Macromolecules **1996,** *29,* 3751−3757

Simultaneous Photoinduced Color Formation and Polymerization: The Formation of Highly Colored Thin Films from Colorless Precursors Due to Formation of Triarylmethane Cations by Acid Generating Decomposition of Iodonium Salts[1]

Yijin Ren, Wolter F. Jager, and Douglas C. Neckers*

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

Received December 18, 1995; Revised Manuscript Received February 16, 1996⊗

ABSTRACT: Highly colored thin films were prepared by irradiating transparent resins consisting of the iodonium salt [4-[(octyloxy)phenyl]phenyl]iodonium hexafluoroantimonate (OPPI, **1**) and a dye precursor such as crystal violet lactone (CVL, **2**) dissolved in an acrylate epoxide mixture. It has been demonstrated that a mixture of CVL and OPPI is a very efficient photoinitiator for radical polymerizations. Color formation takes place via the excited state of CVL, that is oxidized by OPPI to a radical cation, that subsequently forms the colored triarylmethane cation by hydrogen abstraction from the solvent. Formation of photoacid via the excited state of OPPI also contributes to color formation. The main advantage of our approach, by which films of different colors can be made, is that highly colored (OD >2.0: 400−700 nm; 15 μm thick) films can be formed at rates comparable with those of noncolored films.

Introduction

Formation of colored thin polymeric films cured photochemically is desirable for many printing applications. Using light for initiating the polymerization is the method of choice because it is fast, environmentally friendly and can be applied locally.[2] Photopolymerization both immobilizes *and* adheres the film to its substrate. Patterns can be generated by printing the resin on a substrate followed by a curing step or, in lithographic applications,[3] by using masks for local irradiation and subsequently washing away the unused resin.

The conventional method for obtaining strongly colored films by photopolymerization is to add a colored dye or pigment to a photocurable resin which consists of monomer and photoinitiator. As long as the added dye does not absorb in the region at which the photoinitiator absorbs, the rate of the polymerization will, assuming the dye does not interact with, or quench, the photoinitiating system, not be affected by its presence. However, if the absorption spectra of the pigment and the photoinitiator seriously overlap, the rate of polymerization will be reduced to an unacceptably low level. Thus it is well-known in the printing art that deeply colored, for example, black, or reflecting monomer mixtures, such as gold or silver, are difficult to cure photochemically.

In specific cases spectral overlap of the initiator with pigment can be avoided by choosing a photoinitiator[4] that absorbs at longer wavelengths than the dye or at regions where the dye absorption has a (local) minimum. Unfortunately, efficient photoinitiators absorbing above 650 nm are not common. In cases where the added dye(s) absorb strongly below 650 nm, photopolymerization, say of an ink at high speed, is no longer possible by conventional means. A black ink, such as one with carbon black or metal oxides, is a classical example of an “uncurable ink”.

In this paper we present a unique approach to producing strongly colored polymer films. We have chosen to target colors the pigments for which would inhibit polymerization through absorption, were they contained in a resin. Our method starts with a colorless or slightly colored resin containing a monomer, acid sensitive dye precursor and diphenyliodonium salt. Upon irradiation, color development and (photo)polymerization occur simultaneously. The photochemical decomposition of the iodonium salt plays a central role in this procedure,[5] in that it generates both radicals and cations which induce polymerization and it forms acid. The dye precursors chosen are the colorless lactones **2**−**9**, which undergo acid induced ring cleavage to yield highly colored species during the photopolymerization process.[6]

Decomposition of Iodonium Salts. Though many initiating systems for radical polymerization exist, iodonium and sulfonium salts[7] having inert non-nucleophilic counterions are, along with cyclopentadienyl metal salts,[8] the only currently commercially available photoinitiators for cationic polymerizations. Recently, Bi and Neckers demonstrated that cationic polymerizations can be performed using visible light in a “free radical promoted cationic polymerization”.[9] In this system, aromatic amine radicals generated in a conventional visible light initiator system[10] are oxidized by a partner iodonium salt to yield amine cations which initiate the polymerization process.

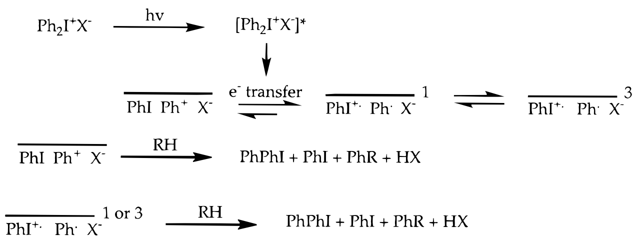
The photochemical and thermal decomposition of diaryliodonium salts has been extensively investigated. The broad literature coverage of iodonium chemistry is, apart from its commercial importance, due to the fact that both radical and ionic processes, which are often closely balanced and in competition with each other, are observed during decomposition of iodonium salts.[11] Recently, it was demonstrated that the quantum yield for the photochemical decomposition of iodonium salts can reach values well above unity due to a radical chain mechanism in which photochemically generated aryl radicals cause decomposition of the onium salt.[12]

The mechanisms by which onium salts decompose are still under debate and are profoundly influenced by other components in solution. In the absence of other substances apart from the solvent, RH, decomposition

⊗ Abstract published in *Advance ACS Abstracts,* April 15, 1996.

