

Vinyl Monomers Bearing Chromophore Moieties and Their Polymers. VII. Synthesis, Photochemical, and Initiation Behavior of Acrylic Monomers Bearing Phenothiazine Oxide Moieties and Their Polymers

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ABSTRACT: Four acrylic monomers bearing phenothiazine oxide moieties, that is, *N*-acryloyl-phenothiazine-5-oxide (APTO), *N*-acryloyl-2-chlorophenothiazine-5-oxide (ACPTO), *N*-acryloyl-phenothiazine-5,5-dioxide (APTDO), and *N*-acryloyl-2-chlorophenothiazine-5,5-dioxide (ACPTDO) were synthesized by oxidation of corresponding *N*-acryloyl-phenothiazine (APT) and *N*-acryloyl-2-chlorophenothiazine (ACPT) using sodium perborate as an oxidant. These monomers could easily be polymerized by initiation of AIBN. The emission fluorescence spectra of the monomers and their polymers were recorded, and the results indicated that these 4 new monomers possess a fluorescence structural self-quenching effect (SSQE), as we have reported previously. Moreover, with the change of the electronic structure of sulfur atom in the phenothiazine chromophore, that is, from sulfide to sulfoxide and sulfone groups, the tendency of SSQE of these monomers is in the order of APT > APTO > APTDO. This would be ascribed mainly to the decrease of electron-donating abilities of monomers in a sequence of sulfide, sulfoxide, and sulfone groups; that is, at the sulfur atom of these monomers, APT has 2 lone-pair electrons, APTO has 1 lone-pair electrons, and APTDO completely loses its lone-pair electrons. Based on the exciplex formation, the monomers APTO, APTDO, ACPTO, and ACPTDO could act as sensitizers for the photopolymerization of acrylonitrile (AN). The combination of APTO or ACPTO with organic peroxides such as BPO could also initiate the polymerization of vinyl monomers, such as AN, by redox nature. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 1191–1199, 1998

Key words: *N*-acryloyl-phenothiazine oxides; fluorescence; fluorescence structural self-quenching effect; polymerizable photosensitizer

INTRODUCTION

A series of acrylic monomers having electron-donating chromophores, namely, *N*-(4-*N'*,*N'*-dimethylamino)-

benzyl methacrylate, *N*-(4-*N'*,*N'*-dimethylamino-phenyl)acrylamides,¹ *N*-acryloyl-*N'*-phenylpiperazines,² *N*-(4-*N'*,*N'*-dimethylaminophenyl)maleimide, *N*-(4-*N'*,*N'*-dimethylaminophenyl)itaconimide,³ 8-acryloyloxyquinolines,⁴ *N*-methyl-*N*-methacryloyl-ethylaniline and *N*-acryloylphenoxazine, as well as their polymers, have been synthesized.^{5,6} Their photochemical behavior, including fluorescence and photoinitiation behavior, have been explored. It has been

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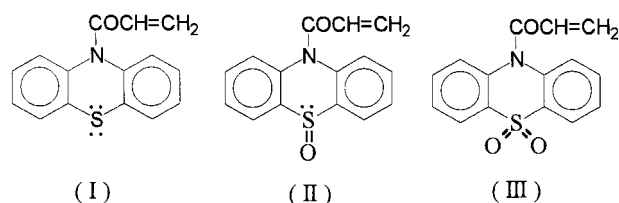
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found that the fluorescence intensities of these monomers are always dramatically lower than those of their corresponding polymers at the same chromophore concentration. We have termed such phenomena as the structural self-quenching effect (SSQE) in order to distinguish it from the fluorescence concentrational self-quenching effect, which is well known thus far.⁷ The fluorescence SSQE are assumed to be due to the intra- or intermolecular charge transfer interaction between the coexisted electron-donating acrylic carbon-carbon double bond and electron donating chromophore moiety in the same molecule upon ultraviolet (UV) light irradiation.

The electron-accepting acrylic carbon-carbon double bond does play a key role in SSQE of the above monomers, which is clarified by the fact that the fluorescence of the polymers in solution can be quenched by adding electron-deficient compounds, such as unsaturated nitriles, like methylacrylonitrile, acrylonitrile (AN), fumaronitrile, and tetracyanoethylene, and unsaturated acrylic esters like methyl acrylate, methyl methacrylate (MMA), and dimethyl fumarate. The above monomers can be photopolymerized in themselves without any other sensitizers. They not only sensitize the photopolymerization of other electron-deficient monomers, such as AN, MMA, and acrylamide, which do not have chromophore moieties but also incorporate into the polymer chains; that is, they act as polymerizable photosensitizers. Based on this fact, it is said that if an acrylic monomer has an electron-donating chromophore, it can act as a polymerizable photosensitizer to initiate the polymerization of electron-deficient monomers, including itself.

