Macromolecules 1991, 24, 4322–4327

Laser-Induced Three-Dimensional Photopolymerization Using Visible Initiators and UV Cross-Linking by Photosensitive Comonomers[1]

G. Sudesh Kumar and D. C. Neckers*

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

Received September 13, 1990; Revised Manuscript Received February 26, 1991

ABSTRACT: In this paper, we report dye-sensitized laser-induced homo- and copolymerization of oxime acrylates with polyfunctional acrylates followed by UV cross-linking of the residual acyloxyimino pendant groups. The primary objectives were to study the photopolymerizability of various oxime acrylates with and without conventional acrylates with visible initiators using an argon ion laser and to investigate the photocross-linking of pendant groups of the resulting homo- and copolymers.

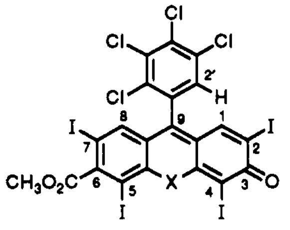
Background

Stereolithography is a new photopolymerization technology linking the power of computer graphics to rapid formation of a solid-shaped object.[2,3] It is entirely a laser-initiated technology that uses multifunctional monomers and oligomers. Control of chemical events resulting from a radical chain reaction initiated at the surface, but proceeding into the polymerizable mixture, is very important. The path where the laser beam hits the surface of the to be polymerized monomer is where the polymer must form for the purposes of end applications, which are generally modeling or prototyping. UV initiators employed in stereolithography, as in other photoinduced polymerizations, generate free radicals by homolytic dissociation. While there are certain visible initiators, such as dye/amine systems, that produce radicals, they do so mostly by electron transfer.[4] This is a subject of current research since many of these visible photoinitiators are more highly absorbing and preclude the formation of polymer in anything but very thin films. In order for a laser-initiated photopolymerization to occur at any depth below the surface plane x,y of a highly functionalized cross-linkable monomer solution, the absorbance of the initiator must disappear at a rate that is essentially comparable to that of the photopolymerization. In other words, concomitant bleaching of the initiator is required during the initiation for an effective laser-controlled imaging in all three directions, x, y, and z.[5] Likewise, increasing emphasis is being placed on the mechanical strength (or the so-called green strength) of the initially formed part, as well as the strength of the final part. This is to maximize cure in the vat in order to reduce the requirement for postcure time and to better control distortions associated with it. A further goal is to reduce the viscosity of the polymerization medium by using reactive diluents. The overall object is to produce three-dimensional (3D) images of a desired texture, mechanical integrity and dimensional stability—soft or hard, rigid, or transparent—models that nearly mimic the target object, and with good layer-to-layer adhesion. Clearly, the development of resin systems is an important target in perfecting stereolithography.

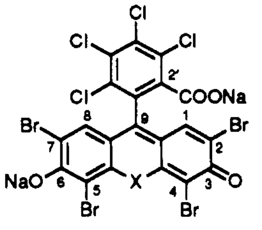
As a part of the "Photopolymerization in Three Dimensions" program, we have sought both better initiators and more photosensitive monomers to control polymerization of a liquid resin in all three dimensions, x, y, and z, relative to an initiating laser beam of some dimension striking an x, y monomer surface in the z direction. In terms of macromolecular engineering, both the polymerization step and cross-linking step may be carried out simultaneously by UV or visible radiation as in current stereolithographic compositions or the two processes may be partly or completely decoupled. One way to effect the latter is to use systems that are sensitive separately to both visible and UV radiations. It is our interest to achieve the required cross-link density of a polymer network by a combination of dye-sensitized photopolymerization using a visible (in the case illustrated, 514 nm) laser and final shaping and dimensional stability of the object by photocross-linking using UV radiation (Scheme I). The application of this two-photon imaging strategy may be either using a combination of visible and ultraviolet lasers or using a UV postcuring procedure.

Acrylate derivatives of various oximes have been selected for this purpose for the following reasons. (1) A wide range of oxime acrylates having desired absorption maxima in the UV range may be prepared by a one-step procedure from corresponding oximes. (2) Polymers bearing (O-acyl)oxyimino groups are reported to be UV-sensitive and participate in photocross-linking or photodegradation.[6–9] (3) (O-Acetyl)oxime esters have been used as photoinitiators, but the photopolymerizability of acrylates with pendant oxime groups has not been studied in detail. Photopolymerization studies involving these nitrogen-containing monomers is of interest. (4) Selection of monofunctional, low-viscosity, UV-sensitive monomers as a reactive diluent introduces a new formulation latitude in image forming.

