95	1.50	1.56	1.53	1.54	1.52	1.50
	quart C (3)		0.96	0.89	0.73	0.66	0.64	0.64
TMPTA	CH_3 (1)	1.25						1.09
DEGDMA	CH_2O (4)	2.13	1.20	1.19	1.26	1.22	1.21	1.18
	quart C (3)		1.10	0.93	0.86	0.79	0.62	0.55
TMPTA	CH_3 (1)	1.22						1.11
TREGDMA	CH_2O (4)	1.50	0.90	0.90	0.93	0.91	0.89	0.79
	quart C (3)		0.96	0.89	0.71	0.65	0.61	0.51
TMPTA	CH_3 (1)	1.22						1.30
TEEGDMA	CH_2O (4)	1.32	0.70	0.69	0.70	0.68	0.70	0.72
	quart C (3)		0.89	0.73	0.61	0.59	0.57	0.45
TMPTA	CH_3 (1)	1.12						1.31

[a–c] See Table 3 for captions.

values is observed. This indicates that the increase in double-bond conversion and the accompanying increase of cross-linking are monitored by main-chain carbons only.

The T_1 values measured for the methyl of TMPTA do not show large differences upon polymerization. In most cases the differences in T_1 values between (concentrated) deuteriochloroform solutions and the fully cured polymer do not exceed 10%. This insensitivity might be explained by the fact that the TMPTA methyl is a freely pending group; it is not directly incorporated in the network, in either the side or main chain.

Rates of spin diffusion[35] have been determined for the species present in the network (the diacrylate (K_{DA}) or dimethacrylate (K_{DMA}) and TMPTA (K_{TA})) by measuring the rotating-frame spin–lattice relaxation time, $T_{1\rho}$.[18]

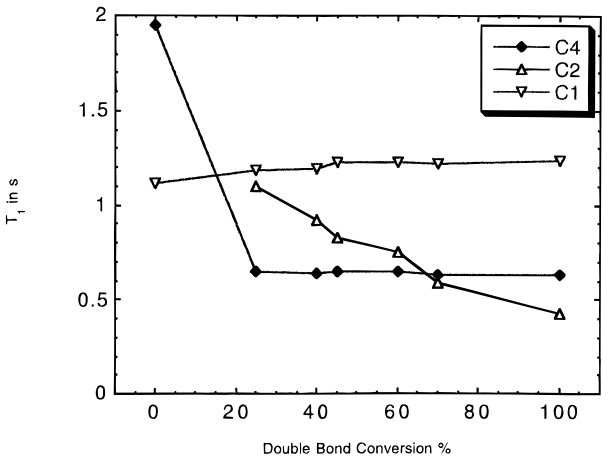

Figure 7. Spin–lattice T_1 relaxation times for different carbons in TMPTA/HEXDA mixtures as a function of double-bond conversion.

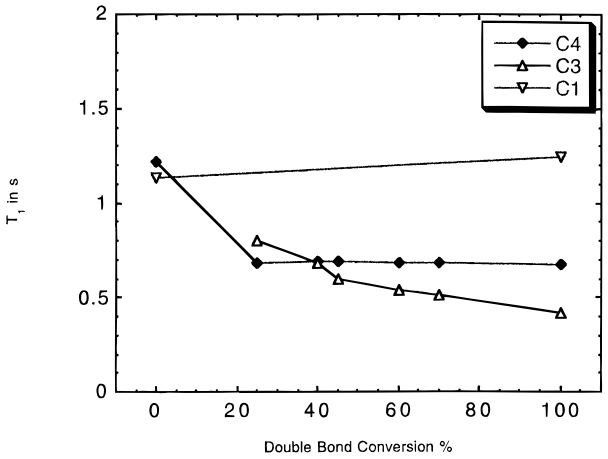

Figure 8. Spin–lattice T_1 relaxation times for different carbons in TMPTA/HEXDMA mixtures as a function of double-bond conversion.

As we previously reported, these values are strongly dependent on the homogeneity of the networks.[18] Closer values imply a more homogeneous network with the compounds in closer, more intimate contact. A clear phase separation has been reported previously as occurring in a polymer formed by the photopolymerization of a mixture of the triacrylate TMPTA, the pentacrylate DPHPA, and the long chain poly(ethylene glycol diacrylate) PEGA 400.[18] Mechanical measurements support these observations[36] and indicate that the diacrylate PEGA 400 is phase separated from the other monomers, has a very low degree of polymerization, and acts as a plasticizer. We have also performed mechanical tests on photopolymers formed from TMPTA/DMA mixtures.[37]

The values for the rates of spin diffusion for 60% cured TMPTA/DA and TMPTA/DMA mixtures are presented in Table 5. Rates of spin diffusion of selected mixtures as a function of the photopolymerization process are given in Table 6. Table 5 reveals that in the TMPTA/DA mixtures the rates of spin diffusion for both components are fairly similar. An increase in homogeneity is observed with an increase in the length of the spacers, especially for the diol diacrylates. For example, in the case of EGDA/TMPTA the values for the rates of spin diffusion are $K_{DA} = 26.0\ s^{-1}$ and $K_T = 37.4\ s^{-1}$ for aged, fully cured samples. When a hexanediol unit was interspersed between the two acrylic groups, the HEXDA/TMPTA case, the rates of spin

