

Development of Pyrene Photosensitizers for Cationic Photopolymerizations

James V. Crivello* and Faming Jiang

New York State Center for Polymer Synthesis, Department of Chemistry,
Rensselaer Polytechnic Institute, 110 8th Street, Troy, New York 12180

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This article describes the preparation of monomeric and oligomeric derivatives of pyrene and their use as electron-transfer photosensitizers for onium-salt-induced cationic photopolymerizations. The synthetic methods that were employed involved simple, straightforward, and high-yield routes to these derivatives. Using Fourier transform real-time infrared spectroscopy, the photoinduced polymerizations of several model epoxide monomers and a vinyl ether monomer were examined in the presence and absence of the photosensitizers. It was observed that in all cases the pyrene derivatives markedly accelerated the rates of the UV-irradiation-induced photopolymerizations. Use of the pyrene derivatives also provided sensitivity to visible light so that photopolymerizations could be carried out in a short time by exposure to direct sunlight. The pyrene compounds investigated in this study are potentially attractive photosensitizers that may find use in many practical photocuring applications.

Introduction

Over the past decade, onium salt photoinitiated cationic polymerizations have become established as both processes of commercial interest and reactions of academic interest. Although these polymerizations are useful, it has been pointed out that the rates of the photoinitiated cationic polymerizations of commercially available epoxides are lower than those of the corresponding photoinduced radical polymerizations of acrylates.¹ To overcome this drawback, it has become common practice to employ photosensitizers in combination with these photoinitiators.² The primary function of the photosensitizer is to provide enhanced sensitivity to the specific light source that is used. Most onium salts possess absorption bands that are confined to the short wavelength region of the UV spectrum. For this reason, much of the energy emitted by broadband emitting light sources such as mercury arc lamps is wasted. The use of long wavelength absorbing photosensitizers permits the capture of a higher fraction of the available emitted light from these sources. This contributes to an overall more efficient photolysis of the photoinitiator and consequently, generates a larger number of initiating species. The end result is that there is an apparent acceleration of the rate of polymerization of the monomer as compared to that when no photosensitizer is used. The accelerating effect of photosensitizers provides the possibility of several tradeoffs, such as increasing productivity, or alternatively, lowered photoinitiator concentrations with resultant lower systems costs. In

addition, monochromatic light or narrow band sources such as lasers and light-emitting diodes are being used increasingly in photoimaging and reprographic technologies. It is important to be able to "tune" the wavelength of sensitivity of onium salt photoinitiators to these emission sources. Last, the use of photosensitizers to enable the employment of solar energy to carry out photopolymerizations is of potentially considerable future importance for the fabrication of a wide assortment of items, as for example, building panels, roofs, and water delivery and sewerage systems.

There are several mechanisms by which the photosensitization of onium salts is known to take place, however, electron-transfer photosensitization is the most efficient and generally applicable process for this class of photoinitiators.^{3,4} Scheme 1 illustrates a generalized mechanism that we have proposed for the electron-transfer photosensitization of diaryliodonium salts.

In the above scheme, 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 and dialkylphenacylsulfonium salt photoinitiators.

Electron-transfer photosensitization relies on, first, the absorption of light by the photosensitizer to give the corresponding excited species $[\text{PS}]^*$ (eq 1). An excited-state complex (exciplex) is often formed as an intermediate between the onium salt and the excited photosensitizer (eq 2). Alternatively, Rodrigues and Neumann^{5,6}

* To whom correspondence should be addressed. Fax: 518-276-2690. E-mail: crivej@rpi.edu.

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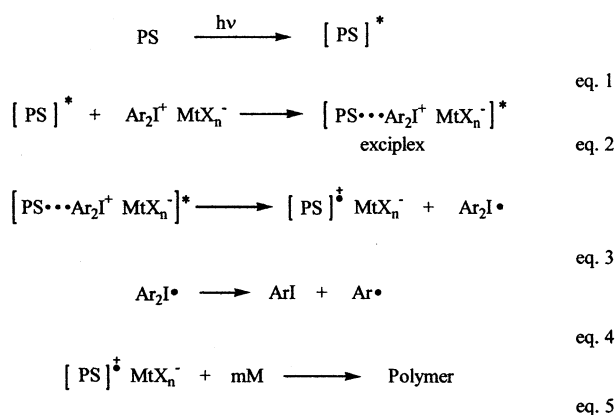
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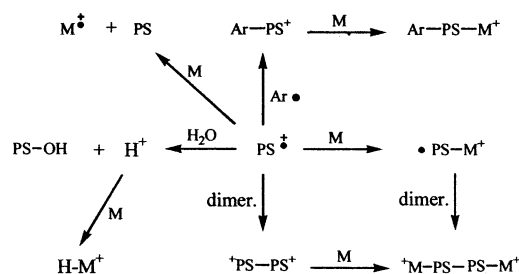
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Scheme 1



Scheme 2



have also suggested the possibility that electron-transfer can occur by the photoinduced excitation of a ground-state complex formed between the onium salt and the photosensitizer. In either case, the onium salt is reduced by a formal one-electron transfer between the two reaction partners (eq 3). The rapid decomposition of the resulting unstable diaryliodonium free radical (eq 4) prevents back electron-transfer and renders the overall process irreversible. Because of their lower reduction potentials, diaryliodonium salts are more easily photosensitized by an electron-transfer process than the corresponding triarylsulfonium or dialkylphenacylsulfonium salts.⁷ Last (eq 5), the photosensitizer cation-radical induces the cationic polymerization of the monomer.

It should be noted that the term "photosensitizer" as applied to electron-transfer photosensitization is a misnomer. As shown in Scheme 1, the photosensitizer undergoes a photoinduced redox reaction to generate the corresponding cation radical, $\text{PS}^{\dot{+}}$. This latter species reacts further via the various mechanisms depicted in Scheme 2 that consume the photosensitizer and induce polymerization of a monomer. Such a mechanism is in direct contrast to the usual energy transfer function in which a "true" photosensitizer is recovered intact at the end of the reaction.

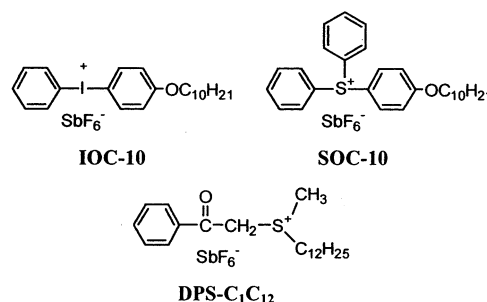
Previously, we have reported that a wide variety of electron-rich polynuclear aromatic compounds such as anthracene, pyrene, and perylene are efficient electron-transfer photosensitizers for onium salt cationic photo-initiators.⁸ Recently, the use of these same photosensitizers for onium salt photolyses has also been studied

by Toba et al.⁹ However, such polynuclear aromatic compounds and their simple substituted derivatives suffer from several serious drawbacks that limit their utility as practical photosensitizers. These compounds generally possess poor solubility in monomers of interest used for cationic photopolymerizations. In addition, they have high vapor pressures at room and elevated temperatures and are readily lost from liquid monomer films by evaporation or sublimation. The most serious problem with these compounds is both their real and perceived toxicity.

