General Photopolymerization Utilizing Colored Merocyanine Form Produced by VP. A photopolymerizable solution prepared by dissolving **6** or **7** in 0.2 mL of VP containing CPB (9.27×10^{-2} M) followed by an addition of 1.8 mL of TMPTA in a glass cuvette was used for the photopolymerization in the normal manner.

Photopolymerization of 6 Using VP as a Color-Developing Solvent by He/Ne Laser. A solution of 2.82 mg (3.15×10^{-3} M) of **6** in 0.2 mL of VP containing CPB (9.27×10^{-2} M) and 1.8 mL of TMPTA was used for the photopolymerization in the normal manner. The 1-, 2-, 4-, 8-, 16-, and 32-s He/Ne laser shots gave 0.65, 1.23, 2.82, 5.78, 13.88, and 18.18 mg of polymeric spikes, respectively.

Photopolymerization of 7 Using VP as a Color-Developing Solvent by He/Ne Laser. A solution of 2.47 mg (2.58×10^{-3} M) of **7** in 0.2 mL of VP containing CPB (9.27×10^{-2} M) and 1.8 mL of TMPTA was used for the photopolymerization in the normal manner. The 1-, 2-, 4-, 8-, 16-, and 32-s He/Ne laser shots gave 1.58, 3.53, 5.91, 16.32, 37.42, and 77.3 mg of polymeric spikes, respectively.

Photopolymerization of 6 Using VP as a Color-Developing Solvent by an Argon Ion Laser. A solution of 2.28 mg (2.54×10^{-3} M) of **6** in 0.2 mL of VP containing CPB (9.27×10^{-2} M) and 1.8 mL of TMPTA was used for the photopolymerization using the argon ion laser (514 nm, 100 mW) in the normal manner. The spots the laser beam hits were bleached but did not give insoluble polymeric spikes.

Photopolymerization of 7 Using VP as a Color-Developing Solvent by an Argon Ion Laser. A solution of 2.34 mg (2.45×10^{-3} M) of **7** in 0.2 mL of VP containing CPB (9.27×10^{-2} M) and 1.8 mL of TMPTA was used for the photopolymerization using the argon ion laser (514 nm, 100 mW) in the normal manner. The 0.25-, 0.5-, 1-, 2-, and 4-s laser shots gave 5.02, 11.29, 26.67, 54.76, and 96.70 mg of polymeric spikes, respectively.

Photopolymerization of a Solution of 7 at Different Dye Concentrations. Each of a different quantity of **7** (0.17, 0.73, 1.07, 1.77, and 3.38 mg, respectively) was dissolved in 0.2 mL of VP containing CPB (9.27×10^{-2} M), and the colored solution was diluted with 1.8 mL of TMPTA under dark. Each of the colored solutions was irradiated for different length of time in the normal manner.

Photopolymerization of a Solution of 7 at Different CPB Concentrations. Each of a solution of 1.77 ± 0.01 mg of **7** (1.85×10^{-3} M) and CPB (2.32, 4.64, 9.27, and 20.6 mM) in 0.2 mL of VP was diluted with 1.8 mL of TMPTA. Each of the colored solutions was irradiated for different lengths of time in the normal manner.

Thermochromic Photopolymerization. A solution of 2.3 mg (3.21×10^{-3} M) of **7**, 8.3 mg of CPB (9.18×10^{-3} M) in 1.5 mL of TMPTA was heated to 55 °C by using a water bath as the heating medium. The colored solution was kept in the water bath during He/Ne laser (632 nm, 16 mW) irradiation. The 9-, 12-, and 16-s laser shots of this solution gave 1.7, 3.2, and 6.0 mg of polymeric spikes, respectively.

Acknowledgment. We are deeply indebted to Dr. O. Valdes-Aguilera for the photochemical study of 6,8-diiodobenzospiropyran (**5**) and to Dr. S. Kumar for valuable discussions. This work has been supported by the National Science Foundation (DMR 8702733). We are grateful for this research support.

Registry No. **3**, 70331-81-6; **5**, 100239-68-7; **6**, 98883-30-8; **7**, 135823-65-3; **8**, 135823-66-4; **9**, 135823-67-5; **10**, 135823-68-6; **11**, 135823-69-7; **12**, 34935-30-3; **13**, 135823-70-0; **14**, 6615-24-3; TMPTA, 15625-89-5; cetylpyridinium butyltrimethylborate, 133521-17-2; *N*-vinylpyrrolidone, 88-12-0; triethylamine, 121-44-8; triethanolamine, 102-71-6.

Two-Photon Radical-Photoinitiator System Based on Iodinated Benzospiropyrans

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Received March 8, 1991. Revised Manuscript Received June 5, 1991

Two-photon photopolymerizations of solutions of benzospiropyrans (BSPs) and *N*-phenylglycine in trimethyltripropane triacrylate (TMPTA) were carried out using both UV and visible lasers. With UV irradiation benzospiropyran solutions generate intensely colored merocyanines and subsequent He/Ne laser irradiation of the colored solutions gave polymer. Benzyldimethyliodomethoxynitrobenzospiropyran (BIMNBSP, **9**) was the most photosensive two-photon initiator among four iodinated BSPs.

Introduction

Stereolithography[2] involves the formation of a three-dimensional object additively, layer by layer. As such it couples the power of computer graphics, through laser-initiated photopolymerization, to the formation of a unique, real plastic form. Stereolithography, in its original manifestation, employs a He/Cd laser (324 nm), a UV photoinitiator (usually an acetophenone acetal) and a mixture of viscous polyolacrylates. The x,y dimension is controlled by scanning the laser beam over the surface of the polyolacrylate/UV initiator mixture at a rate sufficiently fast to form a gelled layer of polymer of fixed depth on an aluminum platform immersed to essentially 100 μm in the polyolacrylate/UV initiator mixture. After formation of the first layer the platform is immersed to a depth of 200 μm, the layer of monomer is leveled, and a second layer is formed on top of the first. This process is continued in an additive modeling fashion[3] until the desired unique object is formed. The entire x,y pattern for each of the successive of layers of the model is controlled from a computer by either vector scanning or raster scanning the laser beam from point x_1y_1 to x_ny_n. Among the applications of stereolithography is in the formation of models from a CAD/CAM input.

The overall slow step in the three-dimensional modeling process when viscous polyacrylates are used as the prepolymer is the leveling process. It takes a substantial time

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[1] Publication No. 110 from the Center for Photochemical Sciences.