S0024-9297(95)01872-9 CCC: $12.00

Scheme 1. The Direct Photochemical Decomposition of a Diaryliodonium Salt in Solvent RH



Scheme 2. The Indirect Decomposition of a Diaryliodonium Salt by Electron Transfer from the Excited State of Anthracene (ArH)

$$\mathrm{ArH} \xrightarrow{h\nu} [\mathrm{ArH}]^*$$

$$[\mathrm{ArH}]^* + \mathrm{Ph_2I^+X^-} \longrightarrow \mathrm{ArH^{+\cdot}} + \mathrm{Ph_2I^\cdot} + \mathrm{X^-}$$

$$\mathrm{ArH^{+\cdot}} + \mathrm{Ph_2I^\cdot} \longrightarrow \mathrm{ArH^{+\cdot}} + \mathrm{Ph^\cdot} + \mathrm{PhI}$$

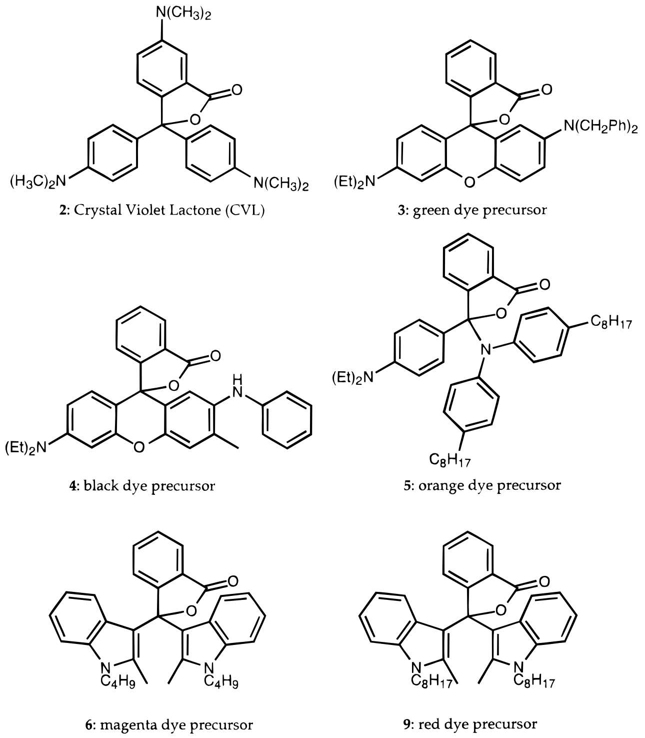
$$\mathrm{ArH^{+\cdot}} + \mathrm{Ph^\cdot} \longrightarrow \mathrm{ArPh} + \mathrm{H^+}$$

of onium salts by direct excitation is expected to occur according to Scheme 1. In this scheme both phenyl cations and phenyl radicals are proposed, and these initiate cationic and radical polymerization. By reacting with the solvent, RH, iodobenzene, (iodo)biphenyl, and the strong acid HX are formed.

Several mechanisms have been proposed for the indirect excitation of iodonium salts including both energy transfer and electron transfer from the excited state of a sensitizer. We reject mechanisms in which sensitizers generate the excited state of the diaryliodonium ion by energy transfer since the triplet or singlet energies of the cyclic lactones of our system are too low to excite iodonium salts.

Electron transfer from an excited state of a sensitizer to an iodonium ion in its ground state is relevant for our system. This mechanism has been demonstrated using anthracene (ArH) as the electron donor and is depicted in Scheme 2. The products of this reaction include iodobenzene, the strong acid HX, and a mixture of phenylanthracenes (ArPh). It should be noted that in this mechanism phenyl radicals are formed, but no phenyl cations.

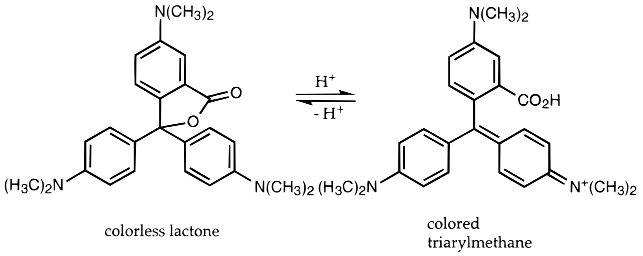
Color Formation by Acidification of Cyclic Lactones. Acid-induced ring opening of colorless lactone dye precursors to form highly colored cationic species is an important step in many imaging systems, including those used in carbonless carbon paper, in monochrome thermal paper, and in color copiers. In carbonless carbon paper, for instance, formation of color is achieved by releasing a solution of a colorless lactone from microcapsules in which it is contained, thus enabling it to migrate to an acid surface (a phenolic resin) on which color is developed. In other more sophisticated systems dye precursors are used in the formation of color copy (Mead Imaging Cycolor®).[13] Once more, removal of the physical barrier (microcapsules) between the lactones and an acidic phase is the basis of color development. Typical, and by far the most important example, of a dye precursor used for carbonless carbon paper applications is crystal violet lactone (CVL, **2**). The acid-catalyzed opening of colorless CVL to the corresponding highly colored triarylmethane cation is demonstrated in Scheme 3.



2: Crystal Violet Lactone (CVL)
3: green dye precursor
4: black dye precursor
5: orange dye precursor
6: magenta dye precursor
9: red dye precursor

Figure 1. Dye precursors for "self-coloring" films.

Scheme 3. The Acid-Induced Opening of CVL (2), a Colorless Lactone, to a Strongly Colored Triarylmethane Cation



The mechanism of this ring opening can be envisaged as first a protonation of the carbonyl oxygen of the lactone, followed by ring opening. The ring opening is facilitated by the donation of an electron pair from a dimethylamino group. It has also been reported that the open, colored form of crystal violet lactone can be obtained by the addition of other Lewis acids such as zinc ions.[14]

Many color forming lactones have been developed, and some representative examples are given in Figure 1. A wide variety of colors can be formed by acidifying these dye precursors. In all dye precursors at least one nitrogen is present that can donate an electron pair to facilitate the opening of the lactone ring.

