tails were correlated with the existence of Curie-law terms in the magnetic susceptibility of $YBa_2Cu_3O_{7-y}$.

Conclusions

Although the local atomic arrangements have close similarities with the structure of the superconducting oxides of the same system, the tubular phase shows an essential difference from all previously reported copper oxide superconductors: the $[CuO_2]$ planes are periodically interrupted by other $[CuO_2]$ planes stacked perpendicularly to them.

The most striking structural consequence of the insertion of such "perpendicular" $[CuO_2]$ planes is the absence of the typical structural modulations associated to the superconductors in the related series $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$. This feature makes the tubular structure an ideal host lattice to study precise structural and crystalochemical changes derivated, for instance, from atomic substitutions or treatment under different atmospheres in order to compare them with those operating in the bismuth cuprate superconductors. Another important probable consequence of the crossing of two perovskite layers is the existence of a heterogeneous charge distribution among copper ions. This charge distribution may be responsible for the sharp change in transport properties observed when going from superconducting $Bi_2Sr_2CuO_{6+y}$ to $Bi_4Sr_8Cu_5O_{19+y}$. In particular, the charge modulation existing in the basal plane reduces the hole mobility, eventually giving rise to a localization at lower temperatures, and, thus, precluding the observation of metallic behavior.

The magnetic susceptibility of these insulating $Bi_4Sr_8Cu_5O_{19+y}$ samples appears to be consistent with that of a strongly correlated 2D antiferromagnetic Heisenberg model. No long-range 3D antiferromagnetic ordering has been observed, however, by either neutron diffraction or muon spin rotation. It would be worthwhile then to fully investigate the magnetic properties of this so-called "tubular" phase as a function of the hole doping. This will help in our understanding of the relationship existing among magnetic order and the insulator–metal transition observed in the layered superconducting copper perovskites.

Acknowledgment. We thank Dr. Pedro Gomez-Romero and Fernando Sapina for helpful discussions. This work has been supported by Grants from the Spanish CICYT (MAT88-0163-C03 and MAT90-1020-C02-01) and from the MIDAS program.

Registry No. $Bi_2Sr_2CuO_6$, 113924-17-7; Bi_2O_3, 1304-76-3; SrC_2O_4, 814-95-9; CuO, 1317-38-0; $SrCuO_2$, 57348-57-9; $Bi_4Sr_8Cu_5O_{19}$, 126653-12-1; Bi_2CuO_4, 39368-32-6.

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(33) Junod, A. In *Physical Properties of High Temperature Superconductors*; Ginsberg, D. M., Ed.; World Scientific: London, 1990; Vol. II.

Benzospiropyrans as Photochromic and/or Thermochromic Photoinitiators

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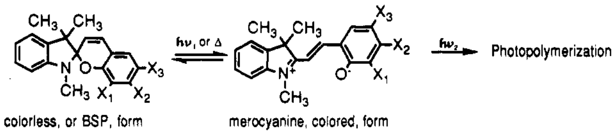
Iodinated merocyanines formed from the benzospiropyrans initiate radical photopolymerizations in the presence of co-initiators including tertiary amines and cetylpyridinium *n*-butyltriphenyl borate (CPB) when irradiated with a He/Ne (632 nm) or argon ion (514 nm) laser. The colored merocyanines were formed by one of four different methods: (1) by neutralization of the respective hydrochloric acid salts with tertiary amines; (2) by irradiation (360 nm) of the benzospiropyrans, (3) by dissolution of benzospiropyrans in *N*-vinylpyrrolidone; (4) by heating the benzospiropyrans.

Introduction

Benzospiropyrans (BSP) are an important class of compounds that undergo reversible intramolecular transformations (Scheme I[2]) forming the merocyanine (colored) isomer either by UV irradiation (photochromic) or by heating (thermochromic).

Our interest in the photoreactions of the BSPs is centered on the utilization of their colored/merocyanine forms as visible light photoinitators. The original notion was to generate a merocyanine from an appropriate benzospiropyran by irradiation and develop specific conditions wherein only radiation from a wavelength absorbed by the merocyanine effected photopolymerization. Rapid reversal of the merocyanine to the benzospiropyran might form the basis of a photochromic, two-photon-photoinitiator system such that polymerization would occur only at a point where two different light sources, one ultraviolet and the other visible, intersected.

Scheme I



A previous attempt to utilize merocyanines as visible light photoinitiators was unsuccessful.[3] However, the

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[1] Publication No. 109 from the Center for Photochemical Sciences.

[2] Tamaki, T.; Sakuragi, M.; Ichimura, K.; Aoki, K. *Chem. Phys. Lett.* **1989**, *161*, 23 and references therein.

[3] Bertelson, R. C.; Becker, W. J. *Research Study on the Application of the NCR Capsular System*; Rept. ASD-TR-61-325, Aug 1961, AD 265564; pp 59–60.