The electron-donating nature of the above-mentioned chromophores is mainly contributed by nitrogen atom. In order to understand whether the atoms other than nitrogen, such as oxygen and sulfur atoms in chromophore, contribute the electron-donating nature in SSQE, we synthesized acrylic monomers having phenothiazine moieties,⁸ that is, *N*-acryloylphenothiazine (APT), *N*-acryloyl-2-chlorophenothiazine (ACPT), *N*-acryloyl-2-acetylphenothiazine, and *N*-acryloyl-1-azaphenothiazine, and phenoxazine moiety, that is, *N*-acryloylphenoxazine, and their polymers.⁶ It has been observed that they also do possess the SSQE and act as a polymerizable photosensitizer to initiate the polymerization of electron-deficient monomers, such as AN, as we have expected.

It is known that the sulfur atom in organic compounds can be oxidized to sulfoxide and sulfone shown as follows:



The sulfur atom in sulfide group of organic compounds has 2 lone pair electrons; that is, (I) has 2, and (II) has 1 lone pair electrons, whereas (III) does not have lone pair electrons at the sulfur atom. Therefore, the understanding of the fluorescence behavior of (I), (II), and (III) is of our interest.

In this article, 4 new acrylic monomers bearing phenothiazine oxide moieties, that is, *N*-acryloylphenothiazine-5-oxide (APTO), *N*-acryloyl-2-chlorophenothiazine-5-oxide (ACPTO), *N*-acryloylphenothiazine-5,5-dioxide (APTDO), and *N*-acryloyl-2-chlorophenothiazine-5,5-dioxide (ACPTDO) were synthesized and radically polymerized aiming at the evaluation of the effect of different electronic states of the sulfur atom in the heterocyclic chromophore on the photochemical behaviors, including fluorescence and sensitizing behaviors. The combination of APTO, which has sulfoxide moiety, with BPO, which forms a redox initiation system to initiate the vinyl polymerization is also of our concern.

EXPERIMENTAL

Materials

Phenothiazine, 2-chlorophenothiazine, 3-bromopropionyl chloride, and 1,8-diazabicyclo[5,4,0] undec-5-ene (DBU) were from Aldrich and used as received. Glacial acetic acid and sodium perborate were analytical grade. Toluene was redistilled after refluxing over metallic sodium for about 2 h. Other solvents and reagents used for spectral measurement were purified by conventional methods and confirmed no existence of interfering impurities.

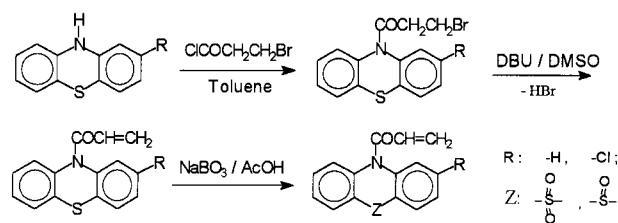
Methods

¹H nuclear magnetic resonance (¹H-NMR) were recorded on a Bruke ARX-400 spectrometer in DMSO-*d*₆ at 25°C, the chemical shifts in parts per million (ppm) are reported downfield from 0.00

ppm using tetramethylsilane (TMS) as an internal reference. Infrared (IR) spectra were recorded on a Nicolet Magna 750 Fourier transform infrared (FTIR) spectrometer. Mass spectra were measured with a ZAB-HS instrument. The UV spectra were recorded on a Shimadzu UV 2100 spectrophotometer. The fluorescence emission spectra were performed on a Hitachi M-850 fluorescence spectrophotometer at room temperature. The slit widths of both monochromators were 5 nm.

Synthesis of Monomers

The monomers were synthesized by a route via acylation, dehydrobromination, and oxidation, as follows:



N-(3-Bromopropionyl) phenothiazine (BPPT)

A solution of 19 g (0.11 mol) of 3-bromopropionyl chloride in 50 mL of dry toluene was added dropwise to a well-stirred solution of 15 g (0.075 mol) of phenothiazine in 150 mL of dry toluene and refluxing. The reaction mixture was kept at refluxing for 30 h. The crude product obtained by removing solvent, and excess 3-bromopropionyl chloride under reduced pressure was recrystallized twice from ethanol to give a white crystal (yield, 80%; mp, 138–140°C).

¹H-NMR (ppm): 3.04 (br. s, 2H); 3.62 (t, 2H); 7.24–7.47 (m, 8H). IR (cm⁻¹): 1676; 1459; 810; 755. MS (m/e): 335; 199. Elemental analysis: calcd for C%, 53.86; H%, 3.59; N%, 4.19. Found: C%, 53.65; H%, 3.68; N% 4.24.

N-(3-Bromopropionyl)-2-chlorophenothiazine (BPCPT)

From 10 g (0.06 mol) of 3-bromopropionyl chloride and 9.8 g (0.04 mol) of 2-chlorophenothiazine, a white crystal was obtained, as described as the procedure of BPPT (yield, 73%; mp, 113–115°C).

¹H-NMR (ppm): 3.10 (br. s, 2H); 3.63 (t, 2H); 7.33–7.74 (m, 7H). IR (cm⁻¹): 1683; 1459; 808; 753. MS (m/e): 369; 287; 233; 198. Elemental analysis: calcd for C%, 48.83; H%, 2.98; N%, 3.80. Found: C%, 49.02; H%, 3.13; N%, 3.88.

