Macromolecules

Volume 27, Number 14 July 4, 1994

A Visible Light Initiating System for Free Radical Promoted Cationic Polymerization

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Received February 15, 1994⊗

ABSTRACT: A visible light initiator system for the photoinduced cationic polymerization of epoxides is reported. The developed system consists of a xanthene dye, an aromatic amine, and a diaryliodonium salt. We describe it as a free radical promoted cationic chain polymerization in that radicals generated from the visible light absorber start a chain process which, after oxidation of the formed radicals, produces a cationic chain initiating carbocation. The system can efficiently photoinitiate the polymerization of certain cyclic ethers at any wavelength of the visible spectrum depending on the dye's absorption spectrum and its oxidation/reduction potentials. Epoxides do not polymerize in the absence of one of the three components or in the absence of light. Aromatic amines of low basicity containing α-hydrogens are the preferred coinitiators for the polymerization of cyclohexene oxide. Studies on photochemical reactions between each two of the three components demonstrate that both oxidative bleaching of the dye by the diaryliodonium salt and reductive bleaching by the aromatic amine contribute to α-amino radical formation. The radical formed can be easily oxidized into an α-aminocarbocation by an onium salt of proper potential. Characterization of the polymer formed from cyclohexene oxide indicates that all the xanthene dye and appreciable amounts of the aromatic amine are incorporated in the polymer. It is believed that the α-aminocarbocation initiates the ring opening cationic polymerization. Dye molecules are incorporated into the polymer in chain terminating processes.

Introduction

Photoinitiated ring opening polymerization of epoxy resins has been the subject of extensive studies during the last two decades.[3] Significant advances in the UV curing of such resins has been achieved since the discovery of thermally stable, but photochemically reactive, cationic initiators such as diaryliodonium,[4] triarylsulfonium,[5] and mixed-ligand arene cyclopentadienyl metal salts.[6] Theoretically, diaryliodonium salts should have the highest efficiency among these initiators owing to their low C-I bond dissociation energy[7] and to the high reactivity of their dissociated species—aryl radicals or ions. However, the major absorption bands of these initiators fall in the deep UV region (210–250 nm), and poor overlap of these bands with the emission spectra of commercial medium and low-pressure mercury lamps limit their sensitivity and make them yield to thiophenoxy substituted triarylsulfonium salts in many important industrial applications. The latter have an additional absorption band at 300–350 nm and possess much higher overall efficiency.

Pappas et al.[8] studied sensitizing the decomposition of iodonium salts with near UV absorbing sensitizers such as anthracene, xanthone, and acetophenone and suggested that either direct or indirect electron transfer from the sensitizer to the iodonium salts enhanced their decomposition. Previously, Crivello and Lam[9] had reported attempts to use visible light absorbing dyes to sensitize the decomposition of iodonium salts to initiate cationic polymerization. Their results were generally negative. After screening nearly 75 different dyes, they reported that only five dyes, all bearing amino or dimethylamino groups in their molecular skeleton, possessed appreciable sensitizing ability. Typical visible sensitizers like rose bengal and methylene blue were found ineffective. Detailed mechanistic investigations were not reported.

Ledwith[10] first proposed the promotion of photoinduced cationic polymerization by photochemical sources of free radicals. In the Ledwith system, common UV free radical sources such as benzophenone/benzhydrol were used as absorbing chromophores, and the oxidation of the formed free radicals by diaryliodonium salts produced cationic species which subsequently, apparently, initiated cationic polymerization, Scheme 1.

⊗ Abstract published in *Advance ACS Abstracts,* May 15, 1994.

0024-9297/94/2227-3683$04.50/0

Scheme 1. Radical Promoted Cationic Polymerization

$$Ph_2C{=}O \xrightarrow{h\nu} Ph_2C{=}O^*$$

$$Ph_2C{=}O^* + Me_2CH{-}OH \rightarrow Ph_2\dot{C}{-}OH + Me_2\dot{C}{-}OH$$

$$Ph_2\dot{C}{-}OH + Ph_2I^+ \rightarrow Ph_2\overset{+}{C}{-}OH + PhI + Ph^{\bullet}$$

$$Me_2\dot{C}{-}OH + Ph_2I^+ \rightarrow Me_2\overset{+}{C}{-}OH + PhI + Ph^{\bullet}$$

$$Ph_2\overset{+}{C}{-}OH \rightarrow Ph_2C{=}O + H^+$$

$$Me_2\overset{+}{C}{-}OH \rightarrow Me_2C{=}O + H^+$$

$$H^+ + \text{monomer} \rightarrow \text{polymer}$$

We reasoned that a visible light free radical initiating system, if carefully selected, might be used successfully to extend the curing wavelength for epoxy resins into the visible by a similar oxidation process. Since it is well-known that halogenated xanthene dyes such as eosin, erythrosin, and rose bengal, in combination with electron donating coinitiators such as aromatic amines, act as efficient visible light photoinitiators for free radical polymerization of acrylic monomers[11] we explore the combination of these dyes, coinitiators, and onium salts as potential visible light initiating systems for cationic polymerization in this paper. As a typical monomer we employed cyclohexene oxide and judged the efficiency of the initiating visible light system by the conversion of this monomer to its polymer by precipitating the formed polymer product from methanol. We report that a system consisting of a diaryliodonium salt, a *N,N*-dimethyl substituted aromatic amine, and a halogenated xanthene dye is an efficient cationic photoinitiator for certain epoxy monomers. A mechanism of the initiation, based on detailed exploration of all the involved photochemical processes, is proposed.

Experimental Section

Materials. All solvents used were spectrograde, dried prior to use over calcium hydride, and then distilled. Cyclohexene oxide (Aldrich), dried over calcium hydride, was purified by fractional distillation under nitrogen. Epichlorohydrin, 2-chloroethyl vinyl ether, trimethylene oxide, and 1,3-dioxolane (Aldrich) and bisphenol-A-diglycidyl ether (PolySciences) were used as received. Rose bengal, eosin B, erythrosin B, rhodamine B, methylene blue, and most aromatic amines were used without further purification. RBAX (acetylated decarboxylated rose bengal),[12] TIHF (2,3,5,7-tetraiodo-6-hydroxyfluorone),[13] and DIEF (2,4-diiodo-6-ethoxyfluorone)[14] were gifts from SGL.[15] Diphenyliodonium hexafluorophosphate, diphenyliodonium hexafluoroarsenate, diphenyliodonium hexafluoroantimonate, diphenyliodonium tetrafluoroborate, 4,4′-dimethyldiphenyliodonium tetrafluoroborate, 4-methoxydiphenyl iodonium tetrafluoroborate, 3,3′-dinitrodiphenyliodonium tetrafluoroborate, and triphenylsulfonium tetrafluoroborate were synthesized according to literature procedures.[4,16]

Light Intensity of Sources. The light source used is a 450-W tungsten lamp equipped with 520-nm cutoff filters to eliminate UV irradiation. Because the light source is multichromatic, its photon flux distribution was calibrated as follows.

The emission spectrum from the filtered tungsten lamp was recorded using a Spex Fluorolog-2 fluorometer. The spectrum gives the relative intensity, measured in counts per second, versus the wavelength of emission.

Absolute light intensity was obtained using a chemical actinometer, Aberchrome 999p,[17] a photochromic fulgide whose quantum yield of bleaching is known at all wavelengths of its absorption ranging from 430 to 630 nm. The procedure is as follows.

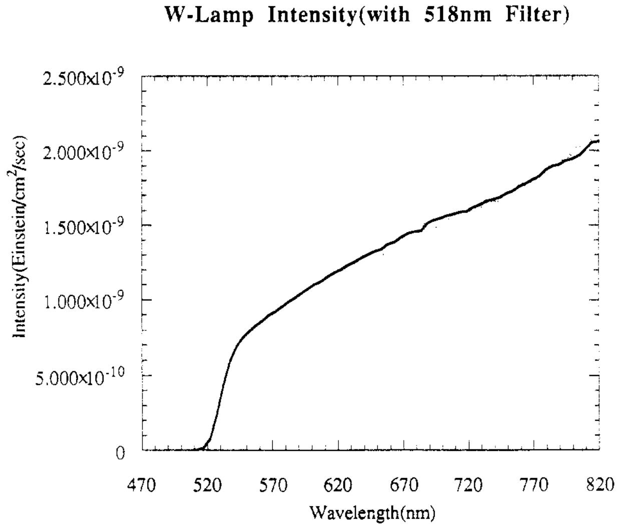


Figure 1. Light intensity of tungsten lamp with 518-nm filter.