Table 5. Rates of Spin Diffusion for Dimethacrylates (K_{DMA}), Diacrylates (K_{DA}), and TMPTA (K_{TA}) (in s^{-1}) in Polymers Obtained from Mixtures of TMPTA/DMA and TMPTA/DA at 60% *Relative* Cure and in Aged Samples (Values in brackets)

	TMPTA/DMA		TMPTA/DA	
	K_{DMA}	K_{TA}	K_{DA}	K_{TA}
EG	7.0 [8.5]	45 [44.6]	17.1 [26.0]	42.4 [37.4]
DEG	6.8 [8.4]	47.5 [46.9]	19.2 [29.8]	42.1 [35.1]
TREG	6.3 [8.1]	49.1 [48.0]	20.8 [30.4]	40.6 [34.7]
TEEG	6.0 [7.7]	52.3 [49.3]	22.1 30.8]	39.3 [31.9]
EG	7.0 [8.5]	45 [44.6]	17.1 [26.0]	42.9 [37.4]
BUD	7.8 [8.9]	46.2 [44.1]	22 [30.8]	40.1 [34.7]
HEX	8.0 [9.1]	47.3 [43.7]	26.3 [32.6]	37.1 [31.7]
DOD	9.6 [9.6]	48.9 [42.0]		

Table 6. Rates of Spin Diffusion in (s^{-1}) at Different Stages of the Photopolymerization of TMPTA/DA and TMPTA/DMA Mixtures

	conversion[a]					
	25%	40%	45%	60%	70%	aged
EGDA	13.1	13.9	15.1	17.1	23.1	26.0
TMPTA	46.2	45.2	43.6	42.9	39.6	37.4
DEGDA	14.0	14.3	16.9	19.1	26.2	29.8
TMPTA	45.7	44.0	42.9	42.1	38.7	35.1
HEXDA	17.6	20.1	24.0	26.3	29.6	32.6
TMPTA	43.0	41.9	39.3	37.1	33.9	31.7
TREGDMA	6.3	6.4	6.5	6.3	6.9	8.1
TMPTA	49.0	49.2	48.9	49.1	48.3	48.0

[a] See Table 3 for captions.

diffusion for both monomeric units are identical, $K_{DA} = 32.6\ s^{-1}$ and $K_T = 31.7\ s^{-1}$, indicating the formation of a perfectly homogeneous network. The homogeneity of the network also increases as a function of the double-bond conversion (see Table 6). For TMPTA/DMA mixtures heterogeneous networks are formed, as expected. The rates of spin diffusion for the dimethacrylates and TMPTA in their polymeric mixtures were similar to those obtained of the homopolymers formed by the photopolymerization of DMA or TMPTA. No significant increase in homogeneity during the photopolymerization process was observed for the TMPTA/TREGDMA mixture (Table 6).

These results lead to the general conclusion that TMPTA/DA mixtures form networks that are homogeneous, while TMPTA/DMA mixtures form networks that are heterogeneous. Homogeneity in TMPTA/DA networks increases with time. Increased homogeneity in the networks made with diacrylates having longer spacers is present from the start of the polymerization process.

Mole fractions of repeat units in the cross-links were calculated for both TMPTA and the difunctional monomers using a modification of the method developed by Rawland and Labun.[20] In their paper they used the differences in the proton spin−lattice relaxation time T_1 in cross-links and in the non-cross-linked parts of some polymers. Details of this method will be described elsewhere.[38] The relative contributions of DA or DMA in the cross-links for all DMA/TMPTA and DMA/TMPTA mixtures are compiled in Table 7,[39] where the mole fraction of (meth)acrylates in the mixture provided by DA or DMA are displayed for comparison. The fully reacted TMPTA is counted as two cross-links.

Table 7 shows that in the case of DA/TMPTA mixtures, the distribution of the repeat units of both monomers in the cross-links is close to the ratio of acrylate functionalities contributed by both components,

Table 7. Mole Fractions of the Cross-Links in Polymers Formed from TMPTA/DMA or TMPTA/DA Mixtures[a]

	DMA	DA
EG	0.46 (0.50)	0.68 (0.54)
DEG	0.42 (0.45)	0.66 (0.48)
TREG	0.16 (0.41)	0.60 (0.43)
TEEG	0.06 (0.37)	0.39 (0.40)
EG	0.46 (0.50)	0.68 (0.54)
BU	0.45 (0.47)	0.50 (0.50)
HEX	0.39 (0.44)	0.49 (0.47)
DOD	0.39 (0.37)	

[a] The fractions of the (meth)acrylates provided by DMA or DA are shown in parentheses.

Table 8. Emission Maxima (nm) of 1 in Different Resins before and after Photopolymerization (15 μm films between glass plates)

		resin			
resin	phase	DMA	DA	DMA/TMPTA	DA/TMPTA
DOD	mono	639		660	
	poly	555		568	
	diff	84		92	
HEX	mono	664	684	653	682
	poly	570	583	559	584
	diff	94	101	94	98
BUD	mono	677	698	663	689
	poly	576	597	565	588
	diff	101	102	98	101
EG	mono	691	721	683	696
	poly	585	607	572	592
	diff	106	114	111	104
DEG	mono	699	714	690	695
	poly	595	610	584	598
	diff	104	104	106	97
TREG	mono	695	714	686	694
	poly	601	615	594	600
	diff	94	99	92	94
TEEG	mono	704	701	687	679
	poly	613	629	594	604
	diff	91	72	93	75
TMPTA	mono	660			
	poly	580			
	diff	80			

especially for the acrylates that have a long spacer. Since the inherent reactivity of the acrylic groups is the same, and statistical heteropolymeric networks are expected, this result is not surprising. A higher mobility of the small chain monomers, especially in the polymeric gel, might explain the higher mole fraction of these species in the cross-links. For the TMPTA/DMA mixtures the mole fractions of the difunctional monomers in the cross-links are lower in all cases. For the poly(ethylene glycol) series a sharp decrease in the mole fraction of the cross-links for the dimethacrylates is observed. This is a clear indication of a heterogeneous network.