The CVL/OPPI System. In our approach the acidic phase for color development is created by a chemical process, that being the photodecomposition of the iodonium salt OPPI. Decomposition of OPPI can be achieved photochemically by direct excitation, and thermally by heating to ±120 °C. Acid as well as cation and radical intermediates are the anticipated reaction products; see Scheme 1. In addition, the photochemical decomposition of OPPI might also occur indirectly via electron transfer from the excited state of CVL in a mechanism which closely resembles the mechanism depicted in Scheme 2.

Experimental Section

Materials. The iodonium salt [4-[(octyloxy)phenyl]phenyl]-iodonium hexafluoroantimonate (OPPI, **1**) was a gift from GE

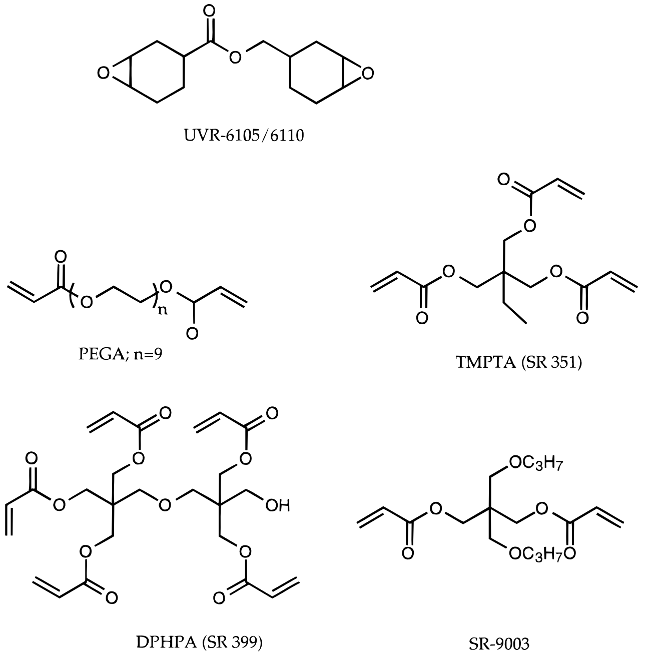


Figure 2. Monomers used in this research.

Silicones in Waterford, NY. Crystal violet lactone (CVL, **2**), 1,4-dicyanobenzene, and 9-cyanoanthracene were obtained from Aldrich. Additional cyclic lactone dye precursors **3**−**8** (trade name Copikem, see Figure 1) were obtained from Hilton Davis, Inc., in Cincinnati, OH, and Mead Corp. in Chillicothe, OH. The dye precursor **9** (Pergascript Red I-6B) and the photoinitiator Irgacure 907 were obtained from Ciba Geigy. 2,4-Diiodo-6-butoxy-3-fluorone was synthesized in our labs.[8] Trimethylolpropane triacrylate (TMPTA, Sartomer 351), dipentaerythritol pentaacrylate (DPHPA, Sartomer 399), and propoxylated neopentyl glycol diacrylate (Sartomer 9003) were obtained from Sartomer Co., while polyethylene glycol-400 (PEGA) was obtained from Scientific Polymer Products. 3,4-Epoxycyclohexylmethyl 3′,4′-epoxycyclohexanecarboxylate, sold with epoxy equivalent weight 130−135 (UVR 6105) and 131−143 (UVR 6110), and the photoinitiator UVI-6974 were obtained from Union Carbide. All monomers were used without further purification.

Two different monomer formulations were used (Figure 2): The standard resin (STDR), an acrylate system that has been used in our group for stereolithography,[15] consists of a di-, a tri-, and a pentaacrylate. In some applications the STDR is mixed with various fractions (10−50 wt %) of the epoxide UVR 6110. The hybrid system (HBRD) used consists of two acrylates and an epoxide and contains two photoinitiators. In some cases, HBRD was used without photoinitiators. The composition of both resins is given below:

Standard Resin (STDR)

component	wt %	
PEGA	20	diacrylate
TMPTA	40	triacrylate
DPHPA	40	pentaacrylate

Hybrid (HBRD)

component	wt %	
UVR 6105	48.8	epoxide, also called ERL 4221
UVI-6974	1.5	sulfonium salt, cationic initiator
DAROCUR 4265	1	radical initiator
SR-399 (DPHPA)	29.3	pentaacrylate
SR-9003	19.5	diacrylate

Sample Preparation: General Procedure. Dye precursor was added to 1.0 g of resin, ethyl acetate (1 mL) was added as a solubilizing agent, and the dye was dissolved in the mixture by ultrasound. After the solvent was evaporated by leaving the bottle open overnight, OPPI, which is readily soluble in the resins used, was dissolved in the monomer in a darkened room. Polymer films were made by exposing 15 μm films of the appropriate resin to UV light in a Colight M218 lightbath using two 400-W medium-pressure Hg lamps. Films were made by squeezing a drop of resin between two transparent plates divided by a 15 μm Teflon spacer. When the degree of cure of the resin was followed, sodium chloride plates were used. In all other applications quartz or glass plates were used. Absorption spectra were recorded on a HP 8452A diode array spectrophotometer. A 6020 Galaxy Series FT-IR spectrometer was used to measure the degree of cure of both acrylates and epoxides by monitoring the decrease of the absorptions at 810 cm^{-1} (acrylic CH bend vibration) and 915 cm^{-1} (bend vibration of the epoxy CH), respectively.