An approximately 1.5 × 10^{-4} M solution was prepared by dissolving Aberchrome 999p in toluene to give an absorbance about 1.2–1.8 at 546 nm. A known volume, *V*, is pipetted into a cuvette, and the absorbance at 546 nm is recorded. The solution is then placed exactly where the polymerization sample is to be placed and irradiated from the filtered tungsten lamp for time, *t*, (in s) until the absorbance at 546 nm is decreased approximately 0.1 from its initial value.

The photon flux $I_0(\lambda)$ at wavelength λ in Einstein cm^{-2} s^{-1} received by the sample from the irradiation sources is calculated according to the following equation:[18]

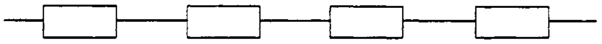
$$I_0(\lambda) = \frac{\Delta A_{546} V I_0^{F}(\lambda)}{\epsilon_{546} b S t \sum I_0^{F}(\lambda)(1 - 10^{-A(\lambda)})\phi(\lambda)}$$

in which $I_0^F(\lambda)$ is the photon flux measured with fluorometer at wavelength λ (unit cps), ΔA_{546} is the absorbance drop of the actinometer at 546 nm in irradiation time *t*, ϵ_{546} is the extinction coefficient of the chemical actinometer at 546 nm, *S* is the exposed area of the cuvette in cm^2, and *b* is the light path in cm, $\phi(\lambda) = 0.0737 - (\lambda - 2.31 \times \theta) \times 10^{-4}$ is the quantum yield of bleaching at temperature θ, and $A(\lambda)$ is the initial absorbance of the artinometer at wavelength λ.

The light intensity measured using this method for the filtered tungsten lamp is shown in Figure 1.

Polymerization. Polymerization initiated by the dye/coinitiator/onium salt system was carried out in a merry-go-round photolysis apparatus. At the center of the apparatus was a Sylvania 120V 500-W tungsten filament immersion lamp placed into a double-walled quartz immersion well through which was pumped cooling water. Compressed dry air was directed continuously to the bottom of the well by a glass tube to cool the lamp. The immersion well was put into a rectangular aluminum well with one window to each side on which a glass filter was fixed. The entire apparatus was placed in a large thermostated water bath, and the temperature was controlled to within 1 °C. Suitable amounts of dye, coinitiator, and onium salt were placed into a predried glass test tube and then sealed with a septum. Dry nitrogen gas was passed through the test tube slowly for several minutes to expel the oxygen trapped in the tube. Monomer, either bulk or in solution, was injected through the septum. The samples were then irradiated on the merry-go-round apparatus, and tubes were withdrawn at regular time intervals. The polymerization was terminated by pouring the reaction mixture into methanol into which a small amount of ammonium hydroxide had been added. The precipitated polymer was isolated by filtration and washed with methanol. It was dried in the oven overnight at 90 °C. Percent conversion was calculated from the weight of the polymer obtained.

Chart 1. Instrumentation for End Group Analysis



GPC column	UV-visible	Fluorescence	Refractive index
10^5 A	detector	detector	detector
10^4 A	220nm	λ_{ex} = 312 nm	
10^3 A	350nm	λ_{em} = 410 nm	
500 A	400nm		

Molecular Weight Determination. Molecular weights of polycyclohexene oxide obtained were measured using gel permeation chromatography (GPC). Four μ-Styragel GPC columns (10^5 A, 10^4, 10^3 A, 500 A) were connected to a Waters HPLC in the order of decreasing pore size to achieve maximum loading. A Waters Associates Differential Refractometer R-400 was used as the detector. HPLC grade THF was the eluent. The molecular weight standards were polystyrene with molecular weights of 4000, 10 200, 17 500, 80 000, 160 000 and 410 000. They were purchased from PolySciences.

End Group Analysis. Fluorescence spectroscopy was used to identify the end groups in the polymer of cyclohexene oxide. *N,N*-Dimethylnaphthylamine (DNA), a compound with high fluorescence quantum yield, was used as the coinitiator. Both manual and GPC methods were used to separate the polymer and free initiator after polymerization.

In the manual method, polymer from cyclohexene oxide obtained through the bulk polymerization initiated by xanthene dye, DPI, and DNA was first dissolved in dichloromethane, and then methanol was added drop by drop to precipitate the polymer. (Direct addition of dichloromethane to methanol causes a rapid precipitation which traps impurities in the polymer during precipitation.) After filtration, the precipitate was dissolved again in dichloromethane and reprecipitated. This dissolution and precipitation was repeated 6 times to remove unreacted amine, DPI, and dye. The fluorescence spectrum of the purified polymer was recorded on the Fluorolog-2 fluorometer.

In the GPC method, the four μ-Styragel columns were connected to a HP1090 liquid chromatograph in the same order as that used for the MW determination. A diode array UV-visible detector, a HP 1046A programmable fluorescence detector and a Waters Associates Differential Refractometer R-400 were hooked to the end of the GPC column, Chart 1. A solution containing 2% polymer in THF was used in GPC analysis.

The absorption, emission, and excitation spectrum of ethyl erythrosin, DPI, and DNA was obtained using the HP8452 diode array UV visible spectrophotometer and the Fluorolog-2 spectrometer, respectively. Three wavelengths were selected on the diode array detector. These wavelengths are 400 nm at which only bleached ethyl erythrosin has absorption, 350 nm at which both the bleached xanthene dye and dimethylaminonaphthylene have absorption, and at 220 nm at which all the three main components of the initiator system have absorption. The excitation wavelength in the fluorescence detector is set at 312 nm which is the wavelength of the maximum absorption of dimethylaminonaphthylene. The emission was monitored at 410 nm. The solvent used in HPLC grade THF, and the rate of solvent flow is 1 mL/min.

Results and Discussion

Table 1. Photopolymerization of Cyclohexene Oxide (Bulk) at 21 °C[a] with Different Photosensitizers

dye	λ (nm)	charge	ϕ_T	E_{ox}	convn (%)
rose bengal	548	−2	0.76	0.95	20.2
eosin	514	−2	0.28	0.80	7.1
erythrosin	525	−2	0.62	0.79	21.8
RBAX	492	0	<0.87	~1.0	17.7
TIHF	538	−1	<0.87	1.34	12.5
methylene blue	656	+1	0.58	1.17	4.6
rhodamine B	556	+1	<0.01	0.95	9.5

[a] Dye concentration, 2×10^{-3} M; 4,4′-dimethyldiphenyliodonium tetrafluoroborate, 5×10^{-2} M; *N,N*-dimethylaniline, 1.0×10^{-2} M; irradiation time, 4 h.

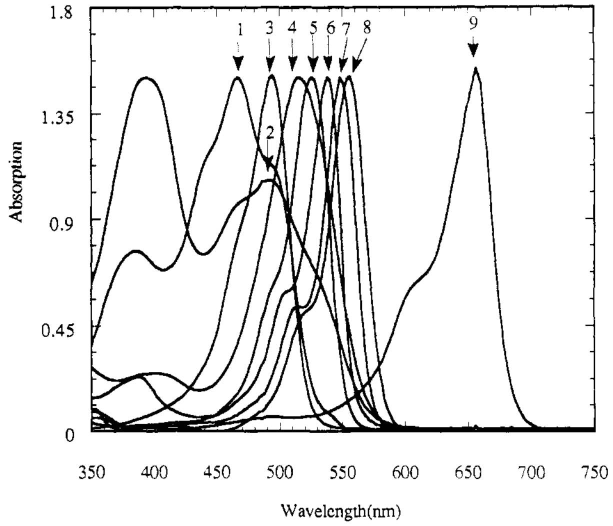


Figure 2. Normalized absorption spectra of different sensitizers: 1, DIEF; 2, RBAX; 3, acridine orange; 4 eosin B; 5, erythrosin B; 6, TIHF; 7, rose bengal; 8, rhodamine B; and 9, methylene blue.

