Monomeric and Polymeric Phenothiazine Photosensitizers for Photoinitiated Cationic Polymerization

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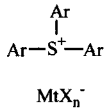
ABSTRACT: The syntheses of several phenothiazine compounds bearing cationically polymerizable vinyl, vinyl ether and epoxide groups are described. These monomers were rapidly and efficiently polymerized or copolymerized by UV irradiation in the presence of onium salt photoinitiators. In addition, the monomers simultaneously function as efficient photosensitizers for the photolysis of the onium salts. In this article, the use of these polymerizable photosensitizers for the photopolymerizations of epoxide and vinyl ether monomers is reported. The inclusion of a small amount of the monomeric photosensitizer is effective in markedly accelerating the cationic photopolymerization of the bulk monomer. Polymers prepared by the polymerization of the monomeric phenothiazine photosensitizers also exhibit excellent photosensitization activity when used in combination with diaryliodonium, triarylsulfonium, and dialkylphenacylsulfonium salt photoinitiators.

Introduction

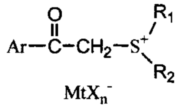
Over the past decade, onium salt photoinitiated cationic polymerizations have found a number of commercial applications that take advantage of the unique processing and mechanical characteristics obtainable by the use of this technology. Among the most notable applications include the following: coatings for metals and plastics, printing inks, adhesives, and stereolithography. Crucial to the success of cationic photopolymerizations in many of these applications is the use of photosensitizers.[1] A photosensitizer may be necessary to provide sensitivity when light sources are used which emit at wavelengths not absorbed by the photoinitiator. 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. This contributes to an overall 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 as compared to when no photosensitizer is used.

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.[2,3] Shown in Scheme 1 is a generalized mechanism proposed for the electron-transfer photosensitization of diaryliodonium salts (**I**).

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 **II** and dialkylphenacylsulfonium **III** salt photoinitiators.


$Ar-\overset{Ar}{S^+}-Ar$ MtX_n^-

II


III

Scheme 1

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

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

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

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

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). Alternatively, Rodrigues and Neumann[4,5] 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 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 or dialkylphenacylsulfonium salts.[6] 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 photoinitiators.[7] Chen et al.[8] and ourselves[9,10] 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.[6,11,12] Recently, Yagci et al.[13] have reported the use of phenothiazine as a photosen-

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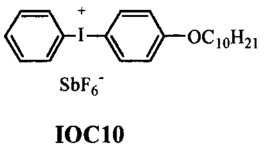
sitizer for the photolysis of allyl sulfonium salts. Phenothiazine compounds are highly attractive as photosensitizers for onium salt photolyses because they can be readily structurally modified to “tune” their spectral absorption characteristics and photosensitizing activity by simple, straightforward chemistry.

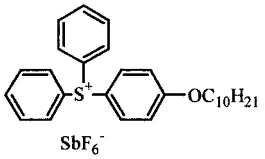
In this article, we describe the synthesis of several phenothiazine monomers, their cationic polymerization and the use of both the monomers and their polymers in the photosensitized cationic polymerizations of epoxide and vinyl ether monomers.

Experimental Section

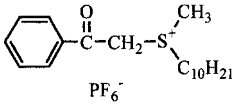
Materials. All organic starting materials and reagents employed in this investigation were reagent quality and were used as purchased from the Aldrich Chemical Co. (Milwaukee, WI) unless otherwise noted. 10*H*-Phenothiazine, allyl bromide, epichlorohydrin, cyclohexene oxide, and 2-chloroethyl vinyl ether were obtained from this same source. Limonene dioxide was obtained from the Elf-Atochem Co. (Blooming Prairie, MN) and purified before use by fractional distillation from calcium hydride. The photoinitiators, (4-*n*-decyloxyphenyl)phenyliodonium hexafluoroantimonate (IOC10)[14] and (4-*n*-decyloxyphenyl)diphenylsulfonium hexafluoroantimonate (SOC10),[15] *S*-dodecyl-*S*-methyl-*S*-phenacylsulfonium hexafluorophosphate (DPS$-$C$_1$C$_{12}$)[16] were prepared as described previously.



IOC10



SOC10



DPS-C$_1$C$_{12}$

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 (cutoff molecular weights 100−5000, 500−30000, and 5000−500000, 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. All molecular weights are reported relative to poly(styrene) standards. NMR Spectra were obtained using a Varian Inova 500-MHz spectrometer. UV spectra were recorded on a Hitachi U-2000 UV−vis spectrophotometer. Elemental analyses were determined by Atlantic Microanalysis (Norcross, GA). The inherent viscosities were measured with an Ubbelohde viscometer at 20 °C in CH$_2$Cl$_2$ or at 25 °C in DMAc.

Synthesis of Monomeric Photosensitizers. Preparation of 10-(2,3-Epoxypropyl)phenothiazine (EPT). EPT was synthesized using the method of Moren.[17] A pale yellow viscous liquid with a bp$_{0.15\mathrm{Torr}}$ of 200−205 °C (lit.[17] bp$_{0.1\mathrm{Torr}}$ 195−200 °C) was obtained by fractional distillation. The yield of EPT was 6.4 g (35.6%).

^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 7.18−6.93 (m; aromatic protons), 4.18 and 3.90 (q,q, O−CH_2), 3.30 (m, N−CH$_2$−CH -O), 2.94−2.78 (t,t; N−CH_2).