0897-4756/91/2803-0852$02.50/0

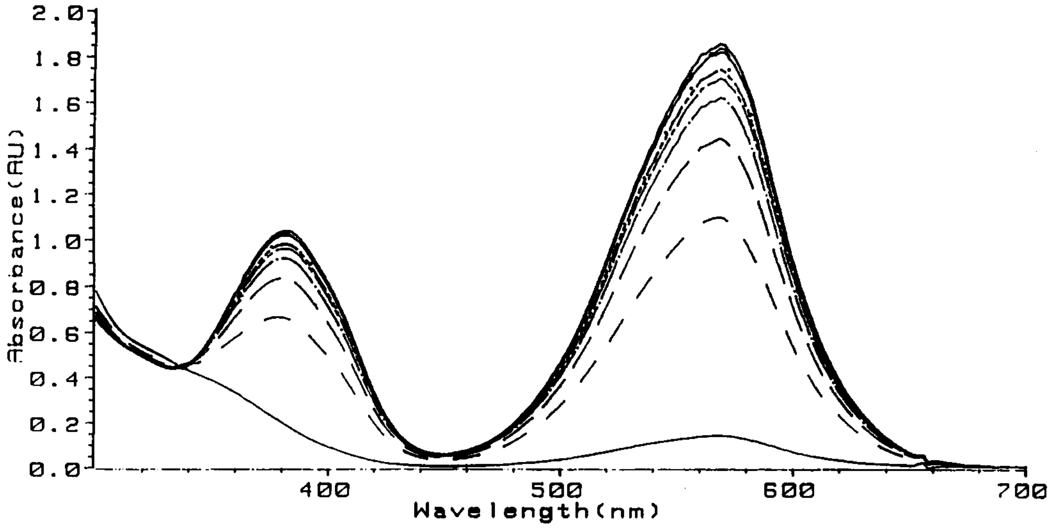

Figure 1. Absorption spectrum of 8-iodo-7-methoxy-6-nitrobenzospiropyran 7 in ethyl acetate *hν* (360 nm, from bottom): 0, 10, 20, 30, 40, 50, 60, and 130 s UV radiation.

merocyanine resulting from a UV-irradiated film of a 6-nitro-substituted BSP ($X_1 = X_2 = H$, $X_3 = NO_2$; Scheme I)[4] caused a layer of poly(methyl methacrylate-*co*-((methacryloyloxy)menthyl)styrene) on an aluminum plate to show enhanced photosensitivity in the presence of diphenyliodonium hexafluorophosphate (DPI) when subsequently exposed to a He/Ne laser. We found that the UV-produced colored solution of 6-nitro-BSP in trimethylolpropane triacrylate (TMPTA) gave no substantial polymer by irradiation with a He/Ne laser (632 nm, 16 mW) or with an argon ion laser (514 nm, 200 mW) in the presence of oxidative coinitiators including DPI and diphenylmethylsulfonium tetrafluoroborate, or reductive initiators such as the ammonium alkyltriphenylborates or tertiary amines.

As a first step in outlining new systems for approaching a photochromic and/or a thermochromic photoinitiator system, we have studied certain mercyanines formed from iodinated BSPs and found that they initiate photopolymerization in the presence of electron-transfer donor co-initiators. We have discovered that a solution of the hydrochloride salt form of 6,8-diiodo-BSP, 8, in TMPTA gives color upon the addition of excess of triethylamine and the colored solution so formed causes polymerization of the TMPTA upon irradiation with a He/Ne laser. This is the first successful example of the concept, and we describe experimental details below.

Results and Discussion

Benzospiropyrans 5–7 are prepared routinely from the corresponding salicyaldehydes and 2-methylene-1,3,3-trimethylindoline (1) in ethanol solution.[5] Iodinated compounds were chosen after an initial screening indicated systems without the heavy atom, iodine, were ineffective.

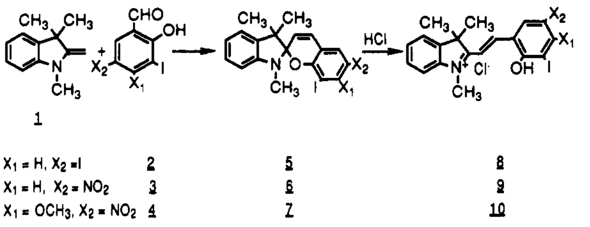

Table I. Spectra and Half-Lives of 11–13 in Ethyl Acetate Solution

	half-life (merocyanine), s	λ_{max} (ϵ),[a] nm	λ_{max} (ϵ^*), nm
$5 \rightarrow 11$	35	394 (ϵ)	606 (ϵ)
$6 \rightarrow 12$	330	376 (1.51×10^4)	572 (2.73×10^4)
$7 \rightarrow 13$	70	382 (1.19×10^4)	568 (2.12×10^4)

[a] These values are obtained by irradiation at 360 nm and simultaneously recording the absorption spectrum. They are thus values for the photostationary state.

Starting material 3 was prepared from the reaction of 5-nitrosalicylaldehyde with CF_3CO_2I.[6] 4 was prepared from 2-hydroxy-4-methoxybenzaldehyde by subsequent nitration and iodination. Hydrochloric acid salt forms (8–10) were prepared by reaction of the corresponding BSPs (5–7) with concentrated HCl.[7]

Photopolymerizations were carried out in a glass cuvette (b = 1 cm) by irradiating a solution of the merocyanine forms (11–13) derived either from the colorless BSP or from the hydrochloric acid salt and a co-initiator such as a tertiary amine or a trialkylaryl borate and TMPTA with either a He/Ne laser (632 nm, 16 mW) or argon ion laser (514 nm, 100 mW). The solid polymeric spikes formed at different irradiation times, t, were washed with acetone (5 × 2 mL) and dried under reduced pressure for 5 h before weighing.

The colored, ring-opened merocyanines (11–13) were formed by one of four different methods: (1) by neutralization of each of the respective hydrochloric acid salts 8–10 with tertiary amines; (2) by UV (360 nm) irradiation of the benzospiropyrans 5–7; (3) by dissolution of the benzospiropyrans in 1-vinyl-2-pyrrolidone, which served as a color developing solvent; (4) by heating the benzospiropyrans. Colored ring-opened merocyanines generated individually by the methods above are spectroscopically identical[8] except for slight difference in the value of λ_{max} deriving from polarity changes in the medium. The absorption spectrum of a solution of 7 in ethyl acetate as a

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(4) Ichimura, K.; Sakuragi, M. *J. Polym. Sci. Part C: Polym. Lett.* 1988, *26*, 185.

(5) Berman, E.; Fox, R. E.; Thomson, F. D. *J. Am. Chem. Soc.* 1959, *81*, 5605.