Monomers that are candidates to be polymerized via a cationic mechanism include cyclic ethers, cyclic formals and acetals, vinyl ethers, and epoxy compounds. Of these, epoxy monomers are the most important class on account of their applications in the coating, paints, and adhesives industries. The relationship between structure and reactivity for epoxy monomers in cationic polymerization is determined not only by the electronic nature of its particular epoxy group, its steric accessibility, and the initiating species but also by properties such as the basicity and the nucleophilicity of other functional groups which coexist within the monomer. Cyclohexene oxide is the simplest monofunctional epoxide with no radical polymerizable functionality and no deactivating group. For this reason it was chosen as a representative of epoxy resins for this study.

1. Effect of Xanthene Dyes on the Efficiency of Cationic Polymerization of Cyclohexene Oxide. Xanthene dye sensitized cationic polymerization has not been investigated since Crivello and Lam's initial work.[9] We have confirmed that xanthene dyes alone do not sensitize the cationic polymerization of an epoxide even in the presence of diaryliodonium salt, though the system bleaches rapidly upon irradiation with visible light.[19] The addition of a small amount of an electron donor such as *N,N*-dimethylaniline, however, causes the system to effectively initiate polymerization of cyclohexene oxide.

The absorption spectra of several common dyes employed in the study are shown in Figure 2. Structures are reported in Figure 3.

Table 1 gives certain physical parameters[20] of the dyes (Figures 2 and 3) and the percentage conversion of cyclohexene oxide monomer to its polymer when they are used as reactants in a standard visible initiating system.

Erythrosin, with the lowest oxidation potential but bearing two negative charges, is the most efficient among these dyes, while rose bengal and RBAX are nearly as efficient. TIHF, with a high quantum yield of intersystem crossing but higher oxidation potential, is less efficient. Methylene blue, bearing a positive charge and a well-known sensitizer of free radical polymerization,[21] gives a very low conversion even though its absorption spectrum is in full overlap with the emission spectrum of the radiation sources used. Rhodamine B, a dye with high fluorescence yield (65%), also gives poor results.

Though it is hard to make an accurate comparison of the photosensitizing efficiency of such different dyes since

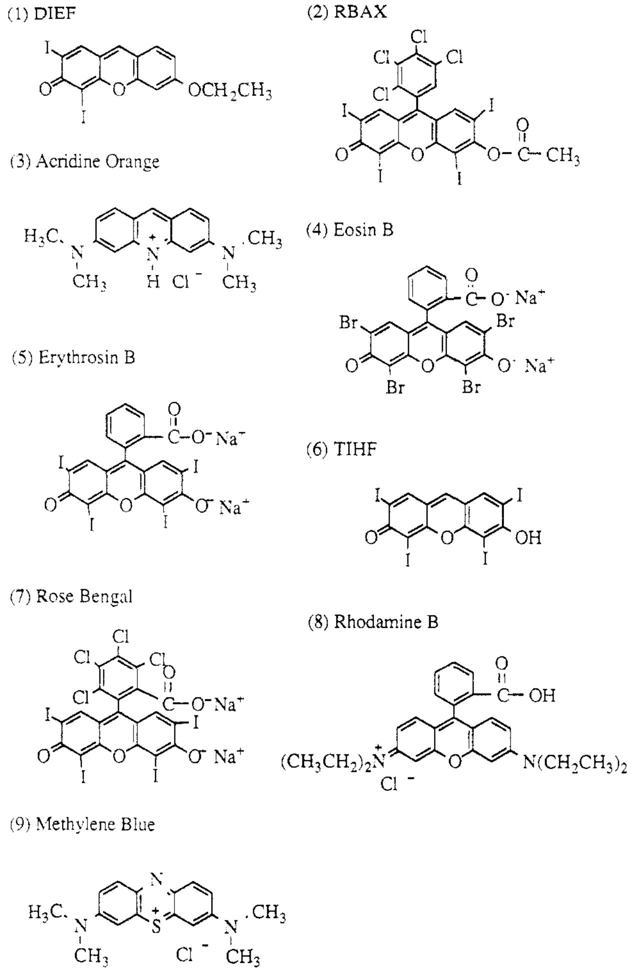


Figure 3. Structures of different photosensitizers.

the dyes have differing absorption band manifolds and extinction coefficients, and different dyes absorb different quantities of photons even if the light source, the dye concentration, and other experimental conditions are kept constant, by irradiating the sample for a long time we believe that we have made the absorption difference less important among the various factors which determine the photoefficiency of the dye. We conclude that xanthene dyes with large quantum yields of intersystem crossing, longer triplet lifetimes, and lower oxidation potentials are better as initiators in the new system.

Figure 4 gives the concentration dependence of conversion of cyclohexene oxide initiated by TIHF and erythrosin. Under the experimental conditions used there is no polymerization in the absence of dye, Figure 4. This is because both the diphenyliodonium salts and *N,N*-dimethylaniline have absorbance only in the UV region. At low dye concentration, erythrosin brought about higher conversion than TIHF. Higher sensitivity of erythrosin has also been found in the dye sensitized decomposition of diazonium salts.[22] At higher dye concentrations however, the efficiency of erythrosin becomes lower than TIHF likely because erythrosin bears two negative charges, one on the phenoxy oxygen of the xanthene ring, the other on the carboxy group of the 9-substituted benzene ring. It appears these negative centers function in the termination step of polymerization but are not important to the initiation step. Ethyl erythrosin shows a much better solubility in the monomers studied, has only one negative charge, and leads to much higher monomer conversion.

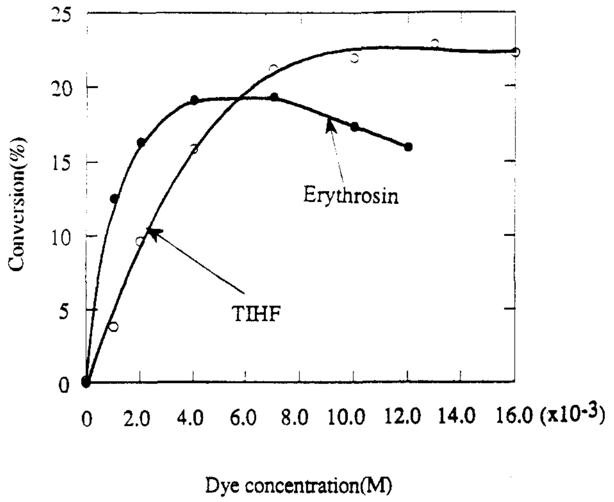
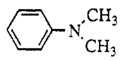
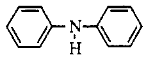
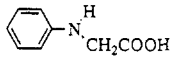
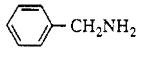
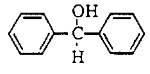
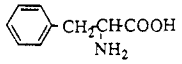
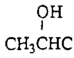


Figure 4. Plot of conversion of cyclohexene oxide monomer vs dye concentration.

Table 2. Photopolymerization of Cyclohexene Oxide (Bulk) at 21 °C[a] with Different Coinitiators

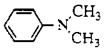
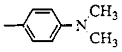
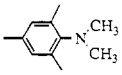
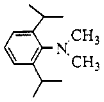
Coinitiator	Conversion(%)	Coinitiator	Conversion(%)
	18.0		<1
		$N(CH_2CH_2OH)_3$	0.2
	15.9	$N(CH_2CH_3)_3$	0.5
	0.7		0.1
	0.1	 $\overset{OH}{CH_3CHCH_3}$	0.02

[a] Decarboxylated rose bengal, 2 × 10^{-3} M; 4,4′-dimethyldiphenyliodonium tetrafluoroborate, 5 × 10^{-2} M; coinitiator, 1 × 10^{-2} M; irradiation time, 4 h.

