Mechanical Properties of Acrylate Networks Formed by Visible Laser-Induced Polymerization. I. Dependence on Photopolymerization Parameters

A. TORRES-FILHO and D. C. NECKERS*

Center for Photochemical Sciences, Department of Chemistry, Bowling Green State University, Bowling Green, Ohio 43403

SYNOPSIS

The mechanical properties of network molecular systems, prepared through visible (Ar^+) laser-induced polymerization of multifunctional acrylates, were studied as a function of some of the photopolymerization parameters. The properties investigated were the Young's modulus of elasticity and the stress-at-break, both derived from the stress versus strain test of dogbone-shaped photopolymerized samples. The parameters studied included the dye and co-initiator concentrations, and the laser power. We also compared the mechanical properties of samples made using different types of fluorone dyes and using two different amines as co-initiator. Better polymers are formed by the dyes with low fluorescence quantum yield. The three photopolymerization parameters modify the mechanical properties in a very similar way: they initially tend to increase both the Young's modulus and the stress-at-break but have a deleterious effect on the material strength if used in excess. N-phenylglycine, NPG, was shown to form stronger polymers (higher Young's modulus) than if N,N-dimethyl-2,6-diisopropylaniline, DIDMA, was used as co-initiator. We discuss the possible molecular mechanisms for such observations. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Stereolithography is a new technology linking the power of computer graphics to the rapid formation of a solid, shaped object. Patented originally by Hull,[1] stereolithography converts CAD/CAM/CAE generated solid or surface model data to a three-dimensional real part synthesized, via polymerization, from a photosensitive mixture of initiators and monomers such as an acrylate. Cured by a laser beam directed across an x, y surface, a liquid monomer mix is converted to a solid plastic object, point by point, layer by layer, as allowed by the photopolymer in all three dimensions x, y, and z.

Ultraviolet (in special HeCd) lasers have been most widely used in stereolithographic systems[1,2] but visible absorbing dyes plus co-initiators have more recently been developed for the same purpose.[3,4] This

has allowed the use of more powerful and reliable visible lasers, like the Ar^+, as the radiation source for the photopolymerization process. Although, in principle, any type of object can be made if the proper file is used to drive the laser beam, one of the most interesting applications of stereolithography involves the use of computer-assisted tomography (CAT) or magnetic resonance image (MRI) digitized data to make plastic replicas of the human organ under medical analysis. Both applications are currently under way in our laboratories at the Center for Photochemical Sciences, Bowling Green State University, using commercially available resins.

During the initial period of this project it was realized that in order to tailor-make polymers for specific industrial or medical applications, it is paramount to establish a good correlation between both the photopolymerization parameters and the molecular composition with the mechanical properties of the formed materials. In this report we present the first results on the study of the effect of various photopolymerization parameters on the mechanical

---
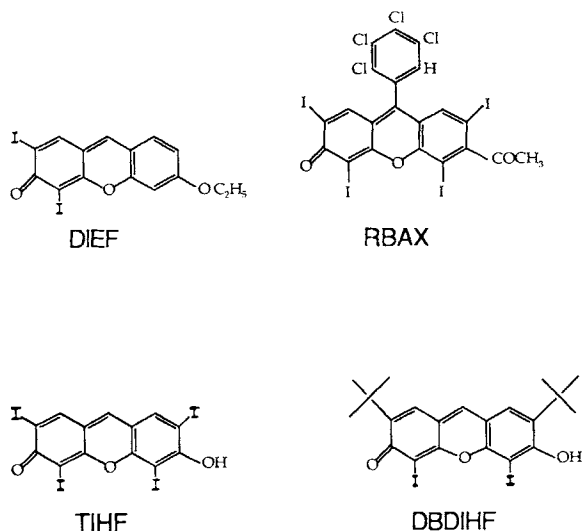
Figure 1   Chemical structure of the 4 fluorone dyes used in this investigation.

properties of solids formed by visible (Ar$^+$) laser-induced polymerization of multifunctional acrylated monomers. The parameters investigated included: the specific dye used; the concentration of the dye; the Ar$^+$ laser power; the concentration of the co-initiator, for example, N,N-dimethyl-2,6-diisopropylaniline (DIDMA). We also compared, through the determination of mechanical properties, the relative efficiency of two co-initiators, namely DIDMA and N-phenylglycine (NPG) at two different concentrations and using the same dye.

