Photosensitized Onium-Salt-Induced Cationic Polymerization with Hydroxymethylated Polynuclear Aromatic Hydrocarbons

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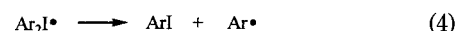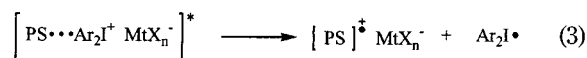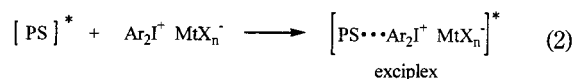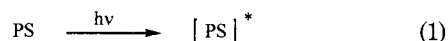
The modification of polynuclear aromatic hydrocarbons by fitting them with hydroxymethyl groups provides a new class of efficient electron-transfer photosensitizers for photoinitiated cationic polymerization that perform several additional highly useful functions. Not only are these compounds capable of photosensitizing the photolysis of a wide variety of onium salt photoinitiators in the long-wavelength UV and visible regions, but the presence of the hydroxymethyl group accelerates the rate of cationic polymerization of many types of vinyl and heterocyclic monomers. In addition, the new photosensitizers become bound as end groups to the chains of the polymers that are formed.
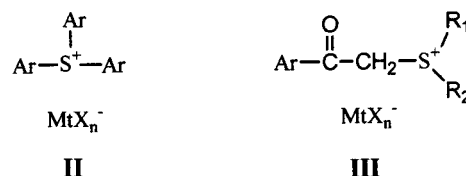
Introduction

As part of the continuing effort to reduce the environmental impact of various industrial chemical processes, there has been a strong emphasis on the devlopment of new methodologies for the application and curing of organic coatings. These ubiquitous materials are absolutely essential to modern life, and yet, they constitute one of the primary industrial sources of emissions of volatile organic solvents that contribute to air and water pollution. The use of photopolymerizations for the fabrication of decorative and protective organic coatings is one solution to this problem that is receiving increasing acceptance as this technology matures and as more users gain experience in applying it to their specific requirements.[1] In a series of publications from this laboratory,[2−4] the development of electron-transfer photosensitizers for onium-salt-induced cationic photopolymerizations was described. The use of photosensitizers is critical to the success of cationic photopolymerizations in many applications in which photopolymerizations are employed. When broad-band-emitting light sources are used, the additional spectral sensitivity provided by a photosensitizer often permits the capture of a higher fraction of the available light emitted from most common UV irradiation sources. As a result, more efficient photolysis of the photoinitiator takes place, generating a larger number of initiating species and producing an apparent acceleration of the rate of

Scheme 1

$$PS \xrightarrow{h\nu} [PS]^* \qquad (1)$$

$$[PS]^* + Ar_2I^+ \, MtX_n^- \longrightarrow \left[PS{\cdots}Ar_2I^+ \, MtX_n^-\right]^* \qquad (2)$$
$$\text{exciplex}$$

$$\left[PS{\cdots}Ar_2I^+ \, MtX_n^-\right]^* \longrightarrow [PS]^{\ddagger} \, MtX_n^- + Ar_2I\bullet \qquad (3)$$

$$Ar_2I\bullet \longrightarrow ArI + Ar\bullet \qquad (4)$$

polymerization of the monomer as compared to the rate when the photosensitizer is absent. In addition, there is currently a tendency toward the use of monochromatic light sources such as lasers and light-emitting diodes for imaging applications. A photosensitizer might be necessary to provide photosensitivity when such light sources emit at wavelengths not absorbed by the photoinitiator.

Shown in Scheme 1 is a generalized mechanism proposed for the electron-transfer photosensitization of diaryliodonium salts (**I**). In Scheme 1, MtX_n^- represents a weakly nucleophilic counterion such as BF_4^-, PF_6^-, or SbF_6^-. Analogous mechanisms can be written for the photosensitization of triarylsulfonium (**II**) and dialkylphenacylsulfonium (**III**) salt photoinitiators.

$$Ar-\overset{\displaystyle Ar}{\underset{\displaystyle MtX_n^-}{S^+}}-Ar \qquad\qquad Ar-\overset{O}{\overset{\|}{C}}-CH_2-\overset{R_1}{\underset{R_2}{S^+}} \\ MtX_n^-$$

II **III**

Electron-transfer photosensitization involves, first, absorption of light by the photosensitizer to give the

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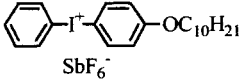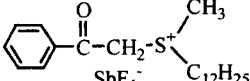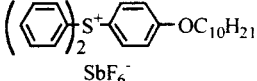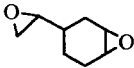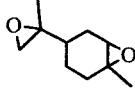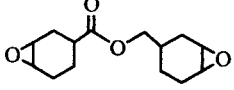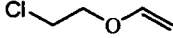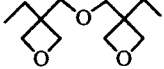
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Table 1. Structures of Photoinitiators and Monomers

Photoinitiators		
IOC10 (4-n-decyloxyphenyl)phenyl-iodonium SbF$_6^-$	**DPS-C$_1$C$_{12}$** S-methyl-S-n-dodecyl phenacylsulfonium SbF$_6^-$	**SOC10** (4-n-decyloxyphenyl)diphenyl-sulfonium SbF$_6^-$

Monomers		
VCDO 4-vinylcyclohexene dioxide	**LDO** limonene dioxide	**CHO** cyclohexene oxide
ERL 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexanecarboxylate	**CEVE** 2-chloroethyl vinyl ether	**BOX** bis(3-ethyl-3-oxetanylmethyl)ether

corresponding excited species [PS]* (eq 1). An excited-state complex (exciplex) is often formed as an intermediate between the onium salt and the excited photosensitizer (eq 2). Subsequently, the onium salt is reduced by a formal electron transfer between the two reaction partners (eq 3). The rapid decomposition of the resulting unstable diaryliodine free radical (eq 4) prevents back electron transfer and renders the overall sequence of reactions irreversible. Because of their lower reduction potentials, diaryliodonium salts are more easily photosensitized by an electron-transfer process than triarylsulfonium or dialkylphenacylsulfonium salts.[5] Chen et al.[6] and we[7,8] have described studies of the photosensitized photolysis of onium salts by various monomeric and polymeric compounds containing the carbazole nucleus. Phenothiazine derivatives have also been reported as a new class of photosensitizers that can be employed for the above-mentioned (**I–III**) classes of onium salt photoinitiators.[9–12] Among the most efficient photosensitizers for onium salts that have been discovered are electron-rich polynuclear aromatic compounds such as anthracene, pyrene, and perylene (dibenz[de,kl]anthracene).[13] Despite the many potential applications for members of this latter class of photosensitizers, they have received little attention. This results from three major deficits associated with these compounds. First, they tend to be poorly soluble in most monomers, and second, many unmodified polynuclear aromatic hydrocarbons are toxic. Last, some of these compounds have high vapor pressures at room temperature and are easily lost from thin film coatings during polymerization.