2. Effect of Coinitiators on the Efficiency of Cationic Polymerization of Cyclohexene Oxide. In most vinyl monomer polymerizations, it is radicals from the coinitiator that initiate polymerization.[23] One of the most ubiquitous classes of coinitiators are photoreducible dye/electron donor systems, such as aliphatic and aromatic amines, which have been extensively used with xanthene dyes and thiazene dyes to induce free radical polymerization.[21] However, the basicity of the amine is a major issue when these amine coinitiators are used in a cationic polymerization system, and it is well-known that aliphatic amines are terminators for such polymerizations. In fact, owing to the living characteristics of cationic polymerization, it is common to use aliphatic amines to terminate cationic chains. In contrast to aliphatic amines, aromatic amines have low basicity. Thus pK_as of most aromatic ammonium salts in aqueous solution are below 5 and can be as low as 2 or 3. (In comparison, the pK_a of trimethylammonium is 9.76.) That acridine orange, a reported sensitizer, bears two dimethylamino groups, is direct evidence that an aromatic amine can be present in a cationically photopolymerizable system without terminating the cationic chain.[9] Thus, we surmised that aromatic amines were potential coinitiators for cationic polymerization and explored more than 50 coinitiators with decarboxylated rose bengal as the sensitizing dye. Typical experimental results are given in Table 2.

In contrast to the Ledwith experiments,[10] no photopolymerization is observed when benzhydrol and isopropyl alcohol are used under our experimental conditions. Benzophenone/isopropyl alcohol promoted cationic polymerization involves hydrogen abstraction by the ben-

Table 3. Photopolymerization of Cyclohexene Oxide (Bulk) at 21 °C[a] with Aromatic Amines Containing α Hydrogens

Coinitiator	Conversion(%)	Coinitiator	Conversion(%)
	9.8		8.9
	16.0		13.3

[a] Decarboxylated rose bengal, 2 × 10^{-3} M; 4,4′-dimethyldiphenyliodonium tetrafluoroborate, 5 × 10^{-2} M; coinitiator, 1 × 10^{-2} M; irradiation time, 1 h.

zophenone from the alcohol as the primary step. For an excited molecular to abstract hydrogen,[24] the activation energy for the reaction must be low enough to allow this reaction to be competitive with the other deactivation processes of the excited states. Thus the energy of the excited state and the bond strength of the hydrogen donor are crucial factors in determining the feasibility of a hydrogen abstraction reaction. Since xanthene dye sensitizers have triplet energies as low as ~43 kcal/mol, hydrogen abstraction from an alcohol such as isopropyl alcohol is not a favorable path in producing radicals from the xanthenes.

Trialkylamines such as triethylamine and triethanolamine have been widely used as coinitiators in photoinduced free radical polymerization. Accumulated evidence suggests that α-amino radicals form from such amines following electron transfer and deprotonation.[22] These compounds, however, fail as coinitiators in initiating cationic polymerization even in the presence of onium salts and dyes. We believe that it is the basicity of the amine that determines if it deactivates the cationic active center responsible for initiation and thus prohibits cationic chain polymerization in the case of trialkylamines. Diphenylamine has a low basicity; the pK_a value of the conjugate acid is 0.97, and this is much lower than acridine orange. It fails to initiate cationic polymerization since no α-amino radical can be produced from it even if an electron is transferred from the amine to the excited dye. In addition, the aminium radical cation such as would be formed from diphenylamine has never been found to initiate either radical polymerization or cationic polymerization. In contrast, both *N*,*N*-dimethylaniline and *N*-phenylglycine are good coinitiators of cationic polymerization.

Summing all the data, we conclude that only aromatic amines with α hydrogens are capable of initiating the polymerization of cyclohexene oxide in our system. Aliphatic amines, aromatic amines without α hydrogen, and non-amine hydrogen donors are incapable of initiation.

Based on this assumption we further explored several aromatic amines, all of which bear an α hydrogen. For a shortened irradiation time to 1 h, results are given in Table 3. 2,4,6-*N*,*N*-Pentamethylaniline gives the highest conversion among these coinitiators. *N*,*N*-Dimethylaniline is included in the table for comparison.

Figure 5 is a plot of the cyclohexene oxide conversion vs coinitiator (*N*,*N*-dimethylaniline) concentration. Conversion increases linearly with coinitiator concentration, levels off, and gradually goes down at higher concentration. Without coinitiator, there is no polymerization under the experimental conditions.

3. Effect of Diaryliodonium Salts on the Efficiency of Cationic Polymerization of Cyclohexene Oxide. The relationship between structure and reactivity of diaryliodonium salts in UV light initiated cationic polymerization of epoxy compounds has been reviewed by Crivello.[25] The counter ion, usually a nonnucleophilic semimetal complex, plays a decisive role in determining the rate of polymerization, and the general order of reactivity was found to be SbF_6^- > AsF_6^- > PF_6^- > BF_4^-. Because the photolysis of diaryliodonium salts with different anions discloses that the quantum yields of photodecomposition are independent of the anionic portion of the salts and also because the iodonium salts with different anions show dramatic differences in the rates of polymerization, the observed differences of polymerization rates must be attributed only to the nature of the anion.[4] This effect has been explained on the basis of the degree of separation in the ion pair. Thus the larger the negatively charged ion, the more loosely it is bound and the more active the propagating cationic species in the monomer solution. An order of reactivity based on the gegen ion is thus a characteristic of a cationic polymerization. We suggest the reverse is also true; i.e., when iodonium salts with different anions are involved in a polymerizable composition, if the rate of polymerization falls in the order of SbF_6^- > AsF_6^- > PF_6^- > BF_4^-, the polymerization must involve a cationic mechanism.

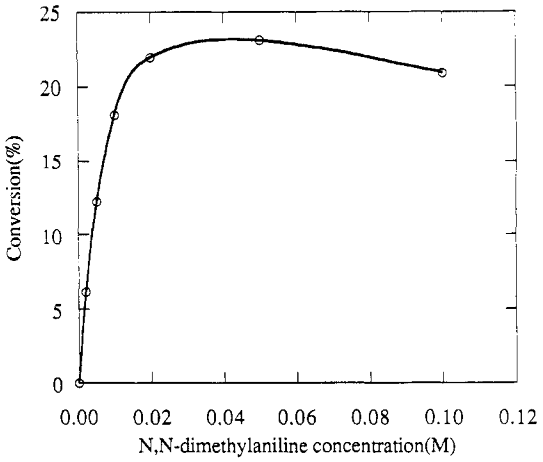
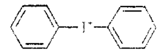
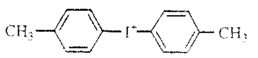
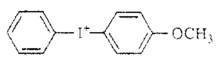
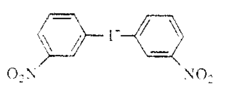
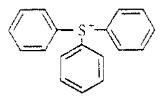
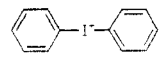
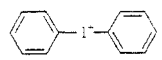
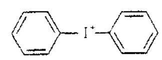
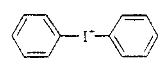


Figure 5. Plot of conversion of cyclohexene oxide vs *N*,*N*-dimethylaniline concentration. Rose bengal, 2 × 10^{-3} M; 4,4′-dimethyldiphenyliodonium tetrafluoroborate, 5 × 10^{-2} M; irradiation time, 2 h.

We synthesized a variety of iodonium salts ranging from a common iodonium cation with different anions to a common anion with different onium cations. We also compared iodonium salts with a sulfonium salt. The experimental results are given in Table 4. A dramatic difference is found in the initiation efficiency of the iodonium salt and the sulfonium salt. The dye/coinitiator system can accelerate diaryliodonium salt initiated cationic polymerization but fails to accelerate the triphenylsulfonium salt initiated cationic polymerization. There is no selectivity based on the diaryliodonium salt if the counter anion is kept the same, and we observed similar conversions no matter what the nature of the substitutent on the aromatic ring. Since both diaryliodonium salts and triarylsulfonium salts are efficient UV cationic initiators, the dramatic difference in their reactivity in the system investigated is related to substantial differences in the reduction potentials of the onium salts. Triphenylsulfonium salts have a reduction potential of ~−1.2 V (vs SME).[26] This is much lower than that of the iodonium salts, which is about −0.2 V (vs SME),[27] meaning that iodonium salts are much more oxidative than are sulfonium salts. Substitution on the benzene ring does not, however, strongly influence the oxidation and reduction properties of iodonium salts. 4-Methoxydiaryliodonium salts, which bear a strongly electron releasing substituent, have an oxidation potential of ~ −0.186, while the 3,3′-dini-

Table 4. Photopolymerization of Cyclohexene Oxide (Bulk) at 21 °C[a] with Different Onium Salts

iodonium salt		irradiation time (min)	convn (%)
cation	anion		
	BF_4^-	240	16.6[b]
	BF_4^-	240	17.7
	BF_4^-	240	19.2
	BF_4^-	240	18.4
	BF_4^-	240	0.0
	BF_4^-	60	8.9[b]
	PF_6^-	30	>90
	AsF_6^-	15	100
	SbF_6^-	10	100

[a] Dye concentration, RBAX = 2×10^{-3} M; diphenyliodonium salt, 5×10^{-2} M; *N,N*-dimethylaniline, 1×10^{-2} M. [b] It was to our disadvantage that we found diphenyliodonium tetrafluorobate has poor solubility in monomer solution. A low concentration was used, and the result was extrapolated to a comparable concentration. A linear conversion dependence on concentration has been found. See Figure 6.

trodiphenyliodonium salt, which bears two strong electron withdrawing groups, has a reduction potential of −0.200 V.[28] This narrow range of the reduction potential parallels with the narrow range of conversions of monomer to polymer in our system so it is apparent that some key step in the initiation involves the iodonium salts in a redox reaction.