In this paper, we report the dye-sensitized laser-induced homo- and copolymerization of oxime acrylates with polyfunctional acrylates. The primary object of this investigation is 2-fold: (1) to study the photopolymerizability of various oxime acrylates, with and without conventional acrylates, with visible initiators using an argon ion laser; (2) to investigate the photocross-linking of pendant groups of resulting homo- and copolymers using He–Cd UV laser and/or high-pressure mercury lamp. The visible initiating systems employed in the present investigation are the RBAX (I)/electron donor and eosin (II)/amine systems.



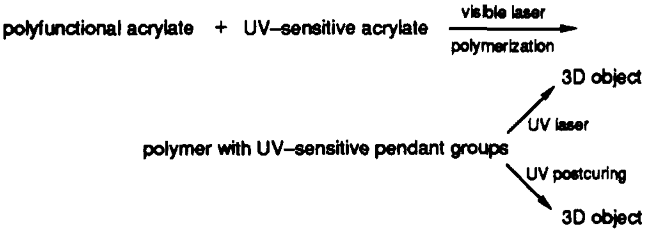
I



II

0024-9297/91/2224-4322$02.50/0

Scheme I[a]



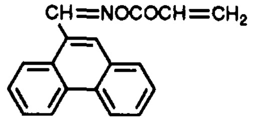
[a] The key to our design is *incorporation of an acrylate monomer* with a UV-sensitive pendant group as a comonomer and/or as a reactive diluent along with di- and trifunctional acrylate monomer compositions.

Experimental Section

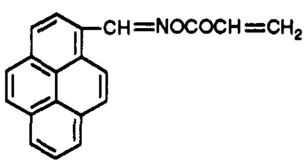
Monomers 1,6-hexanediol diacrylate (HDODA), trimethylolpropane triacrylate (TMPTA), dipentaerythritol pentaacrylate (DPHPA), bisphenol diacrylate (BDA), and *N*-vinylpyrrolidone were purchased from Sartomer and used as received. Monomers 2,3-butanedione monooxime acrylate (BMOA) and cyclohexanone oxime acrylate (COA) were synthesized and purified as reported earlier.[8,9]

Preparation of Triethanolamine Triacrylate (TEAT). Triethanolamine (15 g, 0.1 mol) was dissolved in 100 mL of chloroform, and 30.3 g (0.3 mol) of triethylamine was added. The above mixture was cooled to 0 °C, and 29.8 g (0.33 mol) of acryloyl chloride was added dropwise. The reaction mixture was stirred for 12 h at room temperature, washed with water, and dried over Na_2SO_4, and the solvent was evaporated to give triethanolamine triacrylate. IR 1720 cm^{-1}. NMR δ 6.5 (6 H), 2.5 (triplet, 6 H), 3.7 (triplet).

Preparation of Pyrene-1-carboxaldehyde Oxime Acrylate (IV) (POA). The pyrene-1-carboxaldehyde oxime was obtained from pyrene-1-carboxaldehyde and hydroxylamine hydrochloride. According to the general procedure,[10] oxime (5 g) was dissolved in 20 mL of dichloromethane, and 3 mL of triethylamine was added. An equimolar concentration of acryloyl chloride was added at 0 °C and the mixture stirred for 5 h at room temperature. Further amounts of dichloromethane was added to the reaction mixture, which was then washed with water and dried over sodium sulfate. Evaporation of the solvent resulted in thick viscous liquid that solidified to give a yellow crystalline solid. IR 1735 cm^{-1}. NMR δ 6–6.8 (ABX pattern, quartet, 3 H), 7.5–8.0 (multiplet due to aromatic protons).



III



IV

9-Phenanthrenecarboxaldehyde Oxime Acrylate (III) (PhOA). The 9-phenanthrene oxime[10] was dissolved in chloroform and triethylamine as above, acryloyl chloride was added in equimolar quantities at 0 °C, and the mixture was stirred at room temperature for 6 h. The reaction mixture was washed with water and solvent-evaporated to give yellow solid that was recrystallized from dichloromethane. IR 1735 cm^{-1}. NMR δ 6.0–6.8 (3 H, quartet), 7.5–8.0 (aromatic multiplet).