EXPERIMENTAL

Materials

The monomers and oligomers used were: 1,6 hexanediol diacrylate (HDDA, from Scientific Polymer Products or from Sartomer Co., Sartomer 238; trimethylolpropane triacrylate (TMPTA, Saret 351); dipentaerythritol pentaacrylate (DPHPA, Sartomer 399, both from Sartomer Co.); and polyethyleneglycol 400 diacrylate (PEGA, from Scientific Polymer Products). The stabilizers were not removed from the monomers because it was observed that this procedure generates an instability in the reaction mixture with the polymerization starting before it is really intended. The measurement of the mechanical properties of the materials formed showed much better reproducibility if the monomers were used as received. The concentration of the monomers varied for each experiment but the basic and

most widely used (standard) composition contained, in weight percent, HDDA (10) plus TMPTA (50), and DPHPA (40).

The two main dyes compared were a fluorone derivative (2,4-diiodo-6-ethoxy-3 fluorone),[4] hereafter DIEF, and a decarboxylated and acetylated derivative of Rose Bengal, RBAX.[5] Their concentration was varied from 1.0×10^{-5} to $5 \times 10^{-3} M$, depending on the specific experiment performed. As co-initiators (electron donors in this case) we used DIDMA (Carbolabs, Inc.) but a few experiments were also performed using NPG (Aldrich Chem. Co.). Tests were also made using two other fluorone dyes: the 2,4,5,7-tetraiodo derivative (TIHF) and the 2,7-di-t-butyl(4,6-diiodo) (DBDIHF) derivative. Their structures are shown in Figure 1.

Sample Preparation and Photopolymerization Conditions

For the sample preparation the dye was first dissolved in the monomer where its solubility was the highest. HDDA and PEGA were used for this purpose. This mixture was then submitted to ultrasound for 20 to 40 min. A similar procedure was also utilized to dissolve NPG but the process was carried out in a separate container. The other monomers were added to the solution of dye plus NPG in the dissolving monomer and the whole system was thoroughly homogenized, especially right before the irradiation procedure. When DIDMA was used as co-initiator, it was the last substance added to the mixture immediately before irradiation.

The reaction mixture was poured into dogbone-shaped Teflon molds 2.0-mm deep, 6.0-mm wide, having a gauge length of 70.0 mm, and a total length of 120.0 mm. Although these dimensions do not strictly follow the specifications of the ASTM-D638-82a norm, they are certainly suitable to provide comparison between the mechanical properties of samples prepared under different photopolymerization conditions or with the small changes in composition studied.

The irradiation was carried out in air. An Ar$^+$ laser (Omnichrome, model 543-200 MGS) was used as the irradiation source. The laser beam was directed toward the sample by mirrors positioned above the Teflon molds. These mirrors were controlled by x-y scanners (DX-series servo controller, from General Scanning, Inc.) to form the dogbone-shaped parts. They were driven by digitized computer data from a special file initially designed to generate a solid cube. If the z translation is neglected, the file just controls the laser beam to generate a

square. The file scale option was appropriately modified to span a 200.0 × 200.0 mm square region, large enough to include all the dogbone-shaped molds with the photosensitive mixtures. The laser power varied from 15.0 to 143.0 mW depending on the experiment performed. The beam diameter was typically 1.5 mm. The specific controller file being used is such that the laser beam is scanned through the sample at a speed of about 9 mm/s.

Mechanical Properties

Tensile strength tests were carried out at ambient temperature (typically 23°C), with no strict humidity control, using the photopolymerized dogbone-shaped samples prepared as described. The tests were performed using an L-500 instrument (Lloyd Instruments, Fareham, England), fitted with an NLC-500N load cell. The crosshead speed used was 5.0 mm/s, the sample gauge length was 70.0 mm, and the width was 6.0 mm.