For diaryliodonium salts with different anions, we find exactly the same reactivity as for UV light initiated cationic polymerization: $SbF_6^- > AsF_6^- > PF_6^- > BF_4^-$. For the hexafluoroantimonate salt, cyclohexene oxide can be completely cured to solid polymer in 10 min visible light irradiation under well cooled conditions. (An explosive polymerization in several seconds may result if the solution is not suitably cooled.) We reported the monomer conversion to be 100% in cases where the solid-state polymer is formed, because a routine precipitation method cannot be used to measure the actual conversion. For hexafluorophosphate and hexafluoroarsenate salts the above monomer solution can be completely cured in less than 30 min of irradiation. As to the tetrafluoroborate salt, the rate of polymerization is considerably slower, being less than 10% in 1 h of irradiation. The order of reactivity $S_bF_6^- > A_sF_6^- > PF_6^- > BF_4^-$ reveals a cationic polymerization, even though some radial intermediates might be involved during the reaction.

Figure 6 is a plot of conversion of monomer vs diaryliodonium salt concentration. The straight line obtained with the intercept equal to zero indicates that there is no polymerization in the absence of diaryliodonium salt. Because xanthene dye/electron donor coinitiator is a typical radical polymerization initiating system,[29,11] the fact that no polymerization occurs in the absence of iodonium salt indicates again that cyclohexene oxide is not polymerized via a radical process. All the polymer formed in the presence of the iodonium salt must be formed through a cationic mechanism. At constant dye concentration, a linear relationship between monomer conversion and onium salt concentration is strictly followed. Owing to the absence of absorption of the onium salt in the visible region of the spectrum, the initiating species cannot be generated by the direct interaction of a photon with the onium salt but only through the interaction of the ground-state onium salt with other species which is generated photochemically, for there is no polymerization without irradiation.

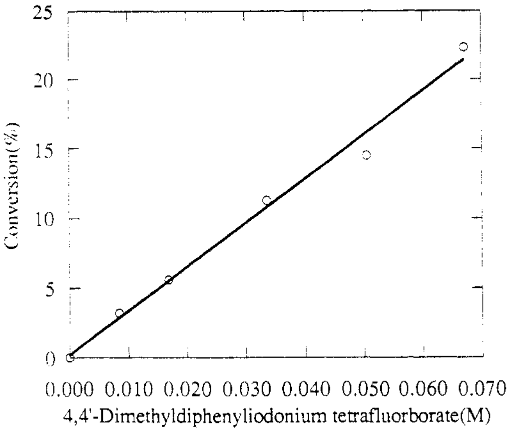


Figure 6. Plot of conversion of cyclohexene oxide vs diaryliodonium salt concentration RBAX; 2×10^{-3} M; *N,N*-dimethylaniline 1×10^{-2} M; irradiation time, 2 h.

4. Influences of Experimental Conditions on the Rate of Polymerization. (1) Influence of Oxygen. Oxygen inhibition is common for light induced free radical polymerizations. It is manifested by an induction period, lower rates, and lower degrees of polymerization.[30] Oxygen, either from air or dissolved in the monomer solution, may interfere with the photopolymerization process by either of the following two mechanisms. First, oxygen may quench the triplet state of the photoinitiator, thereby preventing the formation of primary radicals. Second, oxygen may effectively scavenge the carbon-centered primary radicals or the radicals on the growing polymer chain, thereby terminating the polymerization process.

In contrast to radical polymerization, cationic polymerization initiated by direct photolysis of diphenyliodonium and triphenylsulfonium salts with UV light is insensitive to oxygen. This is because the photolysis of the initiator occurs from the singlet excited state or from a short lived triplet state not quenched by oxygen[31] as well as because the propagating species in the cationic chain is not reactive to oxygen.

Although the polymerization of epoxy monomers by xanthene dye/amine/iodonium salts mechanistically resembles a cationic polymerization, it has been found that oxygen dramatically influences the rate of polymerization.

This implicates a quenchable excited state and/or a radical chain in the process. Figure 7 gives the cyclohexene oxide monomer conversion–irradiation time profile measured at two extreme conditions. The top curve is measured by bubbling dry argon for 10 min into each monomer solution before irradiation, while the bottom curve was measured by bubbling oxygen into the preirradiated solution. At the early stages of the polymerization, the argon bubbled solution polymerized 7–10 times faster than the oxygen saturated solution. This ratio becomes smaller after longer time irradiation, probably because the radical intermediates have exhausted all the oxygen. Also under either of the two conditions, the conversion increases linearly with irradiation time and

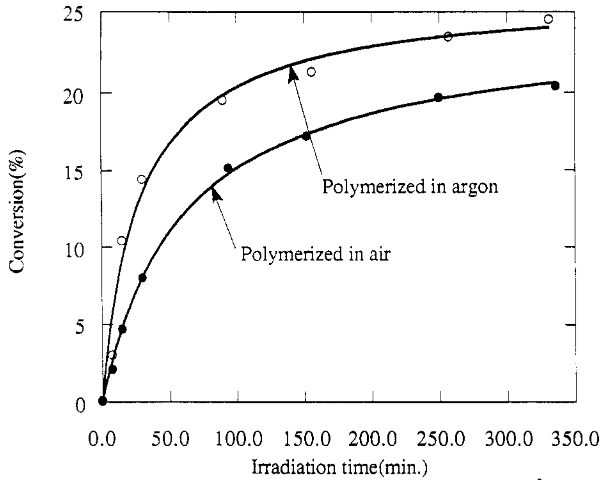


Figure 7. Conversion of cyclohexene oxide vs irradiation time in the presence and absence of oxygen: 4,4′-dimethyldiphenyliodonium tetrafluoroborate, 5 × 10^{-2} M; erythrosin, 4 × 10^{-3} M; *N*,*N*-dimethylaniline, 1 × 10^{-2} M.

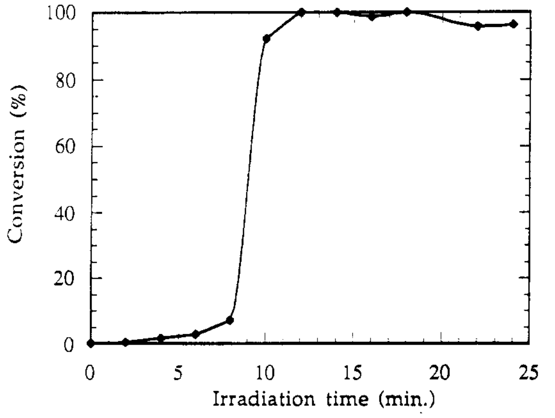


Figure 8. Conversion of cyclohexene oxide vs irradiation time initiated by iodonium hexafluoroantimonate: diphenyliodonium hexafluoroantimonate, 5 × 10^{-2} M; erythrosin, 4 × 10^{-3} M; *N*,*N*-dimethylnaphthylamine, 5 × 10^{-2} M.

levels off beyond 2 h irradiation. This differs from the characteristics of living cationic polymerization in which once a polymerization reaction begins, conversion continues to increase even long after the irradiation ceases.