(6) Merkushev, E. B.; Simakhina, N. D.; Koveshnikova, G. M. *Synthesis*, 1980, 486.

(7) (a) Fox, R. E. *Research Reports and Test Items Pertaining to Eye Protection of Air Crew Personnel* Final Rept. on Contract AF 41(657)-215, April 1961, AD 440226. (b) Shimidzu, I.; Kokado, H.; Inoue, E. *Bull. Chem. Soc. Jpn.* 1969, *42*, 1730.

(8) Hirshberg, Y. *J. Am. Chem. Soc.* 1956, *78*, 2304.

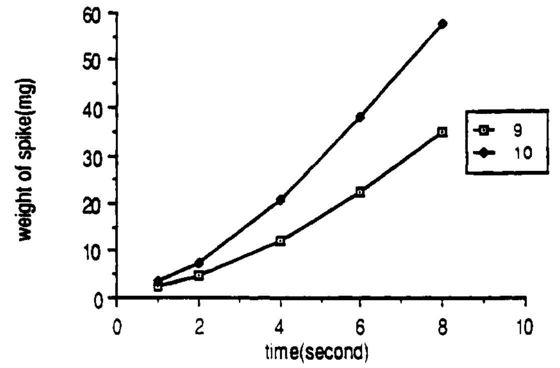


Figure 2. Photopolymerization of a solution of **9** (2.67×10^{-3} M) or **10** (2.67×10^{-3} M) in TMPTA using triethanolamine (0.366 M).

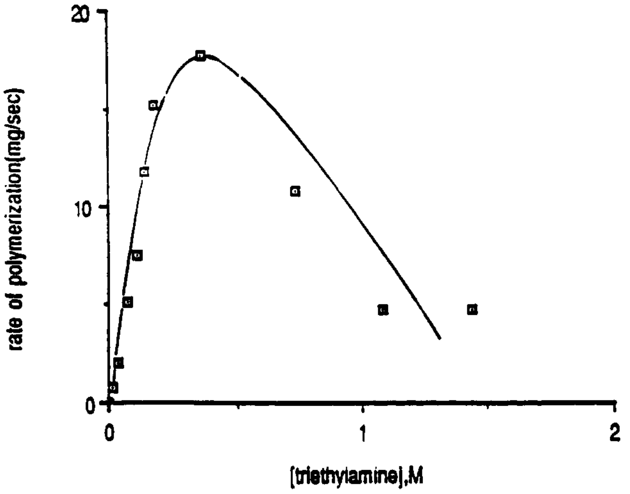
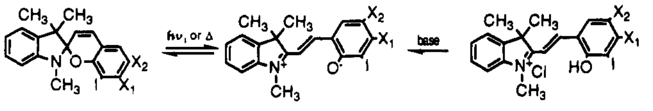


Figure 3. Photopolymerization of **10** (2.7×10^{-3} M) in TMPTA using a He/Ne laser as a function of triethylamine concentration.

function of irradiation (360 nm) time is presented in Figure 1.



X_1=H, X_2=I	5	11	8
X_1=H, X_2=NO_2	6	12	9
X_1=OCH_3, X_2=NO_2	7	13	10

Spectra and half-lives of **11**–**13** in ethyl acetate solution are summarized in Table I.

Photopolymerization Using Amines as a Color Developing Agent. Treatment of **8**–**10** with an excess of a tertiary amine such as triethylamine and triethanolamine gives an intense blue color. Thus a solution of **8** (5.03×10^{-3} M) in TMPTA turned blue upon the addition of triethylamine (1.08×10^{-1} M), and irradiation of this solution with He/Ne laser for 16-, 32-, and 64-s intervals gave 0.1, 0.2, and 0.5 mg of polymer, respectively.[9]

A blue solution was also obtained by treating the hydrochloric acid salts **9** or **10** with triethanolamine, and both colored TMPTA solutions also gave polymer upon irradiation with a He/Ne laser. The colored merocyanine form **13**, derived from **10**, is the fastest visible light initiator among the three iodinated merocyanines. Results are plotted in Figure 2. The relative rates of photopolymerization obtained from Figure 2 were 5.07 and 8.34 mg/s for **9** and **10**, respectively.

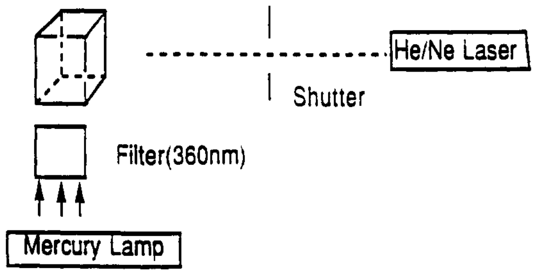


Figure 4. Schematic diagram of photochromic photopolymerization.

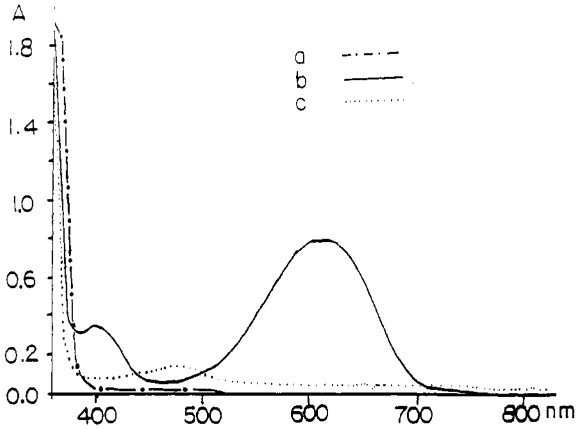


Figure 5. (a) Absorption spectrum of **5** before irradiation at 366 nm in the presence of acetonaphthone in ethyl acetate; (b) absorption spectrum of **5** after irradiation; (c) absorption spectrum after several cycles.