We conclude that the formation of heterogeneous networks can be detected by differences in cross-link densities between the components only in a limited number of cases. A disproportional fraction of cross-links contributed by the components indicates the formation of heterogeneous networks. Clearly a proportional distribution of cross-link density over both components does not imply that a homogeneous network has been formed.

Fluorescence Spectroscopy. Emission maxima obtained before and after 20 min irradiation of 15 μm films for all monomers and monomer combinations are displayed in Table 8. As discussed in the Introduction, **1** monitors both the polarity *and* the rigidity of its environment. This is clearly demonstrated in the series of dimethacrylates, as the emission is red shifted if a

Table 9. Viscosities of the Resins Employed in This Study

	viscosity, cps 25 °C[a]		
resin	DA	DMA	TMPTA
EG	*b*	6	106
DEG	12	8	
TREG	15	11	
TEEG	20	14	
EG	*b*	6	
BU	7	8	
HEX	9	8	

[a] Sartomer Product Catalog. [b] Not reported.

more polar monomer is employed in both the monomeric and polymeric phases; the expected order of increasing polarity, DODDMA → EGDMA → TEEGDMA, is reflected in the emission maxima of the probe. The blue shift observed after photopolymerization clearly increases as the length of the side chain in the networks decreases, despite the fact that significantly lower double-bond conversions are observed for networks with shorter side chains (Table 1). The largest blue shift is obtained in EGDMA, the monomer with the shortest side chain.

In diacrylates almost all emissions are red shifted. Clearly the lack of an α-methyl group makes these resins more polar than the corresponding dimethacrylates. For diacrylates, the order of polarity is expected to be similar to that of the dimethacrylates. However, this is not reflected in the emission of **1**. A blue shift is observed, as expected, in going from EGDA to HEXDA, but the probe's emission undergoes a blue shift as well in going from EGDA to TEEGDA. Two arguments might explain this observation. First, the difference in polarity between an acrylate moiety and an ethylene glycol unit is not as pronounced as between the (less polar) methacrylate moiety and an ethylene glycol unit. This results in a lesser increase in polarity from enlarging the (poly)ethylene glycol chain, from EGDA to TEEGDA. Second, the viscosities of acrylates are higher than those of the corresponding methacrylates (see Table 9)[41] and increase upon increasing the length of the molecule. The effect of increasing the viscosity of a medium is a blue shift in the emission of **1**, as was clearly demonstrated by temperature dependent emission in dimethacrylates.[30] This implies that in going from EGDA to TEEGDA as well as in going from EGDA to HEXDA a blue shift in emission can be expected based on the increasing viscosity of the resins.

In polydiacrylates the expected order of polarity of the monomers is reflected in the emission of the probe. An increase in emission wavelength is observed in going from poly-HEXDA to poly-TEEGDA. For the diacrylates the largest blue shift upon polymerization is observed in EGDA, the monomer with the shortest side chain.

It can be concluded that, apart from the monomeric poly(ethylene glycol) series, the emission of **1** in our dimethacrylates and diacrylates is similar. In general, the spectra in the diacrylates are shifted 15−30 nm to the red compared to the analogous dimethacrylates.

In TMPTA, emission of **1** is observed at 660 nm, a value that is significantly lower than the 698 nm observed for BUDA, a diacrylate of comparable polarity.[40] This 40 nm blue shift can be explained in that TMPTA is a very viscous resin (see Table 9).[41] In poly-TMPTA **1** emits at 580 nm, a value that is 20 nm blue shifted compared to that observed in poly-BUDA (596 nm). This blue shift could be an indication of increased

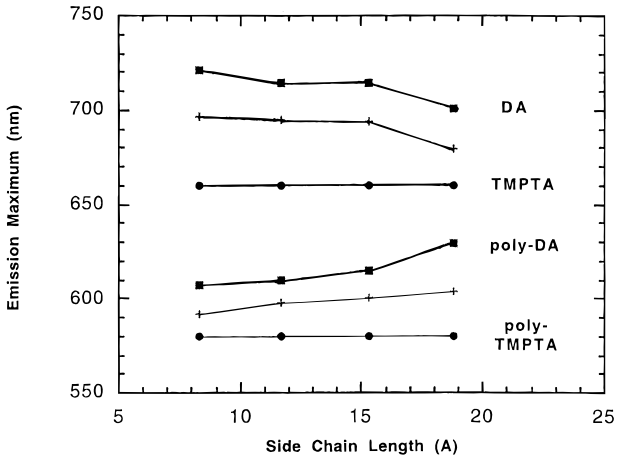

Figure 9. Emission maxima of **1** in DA, TMPTA, and DA/TMPTA mixtures and their photopolymers as a function of the length of the (poly)ethylene glycol spacer in the diacrylates.