Figure 8 gives the conversion of cyclohexene oxide polymerized in air under the same irradiation conditions (>520 nm) except that diaryliodonium hexafluoroantimonate was used instead of the tetrafluoroborate salt. With the time scale more than one order larger than that shown in Figure 7, the induction period at the beginning of the irradiation becomes clear. At an irradiation time of about 8 min, the conversion of the monomer suddenly changes from less than 10% to more than 95%, indicating a nearly explosive polymerization has occurred. In an oxygen free monomer solution, polymerization can be complete in a few minutes if the monomer is suitably cooled.

(2) Influences of Solvents. In the cationic polymerization of cyclic ethers, the growing oxonium ion is postulated to exist in the form of ion pairs and free ions.[32] In either case, the reactivity of the propagating species will be influenced by the media since either monomer or solvent molecules surround the cation. Besides general bases which could terminate polymer chains, any solvent which solvates the propagating ionic species will influence the rate of polymerization.

Polymerization of cyclohexene oxide was conducted in 50% monomer solution in several solvents. The results are listed in Table 5.

Table 5. Influence of Solvents on the Conversion of Cyclohexene Oxide

solvent	viscosity (mPaS)	ϵ	convn (g)	convn (%)
acetonitrile	0.369	37.5	0.015	0.60
acetone	0.306	20.7	0.438	17.52
nitromethane	0.630	38.6	0.745	29.80
nitrobenzene	1.863	34.8	0.749	29.96
chloroform	0.537	4.8	1.810	72.40
dichloromethane	0.413	9.1	2.277	91.08

Table 6. Initiation Efficiency of Xanthene Dye/Coinitiator/Iodonium Salt toward Different Monomeric Systems[a]

monomers	time required for complete curing (min)
trimethylene oxide	<120
1,3-dioxolane	<90
cyclohexene oxide	10
bisphenol-A diglycidyl ether	<300
epichlorohydrin	∞
2-chloroethyl vinyl ether	∞
3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate	∞

[a] Ethyl erythrosin, 2.0 × 10^{-3} M; *N*,*N*-2,4,6-pentamethylaniline, 1 × 10^{-2} M; diphenyliodonium hexafluoroantimonate, 5 × 10^{-2} M.

It can be seen from the data in Table 5 that the influence of solvents on the rate of polymerization is dramatic. In dichloromethane, the polymerization is nearly complete, while in acetonitrile, polymerization essentially does not happen. There is no correlation of solvent viscosity with the rate of polymerization, and the rate of polymerization increases with decreasing dielectric constant. This is because molecules with high polarity tend to stabilize and therefore deactivate the cation and slow down the rate of polymerization. This is another characteristic of cationic polymerization. Radical polymerizations are not sensitive to the polarity of the solvent.

5. Efficiency of Xanthene Dye/Coinitiator/Iodonium Salt Initiating System on Different Monomeric Compositions. Having discovered that the xanthene dye/coinitiator/iodonium salt system efficiently initiates the cationic polymerization of cyclohexene oxide by visible light irradiation, we next explored other monomeric materials.

The polymerizations of trimethylene oxide, 1,3-dioxolane, epichlorohydrin, and 2-chloroethyl vinyl ether were conducted in bulk under the same conditions as used in the polymerization of cyclohexene oxide. Bisphenol-A diglycidyl ether was polymerized in a solution containing 90% monomer and 10% dichloromethane, the solvent being added to decrease the viscosity of the monomer and to improve the solubility of the initiator. Monomer and a suitable amount of initiator were put into a test tube and irradiated (>520 nm) on the merry-go-round apparatus for up to 6 h. The time required to completely cure the monomer was used to measure the efficiency of the initiator toward the monomer. Table 6 gives the results of these experiments.

Cyclohexene oxide is the most reactive monomer, while trimethylene oxide and 1,3-dioxolane processes relatively high reactivity and can be cured by the initiator in less than 2 h of irradiation. Bisphenol-A diglycidyl ether is less reactive. It takes 5 h of irradiation to completely cure it, and the cured polymer has a tacky surface, indicating that oxygen inhibition becomes more significant in the slowly polymerized monomer system. Epichlorohydrin, 2-chloroethyl vinyl ether, and 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate cannot be polymerized

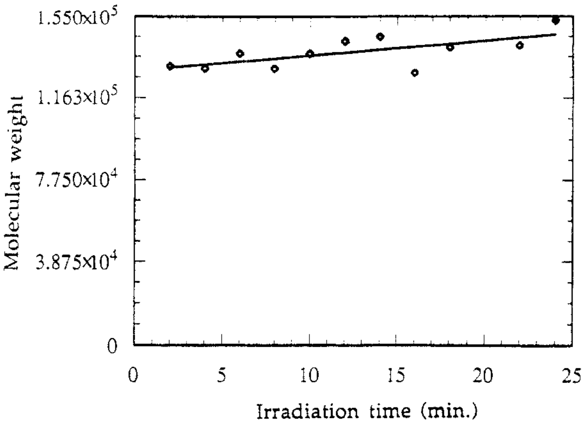


Figure 9. Molecular weight of polycyclohexene oxide vs irradiation time.

by the initiating system. Though it is expected that different monomers have different reactivity toward cationic polymerization, it seems strange that this highly efficient initiating system for cyclohexene oxide does not polymerize an epoxide containing an ester linkage or a vinyl ether monomer particularly since the latter is regarded as the most reactive monomer that can be polymerized by cationic polymerization. We presume it is the basicity and the nucleophilicity of the aromatic amine toward the propagating cationic center that determine the amine's function in the cationic polymerization. If the aromatic amine has low basicity and the carbocation is less electrophilic, for example, the charge is less localized, and the amine mainly functions as a coinitiator. Otherwise, it will function as a terminator.

6. Characterization of Cyclohexene Oxide. Figure 9 gives the molecular weights for a series of samples of polycyclohexene oxides polymerized under the same experimental conditions but with different irradiation times.

The molecular weight of polycyclohexene oxide does not change dramatically with irradiation time nor with conversion. The curves are indicative of the mechanistic character of the fundamental chain polymerization. Moreover, the living cationic polymerization is not so "lively" in this system. This "not-very-living" characteristic is also indicated by the curve of conversion versus irradiation time in Figure 7. The conversion curve of cyclohexene oxide initiated by erythrosin/DPI/BMPI increases first with irradiation time and flattens out after a certain period. This is likely attributed to a low rate of initiation and a fast rate of propagation as well as the presence of some excess of xanthene dye which terminates polymer chains. High molecular weight at low conversion also indicates a back biting process (i.e., the oxygen in the polymer chain attacks the cationic center rather than the monomer to form a small ring) which is common in the polymerization of THF but is not thought to be an important process in the polymerization of cyclohexene oxide.

Determining the initiating species was investigated using a series of detection methods including absorption and fluorescence. The detection limit of fluorescence can easily reach 10^{-8}–10^{-9} M under conventional laboratory conditions. For a polymer with a molecular weight of around 10^5, this method is sensitive enough to detect a fluorescent signal from end groups in a polymer solution of concentration 10^{-3}–10^{-4} g/L if the end group is selected such that it has a high quantum yield of fluorescence.

N,N-Dimethylnaphthylamine (DMNA) is a perfect substitute for DMA as a coinitiator. It contains a *N,N*-dimethyl group which is believed necessary for the proposed initiation process. It also contains a naphthyl group which fluoresces with a high quantum yield, and its characteristic absorption and emission spectra can be differentiated from other compounds in the mixture. The λ_{max} of DMNA's longest absorption band lies at 312 nm. It gives a fluorescence peak at 402 nm at low concentration in acetonitrile solution.

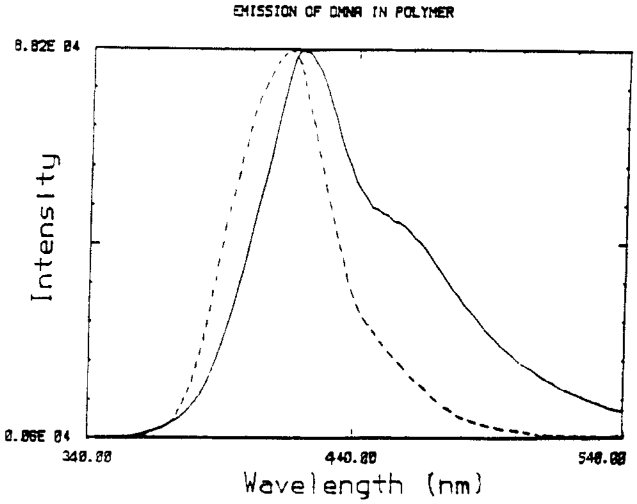


Figure 10. Fluorescence spectrum of polymer sample purified by the dissolution–precipitation method: solid line, polymer solution; dashed line, DMNA.