In this article, we describe the synthesis of several derivatives of pyrene and the results of an evaluation of their sensitizing ability in cationic polymerization.

Experimental Section

Materials and Analytical Methods. All starting materials were purchased from the Aldrich Chemical Co. and used without purification unless otherwise noted. The photoinitiators, (4-*n*-decyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC-10)¹⁰ and (4-*n*-decyloxyphenyl)diphenylsulfonium hexafluoroantimonate (SOC-10),¹¹ and *S*-dodecyl-*S*-methyl-*S*-phenacylsulfonium hexafluoroantimonate (DPS- $\text{C}_{12}\text{C}_{12}$)¹² were prepared as described previously.



Molecular weight determinations were carried out using a Waters (Milford, MA) 515 HPLC apparatus equipped with a 4120 refractive index detector and three Waters μ -styragel HR 1, 3, and 4 columns (cut-off molecular weights 100–5000, 500–30 000, and 5000–500 000 g/mol, 46 mm i.d., 6300 mm). Tetrahydrofuran (THF) was used as the eluent at a flow rate of 0.3 mL/min at 30 °C. Molecular weights are reported relative to poly(styrene) standards. ¹H NMR spectra were obtained using a Varian XL 500 MHz spectrometer at room temperature in CDCl_3 using tetramethylsilane as an internal standard.

Synthesis of Photosensitizers. Given below are typical preparative procedures used for the synthesis of the pyrene derivatives shown in Table 1 that were used as photosensitizers in this work.

Preparation of 1-Pyrenecarboxaldehyde. 1-Pyrenecarboxaldehyde was prepared according to the method of Buckley et al.¹³ To a 250-mL three-necked round-bottom flask containing *N*-methylformamide (6.0 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. Pyrene (7.1 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

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Table 1. UV Absorption Characteristics of Pyrene Photosensitizers

photosensitizer (solvent)	λ_{max}	ϵ
pyrene (methanol)	261	24400
	271	49800
	294	26800
	305	6910
	318	17600
	334	29400
<i>n</i> -dodecyl 1-pyrenyl ether (<i>n</i> -hexane)	264	25560
	275	49430
	312	11990
	325	29670
	341	46010
	264	27780
1-pyrenyl-1-tridecanol (methanol)	297	4890
	312	13180
	325	31070
	341	46160
copolymer IV (THF)	267	31120
	277	49600
	330	28390
	346	40160
	354	31400

solution of sodium acetate (50 g) was added, and then the mixture was stirred for a further 2 h. The mixture was extracted with dichloromethane (10 \times 200 mL). The extractions were combined, washed with distilled water (4 \times 500 mL), and then dried over anhydrous sodium sulfate. The dried solution was concentrated to about 200 mL and left on the bench overnight. A pale yellow crystalline solid (6.5 g) was obtained. The mother liquor was concentrated to give an additional 2.0 g of 3-pyrenecarboxaldehyde, melting point 123–126 °C (lit.^{14,15} mp 123–126 °C). Elemental analysis calculated for C₁₇H₁₀O: %C, 88.70; %H, 4.38. Found: %C, 88.67; %H, 4.37. ¹H NMR (CDCl₃) δ (ppm) 10.75 (s, 1H), 9.38 (d, J = 9.3 Hz, 1H), 8.40 (d, J = 7.8 Hz, 1H), 8.34–8.14 (m, 7H).

Reduction of 1-Pyrenecarboxaldehyde to 1-Pyrenemethanol. A 250-mL three-necked round-bottom flask was charged with 1-pyrenecarboxaldehyde (2.53 g, 0.011 mol), sodium borohydride (2.2 g, 0.058 mol), and dried tetrahydrofuran (60 mL). The mixture was stirred at 80 °C (oil bath) under a nitrogen 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 \times 300 mL), the extractions were combined, washed with 3% Na₂CO₃ (100 mL) and distilled water (4 \times 400 mL), and then dried over anhydrous sodium sulfate. The solution was concentrated to about 50 mL and cooled in the freezer overnight. There were obtained 1-pyrenemethanol, mp 122–124 °C. The ¹H NMR spectrum of this compound corresponded in all respects with an authentic sample obtained from the Aldrich Chemical Co. Elemental analysis calculated for C₁₇H₁₂O: %C, 87.90; %H, 5.21. Found: %C, 87.67; %H, 5.45. ¹H NMR (CDCl₃) δ (ppm) 8.33 (d, J = 9.3 Hz, 1H), 8.20 (d, J = 7.6 Hz, 1H), 8.19 (d, J = 7.6 Hz, 1H), 8.13 (d, J = 7.6 Hz, 1H), 8.12 (d, J = 9.1 Hz, 1H), 8.08–8.00 (m, 4H), 5.37 (d, J = 5.4 Hz, 2H), 1.99 (t, J = 5.4 Hz, 1H).

Preparation of 1-Pyrenyl-1-tridecanol (II). A 100-mL three-necked round-bottom flask was charged with 1-pyrenecarboxaldehyde (0.23 g, 0.0010 mol) and anhydrous diethyl ether (20 mL) and then cooled to –60 °C using a dry ice–acetone bath. *n*-Dodecylmagnesium bromide (prepared from 2.5 g of 1-bromododecane in 10 mL of diethyl ether, 0.010 mol) was added. The mixture was stirred under nitrogen while the temperature of the cooling bath was allowed to increase to –10 °C over 1 h. The reaction mixture was slowly poured into 50 mL of ice-cooled 1 M aqueous HCl. Then, the organic layer was isolated and the aqueous layer was extracted with 30 mL of diethyl

ether. The combined ether organic layers were washed with aqueous Na₂CO₃ (1 M, 20 mL), followed by distilled water (3 \times 100 mL), and then dried over anhydrous sodium sulfate. Ether was removed under vacuum, and the residue was recrystallized with CH₂Cl₂/hexanes to give an off-white product (0.27 g, 67%) with a melting point of 79–80 °C. Elemental analysis calculated for C₂₉H₃₆O: %C, 86.74; %H, 9.03. Found: %C, 86.95; %H, 9.06. ¹H NMR (CDCl₃) δ (ppm) 8.35 (d, J = 9.3 Hz, 1H), 8.22–7.97 (m, 8H), 5.78 (t, J = 8.1 Hz, 1H), 2.10 (s, 1H), 2.10–2.00 (m, 2H), 1.60–1.10 (m, 20H), 0.87 (t, J = 6.7 Hz, 3H).