The effect of triethylamine concentration on the photopolymerization of TMPTA was studied by using solutions of compound **10**. The relative rate of photopolymerization was obtained from plots of time (seconds) vs weight of polymeric spike (milligrams). The results are plotted in Figure 3. The amine is present in substantial excess and above about 0.5 M quenches additional polymerization.

Photopolymerization Using Photochemically Generated Merocyanines. Solutions of BSPs (**5**–**7**) in TMPTA (ca. 2.5×10^{-3} M) were irradiated (360 nm) for 5–10 min to bring them to full coloration. After the irradiation was ceased, borate (ca. 9×10^{-3} M) or tertiary amine (ca. 10^{-1} M) was added immediately, and the solution was irradiated with He/Ne laser as in Figure 4.

The merocyanine derived from **5** slowly gave polymeric spikes in the direction of the He/Ne 632-nm laser beam, whereas solutions of merocyanines derived from **6** or **7** gave no polymeric spike upon irradiation with the He/Ne laser. Though there was no polymerization when held for several days in the dark, solutions of the merocyanines derived from **6** and **7** underwent polymerizations by room light within 12 h. The absorptivity of the colored form of **6** or **7** at 632 nm is 1/7.2 and 1/8.6 of that of the colored form of **6** or **7** at each of the λ_{max}, respectively. Each BSP reaches a photostationary state in merocyanine when irradiated with UV.[10] In the case of merocyanine **13** formed at 360 nm from colorless **7**, we find that only 27.7% of the BSP is in the colored ring-opened form at the UV-derived photostationary state.[11] Among the reasons the He/Ne

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

(10) (a) Heller, C. A.; Fine, D. A.; Henry, R. A. *J. Phy. Chem.* **1961**, *65*, 1908. (b) Heiligman-Rim, R.; Hirshberg, Y.; Fischer, E. *J. Chem. Soc.* **1961**, 156.

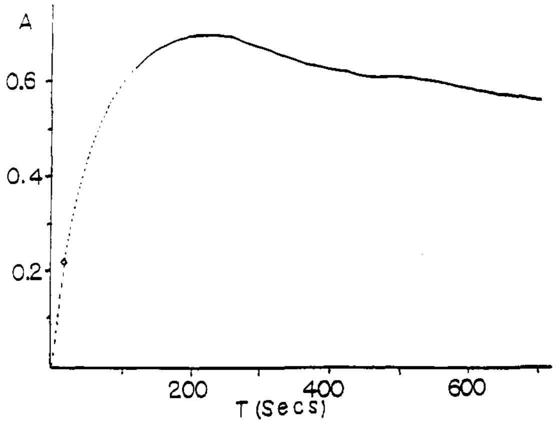

Figure 6. Absorbance from 5 irradiated at 366 nm at 610 nm as a function of time.

Table II. Rates of Merocyanine Formation from Direct and Sensitized Ring Opening of 5

[acetonaphthone]	rate, abs/s	I_a, einsteins/L × s
0	0.27	4.95×10^{-7}
2.6×10^{-2}	0.20	1.37×10^{-5}

laser is not useful for the photopolymerization of polyol-acrylates using the merocyanine forms produced photochemically from 6 or 7 is their low absorptivity. The simultaneous irradiation of a solution of 6 or 7 and triethylamine, triethanolamine, or cetylpyridinium *n*-butyltriphenyl borate at 360 and 632 nm, in general, produces polymer though mostly with the UV light (360 nm).

Photochemistry of 5 under Reductive Conditions. Irradiation in the UV of the colorless 5 results in the formation of the colored merocyanine 11. Figure 5 shows the results of irradiating 5 + acetonaphthone in ethyl acetate as a model system. Figure 5a presents the absorption spectrum before irradiation, and Figure 5b shows the same after irradiation at 366 nm. 11 decays in the dark with the same lifetime as in the absence of acetonaphthone. The maximum concentration of 11 generated decreases with increasing number of cycles (irradiation at 366 nm/dark decay), and the solution turns yellow thus indicating a subsequent chemical reaction between the sensitizer acetonaphthone and 11. The spectrum measured after several cycles is presented in Figure 5c and shows the formation of a new product having an absorption maximum at 480 nm. Presumably this and other product(s) can absorb at 366 nm, thus decreasing the efficiency of the ring-opening reaction of 5. Figure 6 shows the absorbance at 610 nm of 5 in 90% TMPTA (no acetonaphthone) as a function of time. The concentration of 11 reaches a maximum and then decreases, indicating decomposition of the merocyanine and/or BSP. Prolonged irradiation turns the solution yellow, and the final spectrum shows the product absorbing at 480 nm. Because of this, decomposition rates and quantum yields were obtained from the initial slope of the trace.

To determine the sensitization efficiency, 5 (2.3×10^{-4} M) was irradiated at 366 nm in the presence of acetonaphthone (2.6×10^{-2} M) or anthracene (1×10^{-3} M), and the initial rates of the formation of 11 were compared to that obtained with pure 5. The results obtained with acetonaphthone are summarized in Table II (anthracene yields similar results).

Table III

[TEA], M	ϕ	[TEA], M	ϕ
0	0.026	0.71	0.024
0.098	0.023		

The apparent quantum yield (rate/I_a) in the absence of acetonaphthone is 36 times greater than in its presence. If instead of using the total intensity ($I_a = I_a(5) + I_a$(acetonaphthone) in the presence of acetonaphthone) one calculates the quantum yields considering the fraction absorbed by 5 alone, one obtains

$$\phi(\text{no acetonaphthone})/\phi(\text{+acetonaphthone}) = 1.08$$

It is concluded that acetonaphthone decreases the efficiency of the ring-opening reaction by competitive absorption.