N-Acryloylphenothiazine

6.8 g (0.045 mol) of 1,8-diaza-bicyclo[5,4,0]undec-5-ene (DBU) was added to a stirred solution of 15 g (0.045 mol) of BPPT in 60 mL of DMSO. The reaction mixture was kept at 80–90°C for 3 h, then cooled and poured into 600 mL of ice water to give a crude product. After being filtrated, dried, and recrystallized from hexane, a whiter crystal APT was obtained (yield, 57%; mp, 109–110°C).

¹H-NMR (ppm): 5.88–5.91 (q, 1H); 6.43–6.54 (m, 2H); 7.58–7.86 (m, 8H). IR (cm⁻¹): 1671; 1453; 1048; 769. MS (m/e): 269; 253; 198; 55. Elemental analysis: calcd for C%, 71.12; H%, 4.38; N%, 5.53. Found: C%, 71.05; H%, 4.39; N%, 5.69.

N-Acryloyl-2-chlorophenothiazine

From 6.1 g (0.04 mol) of 1,8-diaza-bicyclo[5,4,0]undec-5-ene (DBU) and 15 g (0.04 mol) of BPCPT, a white crystal was obtained, as described as the preparation of APT, and recrystallized from a mixture of petroleum ether and benzene (yield, 31%; mp, 128–130°C).

¹H-NMR (ppm): 5.64–5.79 (m, 3H); 7.10–7.65 (m, 7H). IR (cm⁻¹): 1670; 1620; 960; 750. MS (m/e): 287; 232; 197; 55. Elemental analysis: calcd for C%, 62.62; H%, 3.50; N%, 4.87. Found: C%, 62.65; H%, 3.76; N%, 4.78.

N-Acryloylphenothiazine-5-oxide

2.0 g (0.013 mol) of sodium perborate was added to a stirred solution of 2.5 g (0.01 mmol) of APT in 50 mL of glacial acetic acid. The reaction was kept at 45–50°C until the reaction completion indicated by thin layer chromatography (TLC). The crude product was obtained by pouring the reaction mixture to a stirred 600 mL of ice water and recrystallized from ethyl acetate to give a white crystal (yield, 51%; mp, 178–180°C).

¹H-NMR (ppm): 5.88–5.91 (q, 1H); 6.43–6.54 (m, 2H); 7.58–7.86 (m, 8H). IR (cm⁻¹): 1671; 1453; 1048; 769. MS (m/e): 269; 253; 198; 55. Elemental analysis: calcd for C%, 66.84; H%, 4.08; N%, 5.20. Found: C%, 66.58; H%, 4.05; N%, 5.14.

N-Acryloyl-2-chlorophenothiazine-5-oxide

0.5 g (3.3 mmol) of sodium perborate was added to a stirred solution of 1.0 g (3.4 mmol) of ACPT in 20 mL of glacial acetic acid. The reaction was kept at 45–50°C for 6 h. A white crystal was obtained

by the same way of APTO (yield, 58%; mp, 114–116°C).

¹H-NMR (ppm): 5.92–5.95 (q, 1H); 6.45–6.55 (m, 2H); 7.36–8.01 (m, 7H). IR (cm⁻¹): 1676; 1615; 1450; 1046; 762. MS (m/e): 303; 250; 232; 55. Elemental analysis: calcd for C%, 59.26; H%, 3.29; N%, 4.61. Found: C%, 59.32; H%, 3.74; N%, 4.66.

***N*-Acryloylphenothiazine-5,5-dioxide**

8.2 g (0.054 mol) of sodium perborate was added to a stirred solution of 3.0 g (0.012 mol) of APT in 60 mL of glacial acetic acid. The reaction was kept at 45–50°C for 8 h. The crude product was obtained according to the method of APT and recrystallized from methanol to give a white crystal (yield, 53%; mp, 165–167°C).

¹H-NMR (ppm): 5.92–5.95 (q, 1H); 6.41–6.50 (m, 2H); 7.63–8.05 (m, 8H). IR (cm⁻¹): 1682; 1584; 1314; 1124; 760. MS (m/e): 281; 235; 55. Elemental analysis: calcd for C%, 63.09; H%, 3.56; N%, 4.91. Found: C%, 62.69; H%, 3.42; N%, 4.79.

***N*-Acryloyl-2-chlorophenothiazine-5,5-dioxide**

From 5.0 g (0.033 mol) of sodium perborate and 1.5 g (0.005 mol) of ACPT, a white needle crystal was obtained according to the method of APTDO (yield, 31%; mp, 183–185°C).

¹H-NMR (ppm): 5.96–5.99 (q, 1H); 6.45–6.52 (m, 2H); 7.66–8.13 (m, 7H). IR (cm⁻¹): 1687; 1581; 1320; 1124; 969; 782; 744. MS (m/e): 319; 265; 55. Elemental analysis: calcd for C%, 56.30; H%, 3.13; N%, 4.38. Found: C%, 56.43; H%, 3.16; N%, 4.35.

Polymerization

The polymerization of these monomers were carried out in dimethyl foramide (DMF) by using 2 wt % of AIBN as an initiator in a sealed glass tube at 60°C for 48 h. The polymer was obtained by pouring into a large excess of methanol and purified by reprecipitation from DMF and methanol several times.

