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Development of Polymeric Photosensitizers for Photoinitiated Cationic Polymerization

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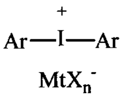
ABSTRACT: Enhancement of the rates of onium salt photoinitiated cationic polymerizations of epoxides and vinyl ethers has been achieved through the use of oligomeric and polymeric electron-transfer photosensitizers. Poly(*N*-vinylcarbazole) (PVK) is an especially attractive and efficient photosensitizer. The use of PVK as a photosensitizer for the cationic photopolymerizations of vinyl ethers and epoxides was examined in detail. PVK functions as an electron-transfer photosensitizer for a wide variety of onium salt cationic photoinitiators, including diaryliodonium, triarylsulfonium, and dialkylphenacylsulfonium salts. The broadening of the spectral response through the use of these photosensitizers accounts for the observed rate enhancement of these polymerization reactions. Alternating copolymers prepared by the free radical polymerization of *N*-vinylcarbazole (NVK) with vinyl monomers also exhibit excellent photosensitization activity. Also described in this paper is the synthesis and use of a dimeric photosensitizer prepared by the hydrosilylation of *N*-vinylcarbazole with 1,1,3,3-tetramethyldisiloxane.

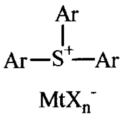
Introduction

In recent years, work in this laboratory has been centered on the synthesis of novel monomers and photoinitiators for cationic photopolymerizations.[1−4] The impetus for much of the work has been due not only to the considerable academic interest in this field of polymer science but also to the rapid implementation of this technology into many commercial applications. In particular, the increasing commercial and technical demands of cationic photopolymerizations have led to an interest in the design and synthesis of optimized monomers and photoinitiator systems. Currently, the most commonly used photoinitiators employed for photoinduced cationic ring-opening polymerizations are diaryliodonium, **I**, and triarylsulfonium salts, **II**, with the general structures shown below in which MtX_n- represents a weakly nucleophilic counterion.



$Ar\text{—}\overset{+}{I}\text{—}Ar \quad MtX_n^-$

I



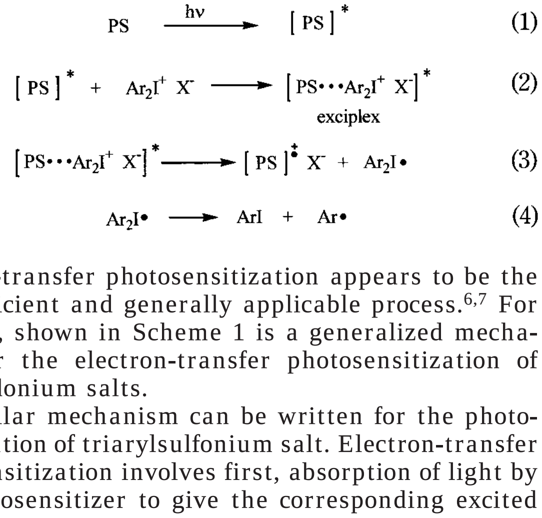
$Ar_3S^+ \quad MtX_n^-$

II

Both classes of photoinitiators possess high quantum yields of photolysis and are efficient initiators of cationic polymerizations when irradiation is carried out using light in the short wavelength UV region (230−300 nm). To further improve the performance of these photoinitiators, a common strategy that is employed is the use of photosensitizers.[5] The broader spectral sensitivity provided by a photosensitizer permits the capture of a higher fraction of the available light emitted from most common UV irradiation sources. This results in a more efficient photolysis of the photoinitiator and, consequently, generates a larger number of initiating species that produce an apparent acceleration of the rate of polymerization of the monomer.

There are several mechanisms by which the photosensitization of onium salts takes place; however, electron-transfer photosensitization appears to be the most efficient and generally applicable process.[6,7] For example, shown in Scheme 1 is a generalized mechanism for the electron-transfer photosensitization of diaryliodonium salts.

Scheme 1



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

$$[PS]^* + Ar_2I^+X^- \longrightarrow \underset{\text{exciplex}}{[PS\cdots Ar_2I^+X^-]^*} \qquad (2)$$

$$[PS\cdots Ar_2I^+X^-]^* \longrightarrow [PS]^{+\bullet}X^- + Ar_2I^\bullet \qquad (3)$$

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

A similar mechanism can be written for the photosensitization of triarylsulfonium salt. Electron-transfer photosensitization involves first, absorption of light by the photosensitizer to give the 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 process irreversible. Because of their lower reduction potentials, diaryliodonium salts are more easily photosensitized by an electron-transfer process than triarylsulfonium salts. Previously, we have reported that a wide variety of electron-rich polynuclear aromatic compounds are efficient electron-transfer photosensitizers for both diaryliodonium and triarylsulfonium salt cationic photoinitiators.[8] While polynuclear aromatic compounds such as anthracene, pyrene, and perylene are excellent photosensitizers for both diaryliodonium and triarylsulfonium salts, unfortunately, these photosensitizers suffer from several drawbacks that have greatly limited their use. Polynuclear aromatic compounds display poor solubility in many polymerizable monomers and have a tendency to be readily lost due to volatilization from thin film coatings,

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Table 1. UV Absorption Characteristics of PVK in THF

wavelength (nm)	ϵ	log ϵ
236[a]	714 300	4.85
294[b]	11 030	4.04
330[b]	3130	3.49
343[b]	3480	3.54

[a] 1.5×10^{-5} M. [b] 6.4×10^{-5} M.