This instrument was controlled by an MCM-4135T Goldstar PC booted with Lloyd's DAPMAT software. This data analysis program allowed direct observation of the load × elongation behavior of the sample during the test. After the test ended it also automatically displayed various physical parameters of interest, including stress at break ($N \cdot mm^{-2}$) and elongation at break, (absolute, in mm, and relative, in %), maximum load (N), work performed ($N \cdot mm$) and Young's modulus of elasticity ($N \cdot mm^{-2}$) among others.

RESULTS AND DISCUSSION

In initial attempts the fluorone dyes DIEF, TIHF, DBDIHF, and RBAX, at concentrations of 5 × $10^{-4} M$, were irradiated in the presence of the following monomer mixture: PEGA 400 (10%) plus TMPTA (50%) plus DPHPA (40%) using DIDMA (0.1M) as co-initiator. The laser power used was 130.0 mW at 514.5 nm.

The samples made with DIEF and RBAX polymerized immediately and formed objects that could be easily removed from the Teflon molds. They also presented good physical stability and did not break during handling. The samples with TIHF formed a very soft gel that could not be handled immediately. These samples were left under room light illumination for about 30 days, after which they could be tested mechanically. A significant color change was also observed with these samples, from red to light pink, an indication of dye bleaching probably in-

duced by room light. However, the TIHF samples were not very strong and delaminate during handling. The samples with DBDIHF could not be photopolymerized under the experimental conditions used.

Table I presents the values for the Young's modulus of elasticity (Y) and for the stress at break (σ) representing an average of about 10 samples for each dye tested. DIEF seems to be clearly the most efficient dye for the photopolymerization of this particular monomer mixture. Also included in Table I are the fluorescence quantum yield (Φ_f) corresponding to the four dyes compared. It is apparent that the mechanical strength of the materials formed is directly related to the nonradiative depletion of the first singlet excited state of the dye. In other words, formation of the dye triplet state certainly increases the chances for electron transfer from the co-initiator, and this triggers the free radical formation that consequently starts the polymerization process. It is worth mentioning that, because of the physical instability (delamination) of the samples formed after TIHF excitation, the corresponding results are to be taken as preliminary values (Table I). The value for the Young's modulus of elasticity for the other two dyes have a 5% error and for the stress-at-break were determined with roughly 20% error.

In a second set of experiments a mixture of HDDA (10%) plus TMPTA (50%) and DPHPA (40%) was polymerized using DIDMA as co-initiator (0.1M), laser power at 130.0 mW, and changing the concentration of the dye DIEF from 1.0 × 10^{-5} to 5.0 × $10^{-3} M$. Table II shows the results of the Young's modulus and stress-at-break, representing an average over at least four samples tested. Figure 2 depicts the initial values of the Young's modulus for concentrations below 1 × $10^{-3} M$. As observed,

Table I   Mechanical Properties of Acrylate Network Formed by Ar+ Laser-Induced Polymerization Using Different Types of Fluorone Dyes

Dye	Y^a ($N \cdot mm^{-2}$)	σ^b ($N \cdot mm^{-2}$)	Φ_f^c
RBAX	15.70	0.84	0.000
DIEF	40.00	2.00	0.004
TIHF	< 2.40	0.10	0.130
DBDIHF	—	—	0.360

^{a} Young's modulus of elasticity as obtained from the stress–strain curve.
^{b} Stress-at-break.
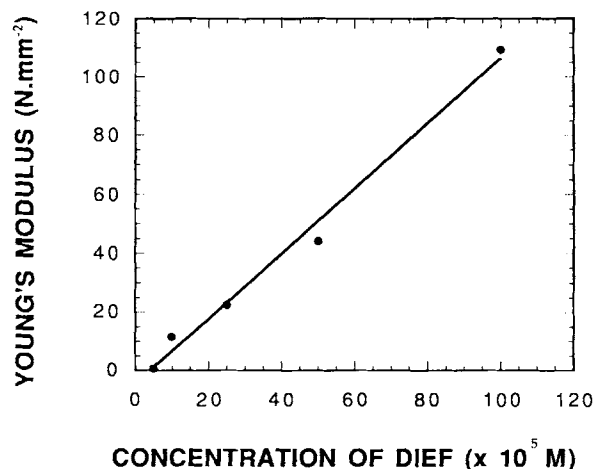^{c} Fluorescence quantum yield for each dye.