Ethyl erythrosin absorbs at λ_{max} 546 nm and emits at λ_{max} 574 nm. Excitation of ethyl erythrosin at 312 nm gives a small, almost negligible emission at 402 nm attributed both to the off peak excitation (312 nm) and off emission observation (402 nm). Because all the dyes are bleached after polymerization, their presence does not interfere with the end group determination.

Dye bleached by DPI has a broad absorption spectrum ranging from the UV to the 550-nm region. Excitation at 312 nm gives a weak emission with a maximum at 484 nm in acetonitrile solution. The emission in the 402-nm region is even weaker. This weak emission may cause a small interference in the fluorescence determination of DMNA, but its maximum emission wavelength is different from DMNA's maximum emission wavelength. Thus the two emissions are easily differentiated.

DPI and its decomposition products such as benzene or iodobenzene do not absorb at 312 nm, so their presence does not influence the determination of other components.

Figure 10 gives the fluorescence spectrum of a cyclohexene oxide polymer photoformed with ethyl erythrosin/DPI/DMNA. The sample was purified by repeated dissolution in dichloromethane and precipitation from methanol solution until no substantial drop of fluorescence occurred after subsequent purification steps. The fluorescence peak (solid line) is exactly the same as that derived from the fluorescence spectrum of DMNA in solution (dashed line), and the shoulder at long wavelength matches with the fluorescence spectrum of bleached ethyl erythrosin. The polymer always remained yellowish, a typical color of the bleached dye, no matter how many times the sample is purified.

Figure 11 gives the normalized elution curves detected by the multiple detectors after GPC separation. Polymer was eluted from the column (retention time = 29.5 minutes) as indicated by the refractive index detector (curve 5).

Curve 1, the 400-nm absorption response from the diode array detector, has a retention time exactly the same as that of the polymer as indicated by curve 5, indicating that most of the 400-nm absorbing component(s) are

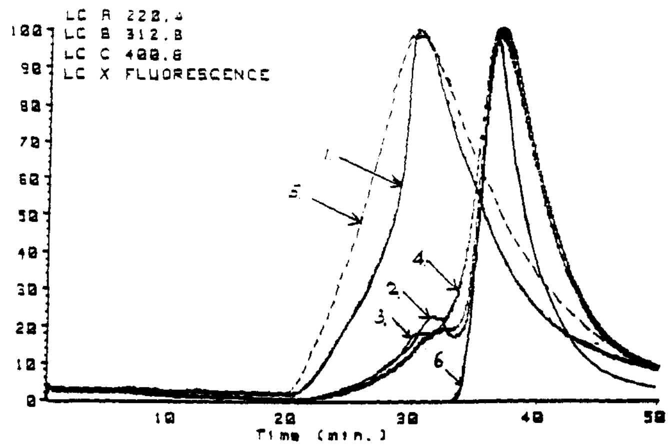


Figure 11. Normalized elution curves of the polymer sample photoformed from ethyl erythrosin/DMNA/DPI: curves 1, 2, and 3, absorption monitored at 400, 220, and 350 nm; curve 4, fluorescence, λ_{ex} = 312 nm, λ_{em} = 400 nm; curve 5, refractive index detector response; curve 6, absorption and fluorescence of DMNA; elution solvent, THF; rate of flow, 1.2 mL/min.

incorporated to polymer molecules. Because only bleached ethyl erythrosin absorbs through 380–550 nm in the system, we conclude that bleached dye molecules are connected to the polymer chain.

Curves 2 and 3 are the 200- and 312-nm absorption responses from diode array detector, and curve 4 is the fluorescence signal at 400 nm. These curves have common peak positions indicating a retention time of 37 min. These peaks are attributed to unreacted small molecules such as unreacted DMNA, DPI, and formed photoproducts like benzene or iodobenzene. Both DMNA and DPI are in large excess and are not exhausted during photopolymerization. Thus they are eluted from the column as individual peaks. Control experiments show that unreacted DMNA gives elution curve expressed in curve 6.

Comparison of curves 2, 3, and 4 with curve 6 in Figure 11 discloses that in front of the large peaks in curve 2, 3, and 4, there are clearly distinct peaks which can be traced as far back as the starting point of the polymer peak. These peaks are caused by the 200- and 312-nm absorbing species and 402 nm fluorescence emitting species.

By scanning the whole fluorescence spectrum at retention time 27.3 min and comparing the spectrum with a sample thermally polymerized in the absence of ethyl erythrosin, we find the main fluorescence species is from the DMNA moiety rather than from the dye, which indicate again the presence of DMNA in the polymer molecules.

7. Mechanism of Photoinitiation. Photochemical reactions between each two of the three components of the initiator system have been intensively studied. Irradiation of acetonitrile solutions of diaryliodonium salts and either ethyl eosin or ethyl erythroson[19] results in immediate bleaching of the dyes. The quantum yield of bleaching was found to be very close to the quantum yield of triplet formation, indicating that triplet formation controlled the efficiency of the photochemical reaction. Product analysis shows that phenyl radicals coupled and substituted on the aromatic nucleus of dyes (Figure 12) indicating the primary photochemical reaction is the electron transfer from the dye to the onium salt as expressed by eq 1 in Figure 13.

In contrast, irradiation of an acetonitrile solution of ethyl erythrosin with *N*,*N*-dimethylaniline for an extended time

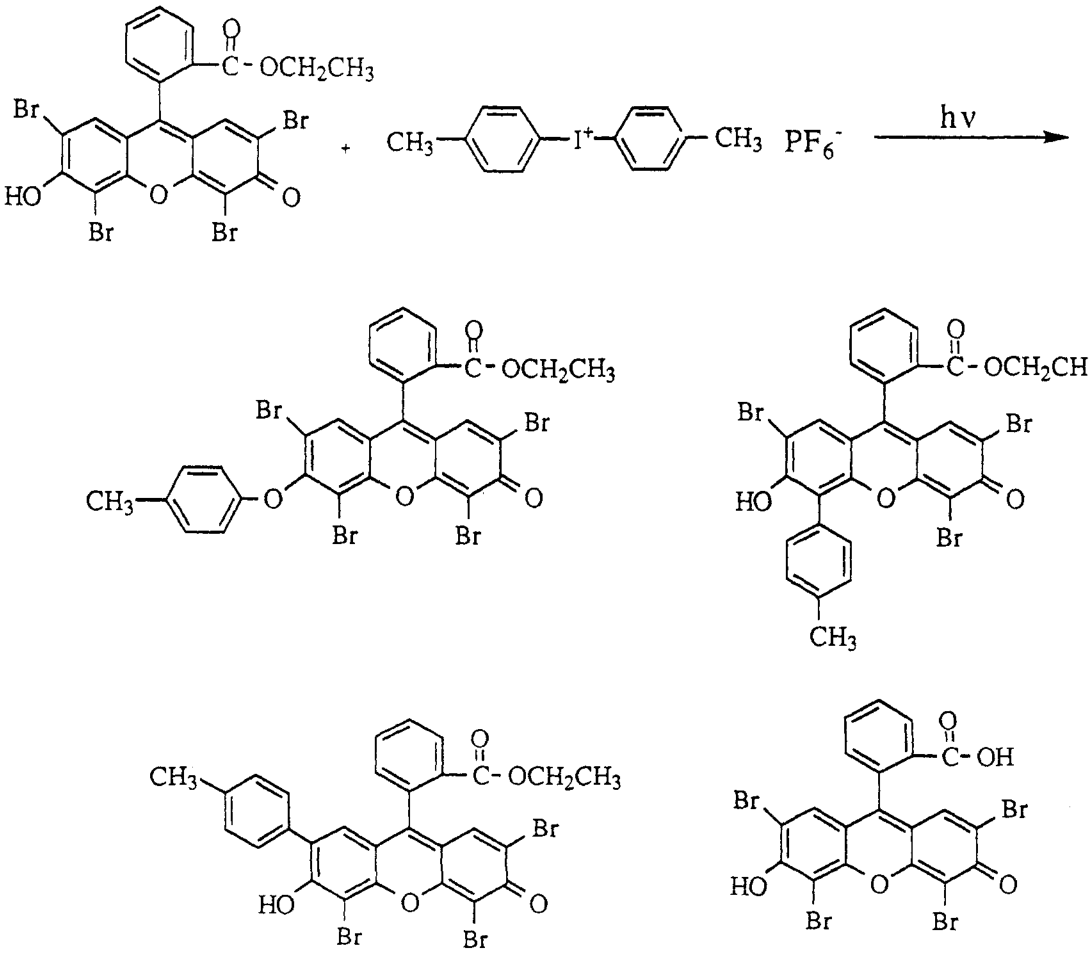


Figure 12. Products of the photochemical reaction between ethyl eosin and iodonium salts.