Preparation of *n*-Dodecyl 1-Pyrenemethyl Ether (I). A 100-mL round-bottom flask was charged with pyrene-1-methanol (1.5 g, 6.5 mmol), *n*-dodecyl bromide (7.0 g, 0.028 mol), sodium hydroxide (1.0 g, 0.025 mol), tetra-*n*-butylammonium bromide (0.5 g, 1.5 mmol), toluene (50 mL), and water (8 mL). The reaction mixture was stirred at 90 °C (oil bath) for 5 h, washed 4 \times with 100-mL portions of distilled water, and then dried over anhydrous magnesium sulfate. Toluene was removed on a rotary evaporator, and the excess *n*-dodecyl bromide was removed under vacuum. The resulting residue was subjected to column (2.5 cm \times 20 cm) chromatography on silica gel first using hexane as the eluent to remove traces of starting alkyl bromide and then followed by a 1:1 mixture of hexane/dichloromethane. A pale yellow fraction was collected and concentrated to give 1.9 g (73%) of pale yellow crystalline *n*-dodecyl 1-pyrenemethyl ether, mp 59–61 °C. The interpretation of the ¹H NMR spectrum is unambiguous and consistent with the structure of this compound. ¹H NMR (CDCl₃) δ (ppm) 8.36 (d, J = 9.3 Hz, 1H), 8.2–8.1 (m, 4H), 8.05–7.95 (m, 4H), 5.19 (s, 2H), 3.59 (t, J = 6.7 Hz, 2H), 1.65 (penta, J = 7.1 Hz, 2H), 1.36 (penta, J = 7.1 Hz, 2H), 1.15–1.30 (br, 16H), 0.87 (t, J = 7.1 Hz, 3H).

Synthesis of Allyl 1-Pyrenemethyl Ether. Allyl 1-pyrenemethyl ether was prepared in a manner identical to that described above for *n*-dodecyl 1-pyrenemethyl ether. The product (83% yield) was obtained as an oil and was dried in a vacuum oven at 60 °C for 5 h. ¹H NMR (CDCl₃) δ (ppm) 8.39 (d, J = 9.3 Hz, 1H), 8.21 (t, J = 7.2 Hz, 2H), 8.18–8.14 (m, 2H), 8.10–8.00 (m, 4H), 6.14–6.02 (m, 1H), 5.42 (d, J = 6.8, 1H), 5.30 (d, J = 10.5 Hz, 1H), 5.25 (s, 2H), 4.20 (d, J = 5.6 Hz, 2H). Elemental analysis calculated for C₂₀H₁₆O: %C, 88.20; %H, 5.92. Found: %C, 88.06; %H, 5.86.

Preparation of 1-Propenyl 1-Pyrenemethyl Ether (III). Into a 100-mL three-necked round-bottom flask fitted with a reflux condenser, nitrogen inlet, and a magnetic stirrer was placed allyl 1-pyrenemethyl ether (3.0 g, 0.011 mol), Ru(PPh₃)₃Cl₂, and toluene (20 mL). The mixture was refluxed overnight under an atmosphere of nitrogen. After cooling, the solvent was removed under reduced pressure and the resulting residue was dissolved in a minimum of dichloromethane, placed on a short (3 \times 5 cm) silica gel chromatography column and eluted with a 5:1 mixture of hexane and dichloromethane. A yellow fraction was collected and the solvent was removed to afford 2.5 g of 1-propenyl 1-pyrenemethyl ether as a 1:1 mixture of cis and trans isomers. ¹H NMR (CDCl₃) δ (ppm) trans isomer 8.33 (d, J = 9.3 Hz, 1H), 8.18 (t, J = 7.3 Hz, 2H), 8.14 (d, 2H), 8.05–7.98 (m, 4H), 6.48 (d, J = 3.9 Hz, 1H), 5.48 (s, 2H), 5.02 (m, 1H), 1.61 (m, 3H). ¹H NMR (CDCl₃) δ (ppm) cis isomer 8.25 (d, J = 9.0 Hz, 1H), 8.18 (t, J = 7.3 Hz, 2H), 8.13 (d, 2H), 8.05–7.98 (m, 4H), 6.48 (d, J = 1.7 Hz, 1H), 5.38 (s, 2H), 4.65 (m, 1H), 1.61 (m, 3H). Elemental analysis calculated for C₂₀H₁₆O: %C, 88.20; %H, 5.92. Found: %C, 87.90; %H, 5.81.

Copolymer of Propenyl Pyrenemethyl Ether and 1-Propenyl *n*-Dodecyl Ether (IV). A clean, dry 25-mL vial was charged with 1-propenyl 1-pyrenemethyl ether (0.8 g, 0.0029 mol), 1-propenyl *n*-dodecyl ether (1.0 g, 0.0042 mol), CH₂Cl₂ (1 mL), and IOC10 (0.095 g, 1.41 \times 10^{–4} mol). The vial was flushed with nitrogen for 2 min, sealed, and allowed to stand on the laboratory bench with exposure to normal laboratory light for one week. The resulting mixture was dissolved 3 \times in dichloromethane and precipitated into methanol. There was obtained 0.5 g of copolymer. The molecular weight is about 800 by GPC.

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Table 2. IR Bands Monitored during FT-RTIR Kinetic Studies^a

monomer	CHO	VCDO	PC-1000	CEVE
IR band (cm ⁻¹)	781	818	886	1620

^a CHO, cyclohexene oxide; VCDO, 4-vinylcyclohexene dioxide; PC-1000, 1,3-bis(3,4-epoxycyclohexyl-2-ethyl)-1,1,3,3-tetramethyldisiloxane; CEVE, 2-chloroethyl vinyl ether.

Integration of the ¹H NMR spectrum is suggestive of a random copolymer. ¹H NMR (CDCl₃) δ (ppm) 8.39–7.05 (broad m, arom. 9H), 5.50–0–5.05 (s, CH₂–O, 2H), 3.80–3.0 (CH₂–O, CH–O, 4H), 1.50 (CH, 2H), 1.42–1.04 (broad m, CH₂, CH₃, 21H), 1.04–0.5 (2d, CH₃, 6H).