Preparation of 10-Allylphenothiazine (APT). APT was prepared according to the method of Gillman and Shirley.[18] The product was obtained as an oil and was purified by distillation at 197−202 °C (0.15 Torr), (lit.[18] bp$_{1.0\mathrm{Torr}}$ 187−195 °C) to give 14.8 g (62%) of APT as a yellow oil.

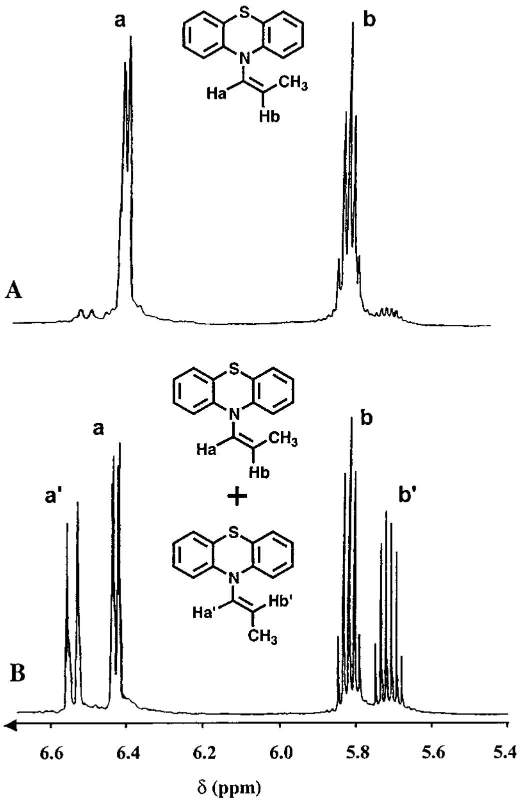


Figure 1. 300 MHz ^{1}H NMR spectra in DMSO-d_6: (A) *cis*-10-propenylphenothiazine; (B) 55:45 mixture of *cis*- and *trans*-10-propenylphenothiazine.

^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 7.12−7.08 (m; aromatic protons), 6.01−5.89 (m, CH$_2$=CH-), 5.36−5.28 (m, −CH=CH_2), 4.47 (d; N−CH_2−CH).

Isomerization of 10-Allylphenothiazine. A. *cis*-10-(1-Propenyl)phenothiazine (*c*-PPT). A 10 mL aliquot of a 0.25 N *t*-BuOK solution in *t*-BuOH was added to 2.4 g (10 mmol) of 10-allylphenothiazine in 25 mL dry DMSO. The mixture was stirred for 6 h at 45 °C and, after cooling, was poured into distilled water. The oil that separated was extracted into toluene. The organic layer was washed with water and dried over anhydrous potassium carbonate, and then the solvent was removed on a rotary evaporator. Recrystallization of the resulting solid from ethanol gave 1.9 g (79%) PPT as gray-white needles with a mp of 32−35 °C (lit.[19] mp 34−35 °C). ^{1}H NMR spectroscopy indicated that the mixture contained 95% pure cis isomer. (Figure 1).

^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 7.12−6.88 (m; aromatic protons), 6.43 (q, N−CH=), 5.81 (m, −CH=CH−), 1.67 (m, =CH−CH_3).

B. Mixture of *cis*- and *trans*-10-(1-Propenyl)phenothiazine *c*- and *t*-PPT. There was added 10 mL of a 0.25 N *t*-BuOK solution in *t*-BuOH to 5 g (21 mmol) of 10-allylphenothiazine dissolved in 25 mL of dry DMSO. The mixture was heated and maintained at 100 °C for 1 h. Isolation of the product was carried out in a manner analogous to the previous procedure. Vacuum distillation at 195 °C/0.25 Torr gave 3.9 g (78%) of a yellow oil (lit. bp[18] 191−193 °C/0.5−0.7 Torr). The ^{1}H NMR spectrum of the product indicated that it was a mixture of cis and trans isomers in a ratio of 55:45.

Preparation of 10-(2-Vinyloxyethyl)phenothiazine (VPT). Combined into a 500 mL round-bottom flask fitted with a magnetic stirrer, reflux condenser, and nitrogen inlet were 5.2 g (0.13 mol) of NaH (60% dispersion in mineral oil) and 350 mL of dry tetrahydrofuran. To this solution was added portion-wise 16 g (0.08 mol) of 10*H*-phenothiazine. The mixture was slowly heated and refluxed for 30 min. After cooling to room temperature, 16.8 mL (0.15 mol) of 2-chloroethyl vinyl ether and 0.40 g tetra-*n*-butylammonium bromide were added, and refluxing continued for 30 h. The cooled reaction mixture was filtered, and the solvent and excess vinyl ether were evaporated under reduced pressure. Toluene was added to the residue, and the precipitated unreacted 10*H*-phenothiazine was removed by filtration. Evaporation of the toluene and distillation of the resulting oil at 170−175 °C (0.01T) afforded 5.4 g of VPT as a pale yellow oil. (lit.[20] $bp_{0.1 Torr}$ 150−170 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.29−6.92 (m; aromatic protons), 6.48 (q, $-CH{=}CH_2$), 4.26−4.20 (m, $N-CH_2-CH_2-N$), 4.08 (m; $CH{=}CH_2$).

Anal. Calcd for $C_{16}H_{15}NOS$: C, 71.34; H, 5.61; N, 5.20; S, 11.90. Found: C. 71.69; H, 5.64; N, 5.23; S, 11.88.

Preparation of 10-Phenothiazine-5-oxide (PTO). PTO was synthesized using the procedure described by Gilman and Nelson.[21] Recrystallization of the crude product from 96% ethanol produced 17 g (93%) of yellow crystals of PTO having a mp 269−272 °C (lit.[21] mp 242−242.5 °C dec). The IR spectrum of the product displayed characteristic sulfoxide bands at 1074 and 1029 cm^{-1}.