The best system so far for two-photon polymerization is 5 (ca. 1 mM) + TEA. Therefore the quantum yield of 11 production and the dark decay of 11 in 90% TMPTA were measured. To calculate the quantum yield, 5.2×10^4 M^{-1} cm^{-1} was used for the molar absorptivity of 11 at 610 nm.

From the initial slope of a kinetic trace for 5 in the absence of the amine, during the irradiation the quantum yield for formation of 11 generation can be obtained. The portion of the trace measured with the light off allows determination of the decay rate constant of 11. The quantum yield is 0.026. The initial slope varies linearly with the absorbed intensity and the effect of TEA is summarized in Table III. From these values it is concluded that TEA has no effect on the quantum yield of the production of 11. Combining the data in the table with those measured at different intensities, one obtains $\phi = 0.024 \pm 0.002$.

The dark decay of 11 follows clean first-order kinetics in the absence of TEA. In the presence of amine the decay is more complex. The first lifetime (where the plot in the presence of amine is linear) is independent of the TEA concentration, and the value for the decay rate constant is $(1.3 \pm 0.1) \times 10^{-2}$ s^{-1}. The decay rate is not affected by irradiation of 11 at 632 nm with an incident intensity of 8×10^{-5} einsteins/L·s.

The decay rate constant depends on the number of cycles (irradiation at 366 nm/dark decay) performed before measuring the lifetime. For example, with TEA (0.5 M) the decay rate constant increases from 1.3×10^{-2} s^{-1} (first cycle) to 2.4×10^{-2} s^{-1} after seven cycles. This effect and the complex decay observed in the presence of TEA are attributed to reaction between 11 and a decomposition product. The fact that complex decay is more readily observed in the presence of amine would indicate product formation is faster in the presence of TEA. However, the deviation from first-order kinetics is less pronounced with the higher concentration of amine.

To find out whether complex decay was specific for TMPTA, experiments was carried out in ethyl acetate. Similar results are obtained under these conditions. This solution was cycled several times to generate the maximum possible concentration of product for identification purposes. The solvent was evaporated, and the resulting solid dissolved in $CDCl_3$. The H^1 NMR spectrum is identical with that of 5.

Photopolymerization Utilizing Colored Merocyanine Form Produced by 1-Vinyl-2-pyrrolidone (VP). 6 or 7 gave intense blue colors upon the addition of 1-vinyl-2-pyrrolidone. In TMPTA with borate as the co-initiator, polymeric spikes formed with the He/Ne laser. The photopolymerization data for 6 and 7 using this me-

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(11) Estimation of the ratio of colored form and colorless form was predicted by $\epsilon_B C_B = \epsilon_C C_C$ assuming no thermal degradation during photolysis. ϵ_B = absorptivity of colorless form at 360 nm; ϵ_C = absorptivity of colored form at 360 nm.

(12) Kometani, T.; Watt, D. S.; Fritz, T. *J. Org. Chem.* **1985**, *50*, 5384.

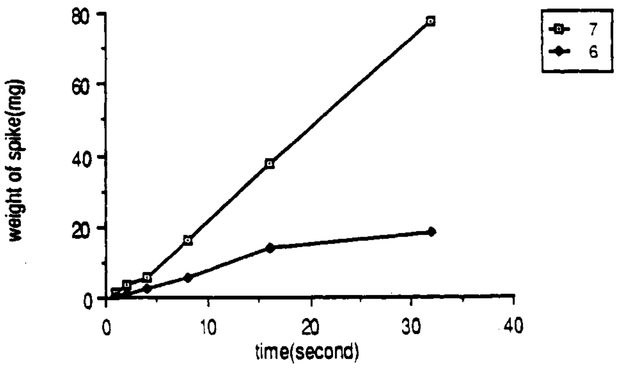

Figure 7. Photopolymerization of **6** (3.15×10^{-3} M) and **7** (2.58×10^{-3} M) using 1-vinyl-2-pyrrolidone as a color-developing solvent by He/Ne laser ([borate] = 9.27×10^{-3} M).

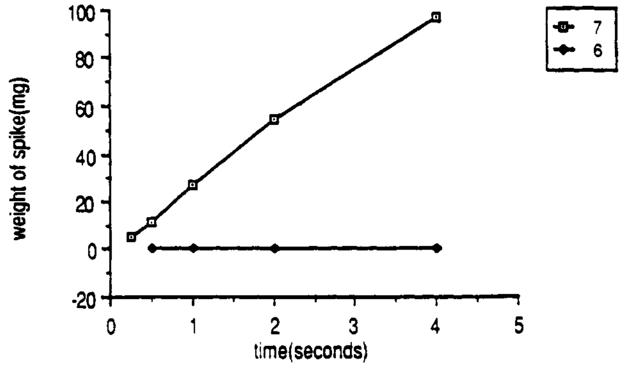

Figure 8. Photopolymerization of **6** (2.54×10^{-3} M) and **7** (2.45×10^{-3} M) using 1-vinyl-2-pyrrolidone as a color-developing solvent by an argon ion laser (514 nm, 100 mW).

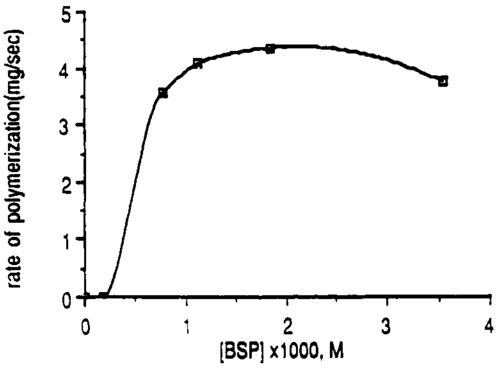

Figure 9. Photopolymerization of 8-iodo-7-methoxy-6-nitrobenzopiropyran (**7**) in TMPTA/VP (9:1 v/v) at different BSP concentrations (borate = 9.27×10^{-3} M).