Kinetic Studies of Photosensitized Cationic Polymerizations. The photosensitized cationic polymerizations of the epoxides and 2-chloroethyl vinyl ether studied in this work were monitored using Fourier transform real-time infrared spectroscopy (FT-RTIR). The apparatus and techniques used in these experiments have been described in previous publications from this laboratory.^{16,17} Unless otherwise noted, all photopolymerizations were conducted under ambient air conditions using broad band UV irradiation with an intensity of 125 mJ/cm² min (2.1 mW/cm²). All studies were conducted using 0.5 mol % of the pyrene-containing photosensitizer based on the monomer used. Thus, for copolymer **IV**, the pyrene content was determined by NMR and an amount containing 0.5 mol % of pyrene groups was used. In each case, a control kinetic study was conducted in which the photosensitizer was omitted. Each photosensitization study consisted of data from three to five kinetic runs that were averaged to give the final conversion versus time curve. Table 2 shows the IR bands that were monitored for each of the monomers studied during the course of this investigation. Because the FT-RTIR method relies on the integration of specific IR bands, it is important to note that it is not always possible to locate unobscured bands and to establish a consistent baseline for each monomer. For this reason, in many cases, the actual conversions may vary slightly from those reported here. However, the relative reaction profiles for each monomer are reliable and completely reproducible within ±5%.

The kinetic parameter, $R_p/[M_0]$, for selected kinetic runs was determined from the initial slopes of the irradiation time-conversion curves according to eq 6

$$R_p/[M_0] = ([\text{conversion}]_{t_2} - [\text{conversion}]_{t_1}) / (t_2 - t_1) \quad (6)$$

where R_p and $[M_0]$ are respectively the rate of polymerization and the initial monomer concentration and the conversions are as determined from the curves at irradiation times t_1 and t_2 .

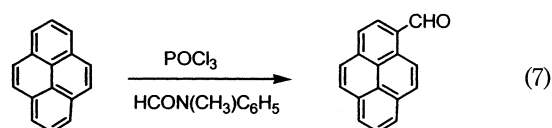
Sunlight-Induced Photopolymerizations. Sunlight-induced solutions were carried out by spreading liquid films of solutions of difunctional epoxy monomers containing various amounts of pyrene derivatives **I** and **II** on glass plates and exposing them to direct sunlight. The exposures were conducted on May 5, 2002 between 11:00 am and 2:00 pm at Troy, New York (42 North latitude).

Results and Discussion

Although pyrene has the deficits of a low solubility, relatively high volatility, and potential toxicity,¹⁸ it is an excellent electron-transfer photosensitizer for diaryliodonium, triarylsulfonium, and dialkylphenacylsul-

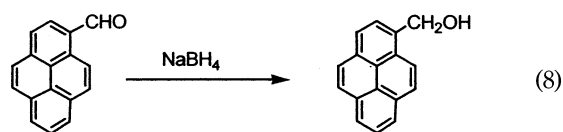
fonium salt cationic photoinitiators. The UV absorption spectrum of pyrene includes bands at wavelengths (Table 1) that are complimentary to those of most onium salt photoinitiators. Pyrene and its simple derivatives are colorless and remain so during and after photolysis. Moreover, pyrene is a readily available and inexpensive starting material. Accordingly, we have centered our attention on this substrate and have employed two different straightforward approaches to its chemical modification. Because it appeared that the problems outlined above result from the low molecular weight and highly crystalline nature (mp 149–151 °C) of pyrene, both of the two approaches we have used in this work are directed toward derivatives of pyrene that possess reduced crystallinity and higher molecular weight.

Synthesis of Low Molar Mass Pyrene Photosensitizers. A particularly facile and high yield method for the derivatization of the pyrene nucleus is the Vilsmeier formylation reaction. Buckley and Thomas¹⁸ and de Clercq and Martin¹⁹ have reported that pyrene can be formylated in high yield (>85%) by treatment with phosphorus oxychloride in the presence of *N*-methylformanilide to give exclusively, 1-pyrenecarboxaldehyde, (eq 7). No di- or multiple formylation was observed.

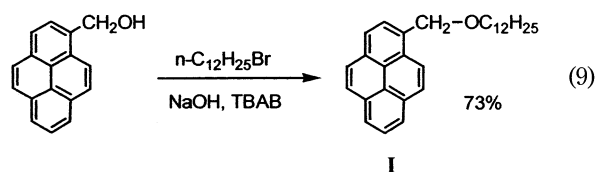


We have reproduced this reaction in this laboratory and have confirmed the high yields reported by the previous authors. Because the formyl group has electron-withdrawing characteristics, it was expected that this would raise the reduction potential of the compound and thus, 1-pyrenecarboxaldehyde should exhibit poor electron-transfer photosensitizing capabilities. This was confirmed in preliminary photosensitization studies. For this reason, 1-pyrenecarboxaldehyde served as a common starting material for the preparation of the other derivatives described in this work. Sodium borohydride reduction of 1-pyrenecarboxaldehyde (eq 8) gave the corresponding pyrene-1-methanol in quantitative yield.

In a subsequent step (eq 9), pyrene-1-methanol was



reacted under phase transfer catalysis (tetra-*n*-butylammonium bromide, TBAB) conditions with 1-bromododecane to give 1-*n*-dodecyl 1-pyrenemethyl ether, **I**, in good yield.



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(17) Gomurashvili, Z.; Crivello, J. V. *J. Polym. Sci. Part A: Polym. Chem. Ed.* **2001**, *39*, 1187.

(18) A literature search for information concerning the toxicity of pyrene revealed that little is known concerning the human toxicity of this compound. Studies conducted in subject animals indicate minimal oral, skin, and eye toxicity. The reader is referred to the website http://risk.lsd.ornl.gov/tox/profiles/pyrene_f_V1.shtml for more information.