Quantitative Stereolithography. Determining the course of a polymerization reaction in the path of a laser source was carried out gravimetrically as follows: Polymerizable monomer compositions were irradiated in 1-cm-diameter Pyrex tube with a 514-nm Ar$^+$ laser for different lengths of time. All the polymerizations were carried out in air and at room temperature. The polymer spike formed in the laser path was washed as free as possible of residual monomer with acetone and dried. The percent conversion at any given time is expressed as the fraction of the total weight of the polymer when spike formation is complete (Figure 1) (i.e., 1 cm). Conversions were taken as 100% *when all the polymer that can be formed in the direction* of a specific radiation beam is formed. Percent conversion is calculated as follows: $(W_t/W)100$, where W_t is the weight of the solid polymer in the laser path after irradiation time t, and W is the weight of the polymer when the spike formation is complete. By using this method, the quantity of the monomer unexposed to laser radiation and hence not participating in the polymerization is eliminated. Samples were irradiated at 514 nm with a Spectra Physics 2016 argon-ion laser. The power delivered was measured with a calibrated Sciencetech 365 power meter. In most cases, the laser power employed was 200 mW equivalent to 8.6×10^{-7} einstein/s. All absorption spectra were determined on a Hewlett-Packard 8652A diode array spectrophotometer. Infrared spectra were recorded by using a Nicolet 20DX FTIR spectrometer.

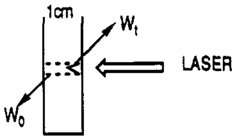


Figure 1. Estimation of percent conversion.

Photocross-linking experiments were carried out by exposing prepolymerized solutions to a monochromator set at the desired wavelength or to a He–Cd laser (320 nm). The insoluble gel formed in the UV-irradiated region was washed free of liquids as above and gravimetrically estimated.

Results and Discussion

Stereolithography converts CAD/CAM/CAE generated solid or surface model data to a three-dimensional real part synthesized, via photopolymerization, from a photosensitive monomer mixture largely composed of polyfunctional acrylates.[2,3] Current stereolithography applications require the formation of mechanically stable photopolymers that are true to within 0.005 in. This means that photopolymer must form, as nearly as possible without deformation, precisely where the laser beam hits the surface of the monomer mixture. In recent years, the use of pulsed UV laser sources to initiate polymerization has increased significantly.[11,12] Since, high-power, stable visible lasers are on the market and convenient, targeting stereolithographic systems aimed at either continuous wave or pulsed lasers is an obvious goal. Eosin's spectral properties in polar solvents such as methanol (λ_{max} 528 nm; ϵ_{max} 1.1×10^5 M^{-1} cm^{-1}; fl = 547 nm; $\phi_f = 0.59$) are such that it is also almost perfectly suited as a potential initiating system for the argon-ion laser.[5] In this case, the excited triplet state of the dye is quenched by an electron-transfer donor such as triethanolamine or triethylamine, which forms the radical anion of the dye. The result is an electron-deficient amine radical partner and electron-rich dye residue.

In the search for visible photoinitiators for three-dimensional imaging applications, our group has also developed new groups of visible systems based on xanthene ring system and spirobenzopyran moieties.[13,14] One such example initiator is the decarboxylated and acetylated derivative of rose bengal (RBAX). Though much of its photochemistry and photophysics will be reported elsewhere, the first step in the mechanism of its action is electron transfer from a nonhydrolytic donor to the xanthene dye moiety, resulting in elimination of acetyl radical.[15] We have chosen to study the suitability of the photoinitiation of RBAX in the presence of electron donors such as triphenyl *n*-butyl borate for the photopolymerization of the oxime acrylates with and without conventional acrylate systems.

Absorption Spectral Characteristics of Oxime Acrylates. The acyl oximes introduced by Delzenne et al.[16] in 1970 have proven to be highly effective in photogenerating free radicals (quantum yields of radicals are of

Scheme II
Decomposition Mechanism of Acyl Oximes

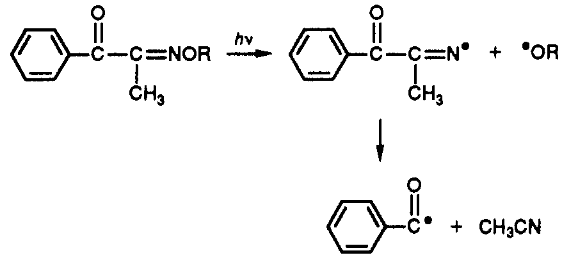


Table I
Spectral Characteristics of Oxime Acrylates

compd	λ_{max}, nm	ϵ_{max}	IR, cm^{-1}
POA	364 290	27 605	1740, 810
PhOA	316 280	11 353	1740, 810
BOA	252	14 500	1740, 810
BMA	228	13 300	1730, 810
COA	<220		1730, 810