Anal. Calcd for $C_{12}H_9NOS$: C, 66.95; H, 4.21; N, 6.51; S, 14.90. Found: C. 67.00; H, 4.26; N, 6.48; S, 14.85.

Preparation of 10*H*-Phenothiazine-5,5-dioxide (PTO_2). The synthetic procedure of Gilman and Eisch was employed for the preparation of PTO_2.[22] After recrystallization from ethanol, an 88% yield of colorless crystalline 10-phenothiazine-5,5-oxide was obtained with a mp range of 264−266 °C. (lit.[22] mp 253.5−255.5 °C). The IR spectrum of the product displayed characteristic sulfone bands at 1153 and 1125 cm^{-1}.

Preparation of 10-(2-Vinyloxyethyl)phenothiazine-5-oxide (VPTO) and 10-(2-Vinyloxyethyl)phenothiazine-5,5-dioxide ($VPTO_2$). The preparation of VPTO and $VPTO_2$ were carried out analogous manner to the synthesis of VPT replacing 10*H*-phenothiazine with 10*H*-phenothiazine-5-oxide and 10*H*-phenothiazine-5,5-dioxide as starting materials. After recrystallization twice from toluene, a 46% yield of off-white colored crystals of VPTO with a mp of 109−111 °C were collected.

^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 7.96−6.27 (m; aromatic protons), 6.54−6.24 (q, $-O-CH{=}$), 4.65−4.14 (t,t, $N-CH_2-CH_2$, 4.25 and 3.99 (q,q; $-CH{=}CH_2$)).

Anal. Calcd for $C_{16}H_{15}NO_2S$: C, 67.35; H, 5.30; N, 4.91; S, 11.24. Found: C, 67.42; H, 5.25; N, 4.96; S, 11.41.

Monomer $VPTO_2$ was obtained after recrystallization from ethanol as a white crystalline powder mp 115−117 °C in a yield of 42%. The IR spectrum of the product $VPTO_2$ displayed characteristic sulfone bands at 1165 and 1141 cm^{-1} (KBr).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.00−7.32 (m; Ar), 6.47 (q; $-CH{=}CH_2$), 4.64 and 4.07 (t,t; $-CH_2-CH_2-N<$), 4.21 and 3.98 (q,q; $-CH{=}CH_2$).

Anal. Calcd for $C_{16}H_{15}NO_3S$: C, 63.77; H, 5.02; N, 4.65; S, 11.24. Found: C, 64.03; H, 5.17; N, 4.61; S, 11.46.

Polymerization of Phenothiazine Monomers EPT, *c*- and *t*-PPT, VPT, and $VPTO_2$. The experimental conditions and results obtained in the cationic polymerizations of the phenothiazine monomers are summarized in Table 1.

Table 1. Cationic Polymerization of Phenothiazine (Pzn) Monomers in CH_2Cl_2

monomer	monomer concn (mol·L^{-1})	Pzn meth	initiator (1.0 wt %)	reacn time (min)	reacn temp (°C)	yield (%)	M_n[a]
EPT	0.9	B	BF_3Et_2O	60	−10	55	*b*
c- and *t*-PPT	2.5	A	IOC10	10	25	85	900
VPT	0.5	B	BF_3Et_2O	45	−45	78	1600
$VPTO_2$	0.5	B	BF_3Et_2O	45	−30	75	*c*

[a] From GPC measurements (in THF, polystyrene standards.). [b] η_{inh} = 0.018 dL/g measured in CH_2Cl_2 at 20 °C, c = 0.5 g/L. [c] η_{inh} = 0.02 dL/g measured in DMAc at 25 °C, c = 0.5 g/L.

Method A. Photoinduced cationic polymerizations were carried out by dissolving 3.0 g of monomer and 1.0% of IOC10 in 5 mL of dry dichloromethane and placing the solutions in sealed 15 mm i.d. quartz reaction tubes. The samples were irradiated at 25 °C in a Rayonet photochemical reactor equipped with 16 low-pressure mercury lamps with an emission wavelength maximum at 250 nm. After 10 min of irradiation, the sample tubes were withdrawn and the contents poured into 50 mL of cold methanol, containing ca. 5 mL of pyridine. The precipitated polymers were isolated by filtration, washed with cold methanol, and dried overnight in a vacuum oven at 45 °C.

Method B. Low-temperature cationic polymerizations were carried out at the designated temperatures by injecting boron triflouride etherate through a rubber septum into a flask that had been charged with a solution of 2.0 g of the monomer and 25 mL of dry dichloromethane. After 45 min of stirring, the reaction was quenched by the addition of 3 mL of cold pyridine and then poured into cold ether. The precipitated polymer was collected by filtration, washed with ether, and dried overnight in a vacuum oven at 45 °C.

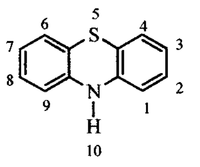
Direct Oxidization of Polymer PVPT. Polymer PVPT (0.5 g) was dissolved in 45 mL of dichloromethane and treated with 6 mL of glacial acetic acid and 2 mL of 30% hydrogen peroxide. The mixture was brought to reflux, and after 2 h, an additional 1 mL of hydrogen peroxide was added and refluxing continued overnight. The oxidized polymer was precipitated into cold methanol, filtered, and dried at 45 °C in a vacuum oven. The polymer, CoPVT, was characterized by FT-IR. The polymer was soluble in dichloromethane and 4-vinylcyclohexene diepoxide but was insoluble in cyclohexene oxide.