both mechanical parameters tend to increase with the dye concentration. In particular, the Young's modulus increases initially in a linear fashion (Fig. 2). This is expected because a larger dye concentration will mean larger absorption, an increase in the number of electrons transferred from the co-initiator, and a consequent increase in the efficiency in transforming the laser light into free radicals. However, as the concentration increases beyond a certain point, in the case of DIEF somewhere between 1×10^{-3} and $5 \times 10^{-3} M$, the dye is not totally dissolved in the medium and it gives visual signs that a dispersion and not a solution is being formed, with clear indication of particle aggregation. As a consequence, a fraction of the Ar^+ laser light will now be scattered and wasted, not performing its real goal of a photopolymerization driving force. This is clearly shown by the decrease in both Y and σ values at a concentration of $5 \times 10^{-3} M$ (Table II). Besides that, the surface of the sample formed with this highest concentration showed some rugosity. This certainly increases the uncertainty in the determination of the thickness of the sample and the values of the mechanical properties are also affected.

There is another striking point when looking at Figure 2. Although the data show a linear correlation ($R = 0.99$) between the Young's modulus and the dye concentration, the line apparently does not pass through the origin. The x (dye concentration)-intercept seems to reflect the fact that there is a minimum dye concentration necessary to generate a density of "real" initiators (free radicals) high enough for gelation to occur. Consequently, there is a concentration threshold (minimum) value below which no extensive cross-linking is observed.

We have also fixed the dye (DIEF) concentration at $5 \times 10^{-4} M$, plus the DIDMA concentration at $0.1 M$, used the standard composition, but changed

Table II   Mechanical Properties of Acrylate Network Formed by Ar^+ Laser-Induced Polymerization Using Different Concentrations of DIEF

Dye Conc. ($\times 10^5 M$)	Y (N·mm^{-2})	σ (N·mm^{-2})
5	0.5	0.15
10	11.7	0.94
25	22.5	1.40
50	44.1	1.66
100	109.3	3.28
500	48.4	1.73

CONCENTRATION OF DIEF (x 10^5 M)

Figure 2   Young's modulus of elasticity of an acrylate network, [in weight percent: HDDA (10) + TMPTA (50) + DPHPA (40), standard composition], as a function of the fluorone dye (DIEF) concentration. Photopolymerization using an Ar^+ laser at 514.5 nm (Pl = 130.0 mW) and DIDMA (0.1 M) as co-initiator.

the laser power from 15.0 to 130.0 mW. Table III presents the results of both Y and σ as a function of the laser power and Figure 3 depicts the Young's modulus against the laser power. The results of Figure 3 show that the Young's modulus initially increases linearly with the laser power. In other words, the laser light is efficiently channeled into polymerization (cross-linking) of the acrylate moieties. However, at higher laser power the mechanical properties of the materials are somewhat degraded. This can be explained by the increase in heat generated inside the sample at higher power with the possibility of partial depolymerization of some of the cross-linked acrylate domains.[6] A deviation from the expected dependence on the laser power was also seen in the photopolymerization kinetics of acrylated and methacrylated monomers using Camphor Quinone as initiator.[7] It has been attributed to the increase in primary radical recombination under high initiator concentration and high laser power, and this effect may be now being observed in our end product. Similar to what was observed in Figure 2 for the dye concentration-intercept, in Figure 3 the laser power-intercept (Pl) is not at Pl = 0.0 mW. This seems also to be an indication of a laser power threshold (minimum) necessary to gel this specific monomer composition containing the dye and co-initiator used, at the particular concentration chosen.