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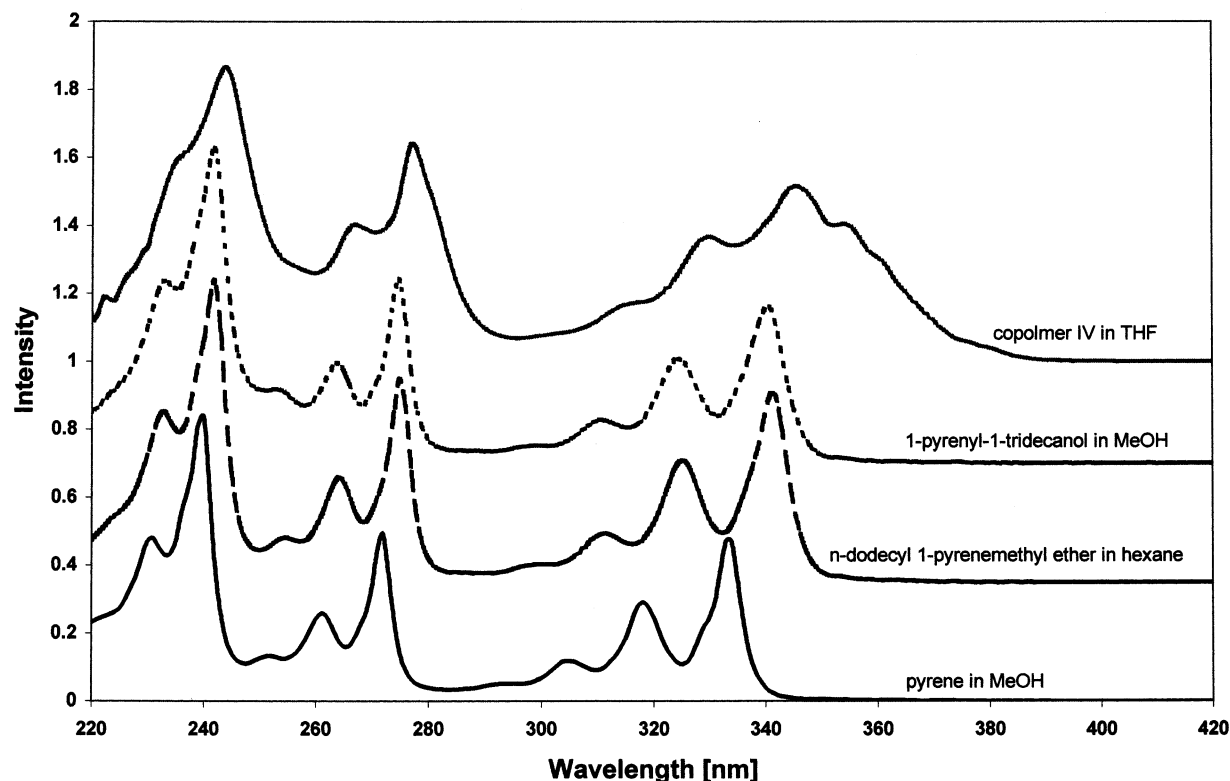
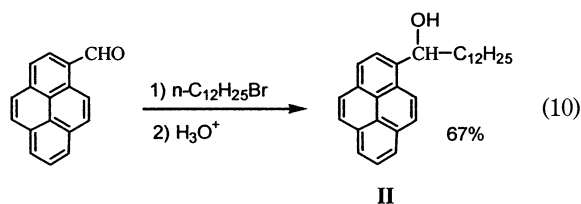


Figure 1. UV spectra of photosensitizers I–IV.

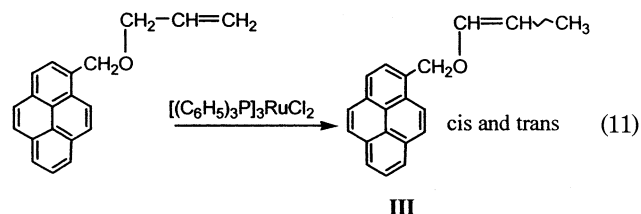
Another approach that was used for the synthesis of pyrene-based photosensitizers consisted of the reaction of 1-pyrenecarboxaldehyde with *n*-dodecylmagnesium bromide to give 1-pyrenyl-1-tridecanol (eq 10).



Photosensitizers **I** and **II** are crystalline compounds with low melting points (79–80 and 59–61 °C, respectively). They display excellent solubility characteristics in a wide variety of polar and nonpolar solvents and monomers.

Synthesis of Polymeric Pyrene Photosensitizers. One method of decreasing volatility and alleviating potential toxicity problems consists of preparing polymeric photosensitizers. In a recent publication from this laboratory,¹⁹ it was shown that poly(*N*-vinylcarbazole) is as highly efficient a photosensitizer for onium salt photolysis as its low molar mass counterparts. Accordingly, it was the intention of this work to investigate the synthesis of polymers bearing pendant pyrene groups. Allyl 1-pyrenyl ether was prepared in a manner analogous to that of 1-*n*-dodecyl 1-pyrenemethyl ether and then isomerized to the corresponding 1-propenyl 1-pyrenemethyl ether using tris(triphenylphosphine)-ruthenium(II) dichloride (eq 11).

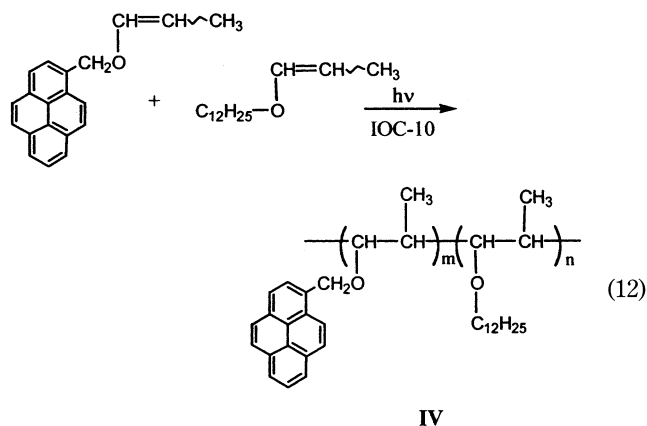
Monomer **III** was obtained as a 1:1 mixture of *cis* and *trans* isomeric products. Previously, we have used this method for the synthesis of a variety of alkyl 1-propenyl



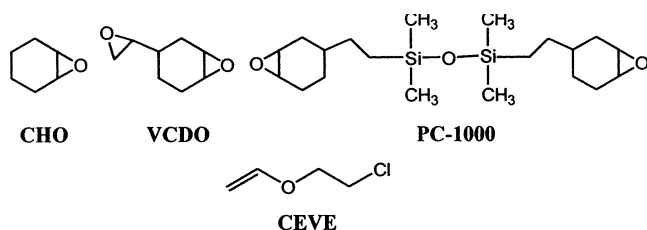
ethers.²⁰ The polymerization of **III** under both photolytic and thermally initiated cationic conditions gave a polymer that was insoluble in most monomeric substrates. For this reason, it was decided to attempt preparation of a copolymer of **III** with another vinyl ether monomer of similar reactivity. For this purpose, the monomer 1-*n*-decyloxy 1-propenyl ether was used as the comonomer. The best copolymerization conditions found were to simply allow a 4:6 stoichiometric mixture of the pyrene and alkyl 1-propenyl ether monomers together with IOC-10 to stand for 1 week under normal laboratory lighting conditions (eq 12). Under these slow polymerization conditions, a broad molecular weight distribution random oligomeric copolymer with a number average molecular weight (GPC, THF, polystyrene standards) of 800 g/mol was obtained. This oligomer (**IV**) was readily soluble in both epoxide and vinyl ether monomers.

Table 1 shows the UV spectral characteristics of the low and high molar mass photosensitizers prepared during the course of this work. In Figure 1, the actual spectra are shown for better comparison. As expected, the UV absorption spectra of these photosensitizers do not differ greatly from those of pyrene.