the order of 90%). Part of their success is based on the fact that primary bond scission is followed in these systems by a rapid second fragmentation step (Scheme II). This puts the final radicals at least 4.5 Å apart outside the primary cage. As a result, the radical pairs do not recombine.[17] In looking for reactive structures that could serve as photolabile side groups, this was an important consideration because cage recombination is an important factor in viscous media such as those used in the polymerization of polyfunctional acrylates. Another important consideration was the fact that the absorption maxima of these monomers could be tuned to the desired wavelength by the selection of desired ketone or aldehyde chromophore from whence the oxime was originally synthesized. In our design, UV photocross-linking follows dye-sensitized visible polymerization. It is very important to be able to choose the absorption window, to prevent interfering absorption, if any, from the residual dye initiator. Acyl oximes as part of the backbone of a photodegrading polymer chain have been studied by Smets.[18] Delzanne et al.[16] and more recently Li et al.[17] have investigated the photofragmentation of linear polymers containing acyl oxime moieties in the main chain and in the cross-links, respectively. Their respective goals were to use the acyl oximes as a means of photodecoupling and eventually in positive photoresists. Preliminary work by Tanaka[6,7] and others shows that acyl oxime pendant groups in the side chain of linear polymers undergo photocross-linking or photodegradation depending on the structure and physical state of the polymer and nature of the oxime.

Table I lists the absorption characteristics of the series of UV-sensitive monomers investigated in our studies. Aliphatic oxime acrylates show absorption maxima below 230 nm, while benzophenone oxime acrylate shows an absorption maximum at 252 nm. It is important to note that while benzophenone has absorption at 360 nm due to n–π* transition, the corresponding oxime has no strong absorption above 300 nm. The two aromatic aldehydes, POA and PhOA, exhibit strong maxima at 325 and 364 nm, respectively, which are due to π–π* transition, and the formation of oxime changes this absorption very little. The spectral characteristics of the oxime acrylates are shown in Figure 2. POA, PhOA, and BOA are yellow solids, while the aliphatic oxime acrylates are low-viscosity liquids that can serve as reactive diluents. The solubility of POA and PhOA was limited in the monomer mixture; hence, small amounts of N-vinylpyrrolidone or chloroform were necessary to make the polymerized monomer mixture homogeneous.

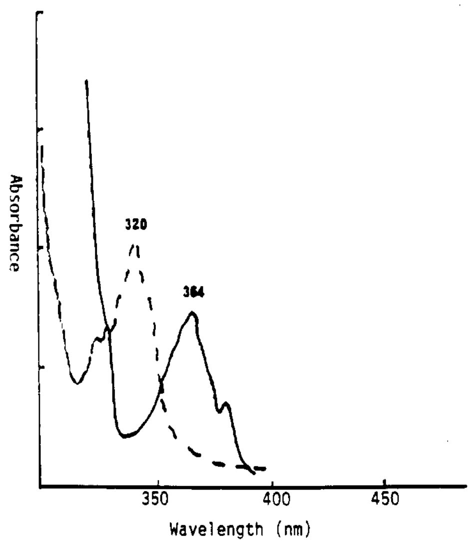


Figure 2. Absorption spectra of pyrene oxime acrylate (—) and phenanthrene oxime acrylate (- - -).

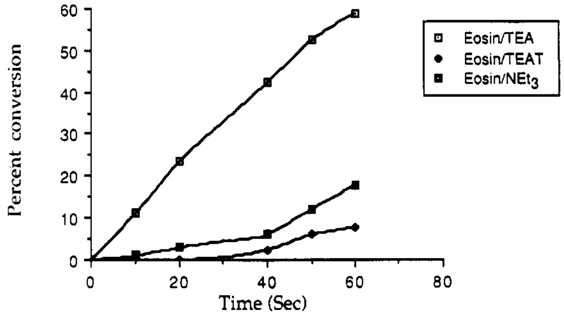


Figure 3. Eosin-sensitized polymerization of BMOA at 516 nm. Conditions: eosin 2.5 × 10^{-6} mol; amine 0.8 × 10^{-3} mol; power = 200 mW.