Kinetic Study for the Photopolymerization of AN

The kinetics for the photopolymerization of AN sensitized by APT, APTO, or APTDO were performed by a dilatometric method in a thermostat. A 3-mL-volumed dilatometer made of hard glass was used, and the photopolymerizations were carried out in DMF under UV irradiation. 300 W of high-pressure mercury arc lamp was used as a

light source, which was filtered by potassium chromate solution. The distance between the centers of the dilatometer and UV lamp was 6 cm. Oxygen in the polymerization system was purged out beforehand.

The thermopolymerization of AN initiated by APTO–BPO system in DMF was pursued by dilatometric method. A 3-mL-volumed dilatometer was used in a thermostat. Oxygen was purged out from the polymerization system beforehand.

RESULTS AND DISCUSSION

Monomer Synthesis and Polymerization

As mentioned in our previous article, acrylic *N*-substituted monomers having aromatic heterocyclic chromophores, such as *N*-acrylylcarbazole and *N*-acrylylphenothiazines, cannot be obtained directly by the reaction of acrylyl chloride with the corresponding heterocyclic compounds, may be due to the weak acidity of H atom on the —NH— group between the 2 aromatic rings. Thus, these monomers were usually obtained by the reactions via acylation of nitrogen atom of heterocyclic compounds with β -halogenated propionyl chloride, followed by dehydrohalogenation of related compounds. In our previous work, we successfully obtained those monomers using β -chloropropionyl chloride as an acylation reagent, followed by dehydrohalogenation with DBU.

It is reported that sodium perborate can selectively oxidize the sulfur atom of organic sulfides to sulfoxide and sulfone groups.^{9,10} APTO and APTDO can be obtained easily by controlled oxidation of APT with certain amount of sodium perborate in glacial acetic acid at 45–50°C.

The 4 new monomers APTO, APTDO, ACPTO, and ACPTDO can be radically polymerized by using AIBN as an initiator, and the polymers are confirmed by the disappearance of 1620 cm⁻¹ in IR spectra of the polymers.

Absorption Spectra of These Monomers and Their Polymers

All of the new monomers are strong UV absorbing compounds, which might be used in manufacture of lenses, optical devices, plastic films, and hydrogels.¹¹ Shown in Figure 1 is the absorption spectra of the oxides of APT, as well as their polymers in dichloroethane. The absorption wavelength

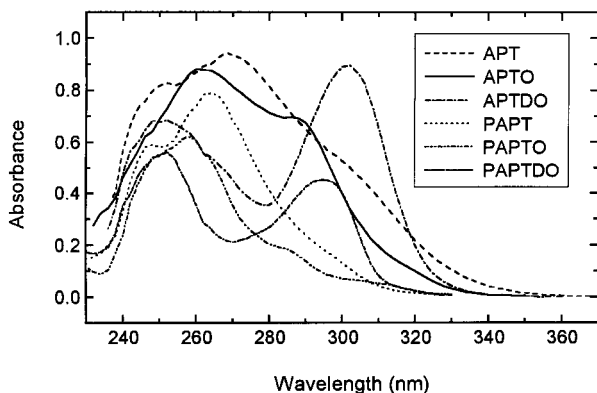


Figure 1 Absorption spectra of the APT oxides and their polymers in 1,2-dichloroethane (conc: 1.0×10^{-4} mol/L).

maximum ($\lambda_{\max}$), and the corresponding molar extinction coefficient (ϵ) of APT, APTO, APTDO, and their polymers in DCE, are summarized in Table I. It shows that the absorption band of these polymers has little more blue shift than that of the corresponding monomers, likely due to the disappearance of the carbon–carbon double bond in polymers, which lessens the conjugation of the polymers. The new peak appeared at 300 nm in APTDO and ACPTDO, which may be attributed to the intermolecular action between newly formed oxides of sulfur atom of APTDO and ACPTDO molecules, but the details still need further exploration.

Fluorescence Behavior of the Monomers and Polymers

The monomers APTO and ACPTO contain both an electron-accepting acrylic carbon–carbon dou-

ble bond and an electron-donating chromophore in the same molecules. The electron-donating nature of these chromophores is contributed mainly by 1 lone pair electrons of sulfides. As regards to the electron-donating nature of the sulfone groups of APTDO and ACPTDO, it was likely contributed by the lone pair electrons of oxygen atoms. Shown in Figures 2 and 3 are the emission fluorescence spectra of APTO and APTDO, as well as their polymers, which were recorded by excitation at 402 nm. Obviously, the fluorescence intensities of the monomers are much lower than those of their corresponding polymers at the same chromophore concentration. A SSQE is also observed on this kind of monomers, as we have reported previously.⁸ The similar results are also recorded for ACPTO, ACPTDO, and their polymers. It means that upon UV light irradiation, a charge transfer interaction took place between sulfur-containing electron-donating chromophores and electron-accepting C=C double bonds.