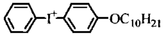
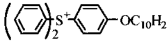
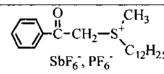
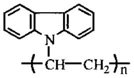
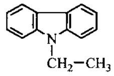
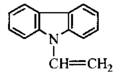
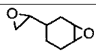
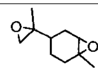
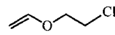
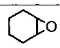
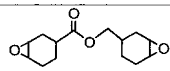
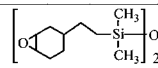
adhesives and printing inks. More seriously, these compounds are regarded as toxic and potentially carcinogenic and are excluded from use in many commercial applications on this basis. Work in this laboratory has been proceeding to overcome the above-mentioned drawbacks by designing novel classes of electron-transfer photosensitizers.

Chen, Yamamura, and Igarashi[9] have recently described studies of the photosensitization of onium salt photolysis by various compounds containing the carbazole nucleus. These authors report the efficient photosensitization of both diaryliodonium and triarylsulfonium salts by carbazole compounds. In this laboratory, we have reported that *N*-vinylcarbazole (NVK) is an excellent electron-transfer photosensitizer for onium salt photoinitiators.[10] Moreover, it was shown that NVK undergoes rapid, photoinduced cationic polymerization by these photoinitiators and that the resulting poly(*N*-vinylcarbazole) (poly(9-vinylcarbazole), PVK) is also an efficient photosensitizer for these same photoinitiators. The observation that polymers such as PVK can function as efficient photosensitizers for onium salt photolyses appeared novel and very interesting. Furthermore, polymeric photosensitizers are practical alternatives to the present monomolecular polynuclear aromatic compounds used as photosensitizers since they are nonvolatile and in addition, would be expected to display a low order of toxicity. In addition, PVK is very interesting as a potential photosensitizer for onium salt photolysis due to its rich and broad UV absorption spectra. The spectral characteristics of PVK as measured in this laboratory are given in Table 1.

The UV spectrum of PVK, although broader and less resolved, is very similar to simple *N*-alkylated carbazole compounds such as *N*-methyl- and *N*-ethylcarbazole. This has been noted previously[11] and it was suggested that this effect is indicative of a very weak ground-state interaction of the carbazole chromophores along the polymer backbone.

Of particular interest are the well-known and unusual photooptical properties of PVK. In 1969 Klöpffer first reported that electronic energy migration occurs in solid films of PVK.[12] This energy transfer process takes place by singlet exciton migration via the carbazole groups involving both inter- and intrachain processes. Triplet energy migration was also observed in films of PVK. Triplet energy migration was found to be extraordinarily efficient and to proceed in intramolecular fashion down the polymer chain at a rate of approximately 1000 carbazole repeat units/s.[13,14] This “antenna effect” has been previously described by Guilette in such polymers as poly(1-vinylnaphthalene) and poly(acenaphthalene) that contain pendant aromatic rings.[15,16] If this “antenna effect” takes place with PVK in solution, it should improve the efficiency of PVK as compared to monomeric photosensitizers by effectively increasing the overall crossection of photosensitizer in a kind of “light harvesting effect.” The high efficiency of photosynthesis in certain biological systems such as chlorophyll[17] and DNA[18] has been attributed to such antenna effects.

Table 2. Structures of Photoinitiators, Photosensitizers, and Monomer

Photoinitiators		
 SbF_6^- **IOC10**	 SbF_6^- **SOC10**	 SbF_6^-, PF_6^- **DPS-C_1C_{12}**
Photosensitizers		
 **PVK**	 **NEK**	 **NVK**
Monomers		
 **VCDO**	 **LDO**	 **CEVE**
 **CHO**	 **ERL**	 **PC-1000**

Accordingly, we decided to conduct a more in-depth study of PVK and other related polymers as photosensitizers for onium salt photolyses. The results of these investigations are presented in this article.

Experimental Section

Materials. All organic starting materials and reagents employed in this investigation were reagent quality and were used as purchased from the Aldrich Chemical Co. (Milwaukee, WI) unless otherwise noted. Cyclohexene oxide, 4-vinylcyclohexene dioxide, and 2-chloroethyl vinyl ether were obtained from this same source and had purities of 98, 97 and 99% respectively. Limonene dioxide was obtained from the Elf-Atochem Co. (Blooming Prairie, MN) and purified before use by fractional distillation from calcium hydride. PC-1000 (bis-2(3,4-epoxycyclohexylethyl)-1,3-tetramethyldisiloxane) was used as obtained as a gift from the Polyset Co., Mechanicville, NY. ERL-4221E (3,4-epoxycyclohexylmethyl 3′,4′-epoxycyclohexanecarboxylate, ERL) was obtained and used without purification from the Union Carbide Corp. (Bound Brook, NJ). Poly(*N*-vinylcarbazole) (PVK, MW = 256 700 g/mol MWD = 3.3) was purchased from Polysciences, Inc. (Warrington, PA). Prior to use, the polymer was twice purified by dissolving it in chloroform and precipitating it into acetone. 1,1,3,3-Tetramethyldisiloxane was purchased from the Gelest Co. (Tullytown, PA) and purified by distillation prior to use. Polymer-bound Wilkinson’s catalyst (polymer-bound chlorotris(triphenylphosphine)rhodium(I) on styrene−divinylbenzene copolymer) was purchased from Strem Chemicals (Newburyport, MA). Shown in Table 2 are the structures of the monomers and photoinitiators employed in this investigation. The photoinitiators, (4-*n*-decyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC10),[19] (4-*n*-decyloxyphenyl)diphenylsulfonium hexafluoroantimonate (SOC10),[20] *S*-dodecyl-*S*-methyl-*S*-phenacylsulfonium hexafluoroantimonate ($DPS-C_1C_{12}SbF_6^-$),[21] and *S*-dodecyl-*S*-methyl-*S*-phenacylsulfonium hexafluorophosphate ($DPS-C_1C_{12}PF_6^-$)[21] were prepared as described previously.