Polymerization Kinetics. Irradiations were carried out with the argon-ion laser tuned to its emission line at 514 nm. The to be polymerized mixture consisted of an initiator/cocatalyst, monomer mixture, and a reactive diluent such as N-vinylpyrrolidone included at 5% by weight where necessary. Where the laser strikes the monomer solution, solid polymer formed and the length of the spike so obtained in the direction of the laser beam increased with irradiation time.[19] Where the polymerization was carried to completion, the spikes formed were nearly colorless, indicating bleaching of the dye occurred during polymerization.[20] In all cases, the experiments were carried out in duplicate, and the average value of the weight of the polymer was taken to measure percent conversion. The nature of the polymer varied depending on the selection of the monomer, initiator, and the extent of polymerization. The solid polymer still contained some unreacted double bonds as determined from the IR absorption peaks at 810 cm^{-1}.

Effect of Initiator Concentration. We have used eosin/amine systems and RBAX/electron-donor systems to initiate copolymerization of a number of diacrylates and the oxime acrylates (Figures 2–5). The concentration range of the dye was approximately 10^{-4} mol/L with the electron donor present in substantial molar excess (0.05–0.1 M). Photopolymerization was quite rapid, and the depth to which polymerization occurred could be controlled by laser power and time.

Figure 3 presents results of the homopolymerization of BMOA with a 514-nm laser when eosin/triethanolamine,

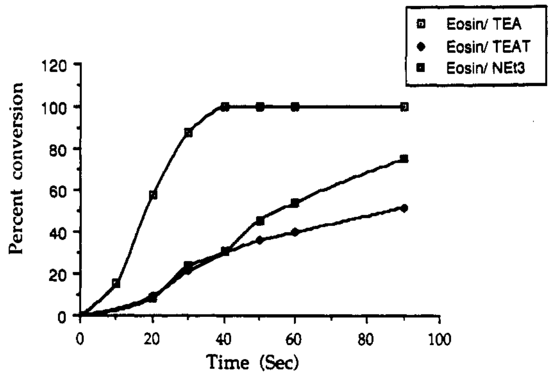


Figure 4. Eosin-sensitized copolymerization of BMOA and Bisphenol diacrylate (1:1) using argon-ion laser (514 nm): eosin 2.5 × 10^{-6} mol; amine 0.8 × 10^{-3} mol; power = 200 mW.

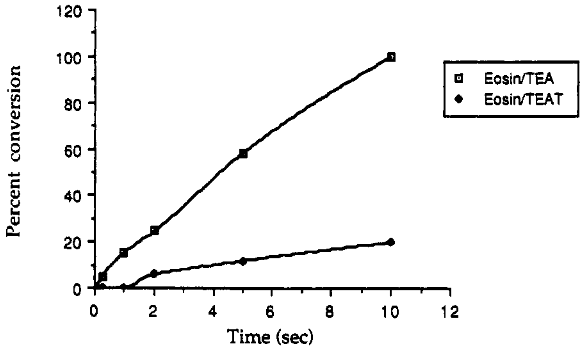
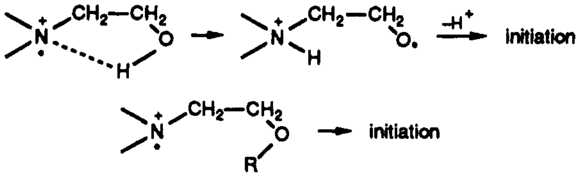


Figure 5. Eosin-sensitized copolymerization of DPHPA with BOA (1:1) using argon-ion laser (514 nm): eosin 2.5 × 10^{-6} mol; amine 0.8 × 10^{-3} mol; power = 200 mW.

Scheme III
Mechanism of Initiating Radical Formation in Triethanolamine and Its O-Substituted Derivatives



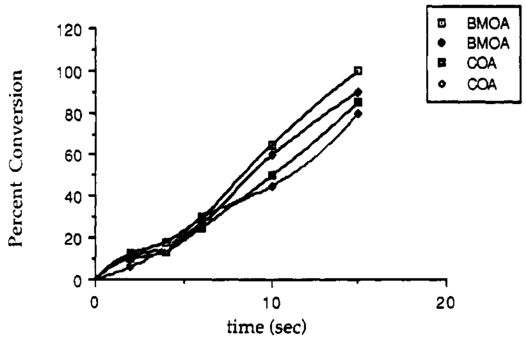


Figure 6. Comparison of eosin/TEA and RBAX/borate as visible photoinitiators. Using DPHPA with BOA and COA (1: 1). In each case initiator 2.5 × 10^{-6} mol, coinitiator 2.5 × 10^{-5} mol.