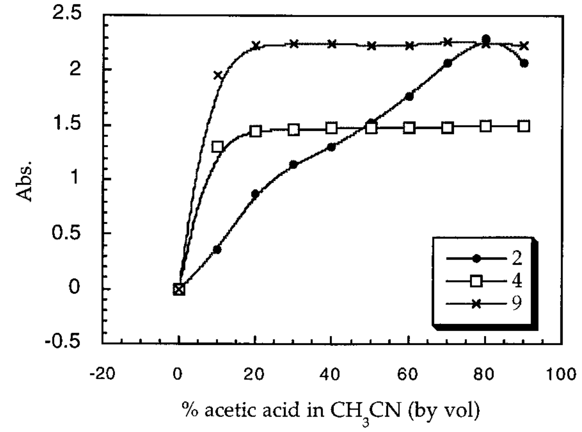


Figure 3. Absorption of solutions of CVL (**2**) (9.9 × 10^{-5} M), **4** (9.9 × 10^{-5} M), and **9** (8.1 × 10^{-5} M) at 604, 446, and 534 nm, respectively, as a function of the fraction of acetic acid in acetonitrile (by volume).

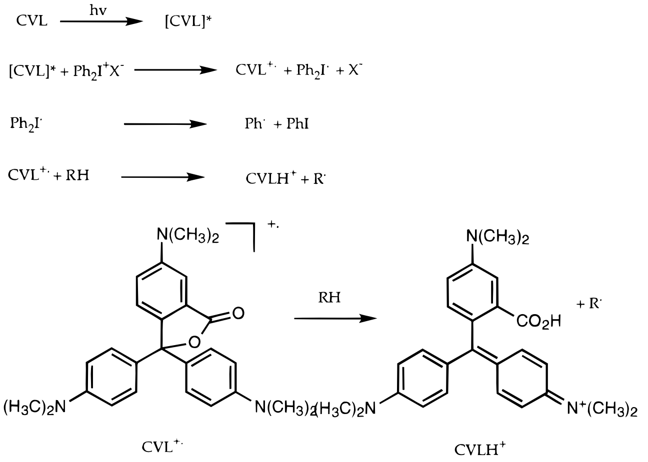
Model Studies in Solution. The photodecomposition of OPPI in the presence of CVL and the photodecomposition of CVL in the presence of electron acceptors were studied in acetonitrile solutions. Solutions were irradiated in 1 × 1 × 3 cm rectangular quartz cuvettes using a 200-W high-pressure mercury lamp in combination with 365 or 435 nm interference filters. The components of the irradiated solutions were analysed using GC and GC-MS. Gas chromatographic analyses were performed on a Hewlett Packard HP-5890 gas chromatograph equipped with a J&W Scientific DB-1 15 m fused silica capillary column and a flame ionization detector. Gas chromatography/mass spectrometry analyses were performed on a HP 5987A GC-MS system using a J&W Scientific DB 5MS 30 m fused silica capillary column. Formation of blue color was monitored by UV−vis spectroscopy.

Results

Relationship between Acidity and Color Intensity. When CVL (10^{-4} M) is dissolved in acetonitrile/acetic acid mixtures, a steady increase of the absorption at 604 nm is observed upon increasing the fraction of acetic acid. A maximum was reached at 90% acetic acid. Further increase results in a decreased absorption, as illustrated in Figure 3.[16] A similar behavior, being maximum color development in 90% acetic acid, was found for **8**.

The increase in color is a clear indication that the equilibrium shown in Scheme 3 is shifted to the right upon addition of acid. It is obvious that acetic acid is too weak an acid to open the lactone ring in **2** efficiently, since a huge excess must be added.[17] A situation in which all CVL is converted to the open colored form never results. Based on the extinction coefficient of crystal violet[18] (109 000 at 610 nm), and assuming the open colored form of CVL has the same extinction coefficient, we calculate that in 90% acetic acid 21% CVL is in the open colored form.

Scheme 4. Proposed Photodecomposition of a Diphenyliodonium Salt in the Presence of CVL



$$\mathrm{CVL} \xrightarrow{h\nu} [\mathrm{CVL}]^*$$

$$[\mathrm{CVL}]^* + \mathrm{Ph_2I^+X^-} \longrightarrow \mathrm{CVL^{+\cdot}} + \mathrm{Ph_2I^\cdot} + \mathrm{X^-}$$

$$\mathrm{Ph_2I^\cdot} \longrightarrow \mathrm{Ph^\cdot} + \mathrm{PhI}$$

$$\mathrm{CVL^{+\cdot}} + \mathrm{RH} \longrightarrow \mathrm{CVLH^+} + \mathrm{R^\cdot}$$

We carried out the same experiment with the other dye precursors **3**−**7** and **9**. The results obtained with these dyes are similar and illustrated for the black dye precursor **4** and red dye precursor **9** in Figure 3. At 20% acetic acid in acetonitrile, the color intensity reaches a maximum, and further addition of acid causes no change in intensity. These results indicate that the opening of the lactone ring takes place at a lower acid strength for **3**−**7** and **9** than it does for **2** and **8**. Based on the extinction coefficients at visible wavelengths, it is clear that conversion to the colored forms does not occur quantitatively for any dye precursor.