Analytical Techniques. Molecular weight determinations were carried out at room temperature using a Hewlett-Packard (Palo Alto, CA) HP-1090 M HPLC equipped with a refractive index detector and a μ-styragel column (particle size 5 μm, mixed 24−34 Å pores). THF was used as the eluent at a flow rate of 1.0 mL/min. All molecular weights are reported relative to poly(styrene) standards. NMR spectra were obtained using a Varian Inova 300 MHz spectrometer. UV spectra were recorded on a Hitachi U-2000 UV−vis spectrophotometer.

Synthesis of NVK-Diethylfumarate Copolymers. The following procedure is typical for that employed for the synthesis of all the copolymers prepared during the course of this work and shown in Table 3.

NVK (2.24 g, 0.0116 mol) was dissolved in diethyl fumarate (2.00 g, 0.0116 mol) in a clean, dry glass vial, 2,2-azobisisobutyronitrile (0.076 g, 0.00046 mol) added, and the mixture

Table 3. Copolymerization[a] of NVK with Diethyl Furmarate and Butyl Acrylate

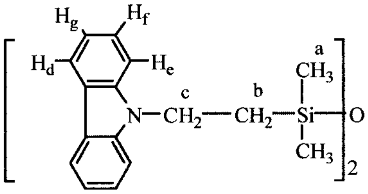
cop.	monomer	LM[b] (%)	M_w (g/mol)	MWD	yield (%)	NVK in copolymer (mol %)	NVK in copolymer (wt %)
1	DEF[c]		42 400	4.4	52	47	50
2	DEF[c]	2.0	11 500	3.8	65	50	53
3	DEF[c]	4.0	9200	2.2	71	49	51
4	BA[d]	2.0	17 000	5.0	69	44	54
5	BA[d]	4.0	10 000	3.8	67	43	53

[a] Equimolar mixture of NVK with the indicated monomer using 2% 2,2′-azobis(isobutyronitrile). [b] Lauryl mercaptan. [c] Diethylfumarate. [d] *n*-Butyl acrylate.

purged with nitrogen and sealed. The mixture was placed in an ultrasonic water bath at 25–35 °C to dissolve the initiator. The resulting pale yellow solution was placed in an oil bath at 78 °C. After 5–10 min under nitrogen, a foamed solid polymer formed. The polymer was dissolved in chloroform and precipitated in methanol. After the product was dried in a vacuum oven at 50 °C, 2.2 g of a white polymer powder was obtained. GPC measurement of the molecular weight gave a $M_w = 42\ 400$ g/mol and a $M_w/M_n = 4.4$.

Preparation of 1,3-Bis(2-carbazoloethyl)-1,1,3,3-tetramethyldisiloxane (IV). Into a 25 mL round-bottom flask equipped with a magnetic stirrer and reflux condenser were placed 5.1 g (0.026 mol) of *N*-vinylcarbazole, 10 mL of toluene that was freshly distilled from sodium metal, 1.8 g (0.013 mol) of 1,1,3,3-tetramethyldisiloxane, and 3 mg of polymer-bound Wilkinson's catalyst. The reaction mixture was heated to 80 °C and maintained at that temperature for 24 h. During reaction, the reaction mixture became increasingly more viscous as reaction proceeded. Upon cooling to room temperature, the product solidified. The crude product was purified by dissolving it in a small amount of THF and slowly adding the resulting solution to cold methanol. The product, **IV**, was obtained as a colorless powder and was recovered by filtration. After drying under vacuum, there were obtained 3.5 g (51% yield) of pure **IV**.

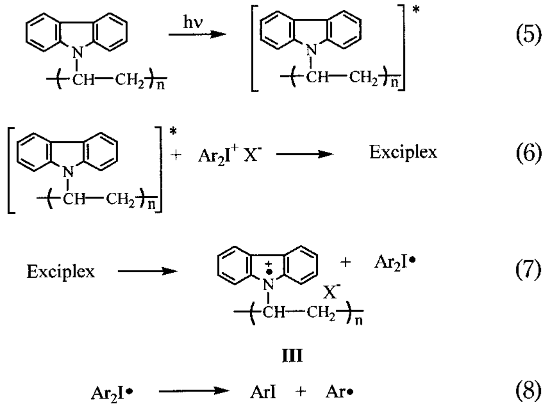
^{1}H NMR spectrum in $CDCl_3$ δ (ppm) H_a, s, 0.24; H_b, m, 1.3; H_c, m, 4.4; H_d, d, 8.1; $H_{e,f,g}$, m, 7.2–7.5.



Photopolymerization Studies Using Fourier Transform Real-Time Infrared Spectroscopy (FT-RTIR). Photopolymerizations of all the monomers were monitored using Fourier transform real-time infrared spectroscopy (FT-RTIR). A Midac M-1300 FTIR spectrometer (Midac Corp., Irvine, CA) equipped with a liquid-nitrogen-cooled MCT detector was used. The instrument was fitted with a UVEXS model SCU-110 mercury arc lamp (Sunnyvale, CA) equipped with a flexible liquid optic wand. The end of this wand was placed at a distance of 4–20 cm and directed at an incident angle of 45° onto the sample window. UV light intensities were measured with the aid of a UV Process Supply, Inc. radiometer (Chicago, IL) at the sample window.