To confirm that such a low-emission fluorescence intensity of the monomers is not caused by concentrational factor, we recorded the fluorescence emission of the monomer APTO, a representative of this kind of monomers, and its polymer at different concentrations (as shown in Fig. 4). It is significant that the fluorescence intensities of APTO are always lower than those of its polymer P(APTO) at any concentrations. Since the difference between APTO and its polymer in structure is only in the disappearance of acrylic carbon–carbon double bond of the polymer, it is presumed that the lower emission fluorescence of the monomer is attributed to the fluorescence-

Table I $\lambda_{\max}$ (nm) and Extinction Coefficient (ϵ ; mol⁻¹; 1 cm⁻¹) of Monomers and Their Polymers in 1,2-Dichloroethane ($1.0 \times 10^{-4}M$)

Monomer	Polymer	λ_1 (nm)	ϵ_1 (10^3)	λ_2 (nm)	ϵ_2 (10^3)
APT		268	7.2	251	9.4
	P (APT)	261	7.6	252	6.5
APTO		286	7.0	263	8.7
	P (APTO)	286	1.8	257	6.6
APTDO		301	9.0	251	7.3
	P (APTDO)	295	4.5	252	5.9
ACPT		272	9.8	251	9.4
	P (ACPT)	264	9.9	251	8.0
ACPTO		295	5.2	263	9.8
	P (ACPTO)	262	7.5	251	8.2
ACPTDO		302	7.8	253	10.0
	P (ACPTDO)	296	6.2	251	11.0

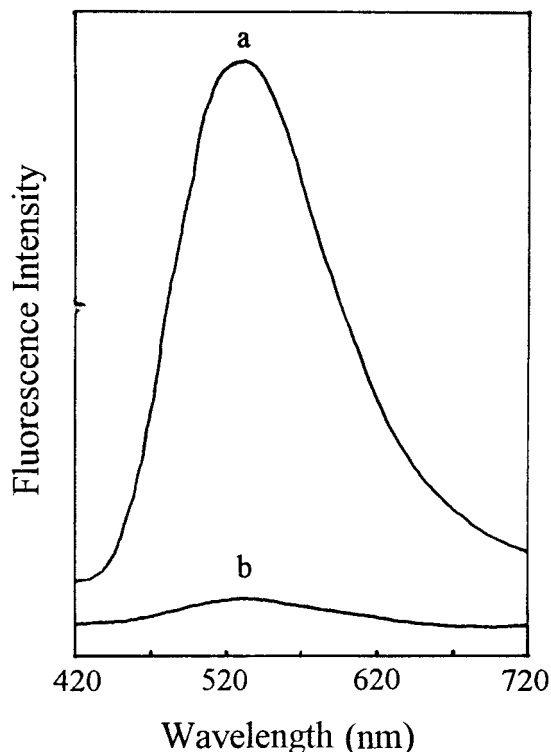


Figure 2 Fluorescence spectra of (a) P(APTO) and (b) APTO in 1,2-dichloroethane. [Chromophore] = 0.01 mol/L; λ_{ex} = 402 nm.

quenching of the chromophore by the coexisted acrylic carbon-carbon double bond in the same molecule.

To clarify that the carbon-carbon double bonds do play an important role in the SSQE of APTO, we added electron-deficient unsaturated compounds, which do not have chromophores, such as MMA, dimethyl fumarate (DMFM), fumaronitrile (FN), tetracyanoethene (TCNE), and tetracyano-*p*-quinodimethane (TCNQ) to the P(APTO) solution. It was observed that the fluorescence intensities of the polymers decreased gradually as the concentration of the quenchers increased. Shown in Figure 5 is the fluorescence-quenching of P(APTO) in 1,2-dichloroethane by adding TCNQ. The same facts were also observed in the other quenchers. It can be seen that with the increase of electron-deficiency of the carbon-carbon double bond of the quenchers, the quenching efficiency increases in the order of MMA < DMFM < FN < TCNE < TCNQ. It is obvious that the more electron deficiency the double bond of the quenchers has, the easier to form an exciplex with the electron donors; thus, the quenching efficiency increases.

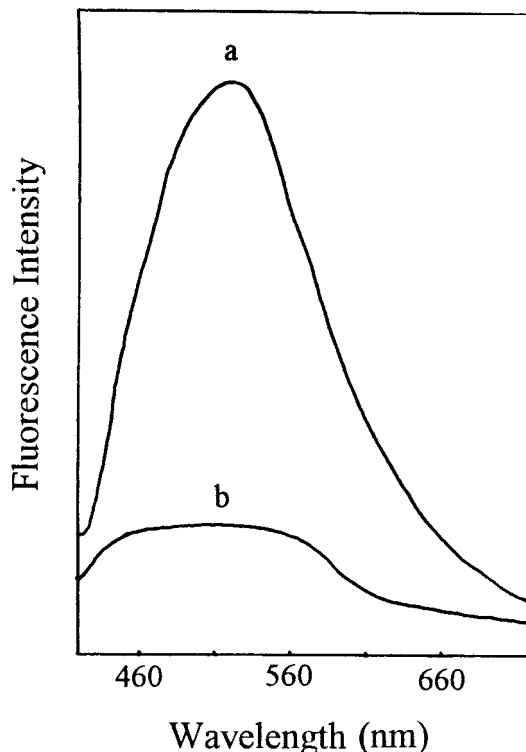


Figure 3 Fluorescence spectra of (a) P(APTDO) and (b) APTDO in 1,2-dichloroethane. [Chromophore] = 0.01 mol/L; λ_{ex} = 402 nm.