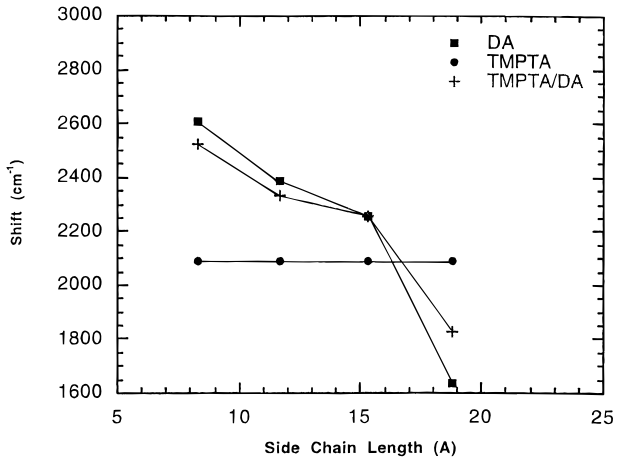

Figure 10. Shift in emission of **1** in DA, TMPTA, and DA/TMPTA mixtures upon photopolymerization as a function of the length of the (poly)ethylene glycol spacer in the diacrylates.

rigidity in poly-TMPTA compared to poly-BUDA. Both the shorter length of the spacer between the acrylate functionalities[42] and the fact that TMPTA is a trifunctional monomer are good arguments for such an assumption. The blue shift of TMPTA upon photopolymerization is 80 nm, a value that is considerably lower than those observed for comparable diacrylates. Our general conclusion is that the shift upon polymerization of TMPTA is reduced to this relatively low value due to the high viscosity of the monomer.

The emission maxima of **1** in monomeric and polymeric phases for TMPTA/DA mixtures are displayed in Figure 9. In monomers the emissions in the mixtures lie between those of TMPTA and the diacrylate. In polymers all emission maxima are the exact averages of those in the corresponding (homo)polymers. The shifts observed upon polymerization are displayed in Figure 10. The blue shifts observed for the mixtures are between those of the components but usually closer to those of the diacrylates.

For the peak widths of the emissions of **1** in poly-TMPTA/DA, intermediate values, between those of poly-TMPTA and the respective poly-DA's, were obtained in all stages of the reaction.[43] Also we observed that the emission maxima at a certain double-bond conversion for the DEGDA/TMPTA mixture are always between those of DEGDA and TMPTA, as displayed in Figure 11. These observations, combined with the kinetics of

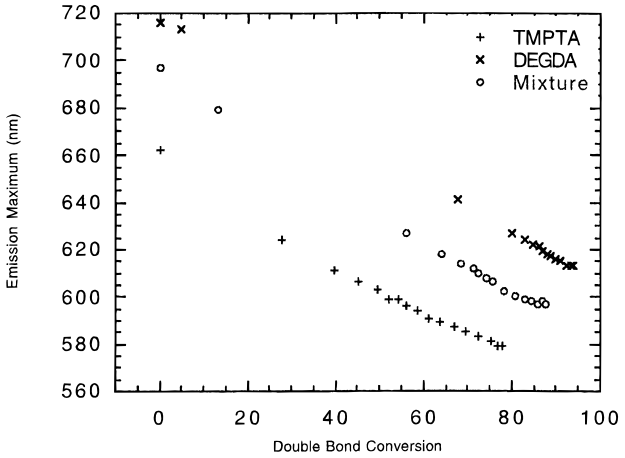

Figure 11. Emission maxima of **1** in DEGDA, TMPTA, and a 1:1 DEGDA/TMPTA mixture as a function of the double-bond conversion (determined by IR).

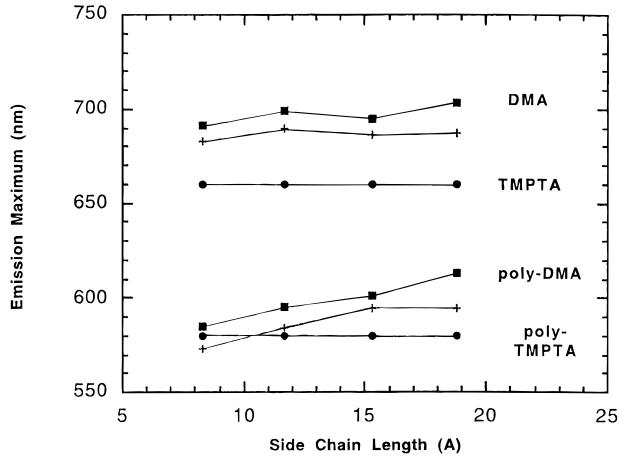

Figure 12. Emission of **1** in DMA, TMPTA, and DMA/TMPTA mixtures and their photopolymers as a function of the length of the (poly)ethylene glycol spacer in the diacrylates.

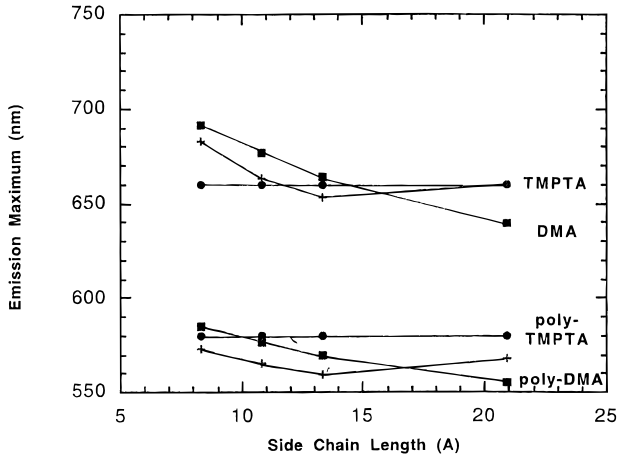

Figure 13. Emission of **1** in DMA, TMPTA, and DMA/TMPTA mixtures and their photopolymers as a function of the length of the diol spacer in the diacrylates.

the double-bond conversions discussed earlier, lead us to the conclusion that the polymeric networks formed from TMPTA/DA mixtures are homogeneous.