Mechanism for Conversion of CVL to CVL Colored Form in the Presence of OPPI. We have established that, for OPPI/CVL solutions in acetonitrile, decomposition of OPPI and the formation of blue color from CVL take place upon irradiation at 365 nm light. Since OPPI absorbs virtually no light at this wavelength, this strongly indicates this is initiated by the excitation of CVL. By varying the concentrations of OPPI and CVL independently and following the kinetics of the color formation, we have demonstrated that, upon irradiation at 365 nm, color formation takes place exclusively via an excited state of CVL. We propose that a diaryliodonium radical, formed after electron transfer from the excited state of CVL, forms iodobenzene and phenyl radicals upon decomposition (Scheme 4). The CVL radical cation abstracts a hydrogen atom from the solvent RH and generates the cationic colored form ($\mathrm{CVLH^+}$) and the radical $\mathrm{R^\bullet}$.[19] This mechanism is supported by the observation of 4-(octyloxy)iodobenzene and (octyloxy)benzene accompanying the formation of blue color.

Further support for this comes from the following: Solutions of CVL and a strong electron acceptor, 1,4-dicyanobenzene, in acetonitrile gave blue color when irradiated at 365 nm. Mixtures of CVL and 9-cyanoanthracene or 2,4-diiodo-6-butoxy-3-fluorone (DIBF) in acetonitrile gave blue color when excited at 435 nm.[20] These experiments prove that color formation takes place when CVL is excited in the presence of an electron donor (1,4-dicyanobenzene) and when an electron acceptor (9-cyanoanthracene or 2,4-diiodo-6-butoxy-3-fluorone) is excited in the presence of CVL.

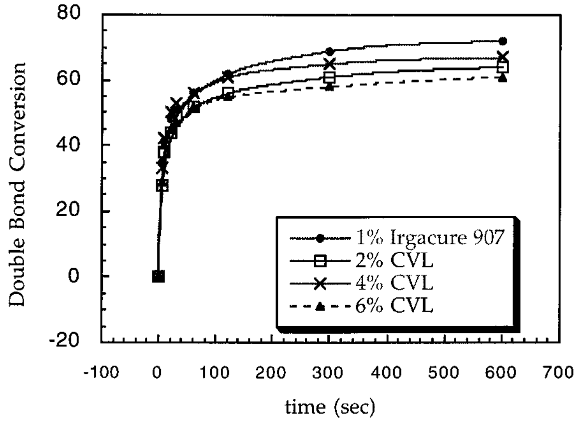


Figure 4. Double bond conversion in the standard resin STDR as a function of the irradiation time, at different CVL concentrations, [OPPI] = 4.5% by weight. For comparison Irgacure 907, 1%, in STDR.

Polymerization Reactions. When solutions of OPPI and CVL in the standard resin (STDR) were irradiated with light from unfiltered medium-pressure Hg lamps (Colight lightbath), fast and efficient polymerization reactions were observed. The degree of double bond conversion as a function of the irradiation time at different CVL concentrations is compared with that of Irgacure 907, a commercial photoinitiator, and both are shown in Figure 4. No photoinitiator other than OPPI/CVL is needed for this polymerization, nor does CVL or OPPI alone initiate this polymerization. We also observe that an excess of CVL decreases the rate of photopolymerization. We conclude that the combination OPPI and CVL acts as an efficient photoinitiator for the polymerization of acrylates. Best results are obtained when CVL and OPPI are used in a 1:1 ratio.

Irradiation of solutions of OPPI and CVL in the hybrid resin HBRD, in the absence other photoinitiators, demonstrated that the combination OPPI and CVL is an efficient photoinitiator for this resin too. Stable, intensely blue polymer films result, suggesting that not only the acrylate but also the epoxide in this hybrid is fully polymerized.

UVR 6110 can be polymerized with CVL and OPPI, but the rate of this process is a few orders of magnitude lower than for the standard resin STDR under the same conditions.[21] We also established that the polymerization rate for UVR 6110/OPPI/CVL was significantly slower than for the UVR 6110/OPPI under identical conditions. From these observations we conclude that in epoxide polymerization takes place via direct excitation of OPPI. Addition of CVL decreases the polymerization rate significantly, most likely due to competitive absorption and because CVL, like all tertiary amines, retards cationic polymerization. It should be noted that excited CVL decomposes OPPI (see Scheme 4), but does not produce reactive cationic species.

Combining these data, we conclude that the combination OPPI/CVL is an excellent photoinitiator for acrylates. For epoxides, photopolymerization can be achieved using CVL/OPPI mixtures, but the rate of the photopolymerization is significantly lower than for cases were OPPI alone was used. For hybrid systems, consisting of equal amounts of acrylates and epoxides, a polymerization of both monomers can be obtained using CVL/OPPI as photoinitiator. We presume acrylate polymerization takes place first, followed by the slow polymerization of the epoxide.

In all resins, acrylate (STDR), epoxide (UVR 6110), or hybrid (HBRD) irradiation in the presence of CVL/OPPI results in both polymerization and the formation of blue color. For STDR, the blue color fades upon continued irradiation or even upon standing in room light. In order to form intensely blue films stable upon

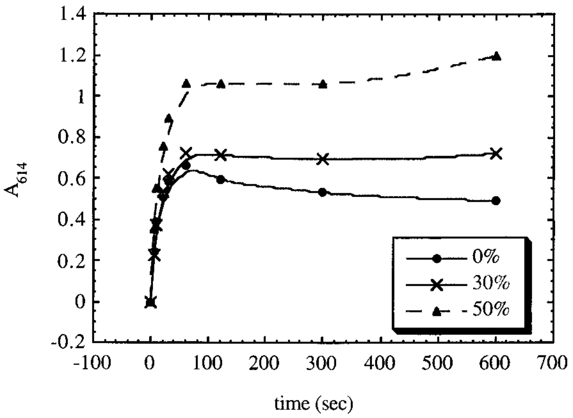


Figure 5. Absorption at 614 nm of CVL in STDR/UVR 6110 mixtures of different compositions as a function of the irradiation time (15 μm films, [CVL] = 2%, [OPPI] = 9%).