Considering the oxides of PAPT as examples, the sulfur atom of phenothiazine moiety has 2 lone-pair electrons, its mono-oxide PAPTDO has one lone-pair electrons at the sulfur atom of sulfoxide moiety, and its dioxide PAPTDO does not have lone-pair electrons at the sulfur atom of

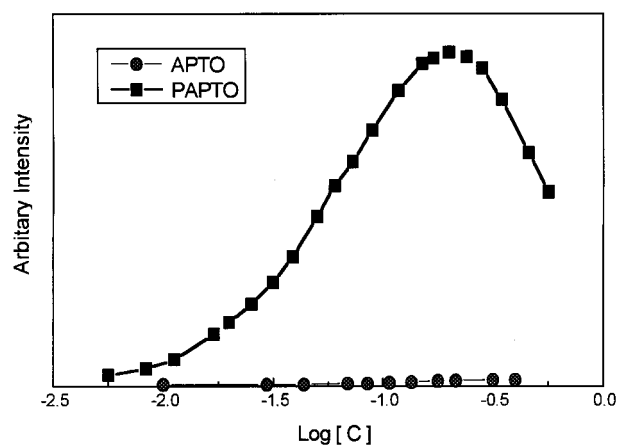


Figure 4 Emission fluorescence intensities of APTO at different chromophore concentrations: λ_{ex} = 402 nm; λ_{em} = 525 nm.

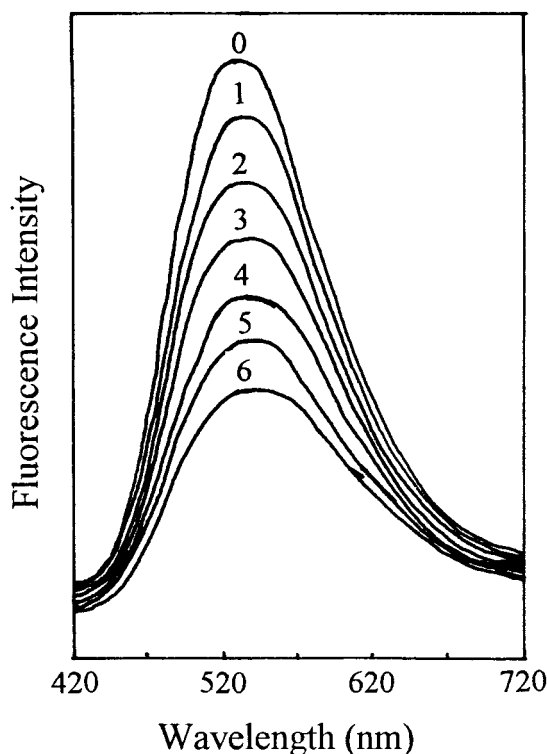


Figure 5 Fluorescence spectra of P(APTO) quenched by TCNQ in 1,2-dichloro ethane. [Chromophore] = 0.01 mol/L; λ_{ex} = 402 nm, [TCNQ] (10^{-5} mol/L): (0) 0; (1) 0.1; (2) 0.3; (3) 0.5; (4) 0.75; (5) 1.0; (6) 1.4.

sulfone moiety; thus, the tendency of the electron-donating ability of these three polymers are in the order of PAPT > PAPTO > PAPTDO. The tendency of the electron-deficiency, which is represented by “e” values, of these quenchers is in the order of TCNQ > TCNE > FN > MMA. Therefore, for any one of the polymers, the Stern–Volmer constants of these quenchers would be in the order of $Kq \cdot \tau_{0(\text{TCNQ})} > Kq \cdot \tau_{0(\text{TCNE})} > Kq \cdot \tau_{0(\text{FN})} > Kq \cdot \tau_{0(\text{DMFM})} > Kq \cdot \tau_{0(\text{MMA})}$. The experimental results show the tendency well, as we have expected.

The correlation between “e” values and the Stern–Volmer constants for these oxides are summarized in Table II.

From Table II, it can also be seen that the Stern–Volmer quenching constants $Kq \cdot \tau_0$ of each quencher used show the same order for these polymers, as follows: $Kq \cdot \tau_{0[\text{P(APT)}]} > Kq \cdot \tau_{0[\text{P(APTO)}]} > Kq \cdot \tau_{0[\text{P(APTDO)}]}$. That is, the electron-donating ability of a lone-pair electron at sulfur in sulfoxide or at oxygen in the sulfone group is lower than that of sulfur atom in phenothiazine moieties. Even though the lone-pair electrons at sulfur atom have disappeared in APTDO and ACPTDO, they also exhibited relatively lower SSQE than the other monomers, that is, APT, ACPT, APTO, and ACPTO, likely due to the existence of lone-pair electron at oxygen atom in sulfone group of PAPTDO and PACPTDO.

Sensitizing Behavior of APT and Its Oxides for the Photopolymerization of AN

As mentioned above, these 4 new monomers, APTO, APTDO, ACPTO, and ACPTDO, display SSQE, which means that they can act as polymerizable photosensitizers to initiate the photopolymerization of electron-deficient monomers, which do not have chromophore moieties, such as MMA and AN.