Accordingly, a program of research was undertaken to address the above-mentioned deficits associated with polynuclear aromatic hydrocarbon photosensitizers. In this article, we report the results of those investigations

that have led to the development of a novel class of highly reactive photosensitizers for onium salt photolysis.

Experimental Section

Materials. Benzyl alcohol, 9-fluorenemethanol, 9-anthracene-methanol, 2-chloroethylvinyl ether, cyclohexene oxide and 4-vinylcyclohexene dioxide (VCDO) employed in this investigation were used as purchased from the Aldrich Chemical Co. (Milwaukee, WI) unless otherwise noted. Bis(3-ethyl-3-oxetanylmethyl) ether was kindly supplied by Toagosei Chemical Company, Ltd. (Nagoya, Japan). Limonene dioxide (LDO) was obtained as a gift from the Witco Chemical Co. (Blooming Prairie, MN). 3,4-Epoxycyclohexylmethyl-3′,4′-epoxycyclo-hexancarboxylate (ERL-4221E, ERL) was purchased from the Union Carbide Corp. (Bound Brook, NJ). The onium salt cationic photoinitiators (4-n-decyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC10),[14] (4-n-decyloxyphenyl)diphenylsulfonium hexafluoroantimonate (SOC10),[15] and S-methyl-*S-n*-dodecylphenacylsulfonium hexafluoroantimonate (DPS−C$_1$C$_{12}$)[16] were prepared as described previously. The structures of the respective monomers and photoinitiators are shown in Table 1. ^{1}H NMR spectra were obtained using a

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Varian XL 500-MHz spectrometer at room temperature in CDCl$_3$ using tetramethylsilane as the internal standard.

Preparation of 3-Perylenemethanol and 1-Pyrenemethanol. To a 250-mL three-necked round-bottom flask containing *N*-methylformanilide (11.0 g, 0.081 mol) and freshly distilled *o*-dichlorobenzene (20 mL) was added phosphorus oxychloride (11.0 g, 0.072 mol). The mixture was stirred at room temperature under N$_2$ for 15 min. Perylene (8.8 g, 0.035 mol) was added into the flask, and the reaction mixture was stirred at 80–85 °C under N$_2$ atmosphere for 18 h. A concentrated aqueous solution of sodium acetate (50 g) was added, and then the mixture was stirred for 2 h. The mixture was extracted with dichloromethane (10 × 200 mL). The extractions were combined, washed with distilled water (4 × 500 mL), and then dried over anhydrous sodium sulfate. The dried intensely violet colored solution was concentrated to about 200 mL and left on the bench overnight. A yellow-brown crystalline solid (6.5 g) was obtained. The mother liquor was concentrated to give an additional 2.0 g of 3-perylenecarboxaldehyde, melting point 232–234 °C (lit. 236 °C).[17]

^{1}H NMR δ (CDCl$_3$): 10.29 (s, 1H), 9.14 (d, J = 8.5 Hz, 1H), 8.3–8.20 (m, 4H), 7.89 (d, J = 7.8 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.73 (d, J = 8.1 Hz, 1H), 7.66 (t, J = 7.7 Hz, 1H), 7.58–7.48 (m, 2H).

A 250-mL three-necked round-bottom flask was charged with 3-perylenecarboxaldehyde (3.0 g, 0.011 mol), sodium borohydride (2.2 g, 0.058 mol), and dried THF (60 mL). The mixture was stirred at 80 °C (oil bath) under N$_2$ atmosphere for 15 h. The flask was cooled in an ice–water bath, and 1 M HCl solution was slowly added until no reaction was observed (~50 mL). After the mixture was extracted with dichloromethane (4 × 300 mL), the extractions were combined, washed with 3% Na$_2$CO$_3$ (100 mL) and distilled water (4 × 400 mL), and then dried over anhydrous sodium sulfate. The dried red solution was concentrated to about 50 mL and cooled in a freezer overnight. A brown solid (2.3 g) was obtained having a melting point of 207–209 °C.

^{1}H NMR δ (CDCl$_3$): 8.20 (d, J = 7.6 Hz, 1H), 8.17 (d, J = 7.5 Hz, 2H), 8.12 (d, J = 7.8 Hz, 1H), 7.92 (d, J = 8.3 Hz, 1H), 7.68 (d, J = 8.1 Hz, 2H), 7.56–7.44 (m, 4H), 5.07 (d, J = 5.6 Hz, 2H), 1.76 (t, J = 5.8 Hz, 1H).

Elemental analysis. Calcd for C$_{17}$H$_{12}$O (%): C, 87.90; H, 5.21. Found (%): C, 87.67; H, 5.45.

In a similar manner, 1-pyrenecarboxaldehyde was prepared using the method of Buckley et al.[18] and employing *N*-methylformanilide instead of *N*-methylformamide. After reduction with sodium borohydride, 1-pyrenemethanol was obtained, mp 122–124 °C (lit. 125–126 °C[19]). The ^{1}H NMR spectrum of this compound corresponded in all respects to that of a sample obtained from the Aldrich Chemical Co.

Elemental analysis. Calcd for C$_{21}$H$_{14}$O (%): C, 89.36; H, 5.00. Found (%): C, 89.55; H, 5.15.

Photopolymerization of Cyclohexene Oxide. Into a dry vial was placed 0.98 g of cyclohexene oxide in which was dissolved 0.1 mol % IOC10 and 2.0 mol % 1-pyrenemethanol. The mixture was degassed using a stream of nitrogen and sealed with a rubber septum. Irradiation of the sample was conducted for 10 min at room temperature in a Rayonet ultraviolet irradiator (Southern New England Ultraviolet Co.) equipped with 16 lamps with an emission centered at 300 nm. Then, the semisolid polymer was dissolved in dichloromethane containing a drop of triethylamine and precipitated into methanol. This process was repeated two more times to ensure the removal of small-molecule starting materials and products. Finally, the polymer was dried overnight in a vacuum oven and dissolved in THF, and the UV spectrum was recorded.