[2] Hull, Charles U.S. Patent 4,575,330; March 11, 1986.

[3] Herbert, A., unpublished research report; 3 M Corporation.

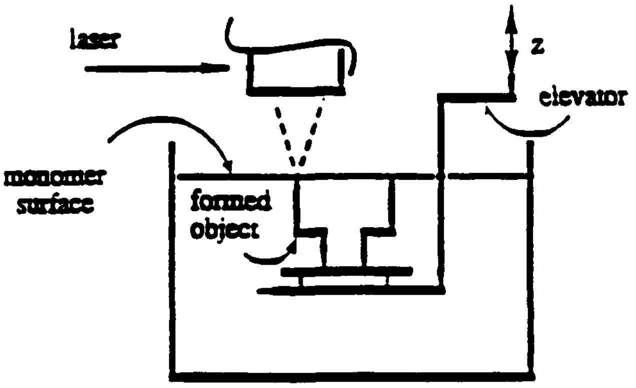
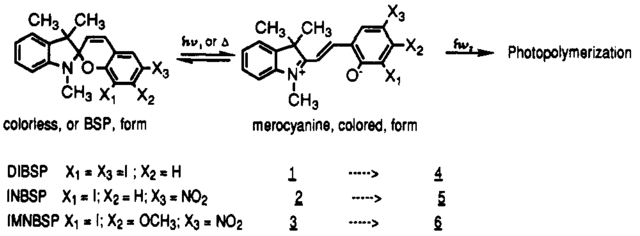


Figure 1. Basic stereolithography.

Scheme I



period for the polyolacrylate mixture to come to dimensional equilibrium after the movement of the platform into the vessel following the formation of the first layer of stereolithogram (Figure 1).

Many commercial methods have been conceived to obviate this. In this publication we concentrate on a chemical solution to the problem of the formation of product under the surface of a monomer mixture rather than at the surface. We have devised a system wherein a first process is used to activate a photoinitiator moiety and a photon subsequently absorbed triggers a photopolymerization event. The former process may involve a photochromic change[4] wherein the triggering process is the absorption of a photon from either a lamp or a laser. The initiation process may be any of several; in the example it is by electron transfer.

Benzospiropyrans (BSP) are an important class of compounds that undergo reversible intramolecular transformations (Scheme I) forming merocyanines either with UV irradiation (photochromic change) or by heating (thermochromic change).[5]

Our interest is centered on the utilization of the colored merocyanine forms as visible light photoinitiator.[6] The original notion was that one form from an appropriate benzospiropyran its merocyanine by irradiation at one wavelength and develop specific conditions wherein only radiation from a second wavelength absorbed solely by the merocyanine effected photopolymerization. If a rapid reversal of the merocyanine to the benzospiropyran followed, a photochromic, two-photon-photoinitiator system such that polymerization would occur only at a point where the two different light sources, intersected, was expected.[7] Such two-photon-photopolymerization events, when coupled with stereolithographic techniques, represent a still additional method of forming a three-dimensional object

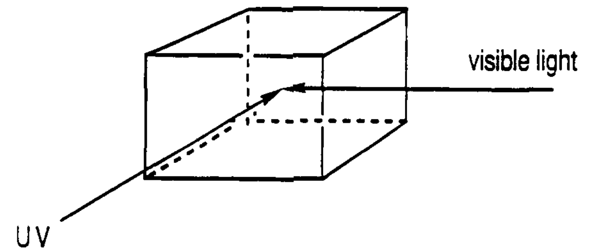


Figure 2. Photopolymerization at the intersection of two lasers.

Table I. Absorption Maxima and Half-Lives of Merocyanines (MC) in Ethyl Acetate

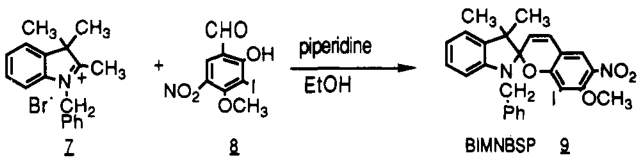
	half-life (merocyanine), s	λ_{max}, nm	λ_{max}, nm
4	35	394	606
5	330	376	572
6	70	382	568
9	15	384	578

by moving through a photopolymerizable monomer at a series of intersection points (Figure 2).[8]

As a first step in outlining the chemistry for this new approach to building a three-dimensional object, we have studied the two-photon-photoinitiator system based on photochromic iodinated BSPs. This is the first successful example of the concept, and we describe the experimental details below.

Results and Discussion

Benzospiropyrans 1–3 are prepared routinely from the corresponding salicylaldehydes and 2-methylene-1,3,3-trimethylindoline in ethanol solution. 1′-Benzyl-3′,3′-dimethyl-8-iodo-7-methoxy-6-nitrobenzospiropyran (BIMNBSP, 9) was prepared from 1-benzyl-2,3,3-trimethylindolenium bromide (7) and 2-hydroxy-3-iodo-4-methoxy-5-nitrobenzaldehyde (8) in an ethanolic solution of piperidine.



The stationary-state absorption spectrum of a solution of BIMNBSP (9) in ethyl acetate as a function of He/Cd (324 nm) laser power is presented in Figure 3. Higher UV power produces a more intense absorption from a greater concentration of the more colored merocyanine form.

Color formation by He/Cd (15 mW) irradiation of a solution of BIMNBSP (9) in ethyl acetate and subsequent thermal decay (followed by 580 nm) is presented in Figure 4. Dark decay follows first-order kinetics with a decay rate constant $k = 6.71 \times 10^{-2}\ s^{-1}$ (Figure 5). Spectral data and half-lives of other merocyanines in ethyl acetate so-

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(4) For a recent review of photochromism see: Durr, H.; Bouas-Laurent, H. *Photochromism; Molecules and Systems*, Elsevier: Amsterdam, 1990.

(5) Tamaki, T.; Sakuragi, M.; Ichimura, K.; Aoki, K. *Chem. Phys. Lett.* **1989**, *161*, 23 and references therein.

(6) Lee, S. K.; Neckers, D. C., submitted for publication.

(7) Parthenopoulos, D. A.; Rentzepis, P. M. *Science* **1989**, *245*, 843.

(8) There are several patents by Swainson and assigned to Formigraphic Engine Products which first outlined this notion. The patents were not, however, supported by experiment. To our knowledge this is the first experimental verification of this Swainson concept. See, for example: Swainson, W. K. U.S. Patent, 4,041,476, August 9, 1977. Another of these is misidentified in ref 7, above. Swainson, W. K.; Kramer, S. D. U.S. Patent 4,471,470, 1984. The spelling error is not the authors, but was made by the Patent Office.