Photopolymerization Studies. The cationic 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 mercury−cadmium-telluride 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 room temperature in solutions of the monomers containing various concentrations of IOC10, SOC10, or $DPS-C_1C_{12}PF_6^-$ as the photoinitiator. All photoinitiator concentrations 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 films (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 per second 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}, the 1-propenyl groups at 1661−1669 cm^{-1}or the epoxy groups between 790 and 915 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.

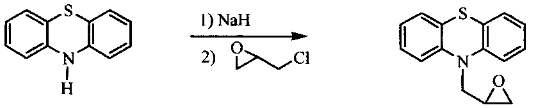
Results and Discussion

Although phenothiazines are an efficient and convenient class of photosensitizers for onium salt photoinitiated cationic polymerizations,[9] they suffer from the drawback that many of these compounds display physiological effects in man. For this reason, it is important that in any application in which they are used, contact with these compounds be minimized. It is also necessary to make certain that residues containing the photosensitizers are not exuded or extracted from the polymers that are produced on photopolymerization. This is an especially important concern when photopolymers are used in applications that come into contact with food. One means of ensuring that the phenothiazine photosensitizers are sequestered is to fit them with functional groups that allow these compounds to be copolymerized into the polymer matrix. Pursuing this approach, we started with 10*H*-phenothiazine (PT) and have prepared several monomers bearing different cationically polymerizable functional groups at the 10 position.



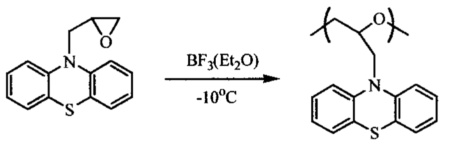
PT

Synthesis of Phenothiazine Monomers and Polymers. The sodium salt of 10*H*-phenothiazine, PT, was prepared by reaction with sodium hydride in THF and then condensed with epichlorohydrin (eq 5) to afford the desired monomer, 10-(2,3-epoxypropyl)phenothiazine, EPT. The ^{1}H NMR spectrum of EPT was identical to that reported by Simov et al. for this compound.[23]

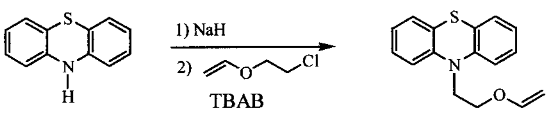


PT **EPT** (5)

EPT was readily polymerized in the presence of boron trifluoride etherate to give PEPT (eq 6). In a similar manner, the sodium salt of PT, was condensed with 2-chloroethyl vinyl ether in THF in the presence of tetra-*n*-butylammonium bromide (TBAB) (eq 7) to give the desired monomer, 10-(2-vinyloxyethyl)phenothiazine, VPT.

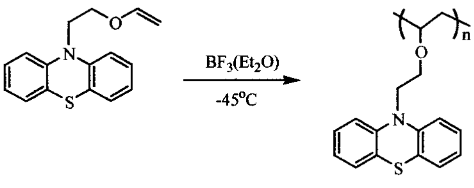


PEPT (6)



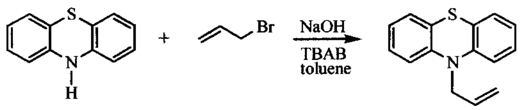
PT **VPT** (7)

The above method is considerably better than the previous synthesis reported for this compound involving a transvinylation reaction.[19] Monomer VPT was successfully polymerized (eq 8) using boron trifluoride etherate as a catalyst. The polymer, PVPT, was obtained as a colorless amorphous solid on precipitation in methanol.



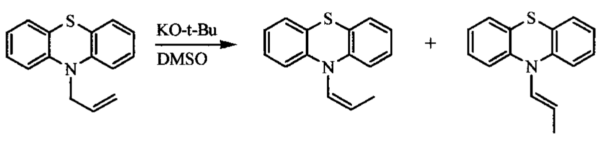
PVPT (8)

10-Allylphenothiazine APT was prepared (eq 9) by the treatment of PT with allyl bromide in the presence of tetra-*n*-butylammonium bromide (TBAB) as a phase transfer catalyst.[17]



APT (9)

Isomerization (eq 10) of APT was carried out in the presence of potassium *tert*-butoxide and dimethyl sulfoxide to give the desired 10-(1-propenyl)phenothiazine.

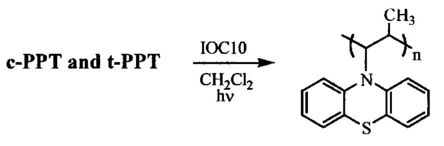


APT **c-PPT** **t-PPT**

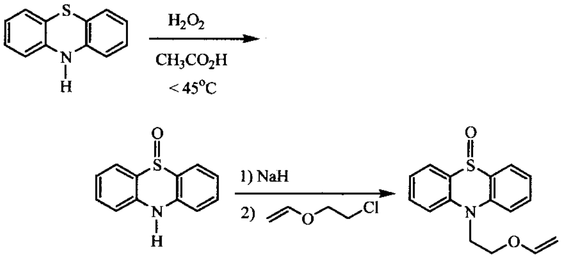
(10)

At 45 °C, the cis isomer (*c*-PPT) was isolated. At 100 °C a 55:45 mixture of cis and trans isomers was obtained. The properties of this compound agreed in all respects with those previously reported properties reported for PPT.[18] Figure 1 shows the ^{1}H NMR spectrum of the pure cis isomer as well as the spectrum of the mixture of cis and trans isomers.