For TMPTA/DMA mixtures the emission maxima **1** in monomeric and polymeric phases are displayed in Figures 12 and 13. In the TMPTA/DMA mixtures, the emission maxima of the probe are between those of TMPTA and the dimethacrylate. In the poly(ethylene glycol) series, the emission wavelength is closer to that

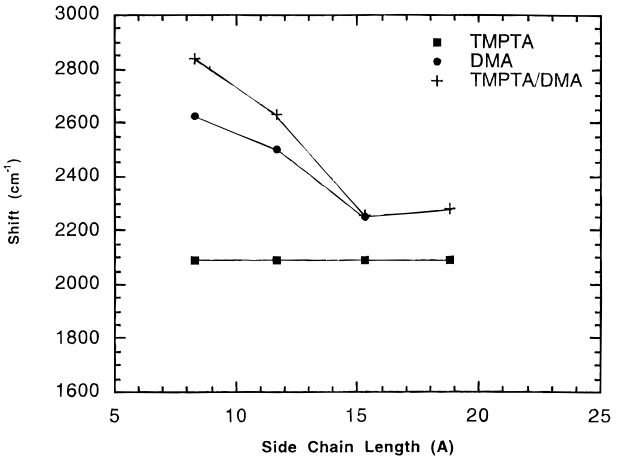

Figure 14. Shift in emission of **1** in DMA, TMPTA, and DMA/TMPTA mixtures upon photopolymerization as a function of the length of the (poly)ethylene glycol spacer in the dimethacrylates.

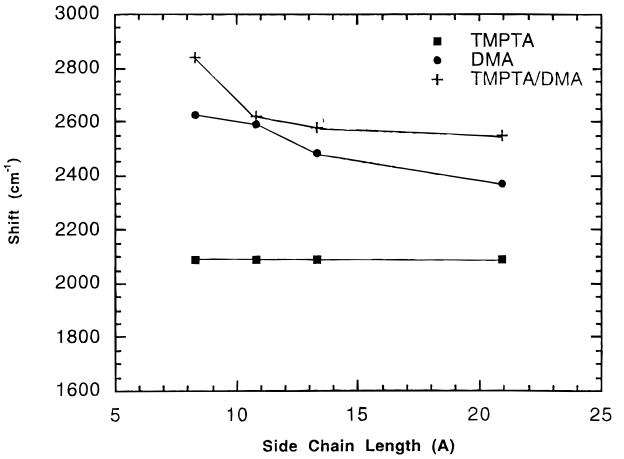

Figure 15. Shift in emission of **1** in DMA, TMPTA, and DMA/TMPTA mixtures upon photopolymerization as a function of the length of the diol spacer in the dimethacrylates.

of the DMA, but in the diol series emission wavelengths close to that of TMPTA are observed. In polymeric networks emission maxima between those in poly-TMPTA and poly-DMA are found in the case of DEGDMA, TREGDMA, TEEGDMA, and DODDMA only. For EGDMA, BUDMA, and HEXDMA the probe in the polymer formed from the TMPTA/DMA mixture emits at a shorter wavelength than either in poly-TMPTA or the respective poly-DMA. Apparently this indicates that the probe senses a polymer that is more rigid in the mixture than in either of the components of the mixture. A migration to the less polar phase, the TMPTA in most cases, might also contribute to this effect. For all mixtures the shift in emission wavelength upon polymerization is larger than that of either of the components (see Figures 14 and 15).

For the peak widths of the emissions of **1** in poly-TMPTA/DMA, intermediate values, between those in poly-TMPTA and the respective poly-DMA's, were measured. This lack of peak broadening indicates that emission of the probe from different phases, being poly-TMPTA and poly-DMA, is not observed.

When the emission maxima for **1** in the DEGDMA/TMPTA mixture are plotted as a function of the double-bond conversion, values between those of DEGDMA and TMPTA are observed (see Figure 16). In the first stages of the photopolymerization, emission maxima closer to

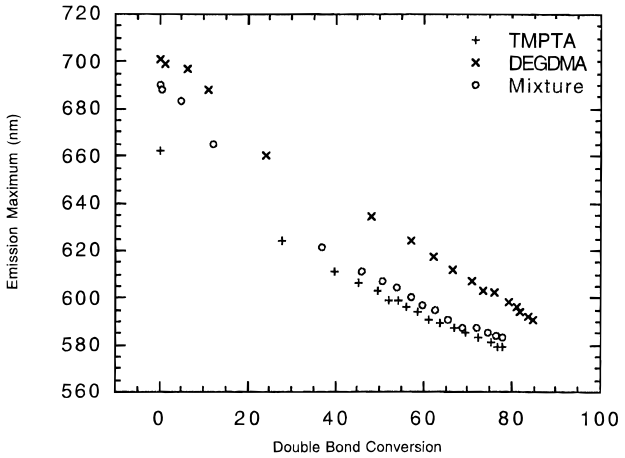

Figure 16. Emission maxima of **1** in DEGDMA, TMPTA, and a 1:1 DEGDMA/TMPTA mixture as a function of the double-bond conversion (determined by IR).