(9) 6-Benzoylbenzylspiropyran/triethanolamine (a) and 6-nitrobenzylspiropyran/diphenyliodonium hexafluorophosphate (b) have been reported to show enhanced photosensitivity by simultaneous irradiation with UV as well as with a He/Ne laser beam. These systems are believed to also cause polymerization by UV irradiation alone. For our application, UV irradiation alone does not cause polymerization at the powers indicated: (a) Jeudy, M. J.; Robillard, J. J. *Opt. Commun.* **1975**, *13*, 25. (b) Ichimura, K.; Sakuragi, M., *J. Polym. Sci. Polym. Lett.* **1988**, *26*, 185.

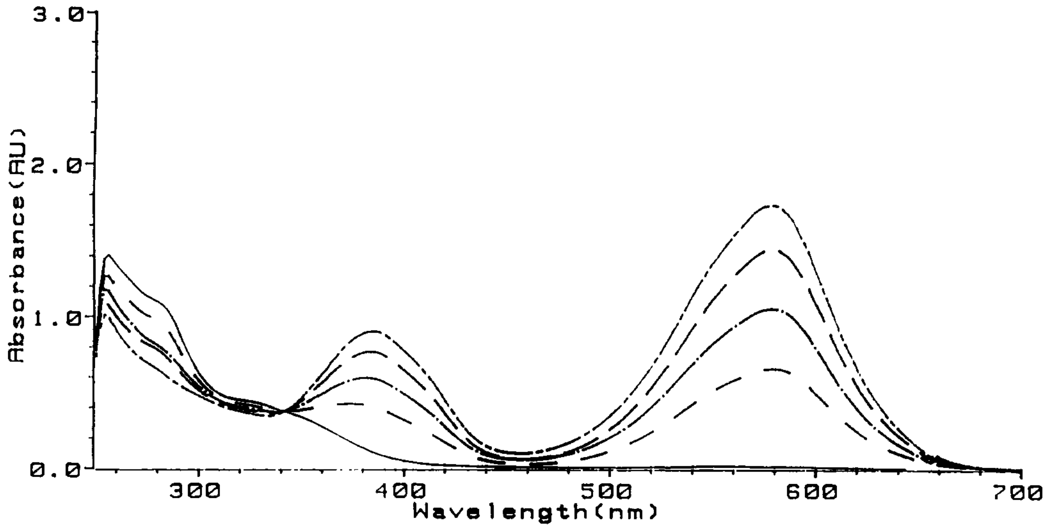

Figure 3. Stationary-state absorption spectrum of **9** in ethyl acetate as a function of irradiation at 324 nm; power (from bottom) 0, 4, 8, 15, 30 mW.

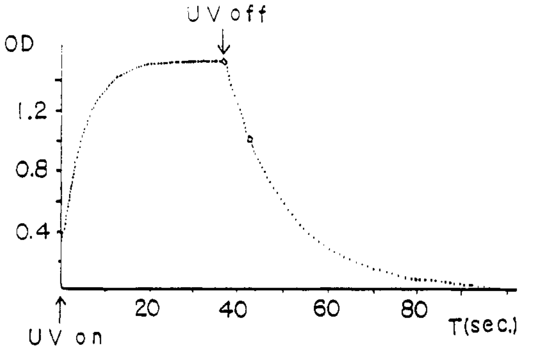

Figure 4. Photocoloration and bleaching of a solution of BIMNBSP **9** in EtOAc generated by 324-nm, 15-mW irradiation followed by thermal decay (spectrum recorded at 580 nm).

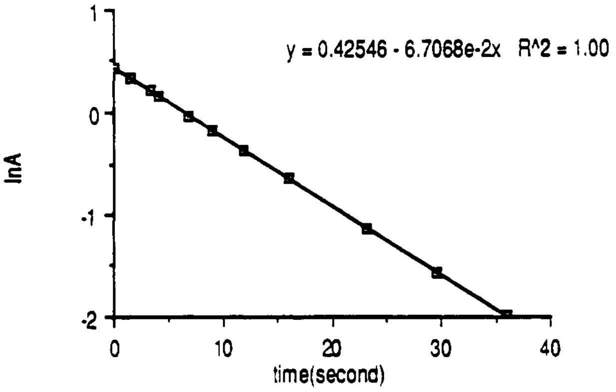

Figure 5. Dark decay of the merocyanine form of BIMNBSP **9**.

lution are summarized in Table I.

Two-Photon Photopolymerizations. Two-photon photopolymerization experiments were carried out by aligning a 324-nm He/Cd laser and 632-nm, 15-mW He/Ne beam and intersecting them as in Figure 6. The He/Ne laser beam was aligned on the edge (d = 1.2 mm) of a UV cell but could be moved from the edge of the cell in a controlled fashion.

The He/Cd 324-nm beam was expanded to 0.7 cm by using a beam spreader. UV laser power was adjusted from 4 to 30 mW by a combination of neutral density filters. Photopolymerizable solutions were prepared by dissolving each of the BSPs, (DIBSP, INBSP, IMNBSP, and BIMNBSP, respectively) and N-phenylglycine in trimethylolpropane triacrylate, TMPTA. N-Phenylglycine was chosen as the co-initiator since it has been shown in other studies to be a most efficient electron donor and it is the least sensitive to 324-nm polymerization with the BSPs among known coinitiators[10] such as triethylamine, triethanolamine, benzyltri-n-butyltin, and cetylpyridinium n-butyltriphenyl borate. A photopolymerizable solution in a quartz cell (b = 0.5 cm) was irradiated at different powers 324 nm to generate a colored spot, after which the colored spot was irradiated with He/Ne laser for different periods of time. Polymeric spikes,[11] which formed only in the direction of the He/Ne laser beam, were washed with acetone, and dried for 2 h before weighing. Data for a solution of DIBSP (**1**, 1.24 × 10^{-3} M) and N-phenyl-

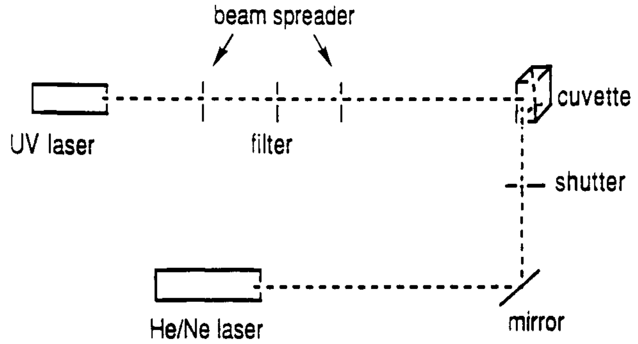

Figure 6. Schematic diagram for a two-photon photopolymerization.