Photoinitiated cationic polymerization of a mixture of isomers *c*-PPT and *t*-PPT (eq 11) gave PPPT. Previously, we had examined oxidized derivatives of N-substituted phenothiazines as photosensitizers for onium salts and found that these compounds displayed interesting behavior that was dependent on the state of oxidation of the sulfur atom.[9] Accordingly, it was of interest to prepare analogous monomers and polymers. Oxidation of PT with 30% hydrogen peroxide in acetic acid solution (eq 12) readily gave the sulfoxide, 10*H*-phenothiazine-5-oxide (PTO). Subsequent treatment with sodium hydride followed by 2-chloroethyl vinyl ether gave the desired monomer, VPTO.



PPPT (11)



PTO **VPTO** (12)

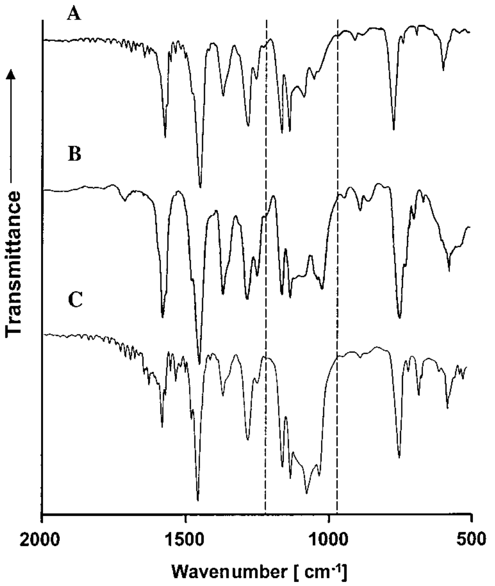
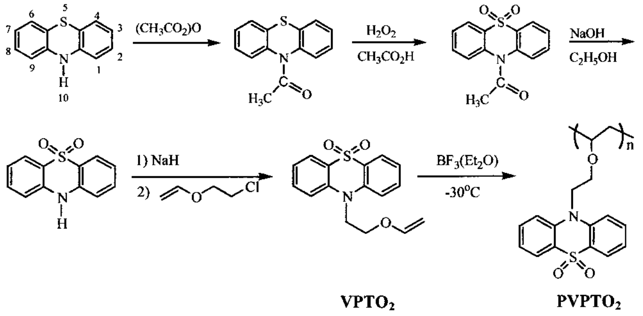


Figure 2. Comparison of the FT-IR spectra (KBr) of polymers: (A) poly(10-(2-vinyloxyethyl)phenothiazine), PVPT; (B) partially oxidized PVPT; (C) poly(10-(2-vinyloxyethyl)phenothiazine-5,5-dioxide), PVPTO$_2$.

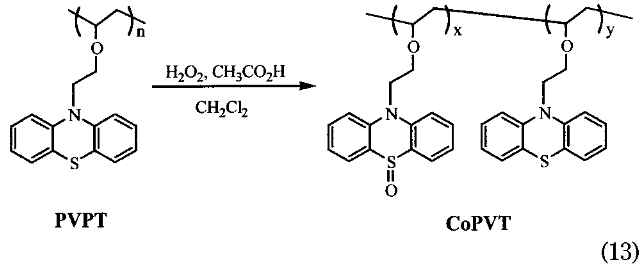
Scheme 2



The corresponding sulfone monomer VPTO$_2$ was prepared and polymerized to give PVPTO$_2$ using the synthetic sequence shown in Scheme 2.

Unfortunately, although PVPTO$_2$ was soluble in DMF and DMAc, it was insoluble in all monomers investigated. For this reason, it could not be used as a photosensitizer in onium salt photopolymerizations.

In an attempt to shorten the synthetic route for the preparation of PVPTO$_2$ and to improve the solubility, the partial oxidation of PVPT (eq 13) with 30% hydrogen peroxide in glacial acetic acid was investigated. Although the original intention was to oxidize PVPT to yield a copolymer containing PVPTO$_2$ repeat units, the infrared spectrum (Figure 2) showed only the presence of bands (1050 cm^{-1}) assigned to the sulfoxide groups. Under these conditions, no evidence of oxidation to the polymeric sulfone (1140 cm^{-1}, 1330 cm^{-1}) was observed.



(13)

Table 2. UV Absorbtion Characteristics of Phenothiazine Monomers and Polymers[a]

monomer or polymer	λ_{max} (ϵ)
10-(2,3-epoxypropyl)phenothizine	255 (45380) 310 (4400)
poly(10-(2,3-epoxypropyl) phenothizine)	254 (12660) 316 (4300)
10-allylphenothiazine	255 (41700) 313 (4660)
cis−10-(1-propenyl)phenothiazine	255 (42870) 311 (4280)
poly(10-(1-propenyl)phenothiazine)	259 (41900) 315 (6180)
2-(10-phenothiazinyl)ethyl vinyl ether	254 (28640) 303 (5,850)
poly(2-(10-phenothiazinyl)ethyl vinyl ether	256 (28,600) 311 (3,600)
2-(10-phenothiazinyl-5,5-dioxide)ethyl vinyl ether	237 (15,000) 271 (17000) 195 (10000) 333 (7000)
10-phenothiazine[b]	253 (43400) 318 (4950)

[a] Measured in THF. [b] From ref 23, measured in methanol.

Attempts to use stronger oxidizing conditions to further oxidize the sulfoxide to the sulfone resulted in the formation of insoluble polymeric products.