Photopolymerizations were carried out at 25 °C in solutions of the monomers containing various concentrations of IOC10, SOC10, $DPS-C_1C_{12}\ SbF_6^-$ or $DPS-C_1C_{12}\ PF_6^-$ as the photoinitiator. All concentrations used in this paper are given in units of mol % with respect to the epoxide or vinyl ether monomer. The monomer/photoinitiator solutions were coated onto a 12 μm oriented and corona treated polypropylene film (General Electric Capacitor Department, Hudson Falls, NY), covered with an identical polypropylene film, and then mounted in 5 cm × 5 cm slide frames. The thickness of the liquid monomer films was estimated at 10–25 μm. Infrared spectra were collected at a rate of 1 spectrum/s using LabCalc, data acquisition software obtained from the Galactic Industries Corp. (Salem, NH), and were processed using GRAMS-386 software from the same company. During irradiation, the decrease of the IR absorbance due to either the vinyl ether double bonds centered at 1610 cm^{-1} or the epoxy groups between 790 and 930 cm^{-1} of the monomers were monitored. In all cases, three to five runs were recorded and the results averaged. Data reduction and subsequent conversion vs time plots were obtained using Excel (Microsoft Corp., Redmond, WA) software. Over many experiments it has been found that the data for a given kinetic run have a variation of plus or minus 5%. Thus, two curves are said to be similar if they are close to the error of measurement and significantly different if the variation is greater.

Scheme 2



Results and Discussion

Photosensitization of Onium Salt Photolysis by PVK. A simple laboratory experiment confirmed that onium salts undergo electron-transfer photosensitization by PVK. When a chloroform solution of PVK was irradiated with broadband UV light in the presence of a diaryliodonium salt, the characteristic intense blue color of the polymeric aminium cation-radical (**III**) was very rapidly generated.[22] Similar observations were made for the other types of polymeric and nonpolymeric photosensitizers employed during the course of this investigation. The aminium ions that are generated are comparatively stable toward oxygen and the color persists for a considerable time after irradiation. In eqs 6–9 of Scheme 2 is shown the mechanism that we propose for this reaction.

Irradiation of PVK leads to the production of the photoexcited polymer (eq 5). This species rapidly interacts with the photoinitiator (a diaryliodonium salt is depicted here) to form an excited-state complex or exciplex (eq 6). The exciplex relaxes (eq 7) with the transfer of an electron from PVK to the onium salt to generate the polymeric cation radical (**III**) and the diaryliodine free radical. **III**, can undergo several types of further reactions including dimerizations (aromatic coupling) leading to cross-linking of the polymer[23] as well as the initiation of the cationic polymerization of reactive monomers. Subsequent, irreversible decomposition of the diaryliodine radical (eq 8) renders the entire process irreversible by preventing back electron transfer. The above mechanism can be characterized as a photoinduced redox reaction in which the onium salt (a diaryliodonium salt is shown here) is reduced by the photoexcited polymer. For this reason, the efficiency of this reaction is governed not only by the spectral ab-

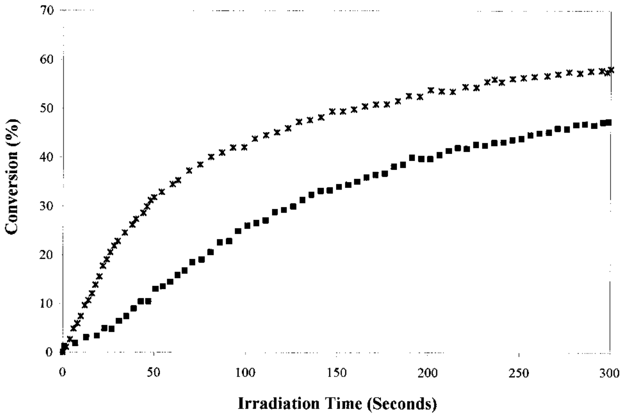


Figure 1. FT-RTIR comparison of the polymerization of 4-vinylcyclohexene dioxide alone (■) and in the presence of 0.1% PVK (∗) (light intensity 131 mJ/cm^2 min; 0.05% IOC10).

sorption characteristics of the polymeric photosensitizer but also by the redox potentials of both the excited photosensitizer and the onium salt employed.

Photoinitiated Cationic Polymerizations Using PVK as a Photosensitizer. It was of considerable interest to determine the range of the ability of PVK to photosensitize the photolysis of different types of onium salts. For this reason, we undertook a brief kinetic study of the rates of polymerization of cationically polymerizable monomers with various types onium salts in the presence and absence of PVK. These kinetic studies were conducted using Fourier transform real-time infrared spectroscopy (FT-RTIR) to follow the photopolymerizations. RTIR has proven to be an extremely useful method for monitoring the kinetics of very rapid photopolymerization reactions and for that reason, has been used by many investigators to probe these types of reactions.[24−27] In our method, thin, homogeneous, liquid samples of mixtures of the monomer containing a photoinitiator were sandwiched between two layers of 12 μm oriented and corona-treated polypropylene film and irradiated with broadband UV light to initiate polymerization. Light intensities of 130−2200 mJ/cm^2 min were used for these studies depending upon the specific monomer-photoinitiator system employed. The progress of both the vinyl ether and epoxide polymerizations were monitored by following the decrease in the absorbance of characteristic IR bands of the epoxide (790−930 cm^{-1}) and vinyl ether (1610 cm^{-1}) groups in the respective two monomers. In the studies reported in this paper, each kinetic run was carried out at 25 °C a minimum of three times. The data were averaged, and the resulting conversion vs time curves are presented here.