Table II. Two-Photon Photopolymerizations of a Solution of DIBSP (1.24 × 10^{-3} M) and N-Phenylglycine (1.89 × 10^{-2} M) in TMPTA at Different UV Irradiation Times and Power As Measured by the Weight and Length of the Spike

He/Ne irradiation time, s	He/Cd (UV) irradiation time (power)			
	20 s (4 mW)	30 s (4 mW)	10 s (15 mW)	20 s (15 mW)[a]
2	none	none	none	0.28 (1.34)[b]
4	none	0.41 (1.95)	0.49 (1.98)	0.38 (2.05)
8	0.62 (4.37)	0.79 (2.97)	0.65 (3.23)	1.09 (4.03)
16	1.08 (5.64)	1.01 (3.67)	1.08 (6.06)	1.51 (4.80)

[a] UV laser time (power). [b] Weight, mg (length of spike, mm).

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(10) Eaton, D. F. *Adv. Photochem.* **1985**, *13*, 427.

(11) The shape of polymer formed is directly related to the photon shape of the laser shot. In this instance, polymeric spikes were formed.

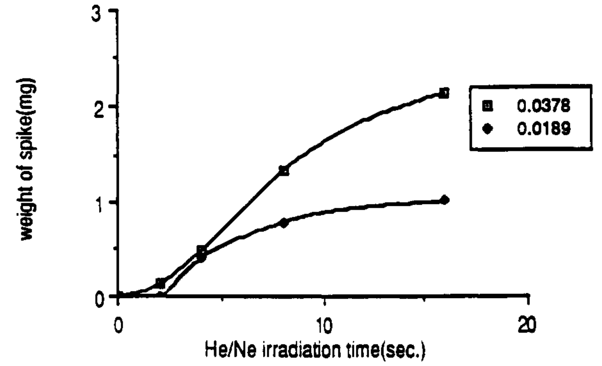

Figure 7. Two-photon photopolymerization of a solution of DIBSP (1.24×10^{-3} M) and *N*-phenylglycine (1.89×10^{-2} M and 3.78×10^{-2} M, respectively) in TMPTA after 30-s UV laser (4 mW) irradiation.

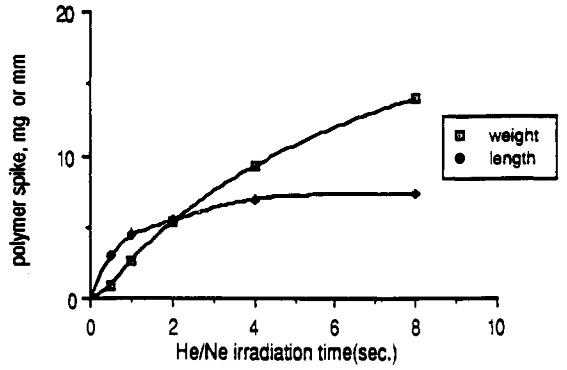

Figure 8. Two-photon photopolymerization of a solution of INBSP (1×10^{-3} M) and *N*-phenylglycine (2×10^{-2} M) in TMPTA for 20-s UV laser (4 mW) irradiation as measured by the weight and length of the spike.

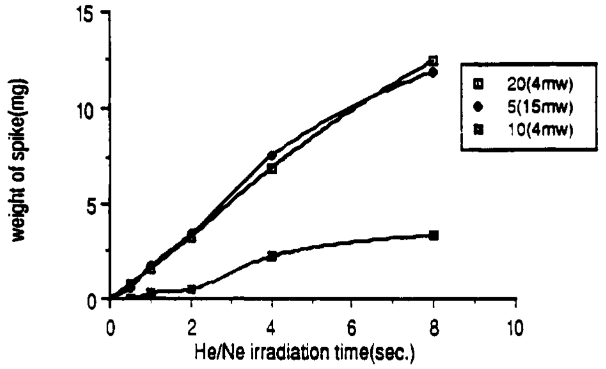

Figure 9. Two-photon photopolymerization of a solution of IMNBSP (1.0×10^{-3} M) and *N*-phenylglycine (2.0×10^{-2} M) in TMPTA. (He/Cd irradiation times and powers inset.)

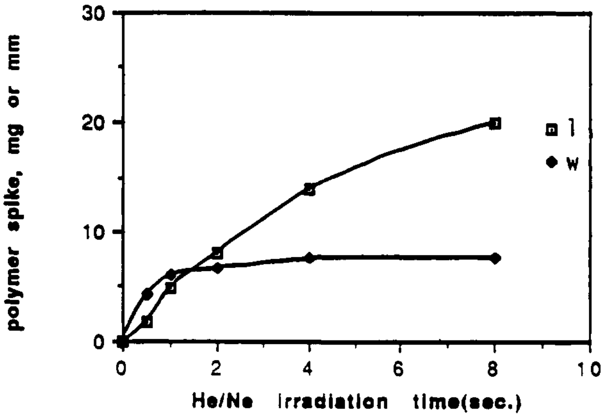

Figure 10. Two-photon photopolymerization of a solution of BIMNBSP (1.0×10^{-3} M) and *N*-phenylglycine (2.0×10^{-2} M) in TMPTA for 10-s UV laser (4 mW) irradiation as measured by the weight and length of the spike.

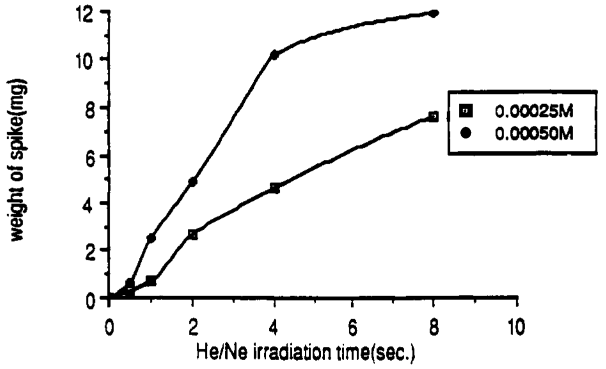

Figure 11. Two-photon photopolymerizations of solutions of BIMNBSP (5.0×10^{-4} M and 2.50×10^{-4} M) and *N*-phenylglycine (2.0×10^{-2} M) in TMPTA for 20-s UV laser (4 mW) irradiation as measured by the weight of spike.

glycine (1.89×10^{-2} M) in TMPTA are summarized in Table II.