Studies of the Rates of Photoinitiated Ring-Opening Cationic Epoxide Polymerization by Fourier Transform

Real-Time IR Spectroscopy (FT-RTIR). The kinetics of the direct and photosensitized cationic photopolymerizations of various epoxy monomers were monitored using FT-RTIR spectroscopy. The configuration of the apparatus used in our experiments has been described previously.[20] A Midac M-1300 FT-IR spectrometer equipped with a liquid-nitrogen-cooled Hg–Cd–Te detector was fitted with a UVEX model SCU-110 mercury lamp in which the light is carried through a flexible wand to the sample compartment. The end of the wand was placed at a predetermined distance from and directed at an incident angle of 45° onto the sample window. The intensity of UV irradiation was measured with a UV Process Supply Inc. Control Cure Radiometer. All kinetic experiments in this investigation were conducted at 25 °C at such light intensities as to permit convenient monitoring and analysis of the data.

Samples for kinetic analysis were prepared as follows: A homogeneous solution of the subject monomer with the designated photoinitiator and photosensitizer was prepared (all concentrations are given in mole percentages with respect to monomer unless otherwise noted). The solutions were spread as thin films between two layers of 12-μm corona-treated oriented polypropylene film and then mounted in 2 cm × 2 cm plastic slide holders. The reproducibility of the sample thickness between various samples was checked by monitoring the peak-to-peak distance recorded by the interferometer. During the photopolymerization, various infrared absorption bands were monitored depending on the specific functional group in the monomer used (VCDO, 926 cm^{-1}; LDO, 800 cm^{-1}; CHO, 781 cm^{-1}; ERL, 750 cm^{-1}; CEVE, 1620 cm^{-1}; BOX, 829 cm^{-1}). Data were collected at a rate of one spectrum per second. Then, the spectral data were converted to conversion versus time curves and plotted using Midac Grams/386 software.

The kinetic parameter, $R_p/[M_o]$, for selected kinetic runs was determined from the slopes of the initial linear portions of the irradiation time–conversion curves according to eq 5.

$$R_p/[M_o] = ([\text{conversion}]_{t_2} - [\text{conversion}]_{t_1})/(t_2 - t_1) \quad (5)$$

where R_p and $[M_o]$ are the rate of polymerization and the initial monomer concentration, respectively, and the conversions are as determined from the curves at irradiation times t_1 and t_2.

Results and Discussion

The stated objective of the work reported in this article is to explore means whereby polynuclear aromatic hydrocarbons can be employed as photosensitizers for onium-salt-mediated cationic photopolymerizations. Despite the drawbacks outlined in the Introduction portion of this paper, polynuclear aromatic hydrocarbons have the advantage that they are readily available and, in many cases, inexpensive starting materials. Further, these compounds generally have very rich and strongly absorbing UV and visible absorption spectra with the potential for sensitization in the very important long-wavelength UV and visible regions. It was our goal to attempt to modify these compounds by fitting them with functional groups that would promote solubility and decrease toxicity. At the same time, it was important to avoid those modifications that could potentially interfere with their absorption and photosensitization characteristics.

As noted in Scheme 1, photosensitization by an electron-transfer mechanism involves the oxidation of the excited photosensitizer by an onium salt to the corresponding cation-radical. The well-known Rehm–Weller equation (eq 6) sets forth the thermodynamic

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requirements necessary for photoinduced electron transfer to take place in any given system.[21]

$$\Delta G = E_{sens}^{*ox} - E_{onium}^{red} \tag{6}$$

The free energy of electron transfer is equal to the difference in the oxidation potential of the excited photosensitizer and the reduction potential of the onium salt (eq 6). The oxidation potential of the excited photosensitizer can be estimated as shown in eq 7 from the difference in the oxidation potential of the photosensitizer and its excited-state energy.

$$E_{sens}^{*ox} = E_{sens}^{ox} - E_{sens}^{*} \tag{7}$$

In all cases, a negative free energy (ΔG) of at least 10 kcal/mol is required for efficient electron transfer to occur. Therefore, to maximize the free energy, it is essential that the photoexcited aromatic hydrocarbons have low oxidation potentials. Substitutents on the rings of a polynuclear aromatic hydrocarbon would be expected to play an important role in determining the magnitude of the oxidation potential. Electron-donating substituents should contribute to a lower oxidation potential in the parent photosensitizer and also stabilize the cation-radical that results from electron transfer. At the same time, electron-withdrawing substituents should correspondingly destabilize these latter species and raise the oxidation potential. For these reasons, we sought convenient, straightforward, and high-yield methods for introducing electron-donating substitutents onto the rings of polynuclear aromatic hydrocarbons.

A survey of the literature revealed that the Vilsmeier reaction has been used to formylate several different polynuclear aromatic hydrocarbons in good to excellent yields. For example, Buckley and Thomas[18] and de Clercq and Martin[19] reported that pyrene was formylated in nearly quantitative yield by treatment with phosphorus oxychloride in the presence of *N*-methylformanilide to give 1-pyrenecarboxaldehyde (eq 8).
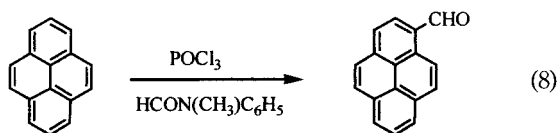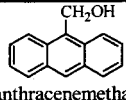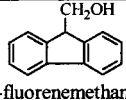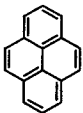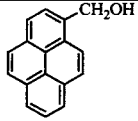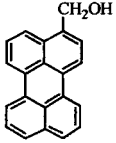

Attempts in this laboratory to introduce a second formyl group into pyrene using this same reaction failed. Because the formyl group has electron-withdrawing characteristics, conversion by reduction with sodium borohydride to the corresponding 1-pyrenemethanol was carried out (eq 9).
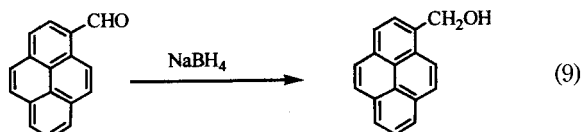
In contrast, the formylation of perylene in the presence of *N*-methylformanilide gave only a low yield of the