Table 2 gives the structures and abbreviated names of the oligomeric or polymeric photosensitizers, photoinitiators, and monomers used in the studies reported in this paper. In all cases, we have elected to employ photoinitiators such as IOC10, SOC10, and DPS$-C_1C_{12}$ salts bearing long chain alkyl groups to provide good solubility in both polar and nonpolar monomers. All of these photoinitiators bear very weakly nucleophilic hexafluoroantimonate (SbF_6^-) or hexafluorophosphate (PF_6^-) counterions that have previously been shown to produce high rates of cationic photopolymerizations.[6]

Shown in Figure 1 is a comparison of the ring-opening epoxide photopolymerization of 4-vinylcyclohexene dioxide (VCDO) with IOC10 as the photoinitiator using broadband UV light in the presence and absence of PVK.

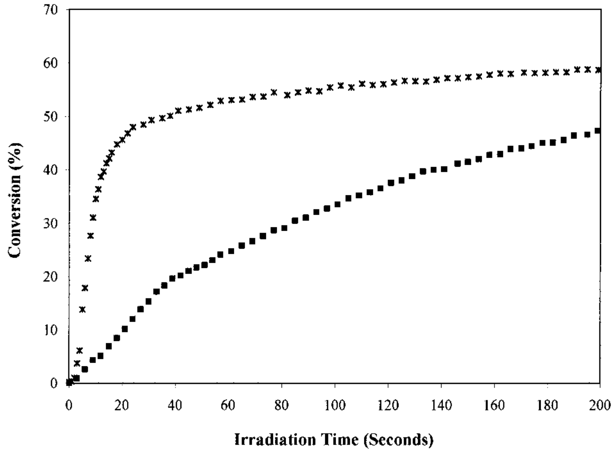


Figure 2. FT-RTIR comparison of the polymerization of limonene dioxide alone (■) and in the presence of 2.0% PVK (∗) (light intensity 265 mJ/cm^2 min; 0.05% SOC10).

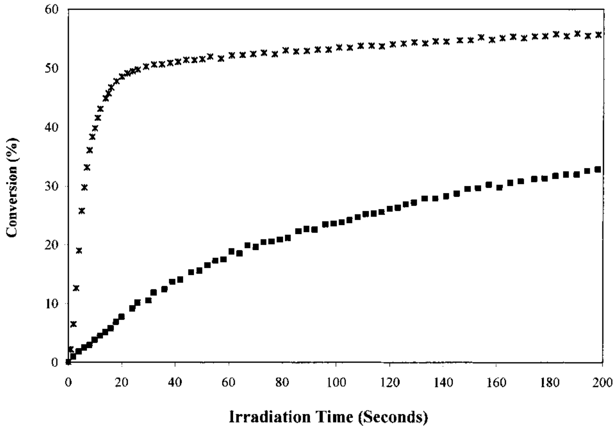


Figure 3. Comparison of the polymerization of limonene dioxide by FT-RTIR alone (■) and in the presence of 2.0% PVK (∗) (light intensity 265 mJ/cm^2 min; 0.05% DPS$-C_1C_{12}$ SbF_6^-).

Similar results were observed for other mono- and difunctional epoxide monomers. For these monomers, there is a dramatic increase in the rate of polymerization in the presence of the polymeric photosensitizer. In all cases, there is no induction period. This suggests that PVK is sufficiently nonbasic that competition with these monomers for initiating protons and propagating oxonium cations does not appear to occur. Attempts were also made to examine the photosensitized polymerizations of vinyl ether monomers. However, these experiments failed due to the insolubility of PVK in those monomers.

In Figures 2 and 3 are shown, respectively, the results obtained for the use of PVK as a photosensitizer for the triarylsulfonium salt, SOC10, and the dialkylphenacylsulfonium salt, DPS$-C_1C_{12}$ SbF_6^-, in the polymerization of limonene dioxide (LDO). For comparison, a curve for the polymerization of LDO in the absence of PVK is included in each of these figures. As was noted above, a dramatic acceleration of the polymerizations took place in the presence of PVK as a result of photosensitization for both of these two different types of sulfonium salts. This implies that the photoexcited PVK is capable of reducing onium salts with very different reduction potentials. Diaryliodonium salts have a rather low reduction potential ($E_{1/2} = -0.2$ V) whereas triarylsulfonium salts have considerably higher redox potentials ($E_{1/2} = -1.01$ to -1.46 V).[28] The reduction potential of DPS salts is intermediate ($E_{1/2} = -0.7$ V) between the

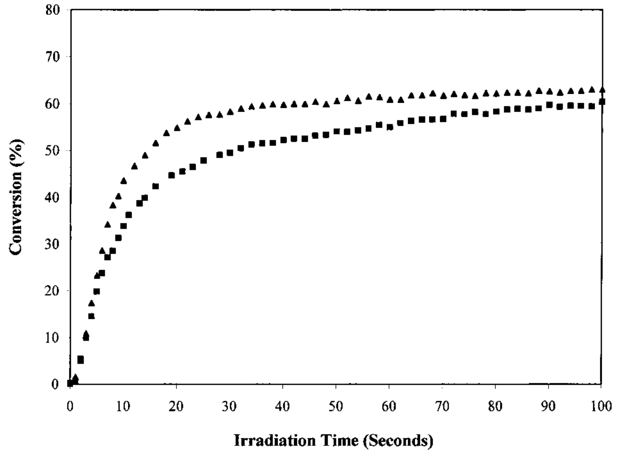


Figure 4. FT-RTIR comparison of the polymerization of limonene dioxide in the presence of 2.0% NVK (■) and PVK (▲) (light intensity 145 mJ/cm^2 min; 0.05% SOC10).