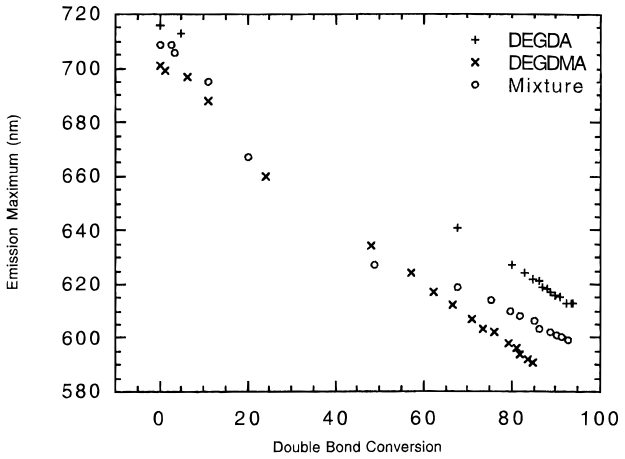

Figure 17. Emission maxima of **1** in DEGDMA, DEGDA, and a 1:1 DEGDMA/DEGDA mixture as a function of the double-bond conversion (determined by IR).

those of DEGDMA are observed, while in the later stages emission maxima approach those of TMPTA. For the DEGDMA/DEGDA mixture a similar behavior, approximating that of the methacrylate in the first stages of the polymerization and swinging back to the diacrylate later on, is observed (see Figure 17). Peak broadening is not observed in the DEGDA/DEGDMA mixture either.

We conclude that fluorescence spectroscopy, based on the emission of **1**, along with the kinetic data discussed in a previous section, indicates that TMPTA/DMA mixtures form inhomogeneous polymeric networks. Both the kinetics of the double-bond conversion versus irradiation time and the emission maximum as a function of the double-bond conversion indicate that incorporation of both monomers is not constant throughout the polymerization process. Therefore the polymer cannot be homogeneous. We have found no significant peak broadening in the mixtures. The reason can be preferential solvation in one of the phases or a large "viewing depth" of the probe compared to the size of the homopolymeric domains. It might even be that inhomogeneities in homopolymeric networks (poly-TMPTA or poly-DMA's) are comparable to those found in the TMPTA/DMA networks. At this stage we are inclined to believe that a large "viewing depth" of the probe is the most likely cause. Studies on materials in which the size of the phase-separated domains can be varied, such as PS/PMMA block copolymers, need to be undertaken to elucidate this matter.

Because peak broadening does not occur, it appears that determining whether a polymeric network is homogeneous or not is not a simple procedure for which an emission spectrum of **1** in the monomer and the polymer would suffice. Kinetic data are needed to find out more about the homogeneity of the photoformed network. The increased blue shift upon polymerization in TMPTA/DMA mixtures indicates that these mixtures form inhomogeneous networks. Whether this increased blue shift is a reliable indication needs further investigation.

Conclusions

We have demonstrated that valuable information concerning the architecture of complex polymeric networks can be obtained by a combination of fluorescence spectroscopy, solid state CPMAS ^{13}C NMR spectroscopy, and FT-IR spectroscopy. Results obtained by these techniques are often complementary, in good agreement with each other, and consistent.

For all polymeric networks, the final degree of cure increased with an increase in the length of the spacer in the difunctional monomer. Double-bond conversions obtained by IR and NMR spectroscopy were virtually identical. Rates of spin diffusion reveal clear phase separations (at a nanoscale, <20 nm) in polymeric networks formed from TMPTA/DMA mixtures, as was expected on the basis of the rates of propagation and the reactivity coefficients of acrylates and methacrylates. Homogeneous networks were obtained by photopolymerization of TMPTA/DA mixtures. The homogeneity of these networks increased by increasing the length of the spacer in the diacrylates and increasing the double-bond conversion.

From ^{13}C T_1 measurements, we determined that after the first stages of the photopolymerization process, a decrease in mobility with a further increase in the degree of double-bond conversion is observed for the main-chain carbons *only*. Only these carbons experience an extra rigidification as a result of further cross-linking. On the basis of T_1 values, we were able to determine the contribution of each monomer to the cross-links in our polymers. In all TMPTA/DA and most of the TMPTA/DMA systems, the contribution to the cross-links made by both species was close to the ratio of (meth)acrylate functions offered by the components. Only for TMPTA/DMA polymers in which a long poly(ethylene glycol) spacer connects the methacrylate units in the DMA did we observe a disproportionately low contribution to the cross-links by the DMA. This indicates that these polymers are heterogeneous and consist of a highly cross-linked TMPTA phase and a slightly cross-linked DMA phase.

Emission maxima of **1** in binary mixtures of TMPTA and DA or DMA as well as in pure TMPTA, DA, or DMA underwent large blue shifts upon photopolymerization of the monomer(s). In all systems the blue shift increased when DA's or DMA's with shorter spacers were employed. In TMPTA/DA mixtures all blue shifts were between those of TMPTA and the DA. For TMPTA/DMA mixtures, however, the blue shift was larger than in TMPTA or the DMA. We think this is an indication that these networks are heterogeneous in nature. Direct evidence of heterogeneity by means of peak broadening of the emission of **1** in polymers formed from TMPTA/DMA mixtures, however, was not obtained.