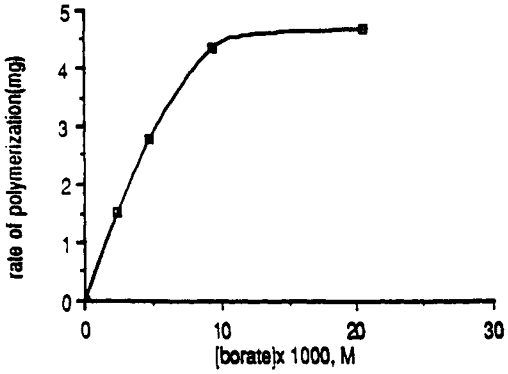

Figure 10. Photopolymerization of 8-iodo-7-methoxy-6-nitrobenzopiropyran (**7**) (1.85×10^{-3} M) in TMPTA/VP (9:1 v/v) at different borate concentrations.

thod are plotted in Figures 7 and 8. A colored solution prepared from **6** (2.54×10^{-3} M) and cetylpyridinium *n*-butyltriphenyl borate (9.27×10^{-3} M) in VP/TMPTA (1:9) produced no polymeric spike from irradiation with an argon ion laser. These data indicate that the colored ring-opened form of **13** initiates photopolymerization much faster than that of **12** either with a He/Ne laser on argon ion laser.

The photopolymerization at different concentrations of **13** and constant borate concentrations (9.27×10^{-3} M) is plotted in Figure 9. No photopolymerization was observed at a 1.8×10^{-4} M concentration of **7**, and the rate of the photopolymerization was independent of the concentration of **7** above 10^{-3} M. The rate of the photopolymerization plotted in Figure 10 increased as the borate concentration increased.

Photopolymerization Using a Thermochromic Process. A solution of **6** or **7** in TMPTA in the presence of co-initiators such as amines or borates produces intense blue colors upon heating. Irradiation of this colored solution with a He/Ne laser gave a polymeric spike. A solution of **7** (3.21×10^{-3} M) in TMPTA was heated to 55 °C by using a water bath, and then the solution was irradiated with He/Ne laser while maintaining temperature at 55 °C with the water bath. Irradiation of this solution for a 9, 12, and 16 s with He/Ne laser gave 1.7, 3.2, and 6.0 mg of the polymeric spike, respectively. At room temperature this solution undergoes no polymerization when irradiated with a He/Ne laser.

Conclusion

To the best of our knowledge, iodinated merocyanines irradiated with co-initiators including triethylamine, triethanolamine, and ammonium alkyltriphenyl borates are the first known photo- and/or thermochromic photoiniator systems. In principle and in fact we have demonstrated that one can develop a colored form of a photochromic material from a colorless form, and use the so-derived colored material in the presence of a co-initiator with a He/Ne laser to form photopolymer. It will be the subject of a future publication to note the relationship of initiator bleaching to polymerization rate; however, it would be the coupling of these two factors that would permit polymerization to occur at a depth beneath the surface.

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 HP 5987A GC/MS system. Infrared spectra (IR) were recorded on Nicolet 20 DX system. Melting points were determined on a Thomas Hoover melting point apparatus and are uncorrected. Absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Elemental analyses were carried out by Galbraith Laboratories, Knoxville, TN. Samples were irradiated with a Melles Griot He/Ne laser or a Spectra Physics 2016 argon ion laser. The power delivered was measured with a calibrated Sciencetech 365 power meter. The 360- and 366-nm radiation was obtained from a Baush & Lomb SP 200 mercury lamp combining a Corning glass filter. Light intensity was measured with a IL 1700 Research Radiometer. Bis(trifluoroacetoxy)iodobenzene, 5-nitrosalicylaldehyde, 3,5-diiodosalicylaldehyde, 2-hydroxy-4-methoxybenzaldehyde, 2-methylene-1,3,3-triethylindoline, 1-vinyl-2-pyrrolidone, and ethyl acetate (HPLC grade) were purchased from Aldrich and used as received. Trimethylolpropane triacrylate (TMPTA) was obtained from Sartomer and used without further purification. Triethylamine and triethanolamine were obtained from Fisher and used as received. Cetylpyridinium *n*-butyltriphenyl borate (CPB) was a gift from Mead Imaging, Miamisburg, OH.

Preparation of 3-Iodo-5-nitrosalicylaldehyde (3). A suspension of 1.0 g (5.98 mmol) of 5-nitrosalicylaldehyde, 2.70 g (6.28 mmol) of bis(trifluoroacetoxy)iodobenzene, and 1.52 g (5.98 mmol) of iodine in 10 mL of carbon tetrachloride was stirred for 15 h at room temperature. The reaction mixture was diluted with 10 mL of hexane, and then the formed solid was collected by filtration, washed with 1% hydrochloric acid, and dried to give 1.6 g of 3[12] (yield 91%): mp 139–141 °C; ^{1}H NMR (CDCl$_3$) δ 12.45 (s, 1 H), 9.91 (s, 1 H), 8.90 (d, *J* = 2.0 Hz, 1 H), 8.59 (d, *J* = 2.0 Hz, 1 H); MS (70 eV) *m/e* (relative intensity) M + 2 = 295 (1.3), M + 1 = 294 (7.8), M = 293 (100), 246 (4.5), 191 (6), 127 (6), 120 (4.8), 92 (16), 91 (7.5), 74 (7), 64 (14), 63 (21), 62 (9.5), 61 (6.5), 53 (6.5); IR (Nujol) 1661, 1607, 1532, 1456 cm^{-1}.