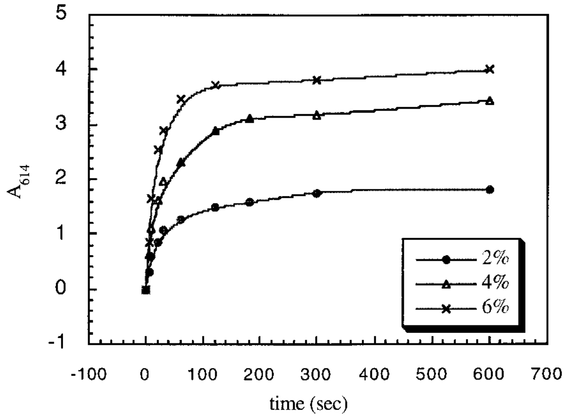


Figure 6. Absorptions at 614 nm as function of the irradiation time for 15 μm HBRD/OPPI/CVL films at different CVL concentrations. HBDR was used without photoinitiators and [OPPI] = 4.5%.

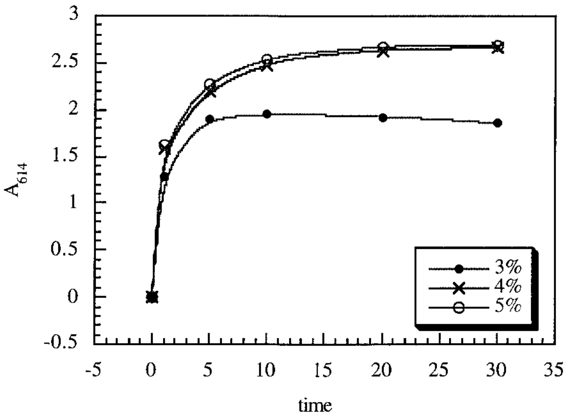


Figure 7. Absorptions at 614 nm as function of the irradiation time for 15 μm HBRD/OPPI/CVL films at different OPPI concentrations. HBDR was used without photoinitiators, [CVL] = 2.0%.

Table 1. Absorptions at 614 nm for 15 μm CVL/OPPI/HBRD Films[a]

	A_{614}			
#1	irr 1 min 1.3	plus heat 1 min 2.4	plus heat 3 min 2.7	plus heat 15 min 3.1
#2	irr 1 min 1.3	plus irr 1 min 1.6	plus irr 3 min 1.9	plus irr 15 min 2.2
#3	heat 10 min 0.2	plus heat 10 min 0.6		

[a] [CVL] = 2%, [OPPI] = 4%, HBRD is used with photoinitiators.

irradiation, addition of epoxide (UVR 6110) was necessary. Figure 5 shows the absorption at 614 nm as a function of the irradiation time for CVL/OPPI/STDR/UVR 6110 mixtures with different acrylate/epoxide ratios. Best results are obtained for 50% acrylate/50% epoxide mixtures. It is not clear why addition of epoxide stabilizes the blue color.

In order to maximize the optical density of the formed films, we have independently varied the concentrations of CVL and OPPI in HBRD. Figure 6 shows the absorption at 614 nm as a function of the irradiation time when [CVL] is varied and [OPPI] = 4.5% by weight. Figure 6 shows that the optical density increases with increasing [CVL], but only slightly at higher concentrations.

Figure 7 shows the absorption at 614 nm as a function of the irradiation time when [OPPI] is varied and [CVL] = 2%. Figure 7 shows that when [OPPI] = 2%, the blue color is not stable and fades upon further irradiation. Comparison with the data in Figure 6 suggests this is due to the low absolute concentrations of CVL and OPPI and has little to do with the concentration ratio. Figure 7 indicates that the optical density increases when [OPPI] is increased, but only slightly at higher concentrations.

Heating OPPI/CVL above 120 °C, either in the standard resin STDR or in the hybrid HBRD, induces polymerization along with the development of blue color. For practical applications, where irradiation times must be minimalized and maximum color development is desired, it has been shown that a fast photopolymerization followed by heating produces stable, strongly colored films. In Table 1 absorptions at 614 nm obtained with a HBRD/CVL/OPPI resin, depending upon the polymerization conditions, are shown. Table 1 shows that heating alone gives lightly colored films. Irradiation alone gives strongly colored films, but the best results in terms of color development are obtained by heating films at 150 °C after a short irradiation period.

The blue color in polymeric films composed of HBRD or STDR/UVR 6110 mixtures is stable toward room light and temperatures up to 150 °C. At 250 °C, the color changes within 30 min, from deep blue to a less intense brownish green, indicating a thermal decomposition of the blue species.

Finally, we have tested the CVL/OPPI/HBRD system in an industrial setting. On a commercial 300 W/inch cure line, using a V bulb, films were made at line speeds of 20 ft/min. In a typical experiment, 15 μm thick films with optical densities exceeding 4 at 614 nm are achieved.

Making Films Using OPPI and Other Dye Precursors. CVL has been employed as the model system, but related acid sensitive dye precursors can also be used to form “self coloring films” of a variaty of colors. Examples of dye precursors are given in Figure 1.