Considering the photopolymerization of AN sensitized by APTO as an example, by varying one of the concentrations of APTO and AN in DMF, the overall rates for the polymerization (R_p) were obtained. And the relationship between R_p and the concentration of AN or APTO was obtained, as shown in Figure 6. The rate equation of the photopolymerization of AN sensitized by APTO can be obtained.

By varying the polymerization temperature from 25–45°C, the overall activation energy for the photopolymerization sensitized by APTO was

Table II Correlation Between “e” Value of Quenchers and Stern–Volmer Constants ($Kq \cdot \tau_0$) for the Polymers with Phenothiazine Moieties and Their Oxides

Quencher	PAPT	PAPTO	PAPTDO	PACPT	PACPTO	PACPTDO
TCNQ (2.8 ^a)	8.7×10^4	8.5×10^4	5.4×10^4	8.2×10^4	6.4×10^4	5.6×10^4
TCNE (2.3 ^a)	230	110	73	220	87	68
FN (1.96 ^a)	23	10.0	4.8	46	12.1	1.26
DMFM	7.6	3.8	3.2	15	4.56	0.11
MMA (0.40 ^a)	0.79	0.31	0.05	1.8	0.58	0.01

^a The data is the “e” value of this quencher.

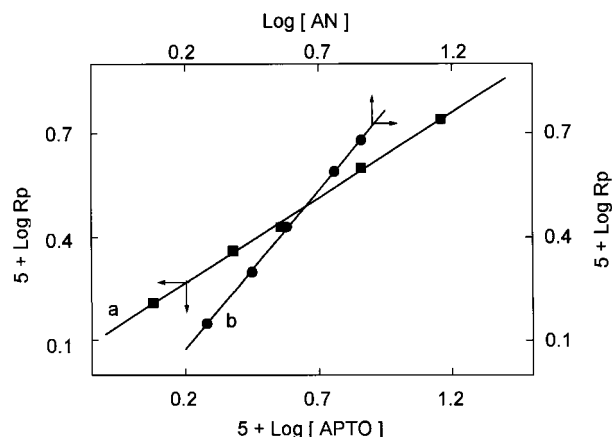


Figure 6 R_p versus [APTO] and R_p versus [AN] plots for AN photopolymerization at 30°C in DMF: (a) [AN] = 3.8 mol/L; (b) [APTO] = 3.6×10^{-4} mol/L.

calculated from the slope of the straight line of $\log R_p$ versus $1/T$ plot, as shown in Figure 7.

Likewise, the rate equations for the photopolymerization of AN sensitized by APT and APTDO were examined as follows.

$$R_p \propto [\text{APT}]^{0.46}[\text{AN}]^{1.02} \quad E_a = 21.1 \text{ kJ/mol}$$

$$R_p \propto [\text{APTO}]^{0.49}[\text{AN}]^{0.92} \quad E_a = 22.4 \text{ kJ/mol}$$

$$R_p \propto [\text{APTDO}]^{0.43}[\text{AN}]^{0.88} \quad E_a = 22.8 \text{ kJ/mol}$$

P(AN) from the photopolymerization of AN sensitized by APTO was extracted with 1,2-di-

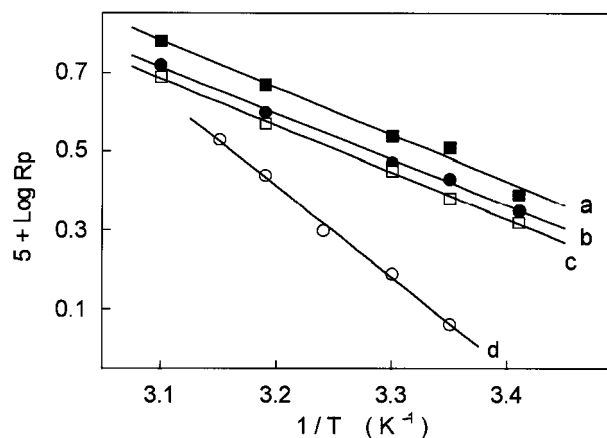


Figure 7 R_p versus $1/T$ plots for AN solution polymerization in DMF; [AN] = 3.8 mol/L. (a) [APT] = 3.6×10^{-4} mol/L; (b) [APTO] = 3.6×10^{-4} mol/L. (c) [APTDO] = 3.6×10^{-4} mol/L. (d) [BPO] = [APTO] = 3.6×10^{-4} mol/L.