The size of the spikes formed increased as the concentration of *N*-phenylglycine increased. The relative rate of polymerization for a solution of DIBSP (1.24×10^{-3} M) and *N*-phenylglycine (3.78×10^{-2} M) in TMPTA was 0.16 and 0.20 mg/sec for 20- and 30-s 324-nm irradiation (4 mW), respectively. The effect of [*N*-phenylglycine] on the rate of photopolymerization is shown in Figure 7.

Results from the two-photon photopolymerizations of a solution of INBSP (1×10^{-3} M) and *N*-phenylglycine (2×10^{-2} M) in TMPTA are plotted in Figure 8. The relative rate of polymerization obtained was 2.2 mg/s.

A solution of IMNBSP (1×10^{-3} M) and *N*-phenylglycine (2×10^{-2} M) in TMPTA was irradiated with a He/Cd (324 nm) to produce a colored spot, and the thus formed colored spot was polymerized at 632 nm with output from a He/Ne laser. These results are summarized in Figure 9.

The relative rates of polymerization of a solution of IMNBSP (1.0×10^{-3} M) and *N*-phenylglycine (2.0×10^{-2} M) in TMPTA obtained were 0.5, 1.6, and 1.6 mg/s for 10- (4 mW), 20- (4 mW), and 5-s (15 mW) UV laser irradiation, respectively (Figure 10).

Irradiation of the same TMPTA/BSP solution but with higher *N*-phenylglycine concentrations (4.17×10^{-2} M) for 20 s (324 nm, 4 mW) gave a smaller amount of polymer. The relative rates of polymerization of a solution of IMNBSP (1.0×10^{-3} M) and *N*-phenylglycine (4.17×10^{-2} M) in TMPTA obtained were 1.9, 0.9, and 2.4 mg/s for 10- (4 mW), 5- (4 mW), and 2-s (15 mW) UV irradiation, respectively. The rate of polymerization increased from 0.5 to 1.9 mg/s in the case of 10-s UV irradiation (4 mW) as the concentration of *N*-phenylglycine increased from 2.00×10^{-2} to 4.17×10^{-2} M.

Two-photon photopolymerization experiments were also carried out with a solution of BIMNBSP (1×10^{-3} M) and *N*-phenylglycine (2×10^{-2} M) in TMPTA. The relative rate of polymerization obtained was 3.0 and 0.5 mg/s for BIMNBSP and IMNBSP, respectively. These results show that BIMNBSP (**9**) is the most efficient among the two-photon photoinitiators described in this publication. Two-photon photopolymerization experiments can be carried out with 1 order of magnitude lower initiator concentration using BIMNBSP (Figure 11). The relative rates of polymerization were 2.7 and 1.0 mg/s for a 5.0×10^{-4} and 2.5×10^{-4} M BIMNBSP solutions, respectively.

The amount of polymer formed by He/Ne laser irradiation of identical duration as a function of depth under

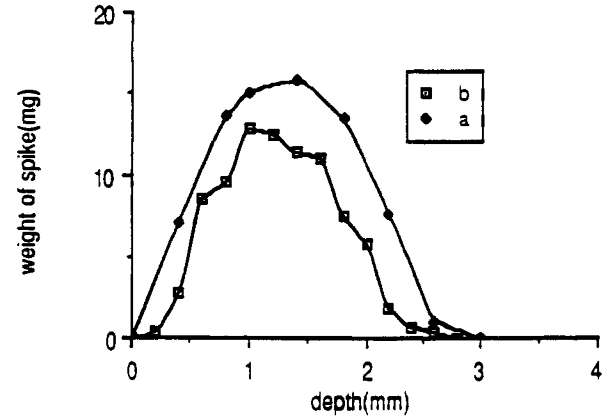

Figure 12. Two-photon photopolymerizations of a solution of BIMNBSP ($a = 2.5 \times 10^{-4}$ M, $b = 5.0 \times 10^{-4}$ M), and *N*-phenylglycine (2.0×10^{-2} M) in TMPTA at different depths under the cell surface (a) 8-s UV irradiation (15 mW) and 8-s He/Ne laser irradiation, (b) 20-s UV irradiation (4 mW) and 4-s He/Ne laser irradiation.

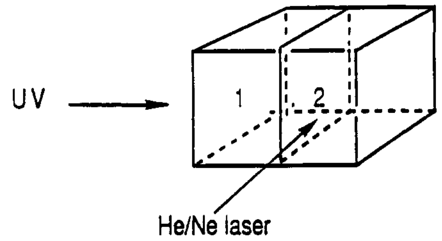

Figure 13. Schematioc diagram of the two-photon photopolymerization experiment using a double cell.

the surface at which the polymerizing beam was focused was determined by using BIMNBSP, and these results are plotted in Figure 12. This figure shows that the depth of UV penetration can never proceed deeper than 3 mm beyond the surface for solutions of BIMNBSP (2.5×10^{-4} and 5.0×10^{-4} M, respectively) in TMPTA.

To determine the cause of the lack of penetration by the UV irradiating beam two-photon photopolymerizations were also carried out using a double UV cell (10 × 12.5 × 45 mm, Figure 13). Cell 1 was filled with different media and cell 2 with polymerizing mixture. Thus in experiment A cell 1 was blank. In B cell 1 was filled with TMPTA; in C a solution of BIMNBSP (1.0×10^{-3} M) in TMPTA; in D a solution of BIMNBSP (1.0×10^{-3} M) in ethyl acetate; in E a solution of BIMNBSP (2.0×10^{-4} M) in ethyl acetate; and in F a solution of BIMNBSP (2.0×10^{-4} M) in TMPTA. A solution of BIMNBSP (1.0×10^{-3} M) and *N*-phenylglycine (2×10^{-2} M) in TMPTA was irradiated for 5 s with a UV laser (15 mW) through the media A–F, respectively, as in Figure 13. The colored spot formed in cell 2 was irradiated with a He/Ne laser for different periods of time. Spikes formed from the He/Ne laser irradiation were washed with acetone and measured. These results are plotted in Figure 14.