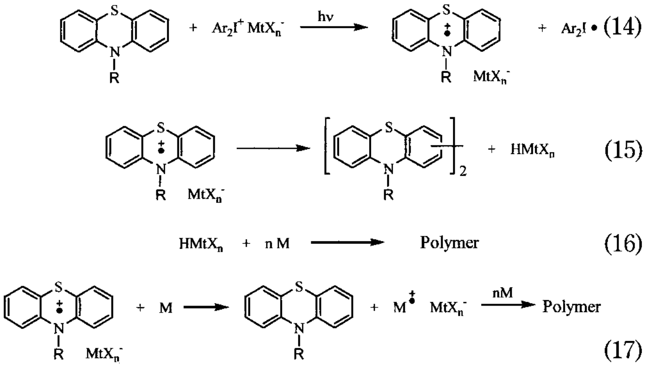
Table 2 gives the UV spectral characteristics for the monomers and polymers prepared during the course of this work. Typically, these materials exhibit two intense absorption bands that overlap well with the major emission bands of mercury arc lamps at 254 and 313 nm.[24]

Photosensitized Cationic Polymerizations using Phenothiazines. Several objectives were set for this portion of the research. First, it was the aim of this investigation to determine whether the phenothiazine monomers prepared during this work would active as photosensitizers for various types of onium salt cationic photoinitiators. Second, we wished to determine whether polymers produced by the polymerization of the monomeric phenothiazines could also be used as photosensitizers. A third objective was to examine both monomeric and polymeric phenothiazines photosensitizers for the cationic photopolymerization of both epoxides and vinyl ether monomers. It is not possible to present in this article all the possible permutations and combinations of photosensitizers, monomers, and onium salt photoinitiators that were examined. Rather, we have elected to present here some representative studies that address and exemplify the objectives outlined above.

Application of the electron-transfer mechanism of onium salt photosensitization proposed in Scheme 1 to phenothiazine monomers or polymers would involve the photoinduced formation of the corresponding phenothiazine cation radicals. In eq 14 of Scheme 3, this is exemplified using a diaryliodonium salt.

Evidence for the formation of phenothiazine cation radicals by onium salt mediated photooxidation was presented previously by us,[9,11] Rodrigues and Neumannn[10] and Yagci et al.[12] The ability of the phenothiazine cation radical to initiate cationic polymerization has been previously reported by several research groups. Nomura et al.[25,26] described studies in which the cation radicals of substituted phenothiazines were prepared by electrochemical methods and used for the polymerization of vinyl ethers and 4-methoxystyrene. Abu-Abdoun and Ledwith[27] prepared stable solutions of the cation radicals 10*H*-phenothiazine and as well as several other

Scheme 3



substituted derivatives by reaction of the parent phenothiazines with the cation radical salt, tris(4-bromophenylamine) hexafluoroantimonate. Depending on whether substitutents were present and their position in the molecule, phenothiazine cation-radical salts were observed to either thermally or photochemically initiate the polymerization of cyclohexene oxide, tetrahydrofuran and *N*-vinylcarbazole. The two mechanisms shown in Scheme 3 were proposed by the Nomura group[24,25] to account for the initiation of cationic polymerization by phenothiazine cation radicals. The first mechanism (eqs 15 and 16) involves coupling of the phenothiazine cation radicals with the concomitant release of a proton. Subsequent polymerization takes place by attack of the Bronstead acid on the monomer. An alternative mechanism (eq 17) consists of an electron transfer between the phenothiazine cation radical with the monomer to form a monomer cation radical. In this latter case, polymerization takes place by interaction of the monomer cation radicals with additional monomer. The second mechanism appears to be operative when vinyl ether monomers are used since these workers showed that the reactivity of the phenothiazine cation radicals could be related to their ionization potentials; the higher the oxidation potential of the parent phenothiazine the greater the reduction potential of the corresponding phenothiazine cation radical and also the greater its activity as an initiator.

The ability of phenothiazine monomers and polymers to photosensitize the cationic photopolymerization of various monomers was evaluated using Fourier transform real-time infrared spectroscopy (FT-RTIR). RTIR has been proven to be an extremely useful method for monitoring the kinetics of very rapid photopolymerization reactions and, for that reason, has been used in this laboratory as well as by many other investigators to probe these types of reactions.[28−31] The apparatus used in these experiments is described in the experimental portion of this article. Samples of liquid monomer containing the photoinitiator and photosensitizer were placed between two poly(propylene) films and irradiated at room temperature using broad band UV light to initiate polymerization. The progress of the polymerizations was monitored by following the decrease in the absorbance of characteristic IR bands of the epoxide (780−915 cm^{-1}), 1-propenyl (1668 cm^{-1}), or vinyl ether (1620 cm^{-1}) groups in the respective monomers. Each kinetic run was carried out a minimum of three times. The resulting data were averaged, and the resulting conversion vs time curves are presented here. It should be noted that since the photopolymerizations were conducted using broadband UV irradiation, the resulting rates are a composite of both direct and photosensitized processes.