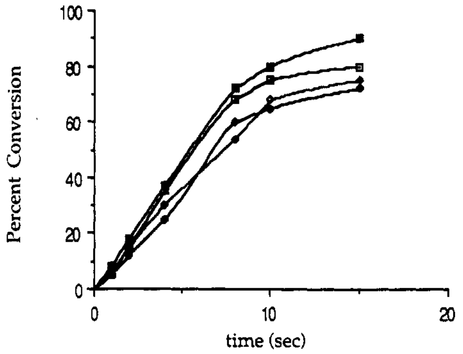


Figure 7. RBAX-sensitized copolymerization of POA and PhOA with bisphenol diacrylate (1:9). POA: PhOA; RBAX 2.5 × 10^{-6} mol; NPG 2.5 × 10^{-5} mol; eosin 2.5 × 10^{-6} mol; TEA 2.5 × 10^{-5} mol; power = 200 mW.

eosin/triethylamine (TA), and eosin/triethanolamine triacrylate were used as the initiating systems. We reasoned that TEAT might serve as an electron donor similar to triethanolamine and in addition might participate in the polymerization process as a trifunctional cross-linker. However, it is evident that conversions are considerably lower when TEAT is used in place of TEA as a cocatalyst. It is known that oxime acrylates undergo thermal radical polymerization without any interference from the pendant groups.[9] However, monofunctional acrylates such as BMOA are expected to give linear, soluble polymers. BMOA, although a monoacrylate, forms insoluble polymer in laser-initiated experiments, suggesting participation of some of the pendant groups as radical sources leading to crosslinking under the photopolymerization conditions.[10] The homopolymerization of cyclohexanone oxime acrylate resulted in viscous solution only under the same experimental conditions.

Figures 4 and 5 show the comparative rates of polymerization using the initiator systems eosin/TEAT, eosin/TEA, and eosin/TEOA for the copolymerization of oxime acrylate and bisphenol diacrylate and DPHPA compositions, respectively. The cross-linked polymers were insoluble in most organic solvents, and molecular weights could not be determined. Again, the results seem to point out that the eosin/TEAT system is less efficient in comparison to the eosin/TEA system with all the monomer systems studied. When triethanolamine triacrylate is used as the polyfunctional monomer, solid polymer was formed at a rate comparable to that of other polyfunctional acrylates. On the basis of this observation, we believe it is likely that intramolecular radical transfer from nitrogen atom to oxygen atom via a five-membered cyclic transition state is one possibility that can take place with TEA but cannot take place in the case of TEAT. The comparable rates with triacrylate and triethylamine seem to confirm this view.

The first step in the mechanism (Scheme III) of RBAX initiating polymerization is electron transfer from a donor to xanthene RBAX, and the radical anion thus formed decays by the elimination of acetyl radical.[15] Acetyl radical is the initiating species in the polymerizations studied. The two electron donors studied, triphenyl *n*-butyl borate and *N*-phenylglycine (NPG), did not exhibit major differences. In both cases, the percent conversions were higher than with eosin/amine systems (Figures 6 and 7). In all the cases, the polymer spike formation proceeded with the bleaching of the dye, resulting in very slightly colored spike.

Effect of Monomer Concentration. The extent of polymerization was dependent on the functionality of the monomer. In general, as the concentration of monofunctional oxime acrylate is increased, the percent conversion correspondingly reduced. Below 10% levels, the presence of these monofunctional acrylates did not influence polymerization rates significantly. The dye-sensitized homopolymerization of COA did not result in spike formation, while BMOA formed a spike under the same conditions. Likewise, a comparison of copolymerization behavior of BMOA and COA indicates faster conversions with BMOA,

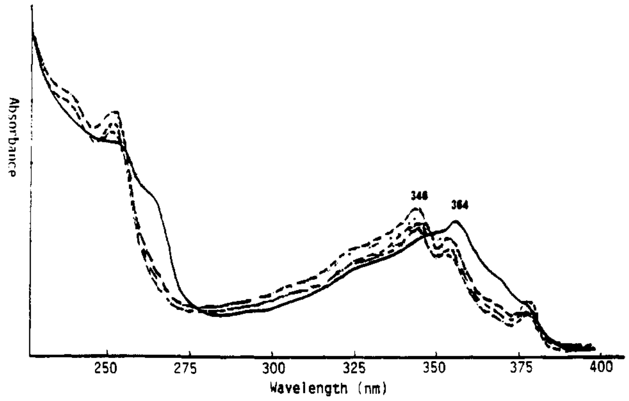


Figure 8. Absorption spectral changes of 1,6-hexanediol diacrylate-*co*-POA (95:5) with UV irradiation. (—) Before irradiation, (- - -) after irradiation.