Preparation of 2-Hydroxy-4-methoxy-5-nitrobenzaldehyde (14). To the stirred solution of 5.4 g (35.5 mmol) of 2-hydroxy-4-methoxybenzaldehyde in 15 mL of acetic acid, 10.1 g of fuming HNO$_3$ (90%) was added dropwise at 0 °C. After the addition was completed, the reaction mixture was slowly warmed to room temperature, and the stirring was continued for 2 h at room temperature. The reaction mixture was poured into cold water, and the formed solid was collected by filtration. The crude product was crystallized from ethanol to give 3.9 g of 14 (yield 56%): mp 167–168 °C; ^{1}H NMR (CDCl$_3$) δ 11.8 (s, 1 H), 9.8 (s, 1 H), 8.3 (s, 1 H), 6.6 (s, 1 H), 4.05 (s, 3 H); MS (70 eV) *m/e* (relative intensity) M + 1 = 198 (14), M = 197 (100), 196 (14), 184 (12), 167 (39), 150 (52), 139 (13), 122 (16), 121 (16), 120 (18), 111 (15), 109 (14), 108 (28), 93 (13), 80 (37), 77 (14), 69 (46), 68 (13), 65 (47), 64 (19), 63 (27), 62 (20), 55 (13), 53 (41), 51 (28); IR (Nujol) 1660, 1641, 1460, 1383, 1299, 725 cm^{-1}.

Preparation of 2-Hydroxy-3-iodo-4-methoxy-5-nitrobenzaldehyde (4). To the stirred solution of 2.0 g (10.2 mmol) of 14, and 2.58 g (10.2 mmol) of iodine in 60 mL of carbon tetrachloride, 4.8 g (11.2 mmol) of bis(trifluoroacetoxy)iodobenzene was added slowly and then the reaction mixture was stirred for 15 h at room temperature. To this reaction mixture 60 mL of hexanes was added, and then the formed solid was collected by filtration, washed with hexanes, dilute HCl, and water, and dried to give 2.4 g of 4 (yield 73%): mp 122 °C; ^{1}H NMR (CDCl$_3$) δ 12.48 (s, 1 H), 9.81 (s, 1 H), 8.35 (s, 1 H), 4.07 (s, 3 H); MS (70 eV) *m/e* (relative intensity) M + 2 = 325 (1.78), M + 1 = 324 (11), M = 323 (100), 293 (41), 276 (51), 262 (11), 120 (8.5), 119 (8.6), 108 (38), 107 (22), 92 (23), 80 (10), 79 (18), 77 (18), 64 (12), 63 (10), 62 (10), 61 (10), 51 (14), 49 (23); IR (Nujol) 1660, 1608, 1557, 1512, 1467, 1376, 1312, 1080, 970, 725 cm^{-1}. Anal. Calcd for C$_8$H$_6$INO$_5$: C, 29.72; H, 1.86; N, 4.33. Found: C, 29.41; H, 1.91; N, 4.27.

Preparation of 6,8-Diiodo-1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2′,2′-(3′*H*)-1*H*-indole] (5). A solution of 3.4 g (9.09 mmol) of 3,5-diiodosalicyaldehyde and 1.58 g (9.12 mmol) of 2-methylene-1,3,3-trimethylindoline in 20 mL of ethanol was heated to reflux for 5 h. After the reaction mixture was cooled to room temperature, the formed solid was collected by filtration to give 3.5 g of 5[3] (yield 73%): mp 105–106 °C; ^{1}H NMR (CDCl$_3$) δ 7.82 (s, 1 H) 7.4–6.5 (m, 6 H) 5.75 (d, *J* = 9.6 Hz, 1 H), 2.68 (s, 3 H), 1.30 (s, 3 H), 1.18 (s, 3 H); MS (70 eV) *m/e* (relative intensity) M = 529 (44), 514 (10), 217 (11), 216 (13), 160 (11), 159 (100), 158 (38), 144 (25); IR (Nujol) 1610, 1460, 1430, 1376, 1351, 1305, 1273, 1157, 957, 880, 751 cm^{-1}.

Preparation of 8-Iodo-6-nitro-1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-(3′*H*)-1*H*-indole] (6). A solution of 1.0 g (3.41 mmol) of 3-iodo-5-nitrosalicyaldehyde (3) and 590 mg (3.41 mmol) of 2-methylene-1,3,3-trimethylindoline (1) in 20 mL of ethanol was heated to reflux for 5 h. After the reaction mixture was cooled to room temperature, the formed solid was collected by filtration to give 1.20 g of 6[3] (yield 75%): ^{1}H NMR (CDCl$_3$) δ 8.8–6.55 (m, 7 H) 5.90 (d, *J* = 9.5 Hz, 1 H), 2.71 (s, 3 H), 1.32 (s, 3 H), 1.23 (s, 3 H); MS (70 eV) *m/e* (relative intensity) M + 1 = 449 (9.6), M = 448 (51), 433 (17), 260 (5), 231 (5), 230 (7), 217 (10), 216 (11), 204 (5), 180 (5), 160 (11), 159 (100), 158 (45), 144 (30); IR (Nujol) 1608, 1525, 1460, 1376, 1305, 1273, 1228, 970, 764 cm^{-1}.

Preparation of 8-Iodo-7-methoxy-6-nitro-1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-(3′*H*)-1*H*-indole] (7). A solution of 500 mg (1.55 mmol) of 2-hydroxy-3-iodo-4-methoxy-5-nitrobenzaldehyde (4) and 268 mg (1.55 mmol) of 2-methylene-1,3,3-trimethylindoline (1) in 10 mL of ethanol was heated to reflux for 6 h. After the reaction mixture was cooled to room temperature, 10 mL of hexanes was added to the reaction mixture. The solid was collected by filtration and washed with hexanes to give 640 mg of 7 (yield 86%): mp 180.5–181 °C; ^{1}H NMR (CDCl$_3$) δ 8.1–6.8 (m, 6 H), 5.83 (d, *J* = 10.4 Hz, 1 H), 3.94 (s, 3 H), 2.70 (s, 3 H), 1.32 (s, 3 H), 1.22 (s, 3 H); MS (70 eV) *m/e* (relative intensity) M + 2 = 480 (3.1), M + 1 = 479 (17), M = 478 (75), 464 (6.5), 463 (27), 448 (3), 416 (5.4), 217 (7), 216 (5), 264 (5), 160 (11), 159 (100), 158 (52), 144 (22) 116 (7), 108 (7), 102 (7); IR (Nujol) 1608, 1460, 1376, 725 cm^{-1}. Anal. Calcd for C$_{20}$H$_{19}$IN$_2$O$_4$: C, 50.21; H, 3.97; N, 5.86. Found: C, 51.50; H, 4.15; N, 5.91.