Scheme 3

$$2\,\mathrm{CZ}^{+\bullet} \longrightarrow {}^{+}\mathrm{CZ\text{-}CZ}^{+} \longrightarrow \mathrm{CZ\text{-}CZ} + 2\mathrm{H}^{+} \qquad (9)$$

$$\mathrm{H}^{+} + \mathrm{M} \longrightarrow \mathrm{H\text{-}M}^{+} \qquad (10)$$

$$\mathrm{CZ}^{+\bullet} + \mathrm{M} \longrightarrow \bullet\mathrm{CZ\text{-}M}^{+} \qquad (11)$$

$$2\,\bullet\mathrm{CZ\text{-}M}^{+} \longrightarrow {}^{+}\mathrm{M\text{-}CZ\text{-}CZ\text{-}M}^{+} \qquad (12)$$

$$\bullet\mathrm{CZ\text{-}M}^{+} + n\mathrm{M} \longrightarrow \bullet\mathrm{CZ\text{-}(M)}_{n}\mathrm{M}^{+} \qquad (13)$$

two former salts.[29] The ability of these polymers to photosensitize a wide range of onium salts is extraordinary and this makes them particularly valuable as a class of universal photosensitizers.

Antenna Effects in Photosensitization by PVK. As mentioned previously, it was of some interest to us to determine whether PVK exhibits any special photosensitization properties for onium salt induced cationic photopolymerizations that would make it more efficient than related monomolecular carbazole compounds. We were especially interested in determining whether an "antenna effect" could be demonstrated. Two brief studies were undertaken to explore this possibility. In Figure 4 is shown a study in which two polymerizations of LDO using IOC10 were carried out comparing NVK and PVK as photosensitizers. Identical molar quantities (2.0 mol % based on the monomer) of carbazole moieties were used in each experiment. Calculations of the initial slopes of the two conversion vs time curves gives 5.0 for PVK and 4.4 for NVK. These results indicate that, under the same experimental conditions, both the monomolecular and polymeric photosensitizers have very similar efficiencies of photosensitization. Analogous results were observed when PVK is compared to *N*-ethylcarbazole (NEK) or *N*-methylcarbazole. These results suggest that both monomolecular and polymeric photosensitizers behave similarly. However, the overall rate of reaction of the complex mechanism depicted in Schemes 1 and 2 is governed by the slowest step. Furthermore, the initiation and propagation steps of the polymerization (Scheme 3) also have to be considered as potentially the slowest steps.

In eqs 9−13, CZ represents either a monomeric carbazole or a polymeric carbazole containing repeat unit. Radical dimerization of the initially formed carbazole cation-radical may occur prior to initiation (eq 9) or during (eq 12) the propagation step. Thus, the polymerizations may be initiated by either protons[9] or carbazole-derived cations.

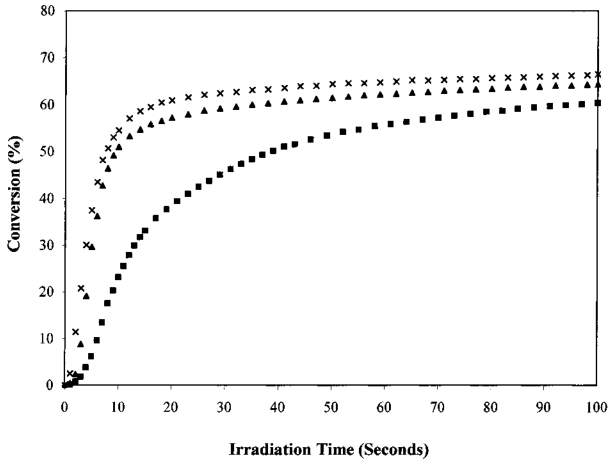


Figure 5. FT-RTIR study of the photopolymerization of cyclohexene oxide in the presence of 0.5% IOC10 alone (■) and using 0.2% PVK (×) and 0.2% NEK (▲) (light intensity 103 mJ/cm^2 min).

To either confirm or exclude the existence of an "antenna effect" the rates of polymerization of a monomer in the presence of various concentrations of PVK and a monomolecular photosensitizer were carried out. If intramolecular energy transfer takes place along the chain of PVK, it should be effective in channeling that energy to sensitize the photolysis of an onium salt remote from the site of excitation. This would be reflected in a higher rate of polymerization for PVK as compared to a monomolecular photosensitizer. This effect should be most readily observable at low photosensitizer/onium salt concentrations. Figure 5 gives the results of an investigation of the photopolymerization of cyclohexene oxide (CHO) in with 0.5% IOC10 using 0.2% of both NEK and PVK. A curve in which no photosensitizer was present is included for comparison. Again, little difference was observed between the initial rates of polymerization using these two photosensitizers. This leads to the conclusion that intramolecular energy transfer in PVK in a monomer solution is most likely very inefficient, and thus, each repeat unit along the chain behaves as an independent photosensitizer entity.

Copolymers of PVK. Thus, while PVK does not exhibit an "antenna effect" that would enhance its activity as a photosensitizer, it also does not display other reported effects that could significantly detract from its efficiency. For example, Klöpffer[12,30] observed that PVK exhibits excimer emission (fluorescence) and, in addition, Johnson[31] also observed a long-lived phosphorescence resulting from interaction respectively, of the presence of singlet and triplet excitons in the photoexcited polymer. These emissions represent energy-wasting, excited-state deactivation processes that can reduce the efficiency of photosensitization.