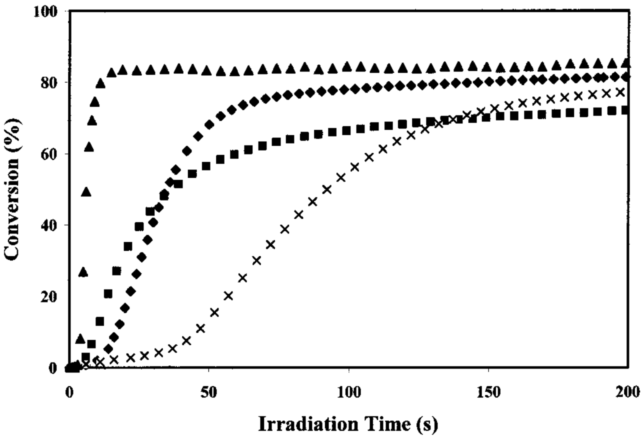


Figure 3. RTIR comparative study of the cationic photopolymerization of cyclohexene oxide using 1.0% IOC10 as the photoinitiator: (◆) alone and (■) in the presence of 0.5% 10-(2-vinyloxyethyl)phenothiazine, (×) 10-(2-vinyloxyethyl)phenothiazine-5-oxide, and (▲) 10-(2-vinyloxyethyl)-phenothiazine-5,5-dioxide. Light intensity: 200 mJ/cm^2·min.

In Figure 3 is shown a study of the photopolymerization of cyclohexene oxide conducted in the presence of 1.0% IOC10 as a photoinitiator using 0.5% VPT, VPTO, and VPTO$_2$ as photosensitizers. Also included in this figure for comparison is a study in which no phenothiazine monomer was used. The epoxide band of the monomer at 780 cm^{-1} was monitored during this kinetic study. When VPT is used as a photosensitizer, a reduction in the induction period for the polymerization was noted. The inclusion of VPTO resulted in an increase in the induction period as well as a retardation of the polymerization rate. In contrast, the sulfone monomer, VPTO$_2$, displays a marked reduction in both the induction period and an increase in the overall rate of polymerization. This is consistent with an efficient photosensitization process that generates considerably more active initiating and propagating species per unit time than the corresponding direct photolysis process. Similar behavior was noted previously[9] in photopolymerizations conducted with simple phenothiazine, phenothiazine-5-oxide and phenothiazine-5,5-dioxide compounds.

A comparison of the photopolymerizations of limonene dioxide carried out using the triarylsulfonium salt, SOC10, as the photoinitiator in the presence and absence of EPT is shown in Figure 4. The epoxy band at 800 cm^{-1} in the infrared spectrum was used to follow the polymerization of this monomer. The efficacy of the inclusion of this photosensitizer on the rate of polymerization can be clearly seen in this figure. The application of EPT as a photosensitizer for the polymerization of 2-chloroethyl vinyl ether is shown in Figure 5. In this case, the dialkylphenacyl sulfonium salt, DPS−C$_1$C$_{12}$PF$_6$, was used as the photoinitiator. Again, a considerable reduction in the induction period and an increase in the rate of polymerization were observed. Figures 3−5 clearly establish that these two phenothiazine monomers are effective as photosensitizers for all three types of onium salt photoinitiators.

A comparison of the photosensitizing effects of *c*-PPT and its corresponding polymer, PPPT, on the polymerization of cyclohexene oxide in the presence of IOC10 is shown in Figure 6. Very similar results are observed

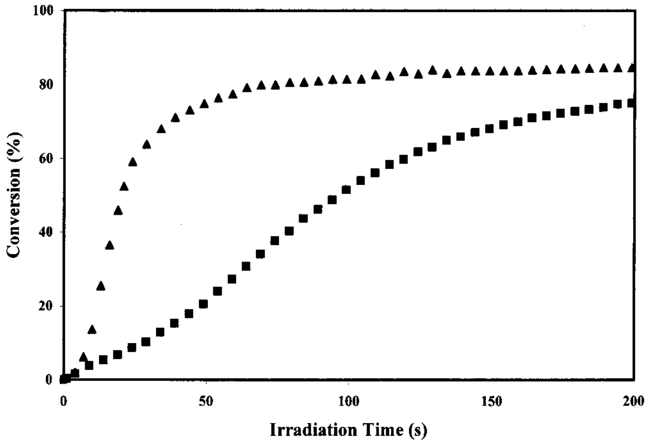


Figure 4. Comparison of the photopolymerization of limonene dioxide in the presence (▲) and absence (■) of 0.5% of 10-(2,3 epoxypropyl)phenothiazine) (EPT), using 1.0% SOC10 as photoinitiator. Light intensity: 250 mJ/cm^2·min.

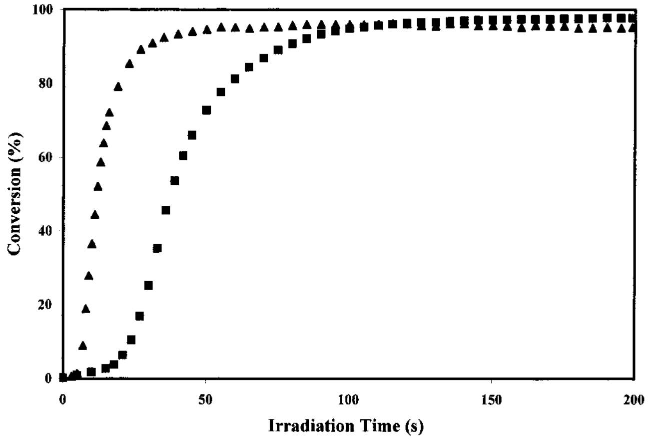


Figure 5. FT-RTIR study of photopolymerization of 2-chloroethyl vinyl ether, EPT: (■) alone and (▲) in the presence of 0.5% 10-(2,3 epoxypropyl)phenothiazine. Light intensity: 250 mJ/cm^2·min; 0.5% DPS$-$C$_1$C$_{12}$PF$_6$.