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Photosensitization Studies. To probe the efficiencies of the low and high molar mass photosensitizers (**I**, **II**, and **IV**) that were prepared, we elected to use Fourier transform infrared spectroscopy (FT-RTIR) to monitor the kinetics of the disappearance of the functional groups undergoing photoinitiated cationic polymerization. The activity of each of the photosensitizers was examined as a function of the photoinitiator and type of monomer employed. As photoinitiators, IOC-10, SOC-10, and DPS-C₁C₁₂ were used all bearing the SbF₆⁻ anion. The four cationically polymerizable monomers with the structures shown below were employed in these studies. In each case, a control kinetic run was included in which the prospective photosensitizer was omitted. Only a few of the most salient results obtained are reported in this article.



All the photopolymerization studies were conducted at a very low light intensity (125 mJ/cm² min) except

where noted to slow the polymerizations sufficiently to enable convenient monitoring of the polymerizations. Since broad band (i.e., unfiltered) UV irradiation was used in all cases, the resulting overall polymerization rates are a combination of the contributions of both direct and photosensitized polymerization processes. Comparison with the control curve gives an estimation of the contribution of photosensitization to the overall rate.

The results of the FT-RTIR kinetic studies of the cationic photopolymerizations of the above four monomers in the presence of pyrene derivatives **I–IV** are summarized in Table 3. This table lists the kinetic parameters $R_p/[M_0]$ determined from the slopes of the initial portion of the conversion versus time curves. This parameter is directly proportional to the rate of polymerization of a specific monomer. To quantify the epoxide rate enhancement in a given monomer system due to photosensitization we have defined, as shown in eq 13, an acceleration factor, AF, as the ratio of the kinetic parameters determined in the presence and absence of the added pyrene photosensitizer compound or polymer.

$$AF = (R_p/[M_0])_{\text{photosens.}} / (R_p/[M_0])_{\text{alone}} \quad (13)$$

Figure 2 shows the results of a FT-RTIR study in which the photopolymerization of CHO was carried out in the presence of the two low molar mass photosensitizers **I** and **II** using DPS-C₁C₁₂ as the photoinitiator. Both photosensitizers are exceedingly efficient (AF = 3.6 and 3.5) in markedly increasing the overall rate of the polymerization of this monomer. Within 10 s, the photosensitized polymerizations proceed to the plateau conversions. In contrast, the polymerization carried out in the absence of a photosensitizer requires more than 160 s to reach the same conversion.

The effect of photosensitizers **I** and **II** on the polymerization of bicyclic monomer, VCHDO, is shown in Figure 3. In this case, IOC-10 was used as the photoinitiator. As in the previous example, there is a dramatic increase in the rate of polymerization (AF = 6.2 and 7.7) in the presence of the two monomolecular

Table 3. FT-RTIR Kinetic Data for Photosensitizers

entry	monomer	photoinitiator (conc. mol %)	photosensitizer ^a	light intensity (mJ/cm ² min)	$R_p/[M_0]$	AF
1	CHO	DPS-C ₁ C ₁₂ (0.5)		125	7.08	
2			I	125	25.2	3.6
3			II	125	25.0	3.5
4	VCHDO	IOC 10 (0.1)		125	0.53	
5			I	125	3.26	6.2
6			II	125	4.90	7.7
7	PC-1000	IOC 10 (0.1)		125	0.83	
8			I	125	2.19	2.6
9			II	125	2.07	2.5
10	CEVE	DPS-C ₁ C ₁₂ (0.5)		1030	0.20	
11			I	125	36.6	183
12			II	125	36.9	189
13	CHO	IOC 10 (0.1)		125	4.08	
14			IV	125	31.4	7.7
15	VCHDO	DPS-C ₁ C ₁₂ (0.2)		125	0.30	
16			IV	125	4.10	14
17	PC-1000	DPS-C ₁ C ₁₂ (0.2)		125	0.59	
18			IV	125	4.13	7.0
19	CEVE	SOC 10 (0.2)		125	0.15	
20			IV	125	26.7	178

^a 0.5 mol % Photosensitizer used based on monomer.

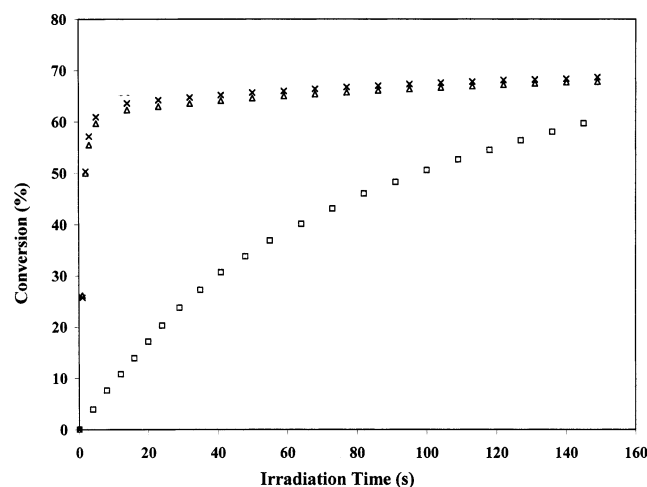


Figure 2. FT-RTIR study of the photopolymerization of CHO in the presence of DPS- C_{12} (0.5 mol %) with no photosensitizer (\square); with 1(1-pyrenyl)tridecan-1-ol (Δ); and with 1-*n*-dodecyl pyrenemethyl ether (\times).

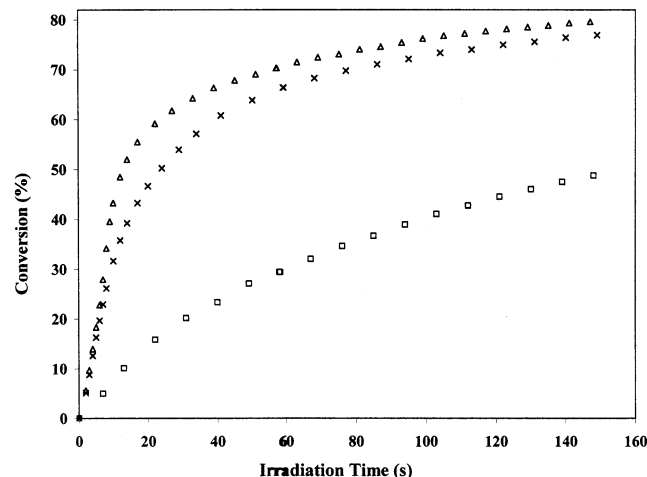


Figure 3. Comparison of the photosensitizing effects of 1(1-pyrenyl)tridecan-1-ol (Δ), 1-*n*-dodecyl pyrenemethyl ether (\times), and no photosensitizer (\square), on the cationic ring-opening photopolymerization of VCHO with IOC-10 (0.1 mol %) as photoinitiator.