Table 2. Structures and Spectral Characteristics of Hydroxymethylated Polynuclear Aromatic Hydrocarbons[a]

Photosensitizer	m.p. (°C)	λ_{max} (nm)	ε	Reference
CH$_2$OH ... 9-anthracenemethanol	162-164[c]	247 322.5 338.5 357 376.5	146600 2890 5650 8330 7840	22
CH$_2$OH ... 9-fluorenemethanol	105-107[c]	220.5 228 265 289 300	16800 6670 19600 5490 7100	23
pyrene	149-151[c]	230.5 239.5 251 261 271 294 305 318 333.5	43400 85100 11800 24400 49800 2680 6910 17600 29400	24
CH$_2$OH ... 1-pyrenemethanol	122-124 123-126[c]	234 243 255 265 276 313 327 343	49430 79880 15450 31090 56700 14470 32100 47030	18,19
CH$_2$OH ... 3-perylenemethanol	207-209	211[b] 255 392 414 441	72880 47810 13300 28180 36780	

[a] Measured in methanol. [b] Measured in THF. [c] Aldrich Handbook of Fine Chemicals and Laboratory Equipment, 2000−2001.

corresponding 3-perylenecarboxaldehyde. However, this compound was readily prepared in good yield by the treatment of perylene with phosphorus oxychloride in *N*-methylformamide.[18] Straightforward reduction of 3-formylperylene with sodium borohydride gave 3-perylenemethanol. 9-Anthracenemethanol and 9-fluorenemethanol were obtained from commercial sources. Table 2 shows the structures, melting points, and UV spectral characteristics of these compounds.

In general, the melting points of the hydroxymethylated compounds that appear in this table are lower than their corresponding parent hydrocarbon precursors and this is also indicative of the enhanced solubility of these former compounds. It is interesting to note that these compounds have UV absorption characteristics that are similar to those of their parent hydrocarbons (perylene is included in this table as an example) and that they provide a large number of bands with appreciable molar absorption coefficients in the long-wavelength UV and visible regions. It can further be observed that, as the number of aromatic rings in a polynuclear hydrocarbon increases, these absorption bands shift to longer wavelengths.

Penczek, Kubisa, and their co-workers[22−29] have reported that alcohols undergo interactions with epoxides during Brønsted-acid-catalyzed ring-opening cat-
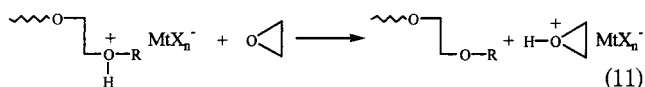
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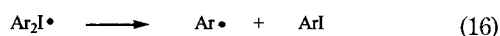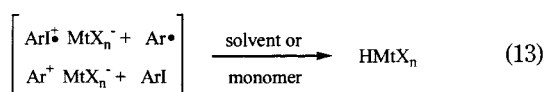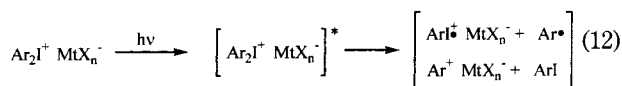(23) Reference 21, Spectrum 19037.

ionic polymerizations by a mechanism they have termed "the activated monomer mechanism". In this mechanism, shown in eqs 10 and 11 (Scheme 2), the propagating oxonium ion species are intercepted by alcohols to give ethers (eq 10).

Scheme 2

$$ROH \ + \ \sim\sim O^+ \hspace{-2pt}\triangleleft \ MtX_n^- \ \longrightarrow \ \sim\sim O\underset{H}{\overset{+}{\underset{|}{O}}}\!-\!R \ \ MtX_n^- \quad (10)$$

$$\sim\sim O\underset{H}{\overset{+}{\underset{|}{O}}}\!-\!R \ \ MtX_n^- \ + \ O\triangleleft \ \longrightarrow \ \sim\sim O\underset{}{\overset{}{\underset{}{O}}}\!-\!R \ + \ H\!-\!O^+\hspace{-2pt}\triangleleft \ MtX_n^- \quad (11)$$

The rapid transfer of a proton from the growing polymer chain end to the monomer (eq 11) results in a chain process in which the propagating species is the protonated epoxide monomer. Simultaneously, the starting alcohol becomes bound to one end of the polymer chain as an ether group. Following the work of Penczek and Kubisa, we have described the use of alcohols as accelerators in the onium-salt-photoinitiated polymerizations of epoxide monomers.[30] Recently, in a publication from this laboratory,[31] it was reported that benzyl alcohols display enhanced rate-accelerating characteristics for these same photopolymerizations. This effect was explained on the basis of the ability of the resulting benzyl ether adducts to participate in a free-radical chain-induced process that results in the decomposition of the onium salt with the cogeneration of cationic species.[32,33] Details of the proposed mechanism are illustrated in Scheme 3 using diaryliodonium salts as the onium salt photoinitiator.

Scheme 3

$$Ar_2I^+ \ MtX_n^- \ \xrightarrow{h\nu} \ \left[Ar_2I^+ \ MtX_n^-\right]^* \ \longrightarrow \ \begin{bmatrix} ArI^{+\bullet} \ MtX_n^- \ + \ Ar\bullet \\ Ar^+ \ MtX_n^- \ + \ ArI \end{bmatrix} \quad (12)$$

$$\begin{bmatrix} ArI^{+\bullet} \ MtX_n^- \ + \ Ar\bullet \\ Ar^+ \ MtX_n^- \ + \ ArI \end{bmatrix} \ \xrightarrow[\text{monomer}]{\text{solvent or}} \ HMtX_n \quad (13)$$

$$Ar\bullet \ + \ RH \ \longrightarrow \ ArH \ + \ R\bullet \quad (14)$$

$$Ar_2I^+ MtX_n^- \ + \ R\bullet \ \longrightarrow \ Ar_2I\bullet \ + \ R^+ MtX_n^- \quad (15)$$

$$Ar_2I\bullet \ \longrightarrow \ Ar\bullet \ + \ ArI \quad (16)$$

$$R^+ MtX_n^- \ + \ nM \ \longrightarrow \ R\text{-}(M)_{n-1}M^+ MtX_n^- \quad (17)$$