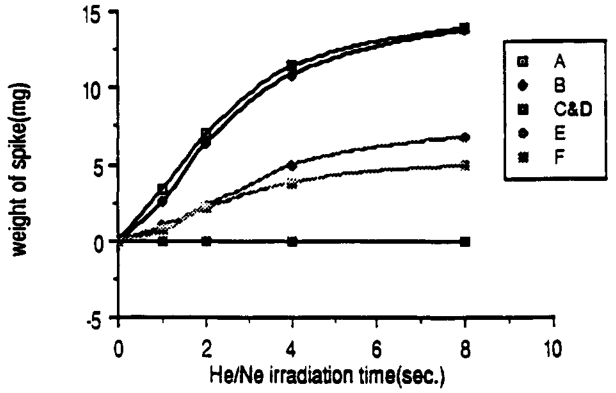

Figure 14. Two-photon photopolymerizations of a solution of BIMNBSP (1.0×10^{-3} M) and *N*-phenylglycine (2.0×10^{-2} M) in TMPTA (cell 2); cell 1; (A) blank, (B) TMPTA, (C) solution of BIMNBSP (1.0×10^{-3} M) in TMPTA, (D) solution of BIMNBSP (1.0×10^{-3} M) in EtOAc, (E) solution of BIMNBSP (2.0×10^{-4} M) in EtOAc, (E) solution of BIMNBSP (2.0×10^{-4} M) in TMPTA.

The relative rates of polymerization (A–F) were 2.70, 2.60, 0, 0, 1.33, and 1.01 mg/s, respectively. Thus the amount of polymer spike formed by the He/Ne laser irradiation reduces when a sufficient concentration of BIMNBSP in either EtOAc or TMPTA is present in cell 1. It is concluded therefore that UV penetration is prevented by absorption from either the BIMNBSP or its merocyanine form and not by other components of the mixture. Since there is little difference in absorbance at 324 nm between BIMNBSP and its merocyanine form (Figure 3), we are certain that the colored MC forms also absorb UV light and thus prevent deep penetration of UV light into the solution. This UV penetration problem might be minimized by using a lower concentration of BSP or a longer wavelength UV irradiation source.

Though we have done no quantitative studies of the mechanism of the polymerization process as initiated by the merocyanine, we suppose it involves electron transfer from the electron-donating borate or tertiary amine to an excited state of the merocyanine. Work is in progress in our laboratories to determine the mechanism of radical formation in the system.

Summary

We have demonstrated for the first time an experimental example of a two-photon-photoinitiator system based on iodinated benzospiropyrans including DIBSP (1), INBSP (2), IMNBSP (3), and BIMNBSP (9). The systems can be used in the area of nonlinear optical recording materials[12] in the building fine objects that require high resolution.

Experimental Section

Methods and Materials. ^{1}H NMR spectra were recorded on Varian XL-200 spectrometer. Chemical shifts are reported in parts per million (δ) from tetramethylsilane (TMS). Mass spectra were measured with a Hewlett-Packard 5987A GC/MS system. Infrared spectra (IR) were recorded on 6020 Galaxy Series FT-IR system. Absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Melting points were determined on a Thomas Hoover melting point apparatus and are uncorrected. Samples were irradiated with Melles Griot He/Ne laser (632 nm) and Omnichrome series 74 He/Cd UV laser (324 nm). The UV laser power was adjusted with Melles Griot neutral density filters, and the power delivered was measured with a calibrated Sciencetech 365 power meter. 2,3,3-Trimethylindolenine, ethyl acetate (HPLC grade), and *N*-phenylglycine were purchased from Aldrich and used as received. Trimethylolpropane triacrylate (TMPTA) was obtained from Sartomer and used without further purification. The preparations of DIBSP, INBSP, and IMNBSP have been described previously.[6]

Preparation of 1-Benzyl-2,3,3-trimethylindolenium Bromide (7). A solution of 5 g (31.4 mmol) of 2,3,3-trimethylindolenine, and 5.91 g (34.54 mmol) of benzyl bromide in 5 mL of ethyl acetate was heated to reflux for 15 h. The reaction mixture was cooled and diluted with 5 mL of hexanes. The solid was collected by filtration and dried under vacuum to give 7.6 g of 7: yield 70%; mp 71–71.5 °C; ^{1}H NMR (CDCl$_3$) δ 7.7–7.1 (m, 9 H), 6.02 (s, 2 H), 3.12 (s, 3 H), 1.67 (s, 6 H); IR (KBr) 3410, 3016,

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[12] Durr, H.; Bouas-Laurent, H. In ref. 4, pp 912–3.

2978, 1732, 1624, 1604, 1464, 1373, 1251, 1031, 769, 750, 692 cm^{-1}.

Preparation of BIMNBSP (9). A solution of 207 mg (0.64 mmol) of 2-hydroxy-3-iodo-4-methoxy-5-nitrobenzaldehyde (8), 210 mg of 1-benzyl-3,3,2-trimethylindolenium (7, 0.64 mmol), and 50 μL of piperidine in 5 mL of ethanol was heated to reflux for 3 h. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography (alumina neutral) using dichloromethane as an eluent to give 220 mg of **9** (yield 52%); mp 161–162 °C; ^{1}H NMR ($CDCl_3$) δ 7.8–6.7 (m, 10 H), 6.37 (d, J = 7.8 Hz, 1 H), 5.87 (d, J = 10.2 Hz, 1 H), 4.36 (d of d, J = 12 and 41 Hz, 1 H), 3.96 (s, 3 H), 1.37 (s, 3 H), 1.32 (s, 3 H); MS (70 eV) m/e (relative intensity) M + 1 = 555 (7), M = 554 (25), 539 (21), 463 (6), 414 (6), 399 (6), 260 (5), 235 (18), 142 (48), 127 (23), 91 (100); IR (KBr) 3055, 2978, 2933, 2870, 1604, 1508, 1489, 1464, 1425, 1334, 1290, 1163, 1090, 1031, 936, 891, 828, 750 cm^{-1}.

General Two-Photon Photopolymerization Procedure. Photopolymerizable solutions were prepared by dissolving a BSP (DIBSP, INBSP, IMNBSP, and BIMNBSP) and *N*-phenylglycine in TMPTA. A photopolymerizable solution in a quartz cell (b = 0.5 cm) was irradiated with different UV powers to generate a colored spot. After the UV irradiation was stopped, the colored spot was irradiated with He/Ne laser for different periods of time. Laser irradiation times were controlled by an electronic time shutter. Spikes that formed only in the direction of He/Ne laser beam were washed with acetone and measured. They were dried for 2 h before weighing.