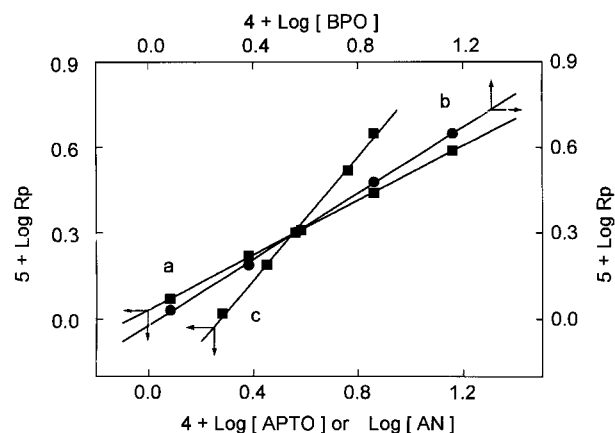
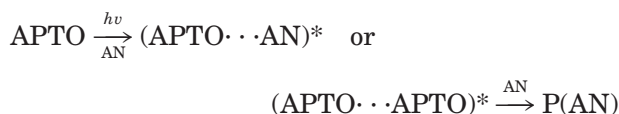


Figure 8 R_p versus [APTO], R_p versus [BPO] and R_p versus [AN] plots for AN polymerization at 40°C in DMF. (a) [AN] = 3.8 mol/L; [BPO] = 3.6×10^{-4} mol/L. (b) [AN] = 3.8 mol/L; [APTO] = 3.6×10^{-4} mol/L. (c) [BPO] = [APTO] = 3.6×10^{-4} mol/L.

chloroethane several times to remove the possibly resulted P(APTO) homopolymers, then it was dissolved in DMF, and the fluorescence of the solution was detected. It was found that P(AN) solution displayed emission fluorescence peak at 525 nm when excited at 402 nm, which was the same as that of P(APTO). The intensity did not change after several times of reprecipitation, while AIBN-initiated P(AN) did not show any fluorescence. All these results revealed that as a sensitizer, APTO not only initiated the polymerization of AN but also entered into the polymer chains. Since the concentration of APTO is much smaller than that of AN, the formation of block copolymer of AN and APTO is less possible. Based on the above results, the mechanism of AN photopolymerization sensitized by APTO could be deduced as follows:



Redox Initiation System by Combination of APTO and BPO

APTO has 1 lone-pair electron. This means that the lone-pair electrons of the sulfoxide group can be further oxidized to sulfone by BPO forming redox initiation system to initiate the polymerization of vinyl monomers. By varying 1 of the concentrations of AN, BPO, and APTO, the plots of R_p versus AN, BPO, and APTO can be obtained,

as shown in Figure 8. The rate equation for the polymerization of AN initiated by APTO-BPO system was obtained as follows:

$$R_p = k_p[\text{APTO}]^{0.48}[\text{BPO}]^{0.58}[\text{AN}]^{1.04}$$

For this polymerization, the overall activation energy were also calculated by varying the polymerization temperature from 30–50°C, as shown in Figure 7. The rate equation and activation energy E_a obtained to be 45.0 kJ/mol indicate that the thermal polymerization of AN initiated by APTO-BPO system is via the redox nature.

CONCLUSION

Four new acrylic monomers bearing phenothiazine oxides moieties are synthesized, and their polymers are obtained by free radical polymerization. Due to the coexistence of a electron-donating chromophore, in which sulfur plays a major role, and an electron-accepting double bond in the same molecule, these 4 new monomers possess fluorescence SSQE, as we have reported previously; that is, the fluorescence intensity of these monomers are much lower than those of their corresponding polymers at the same chromophore concentrations, and the tendency of SSQE of these monomers is in the order of APT > APTO > APTDO.

APTO and APTDO act as polymerizable photosensitizers to initiate the photopolymerization of

AN. Due to APTO, it has sulfoxides moiety, which can act as a reductant to form a redox system by combination with BPO to initiate the polymerization of vinyl monomers.

REFERENCES

1. S. K. Wu and F. M. Li, in *New Trends in Photochemistry of Polymers*, Elsevier, Amsterdam, 1985, p. 85.
2. F. M. Li, S. J. Chen, Z. C. Li, and J. Qiu, *J. Polym. Sci. Part A: Polym. Chem.*, **34**, 1881 (1996).
3. H. Cai, X. H. He, D. Y. Zheng, J. Qiu, Z. C. Li, and F. M. Li, *J. Polym. Sci. Part A: Polym. Chem.*, **34**, 1245 (1996).
4. F. M. Li, Q. Y. Gao, L. Wang, J. X. Zhang, S. J. Chen, and Z. C. Li, *J. Polym. Sci. Part A: Polym. Chem.*, **35**, 1087 (1997).
5. S. J. Chen, D. J. Guo, K. Y. Qiu, and F. M. Li, *Acta Polym. Sin.*, **4**, 501 (1990).
6. S. Y. Yu, J. Qiu, Z. C. Li, G. Q. Yao, Q. Y. Gao, G. X. Yang, J. X. Zhang, and F. M. Li, *J. Appl. Polym. Sci.*, **65**, 481 (1997).
7. F. M. Li, *Kobunshi Kako*, **48**, 185 (1996).
8. J. Qiu, Z. C. Li, Q. Y. Gao, G. Q. Yao, G. X. Yang, J. X. Zhang, and F. M. Li, *J. Polym. Sci., Part A: Polym. Chem.*, **34**, 3015 (1996).
9. A. McKillop and D. Kemp, *Tetrahedron*, **45**, 3299 (1989).
10. A. McKillop and J. A. Tarbin, *Tetrahedron*, **43**, 1753 (1987).
11. E. P. Goldberg, F. M. Li, and C. W. Luo, PCT Int. Appl. WO 8903,386, 1C1 (070279/22) (1989).