On photolysis, diaryliodonium salts undergo fragmentation (eq 12) to yield a variety of species including cations, cation-radicals, and radicals. The cationic species can attack the nucleophilic monomer to directly initiate polymerization, or more commonly, they interact with the monomer, solvent, or traces of protonic impurities present in the reaction mixture to give strong Brønsted acids (eq 13) that serve to initiate polymerization. Aryl radicals are also produced during the course of photolysis (eq 12) that can abstract hydrogen atoms from various hydrogen-donor sources including the monomer (eq 14). If the new radical species, R·, is so designed that it can undergo oxidation, a cation is generated by reaction with the onium salt (eq 15), along with a diaryliodine free radical. Subsequently, the cations so generated can also initiate the cationic polymerization of the monomer (eq 17), while the diaryliodine free radical undegoes further fragmentation to generate an aryliodide and an aryl free radical (eq 16). The overall process (eqs 14–17) defines a photochemically radical-induced chain reaction that catalytically consumes the onium salt while generating cations. We have shown that it is possible to design monomers that function especially well as hydrogen donors in the above process and, as a result, exhibit very high reactivity in photoinitiated cationic polymerization.[34]

Judging from the above discussion, we proposed that the hydroxymethyl-functionallized photosensitizers shown in Table 2 should provide several simultaneous functions when applied to the cationic ring-opening photopolymerization of cyclic ethers such as epoxides and oxetanes. First, the hydroxymethylated polynuclear hydrocarbon should function as an electron-transfer photosensitizer for the onium salt. Second, the presence of the polar alcohol group should contribute to enhanced solubility of the photosensitizers in the monomers. Third, these compounds would be expected to accelerate the polymerization of these monomers through their ability to participate in the activated monomer mechanism. Especially in those cases where multifunctional monomers are employed, the photosensitizers should provide both higher conversions through chain transfer and a delay of the onset of cross-linking. Fourth, the benzylic ethers that result from condensation with the monomer during polymerization can also participate in the free-radical-induced chain decomposition of the onium salt photoinitiator as noted in Scheme 2. Last, the ability of these photosensitizers to form ethers should covalently bind them as end groups into the polymers that are formed, reducing their toxicity and volatility. It is further expected that the polymer-bound benzylic ethers that are formed will have substantially the same UV absorption characteristics as the parent hydroxymethyl compounds and likewise provide a photosensitizing function.

To test the validity of these proposed effects, a systematic investigation of the cationic ring-opening polymerization of several subject monomers was carried

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Table 3. Kinetic Data for Photosensitized Polymerizations

entry	monomer	photosensitizer	conc (mol %)	photoinitiator, conc (mol %)	light intensity [mJ/(cm² min)]	$R_p/[M]_o$ (min⁻¹)	AF
1		1-pyrenemethanol	6.7			13	10
2	VCDO	9-anthracenemethanol	6.7	IOC10, 0.67	175	4.5	3.5
3		none	−			1.3	−
4		1-pyrenemethanol	6.0			11	4.6
5	VCDO	benzyl alcohol	6.0	SOC10, 0.6	180	3.7	1.6
6		none	−			2.3	−
7		1-pyrenemethanol	6.0			9.5	4.1
8	LDO	9-anthracenemethanol	6.0	SOC10, 0.6	173	2.3	1.0
9		none	−			2.3	−
10	CY179	1-pyrenemethanol	6.0	SOC10, 1.0	1250	2.0	9.0
11		none	−			0.23	−
12	VCDO	1-pyrenemethanol	2.0	IOC10, 0.7	176	15	7.0
13		none	−			2.2	−
14	VCDO	1-pyrenemethanol	0.5	IOC10, 0.7	85	8.6	7.2
15		none	−			1.2	−
16		1-pyrenemethanol	6.0			3.9	2.1
17	VCDO	9-anthracenemethanol	6.0	DPS−C₁C₁₂, 0.6	180	2.5	1.4
18		none	−			1.8	−
19	VCDO	9-fluorenemethanol	2.0	IOC10, 0.7	76	2.1	1.7
20		none	−			1.2	−
21			0.5			20	16
22	VCDO	3-perylenemethanol	0.2	IOC10, 0.1	377	18	15
23			−			1.2	−
24	CHO	3-perylenemethanol	0.2	IOC10, 0.01	178	24	11
25						2.1	−

out in the presence of the hydroxymethylated poly-nuclear hydrocarbon photosensitizers shown in Table 2. The cationic photopolymerizations of several vinyl and ring-opening monomers were monitored using Fourier transform real-time infrared spectroscopy (FT-RTIR). Employing this technique, which has been well-documented in the literature,[35,36] polymerizations were carried out in the presence and absence of the above-described photosensitizers. The initial slopes of the conversion versus time plots ($R_p/[M_o]$) were obtained and are directly proportional to the rates of polymerization. Using these values, we determined an acceleration factor, AF, for each photosensitizer−monomer and photoinitiator combination, where AF is the ratio of the rate of epoxide ring-opening polymerization in the presence of the photosensitizer to the rate in its absence (eq 18).

$$AF = \frac{R_p/[M_o]_{(sens)}}{R_p/[M_o]} = R_{p(sens)}/R_p \qquad (18)$$

The data obtained in these studies are tabulated in Table 3, along with a description of the experimental conditions under which they were obtained.

Figure 1 shows the results of a study in which 1-pyrenemethanol and 9-anthracenemethanol were compared as photosensitizers in the polymerization of the difunctional epoxide monomer 4-vinylcyclohexene dioxide (VCDO) using IOC10 as the photoinitiator. Also included in this figure for comparison is a kinetic curve in which no photosensitizer was used. Even at the low light intensity used [175 mJ/(cm² min)] using broad-band UV irradiation, considerable enhancement (Table 3, entries 1 and 2; AF = 10, 1-pyrenemethanol; AF =
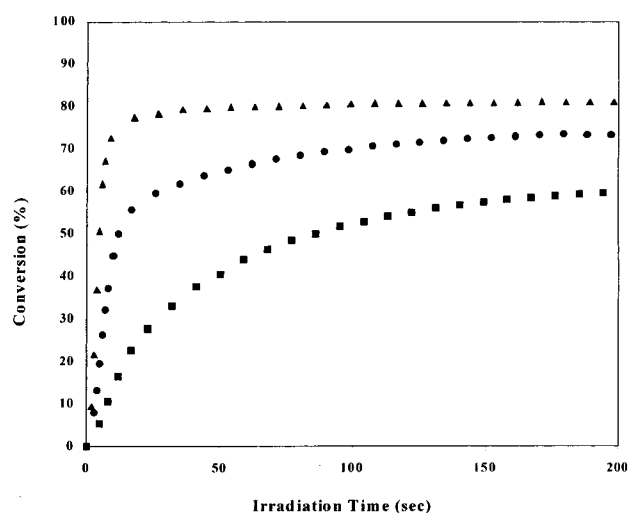

Figure 1. Study of the cationic photopolymerization of 4-vinylcyclohexene dioxide in the presence of 6.7% pyrene-methanol (▲), 6.7% 9-anthracene methanol (●), and without a photosensitizer (■) [0.67% IOC10, light intensity 175 mJ/(cm² min)].