Table II
UV Cross-Linking of Copolymers with Pendant Groups

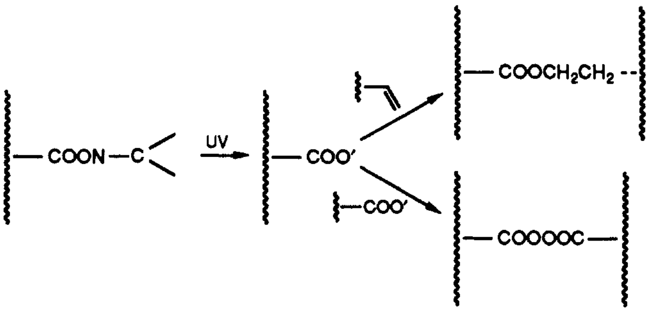
composition	time, min	% gel I	 II
1,6HDA–POA copolymer (95:5)	2	10	3
	5	30	10
	10	60	20
1,6HDA–PhOA copolymer (95:5)	2	5	
	5	10	4
	10	25	10

which may be due to the participation of pendant groups as radical sites for chain growth.[6] Copolymerization studies involving POA and PhOA could not be carried out at higher concentrations because of poor solubility of these monomers in the polyfunctional acrylates (Figure 6). In the case of the RBAX/borate system, *N*-vinylpyrrolidone was used to dissolve the borate salt, which also improved the solubility of these monomers. Polymerizations involving these aromatic oxime acrylates containing 10% by weight of the monomer mixture did not deviate significantly from those of other monomers (Figure 7).

Photocross-Linking of Polymers Bearing Pendant (*O*-Acyl)oxyimino Groups. To demonstrate the UV cross-linkability of the pendant acyloxyimino groups, copolymers of bisphenol diacrylate and 1,6-hexanediol diacrylate were prepared with 5% (by weight) pyrene oxime acrylate and phenanthrene oxime acrylate, both of which have considerable absorption in the region 320–360 nm. Figure 8 shows the absorption characteristics of the polymer prepared from POA (5% by weight) by the benzoyl peroxide initiation at 60 °C. The polymerization was stopped before the gel point, and the solutions were irradiated with light from a monochromator at the maxima of the corresponding oxime acrylate (364 nm). The solution exposed to UV radiation cross-linked within a few minutes, forming a pale yellow film on the wall of the cuvette. The weight of the film was taken as an index for the gelation (Table II). Figure 8 also shows the spectral changes associated with the photocross-linking. These experiments demonstrate the intrinsic photosensitivity of these pendant groups in the absence of any dye absorption that might interfere in the case dye-sensitized copolymer samples.

Parallel sets of polymerization experiments were carried out using the above monomer mixture with an eosin/triethanolamine system (514 nm) but for shorter periods of time, and the resulting prepolymer (or partly polymerized) solution was then exposed to UV radiation as above and the extent of cross-linking was measured.[21] Since the polymerization was not carried out to completion, bleaching of the dye was incomplete at the concentration of the initiator used. As a result, the film formation was observed only after 3 min. The lower levels of cross-linking can be attributed to partial masking of the oxime absorption by the residual initiator. Like experiments with a He–Cd laser (325 nm) produced gel along the laser path. Since the dye-sensitized polymerization was stopped well before the gel point, the polymerization still contained initiator molecule and the penetration of the UV laser was not complete.

Scheme IV
Possible Mechanisms of Cross-Linking



We have explored the possibility of combining visible laser-induced polymerization with UV-induced cross-linking as a means of building a three-dimensional network structure aimed at three-dimensional imaging (Scheme IV). Our investigations have established the possibility of incorporating photosensitive monomers of desired absorption maxima ranging from near UV to deep UV and their polymerizability with other acrylate monomers. Although the quantum yields of chain scission and cross-linking were difficult because of the presence of dye molecule in the polymer matrix, gelation due to ultraviolet exposure (both laser and mercury lamp) indicates that photocross-linking is facile is these systems. As shown by Tanaka et al.,[7–9] photodegradation might be significant in linear polymers over cross-linking, but in the case of branched or cross-linked networks, photocross-linking seems to be the dominant reaction. We believe that the cross-linking following scission of acyl oxime might proceed by two mechanisms. Intermolecular attack of carboxy radicals generated in the polymer side chains due to cleavage of the C=N—O bond, on unreacted double bonds of another chain, is a possibility. In other words, the macroradical generated on the polymer acts as a grafting site, leading to intermolecular cross-links. Alternatively, carboxy macroradicals might react with another carboxy radical, leading to cross-linking.