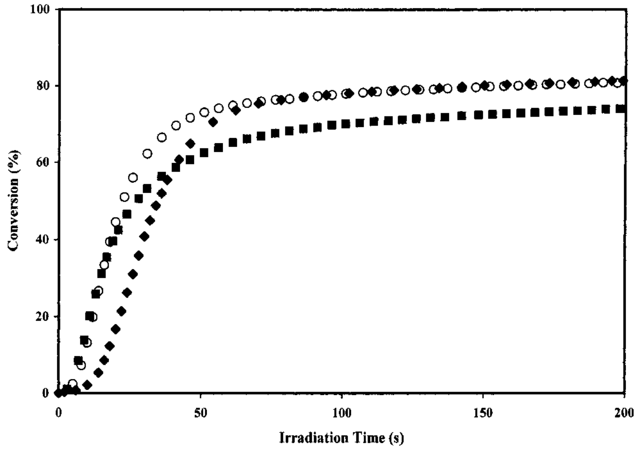


Figure 6. Comparison of the cationic photopolymerization of cyclohexene oxide using 1.0% IOC10 as the photoinitiator: (◆) alone and in the presence of (■) 0.5% *cis*-10-propenylphenothiazine and (○) poly(10-propenylphenothiazine). Light intensity: 200 mJ/cm^2·min.

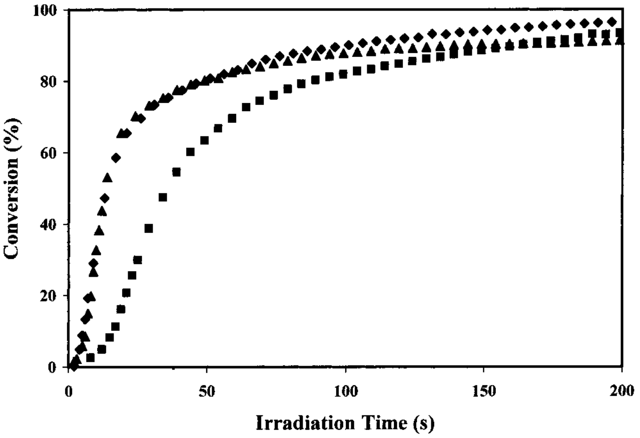


Figure 7. Comparison of the photosensitized polymerization of 4-vinylcyclohexene dioxide carried out with 1.0% IOC10: (■) alone and in the presence of (◆) 0.5% 10-(2-vinyloxyethyl)-phenothiazine and (▲) poly(10-(2-vinyloxyethyl)-phenothiazine). Light intensity: 400 mJ/cm^2·min.

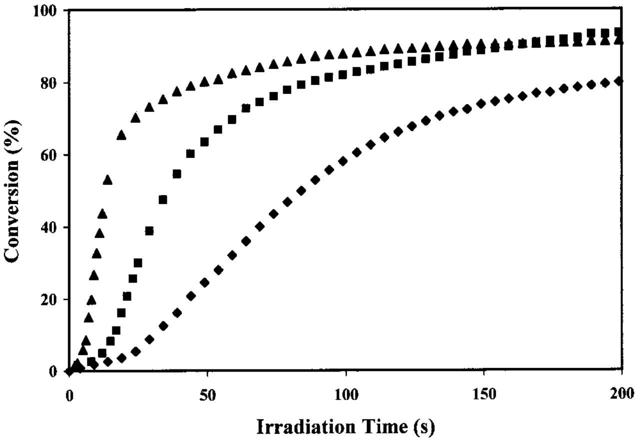


Figure 8. Study of the photopolymerization of 4-vinylcyclohexene dioxide with 1.0% IOC10: (■) alone and using (▲) 0.5% poly(10-(2-vinyloxyethyl)-phenothiazine) and (◆) partially oxidized poly(10-(2-vinyloxyethyl)-phenothiazine). (Light intensity 400 mJ/cm^2·min).

for both the monomer (*c*-PPT) and the polymer. Both photosensitizers decrease the induction period and have a modest effect in increasing the polymerization rate. An analogous study depicted in Figure 7 was carried out using VPT and its polymer, PVPT, in the photopolymerization of 4-vinylcyclohexene dioxide. The epoxide band at 794 cm^{-1} was monitored for this monomer. Again, both monomeric and polymer photosensitizers display very similar behavior in the polymerization of this difunctional epoxide monomer.

Figure 8 shows the results of a study of the photopolymerization of 4-vinyl-cyclohexene dioxide carried out in the presence of PVPT and also with partially oxidized CoPVPT containing sulfoxide groups. As in the study depicted in Figure 3, the introduction of sulfoxide groups has a marked retardation on the rate of polymerization as compared both with polymerization conducted with PVPT and with no photosensitizer present.

Conclusions

Five different cationically polymerizable monomers bearing the phenothiazine group have been prepared by a series of straightforward synthetic reactions at the nitrogen atom of 10*H*-phenothiazine. The monomers were characterized by various analytical techniques and then employed as both comonomers and photosensitizers for the photolysis of diaryliodonium, triarylsulfonium and dialkylphenacylsulfonium salt cationic photoinitiated polymerizations of epoxides and vinyl ether monomers. Marked acceleration of the photopolymerizations of these monomers was observed in the presence of small quantities of the monomeric photosensitizers. It is noteworthy that the phenothiazine monomers serve a dual function in that they photosensitize the photopolymerizations of various monomers to which they are added, further, these monomers copolymerize with the these same monomers to give polymers that also function as photosensitizers. Alternatively, the polymers produced by the independent polymerization of the phenothiazine monomers can also be used as photosensitizers for both vinyl and ring-opening cationic photopolymerizations.

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