3.5, 9-anthracenemethanol) of the rate of photopoly-merization was observed when the photosensitizers were employed. The broader and more intense spectrum of 1-pyrenemethanol makes it a much better photosen-sitizer than 9-anthracenemethanol. Figure 2 compares the photopolymerizations of the same monomer using 1-pyrenemethanol with an equimolar amount of benzyl alcohol, as well as with no photosensitizer present (entries 4−6). This study was carried out using SOC10 as the photoinitiator. The considerably higher rate of photopolymerization observed for 1-pyrenemethanol as compared to benzyl alcohol can be attributed to the effect of the photosensitization and not to acceleration due to involvement of the alcohol portion of this mol-

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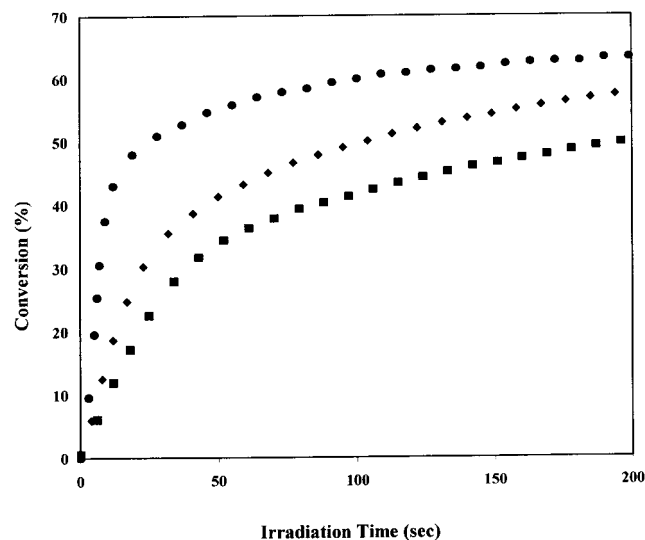(36) Decker, C. *J. Polym. Sci. A: Polym. Chem.* **1992**, *30*, 913.

Figure 2. Comparison of the effects of 6.0% 1-pyrenemethanol (●), 6.0% benzyl alcohol (◆), and no photosensitizer (■) on the photopolymerization of 4-vinylcyclohexene dioxide [0.60% SOC10, light intensity 180 mJ/(cm² min)].
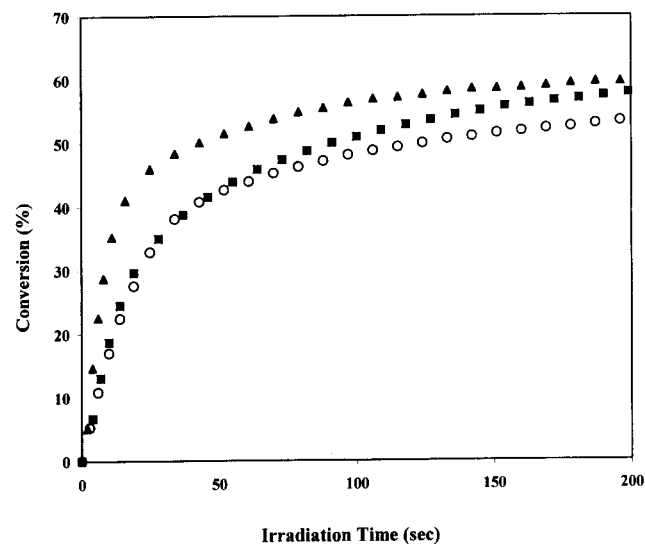

Figure 4. Kinetic study of the cationic photopolymerization of 4-vinylcyclohexene dioxide in the presence of 0% (■), 2.0% (◇), 1.0% (●), and 0.5% (▲) 1-pyrenemethanol [0.70% IOC 10, light intensity 85 mJ/(cm² min)].

Figure 3. Comparison of the effects of 6.0% 1-pyrenemethanol (▲), 6.0% benzyl alcohol (■), and no alcohol (○) on the photopolymerization of 4-vinylcyclohexene dioxide [0.60% DSP−C₁C₁₂, light intensity 180 mJ/(cm² min)].

Figure 5. FT-RTIR study of the cationic photopolymerization of 4-vinylcyclohexene dioxide in the presence of 2.0% 9-fluorenemethanol (■) and in the absence of a photosensitizer (△) (0.70% IOC10, light intensity 75.8 mJ/(cm² min)].