Two-Photon Photopolymerization of a Solution of DIBSP (1.24×10^{-3} M) and *N*-Phenylglycine (1.89×10^{-3} M) in TMPTA. A solution of 6.56 mg (1.24×10^{-3} M) of DIBSP and 28.6 mg (1.89×10^{-2} M) of *N*-phenylglycine in 10 mL of TMPTA was prepared 1 h in advance by using an ultrasonification apparatus. Two-photon photopolymerization was carried out in the normal manner, and the results are summarized in Table II.

Two-Photon Photopolymerization of a Solution of DIBSP (1.24×10^{-3} M) and *N*-Phenylglycine (3.78×10^{-2} M) in TMPTA. A solution of 6.56 mg (1.24×10^{-3} M) of DIBSP and 57.1 mg (3.78×10^{-2} M) of *N*-phenylglycine in 10 mL of TMPTA was prepared 1 h in advance by using ultrasonification. Two-photon photopolymerization was carried out in the normal manner. It gave 0.08 mg (0.83 mm), 0.44 mg (2.60 mm), 1.02 mg (5.50 mm), and 1.36 mg (6.24 mm) of polymer spike for 2-, 4-, 8-; and 16-s He/Ne irradiation, respectively, for 20 s of UV (4 mW) irradiation.

Two-Photon Photopolymerization of a Solution of INBSP (1.00×10^{-3} M) and *N*-Phenylglycine (2.00×10^{-2} M) in TMPTA. A solution of 4.48 mg (1.00×10^{-3} M) of INBSP and 30.2 mg (2.00×10^{-2} M) of *N*-phenylglycine in 10 mL of TMPTA was prepared 5 h in advance by using ultrasonification. Two-photon potopolymerization was carried out in the normal manner. It gave 0.98 mg (2.95 mm), 2.66 mg (4.41 mm), 5.34 mg (5.46 mm), 9.29 mg (6.99 mm), and 14.00 mg (7.36 mm) of polymer spike for 0.5-, 1-, 2-, 4-, and 8-s He/Ne laser irradiation, respectively.

Two-Photon Photopolymerization of a Solution of IMNBSP (1.00×10^{-3} M) and *N*-Phenylglycine (2.00×10^{-2} M) in TMPTA. A solution of 4.78 mg (1.00×10^{-3} M) of IMNBSP and 30.2 mg (2.00×10^{-2} M) of *N*-phenylglycine in 10 mL of TMPTA was prepared 5 h in advance as before. Two-photon photopolymerization was carried out in the normal manner. It gave 0 mg, 0.30 mg (2.52 mm), 0.51 mg (2.68 mm), 2.24 mg (5.69 mm), and 3.35 mg (5.78 mm) of polymer spike for 0.5-, 1-, 2-, 4-, and 8-s He/Ne irradiation, respectively, for 10 s of UV (4 mW) irradiation.

Two-Photon Photopolymerization of a Solution of IMNBSP (1.00×10^{-3} M) and *N*-Phenylglycine (4.17×10^{-2} M) in TMPTA. A solution of 4.78 mg (1.00×10^{-3} M) of IMNBSP and 63 mg (4.17×10^{-2} M) of *N*-phenylglycine in 10 mL of TMPTA was prepared 5 h in advance. Two-photon photopolymerization was carried out in the normal manner. It gave 0.7 mg (0.52 mm), 2.10 mg (4.74 mm), 3.46 mg (6.32 mm), 7.48 mg (6.99 mm), and 12.03 mg (7.14 mm) of polymer spike for 0.5-, 1-, 2-, 4-, and 8-s He/Ne laser irradiation, respectively, for 10 s of UV (4 mW) irradiation.

Two-Photon Photopolymerization of a Solution of BIMNBSP (1.0×10^{-3} M) and *N*-Phenylglycine (2.0×10^{-2} M) in TMPTA. A solution of 5.54 mg (1.0×10^{-3} M) of BIMNBSP and 30.2 mg (2.0×10^{-2} M) of *N*-phenylglycine in 10 mL of TMPTA was prepared 1 h in advance. Two-photon photopolymerization was carried out in the normal manner. It gave 1.81 mg (4.29 mm), 4.95 mg (6.15 mm), 8.10 mg (6.68 mm), 13.9 mg (7.56 mm), and 20.0 mg (7.69 mm) of polymer spike for 0.5-, 1-, 2-, 4-, and 8-s He/Ne laser irradiation, respectively.

Table III. Two-Photon Photopolymerization of a Solution of BIMNBSP (1.0×10^{-3} M) and *N*-Phenylglycine (2.0×10^{-2} M) in TMPTA (Double Cell Experiment)

He/Ne irradiation time, s	wt of polymer spike(mg)				
	A	B	C and D	E	F
1	3.42	2.57	0	0.97	0.70
2	6.98	6.40	0	2.30	2.14
4	11.42	10.87	0	4.97	3.81
8	13.99	13.85	0	6.81	4.95

Two-Photon Photopolymerization of a Solution of BIMNBSP (5.0×10^{-4} M) and *N*-Phenylglycine (2.0×10^{-3} M) in TMPTA. A solution of 2.77 mg (5.0×10^{-4} M) of BIMNBSP and 30.2 mg (2.0×10^{-2} M) of *N*-phenylglycine in 10 mL of TMPTA was prepared 1 h in advance by using an ultrasonification apparatus. Two-photon photopolymerization was carried out in the normal manner. It gave 0.60, 2.53, 4.87, 10.19, and 11.95 mg of spike for 0.5-, 1-, 2-, 4-, and 8-s He/Ne laser irradiation, respectively.

Two-Photon Photopolymerization of a Solution of BIMNBSP (2.5×10^{-4} M) and *N*-Phenylglycine (2.0×10^{-2} M) in TMPTA. A solution of 1.39 mg (2.5×10^{-4} M) of BIMNBSP and 30.2 mg (2.0×10^{-2} M) of *N*-phenylglycine in 10 mL of TMPTA was prepared 1 h in advance. Two-photon photopolymerization was carried out in the normal manner. It gave 0.31, 0.69, 2.68, 4.60, and 7.63 mg of spike for 0.5-, 1-, 2-, 4-, and 8- He/Ne laser irradiation, respectively.