Irradiation of resins consisting of HBRD,[22] a dye precursor, and OPPI results in strongly colored polymeric films in all cases. The rates of polymerization and color formation are comparable to those measured with CVL. We have not investigated if these processes all proceed via the mechanism presented in Scheme 4. As representative examples, color development for films

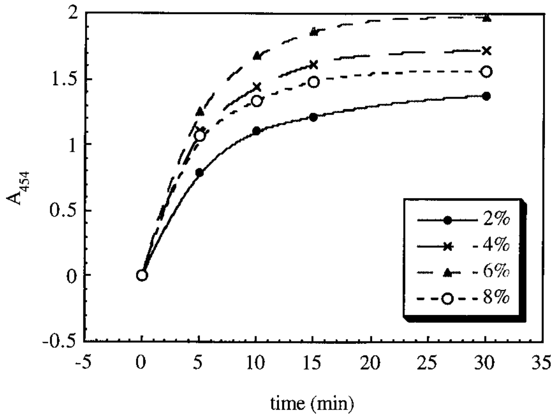


Figure 8. Absorptions at 454 nm as function of the irradiation time for 15 μm HBRD/OPPI/**4** films at different dye precursor concentrations. HBDR was used with photoinitiators and [OPPI] = 4.0%.

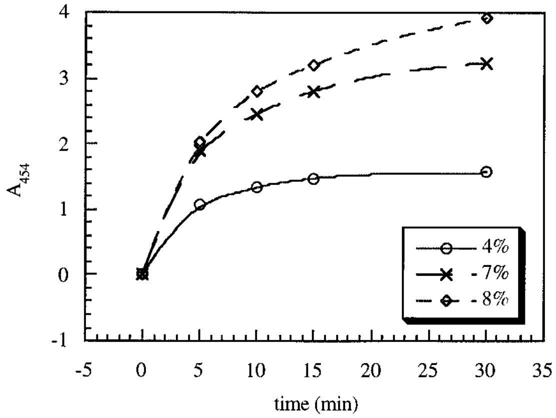


Figure 9. Absorptions at 454 nm as function of the irradiation time for 15 μm HBRD/OPPI/**4** films at different OPPI concentrations. HBDR was used with photoinitiators, [**4**] = 8.0%.

containing OPPI and dye precursor **4** are shown in Figures 8 and 9.

Figure 8 shows that if [OPPI] is 2%, the optical density of the developed film reaches its maximum when [**4**] is 6%. Addition of extra dye precursor results in less colored films. When [**4**] is kept constant and [OPPI] is increased, the situation is less complicated. The optical density steadily increases as [OPPI] increases; see Figure 9. For the dye precursors **3**−**9** similar results are obtained. Optical densities obtained for dye precursor/OPPI combinations in HBRD after irradiation are summarized in Table 2.

We conclude that the optical density of the developed film increases when [OPPI] is increased and that additional [OPPI] *always* leads to more or equally intensely colored films. On the other hand, when OPPI is present in small measure, additional dye precursor does not always lead to more color development; in some cases extra dye precursor leads to less colored films. For each dye precursor there is an optimum dye precursor/OPPI ratio in order to get maximum color. Since the solubility of the dye precursor is poorer than that of iodonium salt, the amount of dye precursor that can be added to the resin usually is the limiting factor for maximizing color development.

Making Films Using OPPI and a Combination of Dye Precursors. We explored formation of colored films by using a combination of dye precursors and OPPI. Our major motivation for exploring this subject is that by combining dye precursors new colors can be generated. We are especially interested in the potential of this technology for creating intensely black films[23] at high speed.

Table 2. Absorptions Obtained for 15 μm Precursor/OPPI/HBRD Films

HBRD with photoinitators		5 min	30 min
6% **2** (blue), 4.5% OPPI[a]	A_{614}	3.82	4.00
8% **3** (green), 8% OPPI	A_{604}	2.14	3.43
10% **4** (black), 10% OPPI	A_{450}	2.20	3.92
10% **5** (orange), 8% OPPI	A_{460}	3.28	3.60
4% **6** (magenta), 4% OPPI	A_{540}	2.24	2.81
4% **7** (yellow), 4% OPPI	A_{442}	3.26	3.22
4% **8** (cyan), 4% OPPI	A_{604}	0.70	1.45
6% **9** (red), 6% OPPI	A_{538}	2.64	3.29

[a] Used without other photoinitiators.

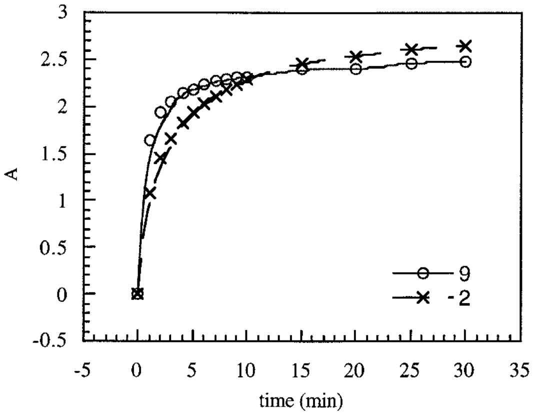


Figure 10. Absorption at 614 and 542 nm of a 15 μm film containing 3% CVL, 1% **9**, and 6% OPPI in HBRD with photoinitiators, as a function of the irradiation time.

When solutions of CVL, dye precursor **9** and OPPI are irradiated, either in acetonitrile or in the hybrid resin HBRD, color formation takes place in a stepwise manner. Figure 10 shows the color development for a solution of CVL and **9** in HBRD as a function of the irradiation time. This figure shows that the absorption at 542 nm, caused by opening the lactone ring in **9**, levels off after 10 min, while the absorption at 614 nm, caused by the same process for CVL, reaches its maximum after 25 min. A similar stepwise color development has been observed by measuring the optical density of a mixture of dye precursors in acetic acid/acetonitrile mixtures, see Figure 3. Color formation from CVL takes place at a later point because CVL needs a stronger acidic medium than does **9**. We also observed that the color development of CVL is strongly reduced in the presence of **9**, while the color development of **9** is not affected by the presence of CVL. For combinations of CVL and the dye precursors **4**−**7**, similar results were achieved.