ecule in the activated monomer. A comparison of the rates of polymerization in the presence and absence of benzyl alcohol shows only a slight elevation of the rate in the presence of 6.0% benzyl alcohol. Previous work[31] has indicated that the acceleration of cationic ring-opening polymerizations due to either the activated monomer mechanism or the free-radical-induced decomposition mechanism requires relatively large (10−20%) amounts of benzyl alcohol. Very similar results were observed when VCDO was replaced by either limonene dioxide (LDO) (entries 7−9) or 3,4-epoxy-cyclohexylmethyl 3′,4′-epoxycyclohexanecarboxylate (ERL) (entries 10 and 11). A reduction in either the relative concentration of the photosensitizer or photoinitiator or the light intensity (entries 12−15) still produces excellent photosensitization effects using 1-pyrenemethanol. When the dialkylphenacylsulfonium salt S-methyl-S-*n*-dodecyl phenacylsulfonium hexafluoroantimonate (DPS−C₁C₁₂), was used as a photoinitiator
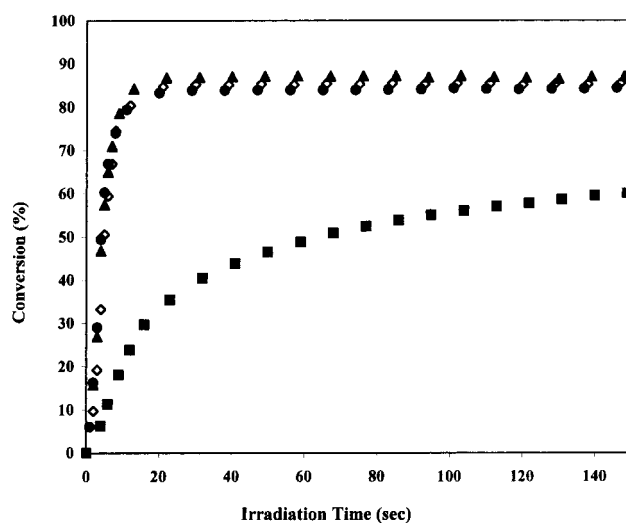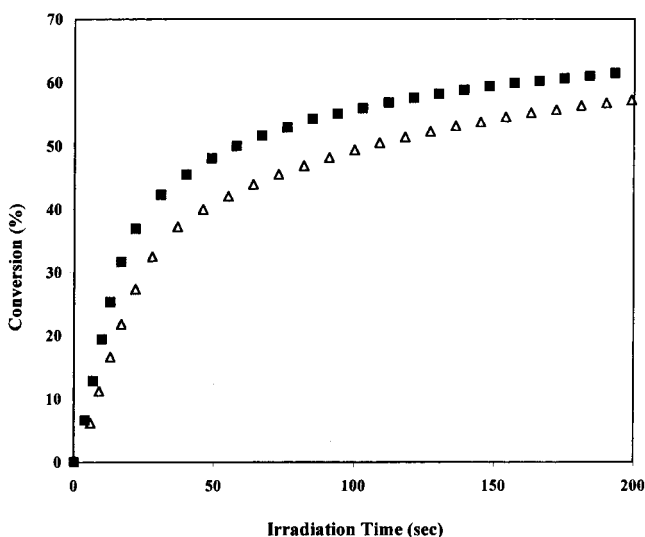
together with photosensitizer 1-pyrenemethanol (Figure 3; Table 3, entries 16−18), a rate enhancement was still observed but its magnitude was 5 times less than that observed with the IOC10 photoinitiator (entries 1 and 16). It might be noted that hydroxymethylated polynuclear hydrocarbon photosensitizers are especially advantageous as they are effective for all three types of onium salt photoinitiators used in this investigation.

In an effort to determine whether there is an optimum concentration of photosensitizer, the polymerization of 4-vinylcyclohexene dioxide was carried out using 0.5, 1.0, and 2.0% 1-pyrenemethanol together with 0.7% IOC10 as the photoinitiator. The results are given in Figure 4. A dramatic acceleration of the polymerization of this monomer is observed at all three concentrations of this photosensitizer and to very nearly the same degree. This indicates that the photosensitization effect is already saturated at 0.5% of 1-pyrenemethanol because of the high optical density of the photosensitizer in the monomer solution in the long-wavelength region
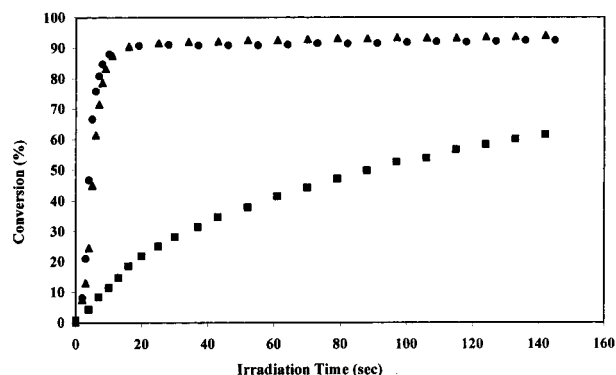
Figure 6. FT-RTIR study of the cationic photopolymerization of 4-vinylcyclohexene dioxide with 0.1 mol % IOC10 in the presence of 0% (■), 0.2% (▲), and 0.5% (●) 3-perylenemethanol [light intensity 377 mJ/(cm² min)].
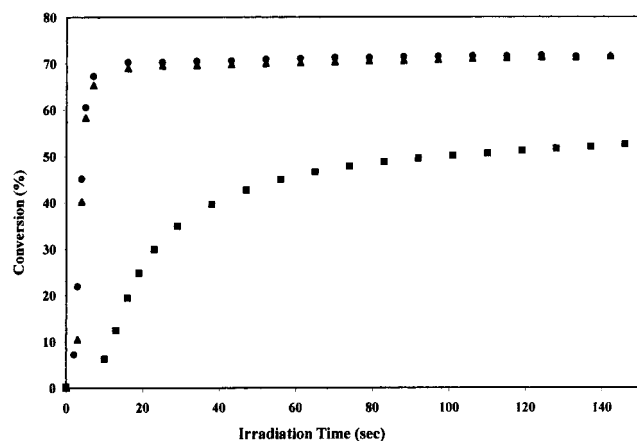

Figure 7. Kinetic study of the cationic photopolymerization of cyclohexene oxide (CHO) using 0.01% IOC10 in the absence of a photosensitizer (■) and with 0.5% (●) and 0.2% (▲) 3-perylenemethanol [light intensity 178 mJ/(cm² min)].

of the UV spectrum. It is also worth noting that the light intensity used in this study was only 85 mJ/(cm² min), and yet, the reactivity of the polymerization mixture under these conditions was still very high. In commercial systems, the light intensity is often on the order of 2000 mJ/(cm² min) or higher.