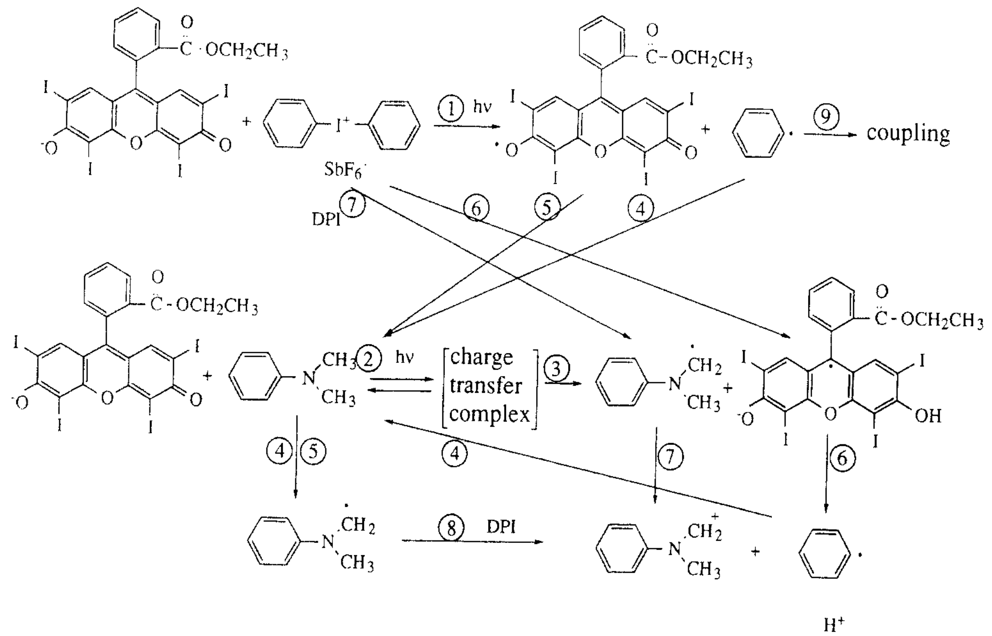
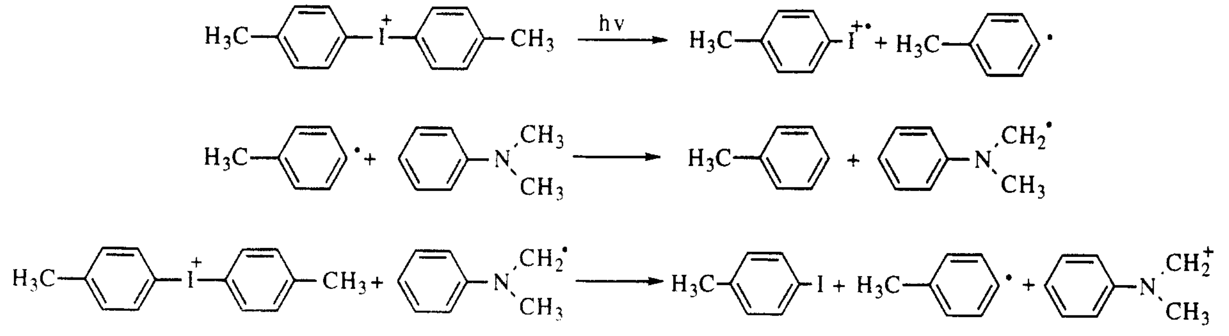


Figure 13. Interaction diagram of ethyl erythrosin/DPI/DMA upon visible light irradiation.

Chart 2



does not cause the dye to bleach, although flash photolysis shows that the amine quenches the triplet states of the dye as efficiently as does the iodonium salt. This indicates both that the electron transfer and the back electron transfer (reaction 2 in Figure 13) are very fast processes in the case of aromatic amine quenching of dye triplet.

Irradiation of an acetonitrile solution of a diphenyl iodonium salt with *N*,*N*-dimethylaniline[33] gives bis-(4,4′-dimethylaminophenyl)methane as the main product and crystal violet and methyl violet as well as the leuco forms of these dyes as minor products. This indicates that the α-amino radical is oxidized into α-aminocarbocation (see Chart 2).

End group analysis[34] by passing the photoinitiated polycyclohexene oxide solution through a series of GPC columns and then detecting the fluorescence and absorbance as well as the refractive index of the polymer demonstrates that both the aniline and dye molecules are incorporated into the polymer. The details of this analysis are presented in the subsequent publication.

Having considered all the possible reactions we propose the mechanism of initiation as shown in Figure 13.

Though we cannot rule out proton initiated polymerization in some small number of cases, it appears that the α-aminocarbocation is mainly responsible for initiation of cationic polymerization because the route of reaction 1 → 4,5 → 8 is favored as compared to 2 → 3 → 6, 7 in which the back electron transfer hinders the free radical formation. Once the radicals are generated, a chain reaction between the diaryliodonium salt and the coinitiator, e.g., the *N*,*N*-dimethylamines, is triggered. Large quantities of reactive cations are produced, and an explosive polymerization results. The dye is incorporated into the polymer mainly by a termination process, although it is essential to the initiation step.

Conclusion

It is clear that in a system consisting of a xanthene dye, a coinitiator, and an oxidative onium salt with a nonnucleophilic anion, the dye functions as a photon acceptor and, together with the coinitiator, produces radicals from visible light. The onium salts are responsible for oxidizing some of the formed radicals to the carbocations, and the latter are responsible for the initiation of cationic polymerization. No polymerization occurs in the absence of any of the three components upon irradiation with visible light (>520 nm) under the described experimental conditions, and every component is essential to this initiating system.

The system in unique in the following ways.

(1) The presence of the dye enables the sensitivity of the cationic initiator to be extended to a majority of visible wavelengths. Sensitivity can be easily adjusted by selecting xanthene dyes with the required absorption maxima.

(2) Since cationic polymerization occurs in the presence of aromatic amines, aromatic amines, if of low basicity, do not always need be terminators of cation polymer chains. A nonnucleophilic amine can be a coinitiator for the polymerization of monomers containing reactive epoxy functions.

(3) The system is relatively stable in the dark, and reactivity can be controlled by selecting an aromatic amine coinitiator with both suitable basicity and oxidation

potential. Substitution on the aromatic ring greatly influences the coinitiator's properties. The polymerization can be made very efficient by choosing suitable iodonium salts and coinitiators, and an explosive polymerization can be achieved for the photopolymerization of cyclohexene oxide under certain conditions.

(4) As has been mentioned in the introduction, acridine yellow and setoflavin T have been found[9] to be efficient sensitizers for the cationic polymerization of some epoxides. These dyes absorb in the longer wavelength region of the spectrum and also possess dimethylamino groups on their aromatic rings. Although both energy-transfer and electron-transfer sensitization have been proposed, we believe the sensitization process may involve similar reactions to those we have described. But our systems provide the freedom to select more efficient dyes, i.e., dyes with different absorption wavelengths and reactivity, more efficient donors, and reasonable ratios of their concentrations to reach maximum efficiency.

Acknowledgment. This work has been supported by the Office of Naval Research (N0014-91-J-1921). The authors are grateful for their support.

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