Conclusions

Eosin-sensitized laser-induced three-dimensional photopolymerization of polyfunctional acrylates incorporating UV cross-linkable (*O*-acyl)oxyimino pendant groups is reported. The visible initiators employed initiate polymerization of these acrylates effectively and undergo concomitant bleaching. UV cross-linking of these prepolymers by irradiation with a mercury lamp and by a UV laser indicates cross-linking, leading to gel formation.

Acknowledgment. This work has been supported by the National Science Foundation (DMR 8702733). We are grateful for this support.

References and Notes

(1) Publication No. 92 from the Center for Photochemical Sciences.
(2) Hull, C. U.S. Patent 4,575,330, March 11, 1986.

(3) Neckers, D. C. *Chem Tech.*, in press.
(4) Zakrewski, A.; Neckers, D. C. *Tetrahedron Lett.* **1987**, *43*, 4507.
(5) Neckers, D. C.; Raghuveer, K. S.; Valdes-Aguilera, O. *Polym. Materials Sci. Eng.* **1989**, *60*, 15.
(6) Tsunooka, M.; Imono, S.; Nakayama, K.; Kuwabara, H.; Tanaka, M. *J. Polym. Sci., Chem. Ed.* **1986**, *24*, 317.
(7) Hong, S.; Kurosaki, T.; Okawara, M. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 2553.
(8) Ghogare, A.; Kumar, G. S. *J. Chem. Soc., Chem. Commun.* **1989**, 1533.
(9) Ghogare, A.; Kumar, G. S. *J. Chem. Soc., Chem. Commun.* **1990**, 134.
(10) *A Text Book of Practical Organic Chemistry*, 3rd ed.; Vogel, A. I., Ed.; Longmans: New York, 1961; p 721.
(11) Hoyle, C. E.; Trapp, M. A. In *Radiation Curing of Polymeric Materials*; Hoyle, C. E., Kinstle, J. E., Eds.; American Chemical Society: Washington, D.C., 1990; p 429.
(12) Decker, C.; Moussa, K. In *Radiation Curing of Polymeric Materials*; Hoyle, C. E., Kinstle, J. E., Eds.; American Chemical Society: Washington, D.C., 1990; p 439.
(13) Watson, D.; Pathak, C. P.; Valdes-Aguilera, O.; Neckers, D. C. Unpublished results.
(14) Lee, S. K.; Neckers, D. C. Unpublished results.
(15) The photochemistry and photophysics of RBAX has been published elsewhere in detail. Watson, D.; Pathak, C. P.; Valdes-Aguilera, O.; Neckers, D. C. patent applied for.
(16) Delzenne, D. A.; Laridon, U.; Peeters, H. *Eur. Polym. J.* **1970**, *6*, 933.
(17) Li, M.; Liang, R. C.; Reiser, A. *Macromolecules* **1990**, *23*, 2704.
(18) Smets, G. *Polym. J.* **1985**, *17*, 153.
(19) Neckers, D. C. U.S. Patent applied for.
(20) From flash photolysis data earlier, we have observed that bleaching quantum yields for eosin in the presence of increasing concentrations of TEA maximize at exactly the TEA concentration where polymerization rates maximize.
(21) Control experiments carried out with partially polymerized monomers at 514 nm but without the photosensitive comonomer took much longer time for gelation, indicating participation of oxyimino pendant groups in the cross-linking.

Registry No. III, 133872-55-6; IV, 133872-54-5; BOA, 62051-35-8; BMOA, 124772-82-3; COA, 86198-29-0; (1,6HDA)(POA) (copolymer), 133872-58-9; (1,6HDA)(PhOA) (copolymer), 133872-59-0; BMOA (homopolymer), 133872-60-3; (DPHPA)(BOA) (copolymer), 133886-94-9; (DHPA)(COA) (copolymer), 133886-95-0; NPG, 103-01-5; TEA, 102-71-6; triethanolamine, 102-71-6; pyrene-1-carboxaldehyde oxime, 3786-56-9; 9-phenanthrene oxime, 126388-91-8; tributylborate, 688-74-4; eosin, 17372-87-1; acryloyl chloride, 814-68-6.