Since each carbazole-containing repeat unit in PVK behaves as an independent sensitizing chromophore, we concluded that the further separation of these chromophores through copolymerization should not appreciably affect their photosensitizing ability. Further, alternating copolymers of NVK with other monomers exhibit no excimer fluorescence emission.[32] Copolymerization is one obvious way of eliminating the formation of intrachain excimers. One additional drawback associated with PVK is its poor solubility in many monomer substrates. Copolymerization of NVK with monomers that either provide flexibilizing and/or polar

Table 4. Solubility Characteristics of PVK Copolymers

polymer	PVK	cop. **1**	cop. **2**	cop. **3**	cop. **4**	cop. **5**
M_w (g/mol)	256 700	42 400	11 500	9200	17 000	10 000
solubility[d]						
PC1000[a]	x	x	x	x	x	x
LDO[b]	+	+	+	+	+	+
ERL[c]	x	+	+	+	+	x

[a] 1,3-Bis(2-(3,4-epoxycyclohexyl)ethyl-1,1,3,3-tetramethyldisiloxane. [b] Limonene dioxide. [c] 3,4-Epoxycyclohexylmethyl 3′,4′-epoxycyclohexanecarboxylate. [d] Key: (x) not soluble; (+) soluble.

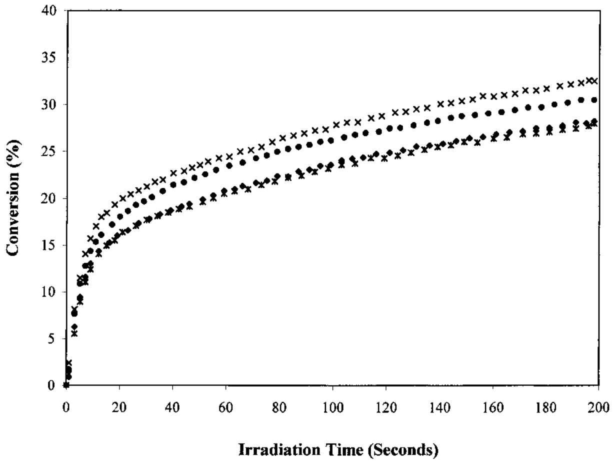


Figure 6. FT-RTIR comparison of the photosensitized polymerization of ERL in the presence of copopolymers **1** (×), **2** (*), and **4** (◆) (1.0% carbazole repeat units) and with 1.0% NEK (●) using 1.0% DPS−C$_1$C$_{12}$ PF$_6^-$ as the photoinitiator (light intensity 2200 mJ/cm^2 min).

moieties should substantially increase the solubility of these materials. Similarly, other carbazole monomers could be employed as, for example, methacrylic polymers[33] and vinyl ether[34] containing pendant carbazole moieties have been recently reported.

Copolymers of NVK with diethylfumarate (DEF) and *n*-butyl acrylate (BA) were prepared by straightforward AIBN-initiated free radical polymerizations. The results are given in Table 3. NVK polymerizes with these two monomers to give largely alternating copolymers.[35] Initially, copolymerization with DEF gave a molecular weight of 42 400 (copolymer **1**). In an attempt to lower the molecular weight somewhat, the copolymerizations were carried out in the presence of lauryl mercaptan as a free radical chain transfer agent. This strategy was successful and lower molecular weight copolymers were obtained. Table 4 shows the solubility of PVK as compared to the NVK copolymers in three different difunctional epoxide monomers. PVK is soluble only in LDO. The silicone diepoxide, PC-1000, is a very poor solvent for PVK and all the NVK copolymers. Good solubility was displayed by the copolymers in LDO and 3,4-epoxycyclohexylmethyl 3′,4′-epoxycyclohexanecarboxylate (ERL).

Figure 6 shows a comparison of the photosensitization of the ring-opening epoxide polymerizations of ERL in the presence of three NVK copolymers (cop. **1**, **2**, **4**) and with NEK using 1.0% DPS−C$_1$C$_{12}$ PF$_6^-$ as the photoinitiator. In each case, equivalent amounts (11.0%) of carbazole groups were used. The results show that the copolymers display essentially the same level of efficiency of photosensitization as NEK in this photopolymerization. In Figure 7 are compared the photosensitized polymerizations of VCDO using 0.1% of copolymer **2** and PVK. Again, this comparison was made using identical molar amounts of carbazole repeat units. The nearly identical results for the two polymeric photosensitizers once again confirm that the carbazole units behave essentially as independent photosensitizing chromophores.

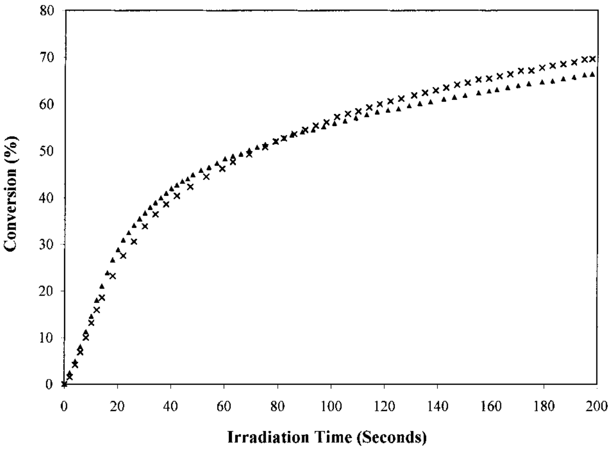


Figure 7. FT-RTIR study of the photosensitized polymerization of VCDO carried out with copolymer **2** (×) and PVK (▲) using equimolar (0.1%) amounts of carbazole repeat units and with 0.05% IOC10 as the photoinitiator (light intensity 228 mJ/cm^2 min).