By measuring double-bond conversions (FT-IR) as a function of the irradiation time, irregular double-bond conversions, meaning conversions that were not between those of both components, were observed for TMPTA/DEGDMA and DEGDA/DEGDMA mixtures. For TMPTA/DEGDA mixtures regular double-bond conversions, conversions that were perfectly in between those of both components, were observed. These are clear indications that inhomogeneous networks are formed with the acrylate/methacrylate mixtures.

We conclude that the sensitivity of CPMAS ^{13}C NMR for detecting inhomogeneity in complex networks is higher. Whether or not a network is homogeneous can be studied on the molecular level, at a scale of less than 20 nm. Fluorescence spectroscopy, in combination with FT-IR spectroscopy, gives indirect indications that a network is inhomogeneous. A peak broadening of the probe's emission in heterogeneous systems was not observed. This lack of peak broadening in heterogeneous systems presumably occurs because the "viewing depth" of the probe exceeds the dimensions of the phases. We will address this question by preparing phases with well-defined dimensions, for instance PMMA−PS block copolymers.[14d]

Another question that needs to be addressed is whether preferential solution of the probe in one of the phases of a heterogeneous system occurs. By using probes in which **1** is covalently attached to either an acrylate or a methacrylate,[44] we will investigate this matter. Using such probes, migration of the probe in the polymeric network will be inhibited, and preferential incorporation of the probe in either of the networks (methacrylate or acrylate) might be achieved.

Finally, more kinetic measurements, plotting double-bond conversions versus irradiation times, need to be undertaken. We will monitor polymerization kinetics in real time by following the emission of **1** using the cure monitor, a fast fiber optics-based device[22b] that was developed in our group.

Our work is continuing in trying to solve the "mystery" of the microstructure of a polymeric network with the help of fluorescence spectroscopy and solid state NMR spectroscopy.

Acknowledgment. This work has been supported by the National Science Foundation (DMR-9013109) and the Office of Naval Research (ONR-N00014-91-J-1921 and ONR-N00014-93-1-0772). The NMR spectrometer used in these experiments was purchased with funds from grants from the NSF (CHE-93-02619), the Ohio Board of Regents, and Bowling Green State University. We are most grateful for the support of these agencies. We thank Dr. Roman Popielarz for helpful suggestions during preparation of the manuscript.

Appendix

The kinetics of binary mixtures containing equal amounts of acrylate (A) and methacrylate (MA) are demonstrated. The rates of propagation K_p for a methacrylate (A) and for a methyl methacrylate (MA) are 1000 and 200 mol s^{-1}. The reactivity coefficients for the A/MA system:

$$r_1 = k_{A-A}/k_{A-MA} = 0.4$$

$$r_2 = k_{MA-MA}/k_{MA-A} = 2$$

From these data we obtain

$$k_{A-A} = 1000$$

$$k_{A-MA} = 2500$$

$$k_{MA-MA} = 200$$

$$k_{MA-A} = 100$$

Initially, more MA is consumed and the expected polymerization rate is close to that of pure MA. After expletion of MA, the rate of the reaction will go up and mainly A will be incorporated. It should be noted that this analysis is only valid in the first stages of the photopolymerization process, as steric factors do not play a significant role.

References and Notes

(1) Contribution No. 300 from the Center for Photochemical Sciences, Bowling Green State University.
(2) Kloosterboer, J. G. *Adv. Polym. Sci.* **1988**, *84*, 1.
(3) Torres-Filho, A.; Neckers, D. C. *J. Appl. Polym. Sci.* **1994**, *51*, 931.
(4) Oldring, P. K. T., Ed. *Chemistry and Technology of UV & EB Formulation for Coatings, Inks & Paints;* SITA Technology Ltd.: London, U.K., 1991; Vol. 4.
(5) (a) Anseth, K. S.; Decker, C.; Bowman, C. N. *Macromolecules* **1995**, *28*, 4040. (b) Dietz, J. E.; Elliott, B. J.; Peppas, N. A. *Macromolecules* **1995**, *28*, 5163.
(6) (a) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953. (b) Stockmayer, W. H. *J. Chem. Phys.* **1943**, *11*, 45.
(7) (a) Reiser, A.; Egerton, P. L. *Macromolecules* **1979**, *12*, 670. (b) Egerton, P. L.; Reiser, A.; Pitts, A. *Macromolecules* **1981**, *14*, 95. (c) Egerton, P. L.; Trigg, J.; Hyde, E. M.; Reiser, A. *Macromolecules* **1981**, *14*, 100.
(8) Broer, D. J.; Mol, G. N. *Integration of Fundamental Polymer Science and Technology;* Elsevier Applied Science: London, 1986; p 669.
(9) Kloosterboer, J. G.; van de Heij, G. M. M.; Boots, H. M. J. *Polymer* **1984**, *25*, 354.
(10) *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; John Wiley and Sons: New York, 1989.
(11) Kloosterboer, J. G.; Lijten, G. F. C. M. *Polymer* **1990**, *31*, 95.
(12) Kloosterboer, J. G.; van de Hei, G. M. M.; Gossink, R. G.; Dortant, G. C. M. *Polymer* **1984**, *25*, 322.
(13) For a review on NMR studies of solid polymers, see: *Polymer Spectroscopy*; Fawcett, A. H., Ed.; John Wiley: Chichester, 1996; Chapters 4 and 5.
(14) (a) Schaefer, J.; Stejskal, E. O.; Buchdahl, R. *Macromolecules* **1977**, *10*, 384. (b) Dejean de la Batie, R.; Laupretre, F.; Monnerie, L. *Macromolecules* **1988**, *21*, 2045. (c) O'Donnell, J. H.; Whittaker, A. K. *J. Polym. Sci., Polym. Chem. Ed.* **1992**, *30*, 185. (d) Sankar, S. S.; Stejskal, E. O.; Fornes, R. E.; Fleming, W. W.; Russell, T. P.; Wade, C. G. In *Polymer and Fiber Science; Recent Advances*; Fornes, R. E., Gilbert, R. D., Eds.; VCH Publishers Inc.: New York, 1992; Chapter 11.
(15) In all cases referring to $T_{1\rho}$, $T_{1\rho}(^1H)$ (relaxation through the hydrogens attached to the polarized carbons) is meant.
(16) (a) Axelson, D. E.; Mandelkern, L.; Levy, G. C. *Macromolecules* **1977**, *10*, 557. (b) Gerard, A.; Laupretre, F.; Monnerie, L. *Polymer* **1994**, *35*, 3402.
(17) Alternatively, identical $T_{1\rho}$ values can be observed if the components are incorporated in different *homogeneously interpenetrating* networks. However, this is not a likely scenario for the resins used in this study.
(18) Lungu, A.; Neckers, D. C. *Macromolecules* **1995**, *28*, 8147.
(19) Allen, P. E. M.; Bennett, D. J.; Hagias, S.; Hounslow, A. M.; Ross, G. S.; Simon, G. P.; Williams, D. R. G.; Willimas, E. H. *Eur. Polym. J.* **1989**, *25*, 785.
(20) Rawland, T. J.; Labun, L. C. *Macromolecules* **1978**, *11*, 467.
(21) Rabek, J. F. *Mechanisms of Photophysical Processes and Photochemical Reactions in Polymers*; John Wiley & Sons: Chichester, U.K., 1987; Chapter 4.
(22) (a) General reference. (b) Popielarz, R.; Neckers, D. C. *Proc. Rad. Tech.* **1996**, *1*, 271. (c) Song, J. C.; Torres-Filho, A.; Neckers, D. C. *Proc. Rad. Tech.* **1994**, 338.
(23) Valdez-Aguilera, O.; Pathak, C. P.; Neckers, D. C. *Macromolecules* **1990**, *23*, 689.