Two-Photon Photopolymerization of a Solution of BIMNBSP (5.0×10^{-4} M) and *N*-Phenylglycine (2.0×10^{-2} M) in TMPTA at Different Depths of UV Penetration into the Cell. A solution of 2.77 mg (5.0×10^{-4} M) of BIMNBSP and 30.2 mg (2×10^{-2} M) of *N*-phenylglycine in 10 mL of TMPTA was prepared 1 h in advance using ultrasonification apparatus. A 1.5-mL portion of this solution in a quartz cell (b = 0.5 cm) was irradiated for 20 s with UV laser (4 mW) followed by a 4-s He/Ne laser irradiation at different depths of UV cell. Spikes formed by subsequent irradiation of UV and He/Ne laser were washed with acetone, dried, and measured. It gave 0, 0.38, 2.76, 8.51, 9.50, 12.80, 12.46, 11.36, 11.00, 7.50, 5.75, 1.87, 0.68, 0.36, and 0 mg of spike for 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, 2.4, 2.6, and 2.8 mm of depth, respectively.

Two-Photon Photopolymerization of a Solution of BIMNBSP (2.5×10^{-4} M) and *N*-Phenylglycine (2.0×10^{-2} M) in TMPTA at Different Depths of UV Penetration into the Cell. A solution of 1.39 mg (2.5×10^{-4} M) of BIMNBSP and 30.2 mg (2×10^{-2} M) of *N*-phenylglycine in 10 mL of TMPTA was prepared 1 h in advance by using ultrasonification apparatus. A 15-mL portion of this solution in a quartz cell (b = 0.5 cm) was irradiated for 8 s with a UV laser (15 mW) followed by an 8-s He/Ne laser irradiation at different depths of UV cell. Spikes formed by subsequent irradiation of UV and He/Ne laser were washed with acetone, dried, and measured. It gave 0, 7.03, 13.55, 15.04, 15.80, 13.40, 7.62, 1.09, and 0 mg of polymer spike for 0, 0.4, 0.8, 1.0, 1.4, 1.8, 2.2, 2.6, and 3.0 mm of depth, respectively.

Two-Photon Photopolymerization of a Solution of BIMNBSP (1.0×10^{-3} M) and *N*-Phenylglycine (2.0×10^{-2} M) in TMPTA Interfering UV Irradiation with a Different Medium. This two-photon photopolymerization experiment was carried out in the normal manner as in Figure 13 by using a double UV cell (10 × 12.5 × 45 mm). Cell 2 was filled with a solution of BIMNBSP (1.0×10^{-3} M) and *N*-phenylglycine (2.0×10^{-2} M) in TMPTA, and cell 1 was filled with different media such as blank (A), TMPTA (B), a solution of BIMNBSP (1.0×10^{-3} M) in TMPTA (C), a solution of BIMNBSP (1.0×10^{-3} M) in ethyl acetate (D), a solution of BIMNBSP (2.0×10^{-4} M) in ethyl acetate (E), and a solution of BIMNBSP (2.0×10^{-4} M) in TMPTA(F). The solution was irradiated for 5 s with a UV laser (15 mW) through the different media (A–F, respectively) to produce colored spots as in Figure 13. The colored spot formed in cell 2 was irradiated with He/Ne laser for different periods of time. Spikes formed by He/Ne laser irradiation were washed with acetone and measured. These results are summarized in Table III.

Acknowledgment. We are deeply indebted to Dr. E. Dolan for the laser setup for two-photon photopolymerization and to Dr. S. Kumar and Dr. J. Paczkowski for valuable discussions. This work has been supported by the National Science Foundation, Division of Materials Research (DMR 8702733). We are grateful for this support.

Registry No. 4, 100239-68-7; 5, 98883-30-8; 6, 135823-65-3; 9, 135823-64-2; TMPTA, 15625-89-5; *N*-phenylglycine, 103-01-5.

Third-Order Optical Nonlinearities of Model Compounds Containing Benzobisthiazole, Benzobisoxazole, and Benzbisimidazole Units

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Received March 12, 1991. Revised Manuscript Received July 22, 1991

As part of a continuing study, a series of highly conjugated aromatic benzobisthiazole, benzobisoxazole, and *N*,*N*-diphenylbenzbisimidazole model compounds were synthesized, and their third-order nonlinear optical properties investigated by using subpicosecond degenerate four-wave mixing. Measurements were made at 602 nm on THF solutions, vacuum-deposited films, or melt-quenched films. In all but one material, the third-order effect was determined to be instantaneous within the employed temporal resolution, suggesting dominance of electronic nonlinearity. From the experimental data it was possible to formulate structure–nonlinear optical property correlations and demonstrate that the molecular second hyperpolarizability can be increased almost 3 orders of magnitude by simple structural modifications.

1. Introduction

A previously coordinated effort of our two laboratories[1] involved the synthesis and third-order nonlinear optical (NLO) susceptibility measurements on a number of aromatic heterocyclic model compounds. This study provided structure–NLO property information for a series of benzothiazole, benzoxazole, and *N*-phenylbenzimidazole molecules with a variety of other structural components. Systematic structure–NLO property correlations were formulated for these materials that demonstrated the effects of the following on the third-order nonlinear susceptibility: (1) nature of the heterocycle, (2) effective conjugation length, (3) electron richness of the nonheterocyclic structural units, and (4) two-dimnesional π-conjugation effects.

In general, heterocyclic conjugated molecules can enhance third-order NLO activity via a number of routes. The incorporation of five-membered heterocyclic rings into the molecular backbone tends to minimize steric interactions, promoting planarity and thus increasing the effective π-conjugation length. In addition, in terms of a coupled anharmonic oscillator model[2] the participation of the atomic orbitals of the heterocyclic atoms in the π-system increases the orbital overlap between units, which leads to either a larger coupling constant or a larger local anharmonicity of the molecular oscillator.

As an extension of our initial study it was deemed necessary to study heterocyclic model compounds containing three fused rings. The existence of such a highly conjugated, rigid structural moiety in the repeat unit of rigid-rod polymers such as PBT[3] is postulated to be a major contributor to the polymer's third-order NLO activity. Not only do such highly conjugated structures enhance NLO activity, but they also tend to impart high melting points and greatly reduced solubility to any molecules into which they are incorporated. The purpose of the current research is therefore 4-fold: first, to synthetically attempt to optimize γ for PBT-like fused ring model compounds; second, to improve solubility/processibility characteristics of these materials to acquire samples suitable for measurements; third, to investigate the third-order NLO behavior of these materials by degenerate four-wave mixing (DFWM); finally, to develop structure–NLO property correlations similar to those developed previously.[1] It was postulated that experimental data of this type would provide baseline data for the synthesis of

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0897-4756/91/2803-0864$02.50/0