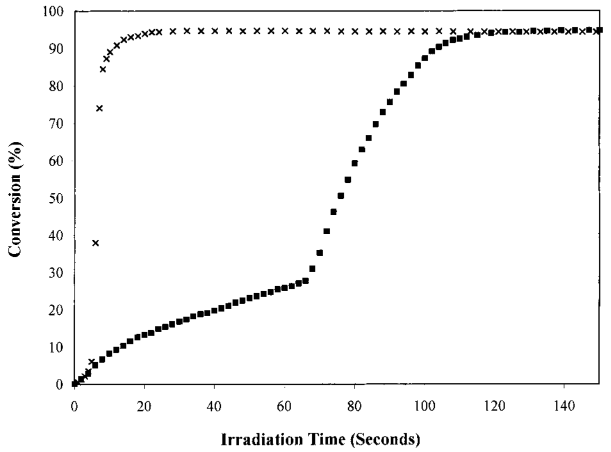


Figure 8. FT-RTIR study of the photopolymerization of 2-chloroethyl vinyl ether alone (■) and in the presence of 0.5% PVK/DEF copolymer **1** (×). (light intensity 245 mJ/cm^2 min; 1.0% SOC10).

As mentioned previously, attempts to carry out the PVK photosensitized polymerization of vinyl ether monomers were frustrated by the insolubility of this latter polymer. However, the copolymers of NVK with DEF display excellent solubility in these monomers. Figure 8 shows one such study in which copolymer **1** was used to photosensitize the polymerization of 2-chloroethyl vinyl ether in the presence of 1.0% SOC10 as a photoinitiator. Marked improvement of the photoresponse of the copolymer photosensitized polymerization using broadband UV light was observed as compared to the parallel polymerization carried out in the absence of a photosensitizer. Direct comparison of copolymer **1** with NVK shows that both exhibit identical levels photosensitization activity in the polymerization of this monomer when compared on the basis of the same molar equivalents of carbazole groups.

Synthesis of a Dimeric Photosensitizer. As noted previously, the silicone diepoxide, PC-1000, is a poor solvent for both PVK and copolymers of NVK with either

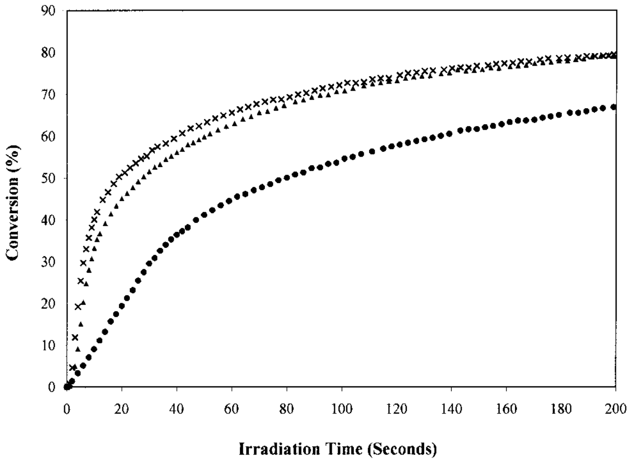
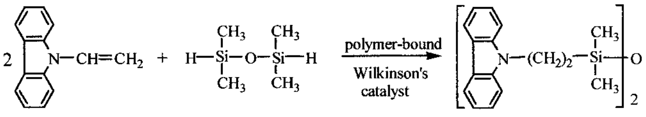


Figure 9. Study of the photosensitized polymerization of PC-1000 by FT-RTIR with 0.5% IOC10 alone (●) and in the presence of 2.0% **IV** (×) (carbazole units) and NEK (▲) as photosensitizers (light intensity 405 mJ/cm^2 min).

DEF or BA (Table 4). To overcome this difficulty, it appeared worthwhile to attempt to prepare a compatible, high molecular weight carbazole photosensitizer. This was accomplished as shown in eq 14 by the hydrosilylation of NVK with 1,1,3,3-tetramethyldisiloxane.



IV (14)

Hydrosilylation proceeded smoothly in the presence of polymer-bound Wilkinson's catalyst to give the desired hydrosilylation dimer **IV** in 51% yield as a colorless powder. ^{1}H NMR spectroscopy confirmed the structure of this compound. It is interesting to note that Si−H addition takes place to the vinyl double bond such that the silicon becomes bonded to the terminal carbon of the double bond (α-addition). There is no evidence in the spectrum of methyl bands arising from the reverse addition (β-addition) to the vinyl double bond. In agreement with this structure, the ^{29}Si NMR spectrum shows only a single resonance located at 7.00 ppm. Recently, Belfield et al.[36] have prepared similar carbazole substituted siloxanes by the hydrosilylation of *N*-allylcarbazole.

Dimer **IV** is readily soluble in PC-1000 and Figure 9 shows a comparison of this photosensitizer with NEK. **IV** displays excellent photosensitization activity that is very similar to NEK in this highly reactive monomer. These results suggest that a wide variety of other oligomeric and polymeric carbazole photosensitizers can be prepared by the hydrosilylation of NVK with the appropriate Si−H functionalized substrates.

Conclusions

Electron-transfer photosensitization of onium salt photoinitiated cationic vinyl and ring-opening polymerizations by polymers, copolymers, and oligomers containing carbazole repeating units is a highly efficient process. These photosensitizers are especially attractive since they are effective for the photosensitization of several different types of onium salt photoinitiators. The polymerization rate enhancement effects in photosensitized polymerizations as compared to photopolymerizations conducted in the absence of such photosensitizers can be rationalized as due to the enhanced UV spectral absorption of these systems. Comparative studies of cationic photopolymerizations using monomolecular carbazoles, PVK and NVK copolymers showed that there was very little difference in the efficiencies of these photosensitizers. This leads to the conclusion that "antenna effects" in the case of PVK either do not occur in solution or are very weak.

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