In another study the amount of the co-initiator, DIDMA, was varied from 0.01 to 0.2 M. A DIEF

Table III   Mechanical Properties of Acrylate Network Formed by Ar⁺ Laser-Induced Polymerization as a Function of the Laser Power

Pl (mW)	Y (N·mm^{-2})	σ (N·mm^{-2})
15	15.4	0.95
40	28.8	1.40
70	43.8	1.72
100	48.0	2.22
130	44.1	1.70

Table IV   Mechanical Properties of Acrylate Network Formed by Ar⁺ Laser-Induced Polymerization Using DIEF and Different Concentrations of DIDMA

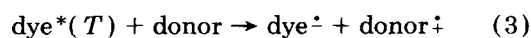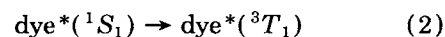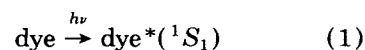| DIDMA Conc. (M)	Y (N·mm^{-2})	σ (N·mm^{-2})
0.010	1.2	0.21
0.025	6.8	0.76
0.050	10.2	0.91
0.075	10.5	1.10
0.100	8.2	0.85
0.150	7.7	0.98
0.200	6.7	0.82

concentration of $1 \times 10^{-4} M$ was used while using the standard monomeric composition and laser power of 40.0 mW. Table IV and Figure 4 present the Y values for each DIDMA concentration. These data show an initial direct relationship between the variables but, after a concentration value somewhere between 0.075 and 0.1M, DIDMA seems to have a negative effect on the strength of the material formed.

The role of a co-initiator in visible light-induced polymerization is worth mentioning at this stage. In the particular case of DIDMA, the co-initiator is an electron donor. According to the accepted mechanism[8] it first loses electrons to the triplet state of the dye. This leads to an unstable species that dissociate into free radicals, and these radicals ini-
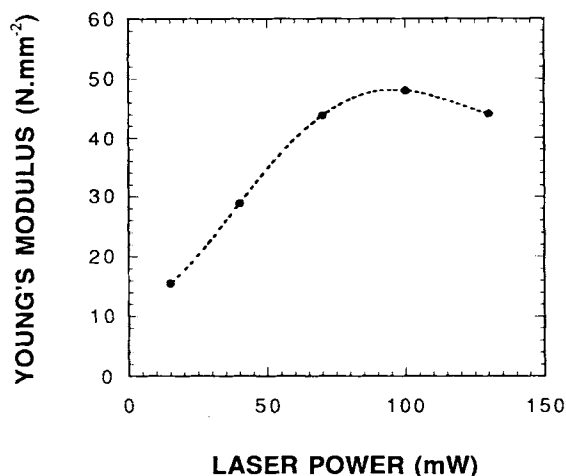
tiate polymerization. Equations (1)–(3) represent the chemical processes just described.

$$\text{dye} \xrightarrow{h\nu} \text{dye}^*(^1S_1) \qquad (1)$$

$$\text{dye}^*(^1S_1) \rightarrow \text{dye}^*(^3T_1) \qquad (2)$$

$$\text{dye}^*(T) + \text{donor} \rightarrow \text{dye}^{\cdot} + \text{donor}^{\cdot+} \qquad (3)$$

$$\text{donor}^{\cdot+} \rightarrow R_1^{\cdot} + \text{acid} \qquad (4)$$

$$R_1^{\cdot} + M \rightarrow M_1^{\cdot}. \qquad (5)$$
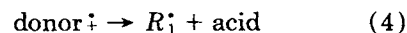
Many amines have been tested as co-initiators before and it was observed that they have different efficiencies in initiating polymerization. This prop-