Different results were obtained when acetonitrile or HBRD solutions, containing OPPI and two dyes from the group **3**−**7** and **9**, are irradiated. We have demonstrated that in these cases dyes develop color simultaneously and the color development of one dye precursor is not retarded or significantly reduced by the presence of the other. As illustrated in Figure 3 for **4** and **9**, color formation takes place at the same acidity for these dyes.

We conclude that, in order to use more dye precursors simultaneously, acid catalyzed opening of the lactone rings must take place at the same acid strength in order to get full and simultaneous color development of all the dye precursors.

Conclusions

We have developed a method for generating "self-coloring" polymeric films. Thin highly colored polymeric films are made in a process where both color formation and polymerization take place. The combination of CVL and OPPI is proven to be an efficient photoinitiator for the radical polymerization of acrylates. The best, most intensely colored films are made in our hybrid resin HBRD, consisting of 50% acrylate and 50% epoxide. In an industrial setting, CVL/OPPI/HBRD 15 μm films, with optical densities exceeding 4 at 614 nm, can be made at line speeds of 20 ft/min.

Films of many different colors can be made, the intensity of which increases as [OPPI] is increased. Increasing the concentration of the dye precursor at a given [OPPI], however, does not always lead to a more intense color; when OPPI is present in short measure, the color intensity decreases when extra dye precursor is added. Color development of resins containing OPPI and different dye precursors is a complex process. In general, a full, synchronous color development can only be obtained when dye precursors develop color at the same medium acidity.

Acknowledgment. This work has been partially supported by the Office of Naval Research (ONR 170014-93-1-0772) and the National Science Foundation (DMR 90 13109). The authors are most grateful for the support of these agencies. Film formation was done on commercial lines at Spectra Group Limited. Dyes were gratiously contributed by both Hilton Davis and Mead Corp.

References and Notes

(1) Contribution No. 257 from the Center for Photochemical Sciences.
(2) For a review on photopolymerization of multifunctional acrylates, see: Kloosterboer, J. G. *Adv. Polym. Sci.* **1988**, *84*, 1.
(3) *Polymers for microelectronics*; Thompson, L. F., Willson, C. G., Tagawa, C. S., Eds.; ACS Symposium Series 537; American Chemical Society, Washington, DC, 1992.
(4) For a review on free-radical initiators, see: Monroe, B. M.; Weed, G. C. *Chem. Rev.* **1993**, *93*, 435.
(5) Crivello, J. V.; Lam, J. H. W. *Macromolecules* **1977**, *10*, 1307.
(6) (a) Leaver, I. H. *Photochem. Photobiol.* **1972**, *16*, 189. (b) Korppi-Tommola, J.; Kolehmainen, E.; Salo, E.; Yip, R. W. *Chem. Phys. Lett.* **1984**, *104*, 373. (c) For a review on triarylmethanes, see: Duxbury, D. F. *Chem. Rev.* **1993**, *93*, 381.
(7) Shi, J.; Zang, X.; Neckers, D. C. *J. Org. Chem.* **1992**, *57*, 4418.
(8) Meier, K.; Bühler, N.; Zweifel, H.; Berner, G.; Lohse, F. Eur. Pat. Appl. 093915 (Prior 19.5.82) to Ciba Geigy AG.
(9) Bi, Y.; Neckers, D. C. *Macromolecules* **1994**, *27*, 3683.
(10) (a) Valdez-Aguilera, O.; Pathak, C. P.; Shi, J.; Watson, D.; Neckers, D. C. *Macromolecules* **1992**, *25*, 541. (b) Zhang, X.-P.; Neckers, D. C. *J. Org. Chem.* **1993**, *58*, 2614.
(11) Dektar, J. L.; Hacker, N. P. *J. Org. Chem.* **1990**, *55*, 639.
(12) Kampmeier, J. A.; Nalli, T. W. *J. Org. Chem.* **1994**, *59*, 1381.
(13) (a) Gottschalk, P.; Davis, P. D.; Schuster, G. B. U.S. Patent #4,772,530, September 1988. (b) Gottschalk, P.; Neckers, D. C.; Schuster, G. B. U.S. Patent #4,772,542, September 1988; E. P. #90201194.9.
(14) Adair, P. C. In *Conference Summary SPSE 40th Annual Conference*, May 17–22, 1987, Rochester, NY, p 113.
(15) Torres-Filho, A.; Neckers, D. C. *J. Appl. Polym. Sci.* **1994**, *51*, 931.
(16) Allen, N. S.; Hughes, N.; Mahon, P. *J. Photochem.* **1987**, *37*, 379.
(17) A stoichiometric amount of acetic acid is present in a solution containing 5×10^{-4}% acetic acid.
(18) Crystal violet equals the open colored form of crystal violet lactone minus the carboxylic acid functionality (see Scheme 3).
(19) Note that in the mechanism in Scheme 4 protonation of CVL takes place in two steps: electron abstraction followed by the addition of a hydrogen atom.
(20) Ren, Y; Jager, W. F.; Neckers, D. C. To be published.
(21) This is no surprise; photopolymerizations of acrylates are known to be much faster than photopolymerizations of epoxides.
(22) For the dye precursors **3**–**9**, HBRD was used with the photoinitiators UVI-6974 and DAROCUR 4265; see Experimental Section.
(23) Strongly absorbing black films cannot be generated with the black dye prcursor **4**. The color developed with **4** is a dark green instead of black, due to a hole in the absorption spectrum at 500 nm.

MA9518722