photosensitizers. A similar study is depicted in Figure 4 in which **I** and **II** are employed as photosensitizers for the polymerization of the very reactive diepoxy siloxane monomer, PC-1000. In this instance, SOC-10 was used as the photoinitiator. Only a modest increase in the rate of the polymerization is noted as compared to the polymerization carried out in the absence of a photosensitizer. It was observed that although electron-transfer photosensitizers are effective for all three types of onium salt photoinitiators: diaryliodonium, triarylsulfonium, and dialkylphenacysulfonium salts, they are less so for triarylsulfonium salts. Because electron-transfer photosensitization takes place by oxidation of the excited photosensitizer and the reduction of the onium salt, it is not surprising that the reduction potential of the onium salt determines the facility with which this reaction proceeds. Despite the similarities of the UV absorption characteristics and the quantum yields of IOC-10 and SOC-10, the higher rate of polymerization in the presence of IOC-10 reflects its lower oxidation potential ($E_{1/2} = -0.2$ V versus typical triar-

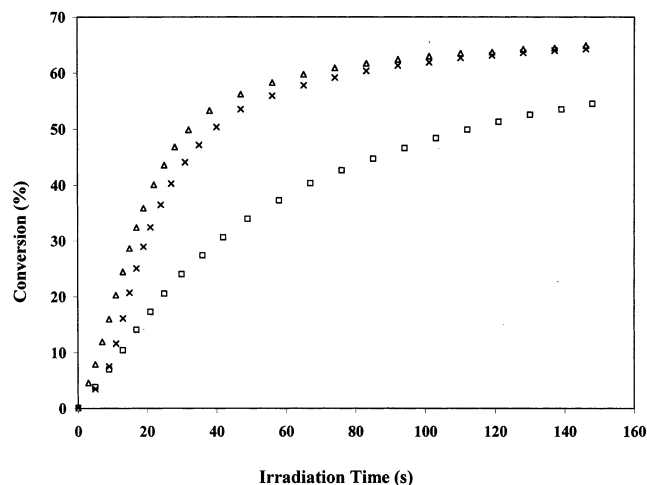


Figure 4. Comparison of the effects of photosensitizers on the cationic ring-opening photopolymerization of PC-1000 using SOC-10 (0.1 mol %) as photoinitiator: no photosensitizer (\square); 1(1-pyrenyl)tridecan-1-ol (Δ); 1-*n*-dodecyl pyrenemethyl ether (\times).

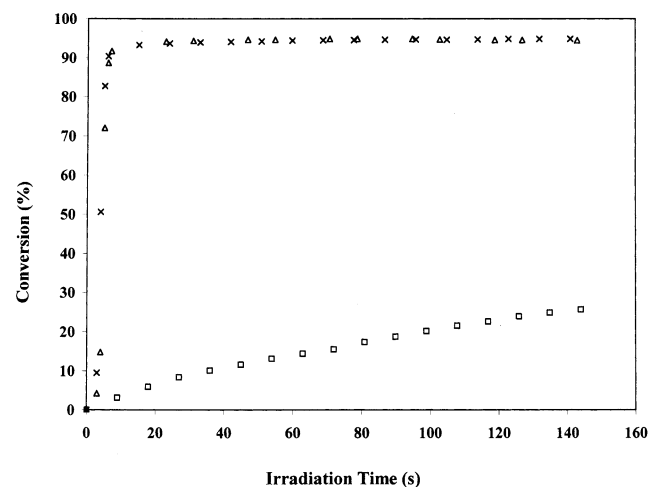


Figure 5. Photopolymerization of CEVE with DPS- C_{12} (0.5 mol %) as the photoinitiator: no photosensitizer, 1030 mJ/cm^2 min (\square); 1(1-pyrenyl)tridecan-1-ol, 125 mJ/cm^2 min (Δ); 1-*n*-dodecyl pyrenemethyl ether, 125 mJ/cm^2 min (\times).

ylsulfonium salts $E_{1/2} = -1.01$ – -1.46 V)²¹ and, accordingly, its greater ability to participate in the mechanism shown above. The reduction potential of DPS salts has been found to be intermediate ($E_{1/2} = -0.7$ V) between that of diaryliodonium and triarylsulfonium salts.²²

2-Chloroethyl vinyl ether (CEVE) is an exceedingly reactive monomer in photoinitiated cationic polymerization. Figure 5 shows the photopolymerization of this monomer in the presence and absence of photoinitiators **I** and **II** with DPS- C_{12} under two different conditions of illumination with UV light. When no photosensitizer is present, the polymerization of CEVE is slow even at 1030 mJ/cm^2 min. However, when the photosensitizers are employed, polymerization is exceedingly rapid even at a fraction of the light intensity (125 mJ/cm^2 min). Although the AF factors were calculated for this study, it is recognized that they do not really reflect true

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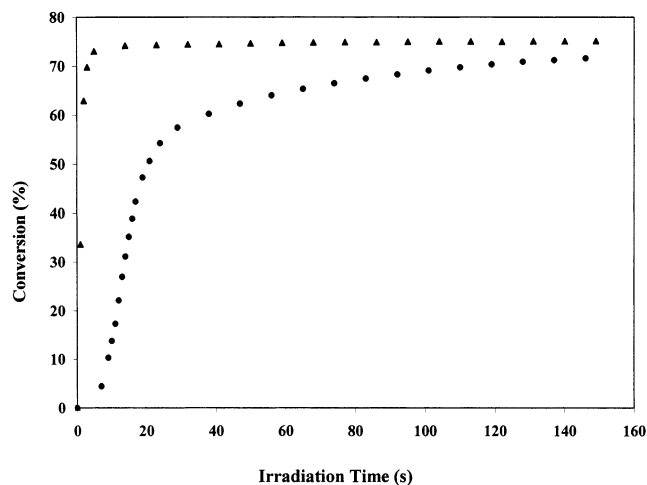


Figure 6. Photosensitized polymerization of CHO with copolymer **IV** in the presence of (0.1 mol %) IOC-10 as a photoinitiator (▲), and with no photosensitizer (●).

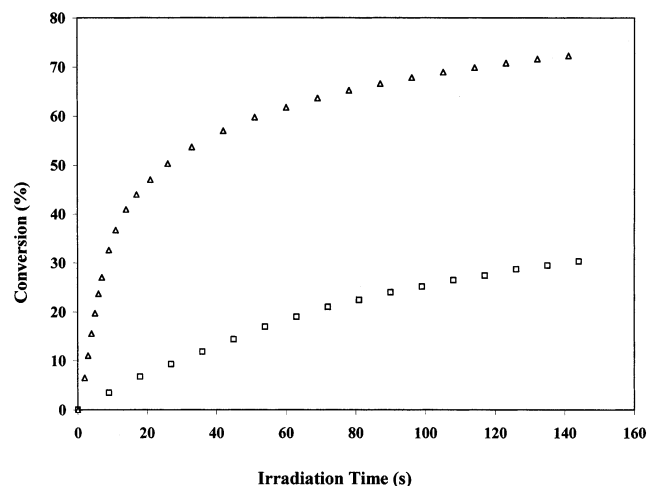


Figure 7. Effect of copolymer **IV** on the DPS- C_{12} (0.2 mol %) photoinitiated photopolymerization of VCDO (Δ); no photosensitizer (□).