Figure 3   Young's modulus of elasticity of an acrylate network, standard composition, as a function of the laser power. Photopolymerization using an Ar⁺ laser at 514.5 nm, DIEF $(5 \times 10^{-4} M)$ and DIDMA $(0.1M)$ as co-initiator.
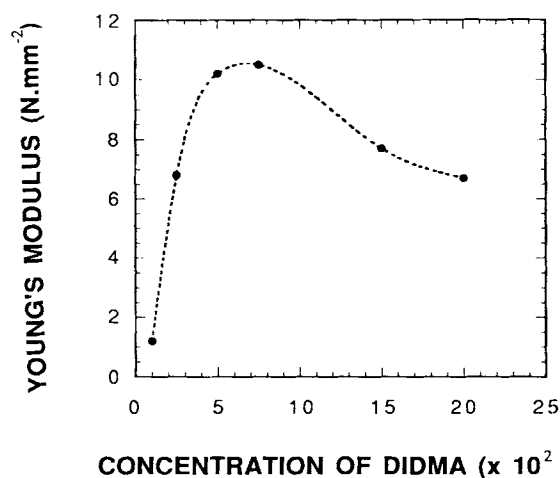
Figure 4   Young's modulus of elasticity of an acrylate network, standard composition, as a function of the co-initiator (DIDMA) concentration. Photopolymerization using an Ar⁺ laser at 514.5 nm (Pl = 40.0 mW) and DIEF at $1 \times 10^{-4} M$.

Table V   Mechanical Properties of Acrylate Networks Formed by Ar$^+$ Laser-Induced Polymerization: Comparison Between DIDMA and NPG

Co-Initiator	Y (N · mm^{-2})	σ (N · mm^{-2})
DIDMA (0.03M)	61.0	3.8
NPG (0.03M)	115.4	5.2
DIDMA (0.05M)	83.7	4.2
NPG (0.05 M)	239.5	9.6

erty is apparently related to their oxidation potential among other factors. However, these materials are generally used in large excess with respect to the dye, for reasons related to the electron transfer mechanism, including the oxidation potential, electron back-transfer, the formation of a dye–amine ground state complex, to name a few. From the experimental results just obtained it is apparent that DIDMA is increasingly efficient in polymerizing the acrylate functions up to a co-initiator-to-dye ratio of about 750. After this point the decrease in Young's modulus values seem to indicate that the excess DIDMA is now acting more like a plasticizer of the acrylate network. Knowing that the degree of polymerization for most of the acrylate monomer mixtures used corresponds to about 20–40% double bond conversion,[9] the molecular structure model that comes to our mind is that of a highly cross-linked acrylate domain, mediated by DIDMA, unpolymerized, and partially polymerized monomers. Because the mechanical strength of networks correlate with the cross-linking density of the formed molecular structure,[10] the excess of unreacted DIDMA certainly contributes to the decrease in cross-linking density.

In the last part of this mechanical properties study, two co-initiators, DIDMA and NPG, were compared. The monomer mixture used consisted of PEGA 400 (20%) plus TMPTA (40%) and DPHPA (40%), all in weight percent. The dye used was still DIEF, at a concentration of $5 \times 10^{-4}M$, and the laser power was 100.0 mW. The co-initiators were used at concentrations of 0.03 and 0.05 M. Table V presents the results for this set of experiments, including the Young's modulus and the stress-at-break. The same data is also represented in Figure 5. They show clearly that NPG is much more efficient as co-initiator than DIDMA. The main problem with the use of NPG as co-initiator is its solubility in most of the acrylates commonly used. HDDA, PEGA, and especially vinyl pyrrolidone can

be effectively used as a solvent for NPG and the dyes tested, in the range of concentrations normally employed.

Laser-induced polymerization of (mono- and multifunctional) acrylate monomers has been studied in detail for quite some time.[11] It is certain that when multifunctional monomers are used the material structure will consist mostly of highly cross-linked domains,[12] namely, a network. The properties of a network are determined mainly by two structural characteristics: the chemical nature of the molecular chains involved in the network formation and the density of cross-linking.[10] In the experiments just described the molecular composition was kept constant while one of the polymerization parameters was changed. Therefore, the mechanical properties observed give an indication on how the cross-linking density of the network formed was affected by the specific change in the photopolymerization parameters. The results clearly indicate that the Young's modulus (and the stress-at-break) tend to increase every time a photopolymerization parameter is changed in the direction of forming a larger number of free radicals, by either improving the energy coupling between the laser source and the initiator:co-initiator system, or changing conditions in order to improve the electron transfer process. It was also shown that the parameters that positively changed the mechanical properties of the network can also be deleterious if "used" in excess. This was clear in