Preparation of Hydrochloric Acid Salt Form of BSPIs, 8–10. To a stirred solution of 500 mg of the corresponding BSPs (5–7) in 5 mL of THF was added dropwise 0.3 mL of concentrated HCl at room temperature. The stirring was continued for 15 h, and then the formed yellow solid was collected by filtration. 8 (yield 80%): mp 204.5–205 °C; ^{1}H NMR (DMSO-d_6) δ 8.9–6.7 (m, 8 H), 5.8 (d, *J* = 10 Hz, 1 H), 4.1 (s, 3 H), 1.73 (s, 6 H). 9 (yield 78%): ^{1}H NMR (DMSO-d_6) δ 8.9–7.4 (m, 9 H), 4.2 (s, 3 H), 1.73 (s, 6 H). 10 (yield 75%): mp 165 °C; ^{1}H NMR (DMSO-d_6) δ 8.9–6.6 (m, 7 H), 5.9 (d, *J* = 9.5 Hz, 1 H), 3.94 (s, 3 H), 3.8 (s, 3 H), 1.74 (s, 6 H).

General Photopolymerization Procedure. Photopolymerization was carried out irradiating photopolymerizable solution (2 mL) with argon ion laser (514 nm) of He/Ne laser (632 nm) in a glass cuvette (12.5 × 12.5 × 44 mm). The laser irradiation time was controlled by an electronic time shutter. The insoluble polymeric spikes formed for different lengths of irradiation time were washed with acetone (5 × 2 mL) and dried under reduced pressure for 5 h before weighing.

General Photopolymerization Procedure Using Hydrochloric Acid Salt Forms of BSP. To a suspension of the corresponding hydrochloric acid salt (8–10) in 2 mL of TMPTA, triethylamine or triethanolamine was added in one portion. The resulting solution was mixed well in the dark, and the colored solution thus formed was irradiated with a He/Ne laser (632 nm, 16 mW) for different lengths of time.

Photopolymerization of a Solution of 8 in TMPTA Using Triethylamine. A solution of 5.68 mg (5.03 × 10^{-3} M) of 8 and 21.8 mg (1.08 × 10^{-1} M) of triethylamine in 2 mL of TMPTA was used for the photopolymerization using the He/Ne laser in the normal manner: 16-, 32-, and 64-s laser irradiations gave 0.1, 0.2, and 0.5 mg of polymeric spikes, respectively.

Photopolymerization of a Solution of 9 in TMPTA Using Triethanolamine. A solution of 3.88 mg (2.67 × 10^{-3} M) of 9 and 199 μL of a triethanolamine solution in DMF (5.87 M) in 3 mL of TMPTA was used for the photopolymerization in the normal manner. The 1-, 2-, 4-, 6-, and 8-s He/Ne laser shots gave 2.21, 4.64, 12.24, 22.49, and 34.99 mg of polymer, respectively.

Photopolymerization of a Solution of 10 in TMPTA Using Triethanolamine. A solution of 4.13 mg (2.67 × 10^{-3} M) of 10 and 199 μL of triethanolamine solution in DMF (5.87 M) in 3 mL of TMPTA was used for the photopolymerization in the normal manner. The 1-, 2-, 4-, 6-, and 8-s He/Ne laser shots gave 3.59, 7.64, 20.82, 38.11, and 57.5 mg of polymeric spikes, respectively.

Photopolymerization of a Solution of 10 in TMPTA at Different Triethylamine Concentrations. Each of a solution of 2.75 ± 0.02 mg of 10 (2.67 × 10^{-3} M) and with different concentrations of triethylamine (0.018, 0.036, 0.072, 0.108, 0.144, 0.18, 0.36, 0.72, 1.08, and 1.44 M) in 2 mL of TMPTA was used for the photopolymerization using He/Ne laser in the normal manner.

Photochromic Photopolymerization. A solution of BSPs (5–7) in TMPTA (ca. 2.5 × 10^{-3} M) was irradiated with a mercury lamp until it reached its full coloration. To this colored solution, CPB (ca. 9 × 10^{-3} M) or triethylamine (ca. 0.1 M) was added immediately, and the resulting solution was irradiated with He/Ne laser as in Figure 4 either with UV on or with UV off. A controlled experiment indicated that a solution of triethylamine (ca. 0.1 M) or CPB (ca. 0.02 M) in TMPTA undergoes photopolymerization by UV light (360 nm) during 5–10-min period.

Two-Photon Photopolymerization. A solution of 5 (1 × 10^{-3} M) and triethylamine (0.1 M) in 1 mL of TMPTA in a test tube (10 × 75 mm) was irradiated at 360 nm with mercury lamp for 2–3 min with the He/Ne laser beam blocked by a screen. After the solution turned blue, the screen was removed, and then the solution was irradiated with both the He/Ne laser beam and UV (360 nm) light on. For 2 min of irradiation with the He/Ne laser the solution gave about 5-mm length of soft and thin spikes in the direction of He/Ne laser beam.

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.

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Two-Photon Radical-Photoinitiator System Based on Iodinated Benzospiropyrans

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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.

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