Two additional photosensitizers, 9-fluorenemethanol and 3-perylenemethanol, were evaluated, and the results are shown in Figures 5 and 6. Whereas 9-fluorenemethanol is a relatively weak photosensitizer (Table 3, entries 19 and 20; AF = 1.7), 3-perylenemethanol displays excellent photosensitization characteristics for IOC10. Essentially identical conversion versus time curves were obtained when 0.5 and 0.2% 3-perylenemethanol were used in the polymerization of VCDO. AF values of 16 and 15, respectively, were determined for these polymerizations (Table 3, entries 21 and 22). The difference between the performances of the two photosensitizers can be rationalized by a comparison of the UV absorption spectra of the two different photosensitizers, as shown in Table 2. The presence of intense, long-wavelength absorption bands in 3-perylenemethanol and their absence in 9-fluorenemethanol accounts for the large difference in their efficiencies in photosensitization. In addition, the electron-rich perylene nucleus is much more easily oxidized than the corresponding fluorene nucleus and, in addition, more readily
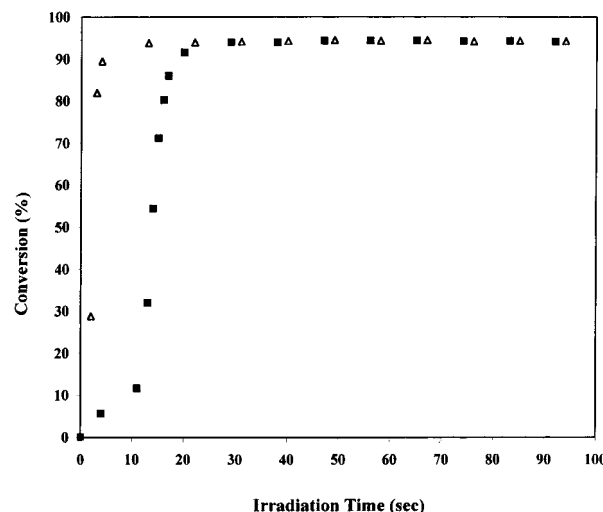

Figure 8. FT-RTIR study of the cationic photopolymerization of 2-chloroethyl vinyl ether (CEVE) with 1.0% IOC10 using 0% (■) and 0.5% (△) 1-pyrenemethanol [light intensity 194 mJ/(cm² min)].
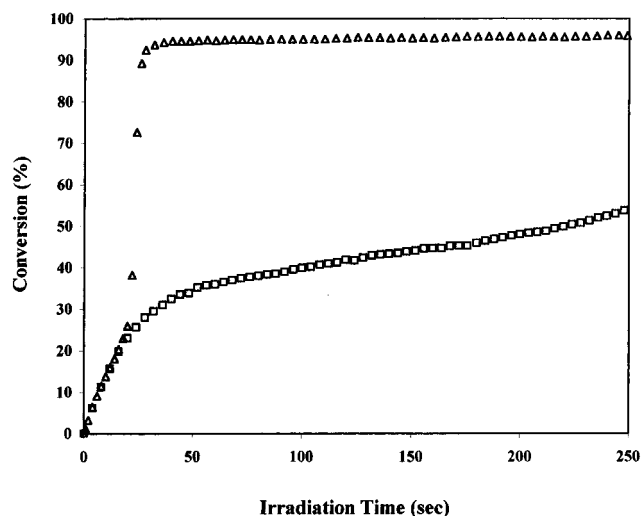

Figure 9. Photopolymerization of bis(3-ethyl-3-oxetanyl-methyl) ether in the presence of 0.5% 1-pyrenemethanol (△) and without a photosensitizer (□) [1.0% IOC10; light intensity 401 mJ/(cm² min)].

stabilizes the cation-radical that is formed. The results of an FT-RTIR study of the 3-perylenemethanol photosensitized polymerization of the monofunctional epoxide, cyclohexene oxide, are shown in Figure 7. At a concentration of 0.2 mol % of the photosensitizer, the polymerization is markedly accelerated (AF = 11) as compared to a parallel experiment in which no photosensitizer is present.

The polymerization of vinyl ethers is much more rapid than that of epoxides. Figure 8 shows the effect of photosensitization by 1-pyrenemethanol on the polymerization of 2-chloroethyl vinyl ether. This very reactive monomer contained traces of base as a polymerization inhibitor that was not removed prior to polymerization. A comparison with a control polymerization in which no photosensitizer was present reveals that, in the presence of the photosensitizer, the inhibition period is markedly reduced. This appears to be due to the photogeneration of a large amount of acid when the photosensitizer is present that rapidly consumes the

basic inhibitor. In contrast, the direct photolysis of the photoinitiator results in the slow consumption of monomer until the inhibitor is consumed. Thereafter, rapid polymerization ensues. The cationic photopolymerization of oxetanes proceeds at rates similar to those of epoxides. The photopolymerization results for the monomer bis(3-ethyl-3-oxetanylmethyl) ether (BOX) are shown in Figure 9 for the reaction carried out in the presence and absence of 1-pyrenemethanol as a photoinitiator. As in the previous case, this difunctional monomer also appears to contain traces of basic inhibitors that slow the initial portion of the polymerization. However, when the photosensitizer is used, the inhibition period is markedly shortened, and polymerization proceeds rapidly to high conversion. In contrast, the direct polymerization without the photosensitizer does not exhibit a rate acceleration, and the conversion remains low even after relatively long irradiation times.

To confirm that the hydroxymethylated polynuclear hydrocarbon photosensitizers were incorporated into the polymers that were formed, the bulk polymerization of cyclohexene oxide was carried out using IOC10 and 1-pyrenemethanol, respectively, as the photoinitiator and photosensitizer. After several dissolutions in dichloromethane and precipitations into methanol to remove low-molecular-weight species and residues of the photosensitizer, the polymers were subjected to UV spectral analysis. The presence of the strong, prominent absorption bands in the spectrum at 234, 243, 265, 276, 314, 327 and 343 nm are indicative of the incorporation of the photosensitizer into the polymer backbones.

Conclusions

A simple, direct, and efficient approach for the photosensitization of onium-salt-induced cationic polymerizations has been described. Four hydroxymethylated polynuclear aromatic hydrocarbons were formylated using the Vilsmeier reaction, and the aldehyde products were further reduced to the corresponding hydroxymethyl compounds. These modified hydrocarbon compounds are very effective at low concentrations for the photosensitization of various types of onium salt photoinitiators in the long-wavelength UV and visible regions. In addition, the photosensitizers are effective in accelerating the rates of photoinitiated cationic ring-opening epoxide and oxetane polymerizations because they can participate in the activated monomer mechanism by reaction at the hydroxymethyl groups. Moreover, these photosensitizers accelerate polymerizations by virtue of the fact that they can participate in the free-radical chain-induced decomposition of the onium salt photoinitiator. Finally, the incorporation of the photosensitizers as ether groups at the polymer chain ends is advantageous in that the photosensitizer cannot migrate once polymerization is complete. This potentially has important consequences for mitigating possible toxic effects of these agents. Among the photosensitizers studied, only 1-perylenemethanol is strongly colored. However, because this photosensitizer is required in extremely small quantities, a very pale yellow color is imparted to the cured resin. This might be tolerable for many applications.