CONCENTRATION OF CO-INITIATOR (x10^2 M)
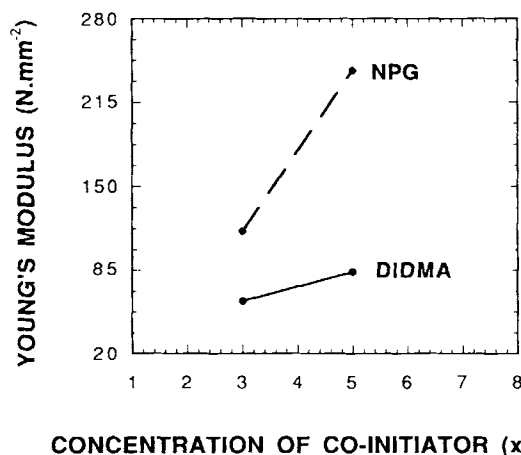
Figure 5   Young's modulus of elasticity of an acrylate network formed from an initial monomeric composition containing, in weight percent, PEGA (20) + TMPTA (50) + DPHPA (40), using DIDMA and NPG as co-initiators, at two different concentrations. Photopolymerization using an Ar$^+$ laser at 514.5 nm (Pl = 100.0 mW) and DIEF at 5.0×10^{-4} M.

the high laser power regime and when an excess of DIDMA was utilized.

It is understandable that the ultimate goal of this work is to develop an in depth understanding of the molecular structure of these networks, using different techniques such as IR and fluorescence spectroscopy, swelling behavior, dynamic mechanical testing, etc. However, because this is a very difficult task, it was not the primary goal at this initial stage of the research. We had just literally "touched the surface" of these materials' properties, but we should go deeper inside their microscopic structure in future work. From what is already known in similar systems, the structure of these photopolymers is probably heterogeneous at the molecular level; it should consist of "microgel-type domains," dispersed in high cross-linking density network regions. Even though the microscopic domains' distribution may be different from sample to sample, formed from the same monomeric composition, and polymerized under the same irradiation conditions, the fact that they show mechanical properties values with a small spread (5–20% error) is an indication that the possible difference in microdomains distribution is not large enough to cause significant variation in the macroscopic properties of the photopolymers.

Another important objective involves the establishment of a good correlation between the monomeric composition, which may contain some oligomers and additives, including cross-linking agents and fillers, and the mechanical property of the final polymeric material formed. This will be the subject of the subsequent research projects to be developed in our laboratories.[13]

REFERENCES

1. C. Hull, U.S. Pat. 4,575,330 (March 11, 1986).
2. C. Hull, M. Sekowski, and R. N. Leyden, Eur. Pat. Appl. EP 420,614 (April 19, 1991).
3. G. S. Kumar and D. C. Neckers, *Macromolecules*, **24**, 4322 (1991).
4. J. Shi, X. Zhang, and D. C. Neckers, *J. Org. Chem.*, **57**, 4418 (1992).
5. O. Valdes-Aguilera, C. P. Pathak, J. Shi, D. Watson, and D. C. Neckers, *Macromolecules*, **24**, 9297 (1991).
6. W. D. Cook, *Polymer*, **33**, 2152 (1992).
7. S. M. Lomakin, R. M. Aseeva, and G. E. Zaikov, *Polym. Degrad. Stab.*, **36**, 187 (1992).
8. A. Zakrewski and D. C. Neckers, *Tetrahedron*, **43**, 4507 (1987).
9. I. Kotchetov and D. C. Neckers, unpublished.
10. A. A. Berlin and N. G. Matvejava, *J. Polym. Sci., Macromol. Rev.*, **15**, 107 (1980).
11. G. E. Frigerio and A. Stefanini, *Lett. Nuovo Cimento Soc. Fis.*, **2**, 810 (1971).
12. G. R. Tryson and A. R. Shultz, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 2059 (1979); C. Decker, ACS Symposium Series 266: *Materials for Microlithography: Radiation Sensitive Polymers*, **9**, 207 (1984).
13. Contribution #173 from the Center for Photochemical Sciences.