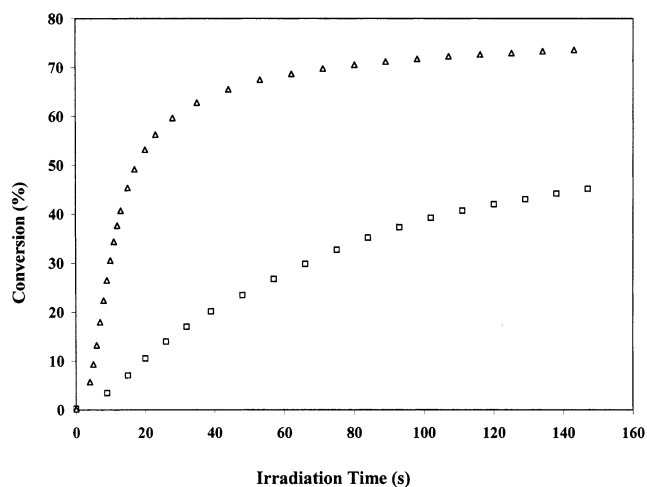


Figure 8. FT-RTIR study of the DPS- C_{12} (0.2 mol %) induced cationic photopolymerizations of PC-1000 alone (□) and with copolymer **IV** (Δ).

acceleration because very little polymerization of CEVE takes place in the absence of a photosensitizer.

In Figures 6–9 are depicted the results of studies of the photosensitizing effects of oligomeric copolymer **IV**

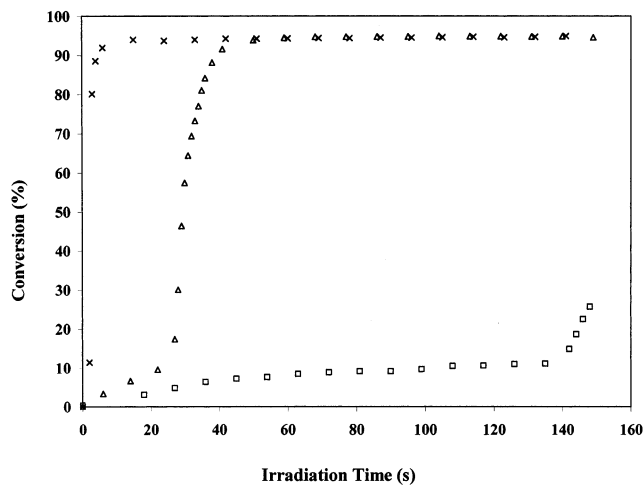


Figure 9. Comparison of effects of photosensitizer and light intensity on the photopolymerization of CEVE in the presence of SOC-10 (0.2 mol %): no photosensitizer, 125 mJ/cm² min (□); no photosensitizer, 1030 mJ/cm² min (Δ); and copolymer **IV**, 125 mJ/cm² min (×).

containing pendant pyrene groups with different monomeric substrates. Figure 6 shows the photosensitizing effect of the copolymer in the IOC-10-induced polymerization of CHO. Not only is the rate of the photosensitized polymerization enhanced ($AF = 7.7$) in the presence of the photosensitizer, but also the induction period is markedly reduced because of the greater amount of initiating Brønsted acid produced in this system. Difunctional monomer, VCDO, also undergoes very rapid copolymer photosensitized polymerization ($AF = 14$) in the presence of DPS- C_{12} as shown in Figure 7. The cross-linking polymerization by DPS- C_{12} of PC-1000 displays a marked enhancement ($AF = 7.0$) when copolymer **IV** is used a photosensitizer (Figure 8) under the same experimental conditions. Last, the vinyl ether polymerization of CEVE in the presence of SOC-10 carried out in the presence of copolymer **IV** is shown in Figure 9. Control polymerizations containing no photosensitizer were conducted at two UV illumination intensities (1030 mJ/cm² min and 125 mJ/cm² min). In the absence of a photosensitizer, this polymerization displayed a prolonged induction period that was reduced but not completely eliminated at the highest illumination intensity. In contrast, at 125 mJ/cm² min, copolymer **IV** accelerates the polymerization at a rate higher than the nonphotosensitized polymerization and, in addition, eliminates the induction period.

In a recent publication from this laboratory,²³ we described a different approach toward photosensitization that made use of hydroxymethylated polynuclear aromatic hydrocarbons including 1-pyrenemethanol. The results obtained using this previous approach and that employed here are similar for several monomer systems. However, for many others, 1-pyrenemethanol displays limited solubility, and the photosensitization effects obtained are poorer than for the more soluble photosensitizers described in this communication.

Because the substituted pyrene derivatives **I** and **II** have absorption bands that possess tails that extend to the near visible region, it was decided to attempt to

conduct the polymerization of epoxy monomers using ambient sunlight. This was readily achieved using both photosensitizers. For example, a thin film of a solution of limonene dioxide containing 1.0 mol % IOC-10 and 0.5 mol % **I** exposed to direct sunlight required approximately 15 s to undergo polymerization to give a cross-linked network polymer. Under the same conditions, an exposure of approximately 20 s of a film of PC-1000 containing 0.2 mol % IOC-10 and 0.5 mol % **I** resulted in a glassy, solid, cross-linked polymeric film.

Conclusions

During the course of this work, we have demonstrated that the facile synthetic modification of the polynuclear aromatic hydrocarbon pyrene can be carried out in a straightforward, simple, and high-yield fashion to yield both low molar mass and oligomeric compounds. These compounds display good solubility in a wide range of both polar and nonpolar solvents and monomers. These photosensitizers display excellent activity as photosensitizers for photoinitiated vinyl ether and epoxide ring-

opening cationic polymerizations employing a broad spectrum of onium salt photoinitiators including diaryliodonium, triarylsulfonium, and dialkylphenacylsulfonium salts. Kinetic studies were carried out using three mono- and difunctional epoxides and a vinyl ether as polymerizable substrates. In all cases, those polymerizations incorporating photosensitizers displayed considerably higher rates of polymerizations than the corresponding control experiments in which the photosensitizer was omitted.

This work shows that it is possible to rationally design highly effective electron-transfer photosensitizers for onium-salt-induced photopolymerizations that also possess other desirable characteristics such as low volatility and good solubility.

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