(24) (a) Paczkowski, J.; Neckers, D. C. *Chemtracts: Macromol. Chem.* **1992**, *3*, 75. (b) Paczkowski, J.; Neckers, D. C. *Macromolecules* **1991**, *24*, 3013. (c) Rettig, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 971.
(25) (a) Jager, W. F.; Volkers, A. A.; Neckers, D. C. *Macromolecules* **1995**, *28*, 8153. (b) Schaeken, T. C.; Warman, J. M. *J. Phys. Chem.* **1995**, *99*, 6145. (c) van Ramensdonk, H. J.; Vos, M.; Verhoeven, J. W.; Möhlmann, G. R.; Tissink, N. A.; Meesen, A. *Polymer* **1987**, *28*, 951.
(26) Jager, W. F.; Kudasheva, D.; Neckers, D. C. *Macromolecules*, accepted for publication.
(27) To our knowledge "Fluoroprobe" is the most sensitive solvatochromic probe discovered so far; see: 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.
(28) (a) Kanis, P. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195. (b) Lippert, E. *Z. Electrochem.* **1957**, *61*, 962. (c) Liptay, W. *Z. Naturforsch.* **1965**, *20a*, 1441.
(29) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH Weinheim, 1988.
(30) Jager, W. F.; Neckers, D. C. Manuscript in preparation.
(31) A lifetime of 3 ns was reported for **1** in benzene; see: Shin, D. M.; Whitten, D. G. *J. Phys. Chem.* **1988**, *92*, 2945.
(32) Apart from cross-linking other factors influence the "rigidity" of a polymer, and a general correlation between the rigidity or microviscosity of a network and the degree of cross-linking can not be made. For example, if **1** is dissolved in MMA a 115 nm shift (from 680 to 565 nm) is observed upon polymerization, despite the fact that PMMA is a linear polymer.
(33) Double emission has been observed for **1** while melting solid dimethacrylates. The large difference of the probe's emission in the solid and liquid states, 565 and 680 nm, respectively, enabled us to observe this dual fluorescence[30]
(34) Neckers, D. C.; Jager, W. F.; Lungu, A.; Popielarz, R. *PMSE Proc.* **1996**, *74*, 352.
(35) Solomon, I. *Phys. Rev.* **1955**, *99*, 559.
(36) Torres-Filho, A.; Neckers, D. C. *Chem. Mater.* **1995**, *7*, 744.
(37) Lungu, A.; Neckers, D. C. *J. Polym. Sci., Part A: Polym. Chem.*, accepted for publication.
(38) Lungu, A.; Neckers, D. C. To be published.
(39) Harrell, J. W., Jr.; Choudhury, M.; Ahuja, S.; Walker, W. *J. Polym. Sci., Polym. Phys. Ed.* **1991**, *29*, 1039.
(40) Based on the ratio between fully saturated alkyl carbons and acrylate groups.
(41) Sartomer Product Catalog, Sartomer Co. Inc., 1993.
(42) From MM2 calculations, using fully stretched chains, side-chain lengths for EGDA, TMPTA, and BUDA of 8.3, 10.0, and 11.7 Å are obtained.
(43) Typical peak widths for **1** in polymers formed from these resins are 130−140 nm.
(44) Jager, W. F.; Sarker, A. M.; Neckers, D. C. Manuscript in preparation.

MA961468I