

Vinyl Monomers Bearing Chromophore Moieties and Their Polymers. VI. Synthesis and Photochemical Behavior of Acrylic Monomer Bearing Phenoxazine Moiety and Its Polymer

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ABSTRACT: An acrylic monomer having phenoxazine moiety, i.e., *N*-acryloylphenoxazine (APO), has been synthesized by dehydrochlorination of *N*-(3-chloropropionyl)phenoxazine with 1,5-diazabicyclo[5.4.0]undec-5-ene in dimethyl sulfoxide. The monomer can be polymerized with AIBN as an initiator. The photochemical behavior, including the fluorescence and photosensitizing properties of this monomer and its polymer, has been studied. It has been recorded that the absorption spectrum of polymer P(APO) displays a few blue shifts compared with its monomer APO. It has also been observed that the fluorescence emission intensity of the monomer is dramatically lower than that of its polymer at the same chromophore concentration. This may be ascribed to the charge transfer interacting between the coexisting electron-accepting acrylic carbon-carbon double bond and the electron-donation phenoxazine moiety in APO, intramolecularly or intermolecularly on excitation. The fluorescence of the APO polymer, which does not have carbon-carbon double bond, can be quenched by electron-deficient unsaturated nitriles and esters, clarifying that the electron-deficient carbon-carbon double bond does play an important role for the fluorescence quenching of the monomer. Thus, we term such phenomena as structural self-quenching effect, differing from the concentrational self-quenching effect, which is caused mainly by concentrational factors. The fluorescence quenching of P(APO) by C₆₀ has also been demonstrated. The formation of the charge transfer complex of P(APO) with C₆₀ in the ground state is revealed by the upward deviation from the linearity of the Stern-Volmer plot. APO can act as a photoinitiator to sensitize the photopolymerization of vinyl monomers such as acrylonitrile in dimethyl formamide and pursued kinetically. From the ultraviolet analysis of the PAN sensitized by APO, it is proved that APO not only sensitizes the photopolymerization of AN, but also incorporates in the PAN chain. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 481–489, 1997

Key words: *N*-acryloylphenoxazine; fluorescence self-quenching effect; C₆₀; Stern-Volmer plot; charge transfer complex; fluorescence lifetime; polymerizable sensitizer

INTRODUCTION

We have reported on the photochemical behavior including fluorescence and photosensitization be-

havior of acrylic monomers having nitrogen-containing, electron-donating chromophore moieties, i.e., *p*-(*N,N*-dimethylamino)benzyl methacrylate,¹ *N*-(4-*N'*,*N'*-dimethylamino phenyl)acrylamides,² *N*-acryloyl-*N'*-phenylpiperazines,³ *N*-(4-*N'*,*N'*-dimethylaminophenyl)maleimide,⁴ *N*-(4-*N'*,*N'*-

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dimethylaminophenyl)itaconimide,⁴ *N*-acryloylphenothiazines,⁵ and acryloyloxyquinolines,⁶ and vinyloxy monomer-bearing, electron-accepting chromophore moiety, *N*-(vinyloxyethyl)-1,8-naphthalimide.⁷ The fluorescence emission intensity of these monomers^{1-4,6,7} is always dramatically lower than that of their corresponding polymers at the same chromophore concentration. This may be ascribed to the occurrence of charge transfer interacting between coexisting electron-deficient acrylic carbon-carbon double bond and nitrogen-containing, electron-donating chromophore moieties intramolecularly or intermolecularly under ultraviolet (UV) light irradiation. In these chromophore moieties, the electron-donating nature is mainly contributed by the nitrogen atom of the *N,N*-dialkylphenyl groups and heterocyclic rings. The fluorescence of these polymers, which do not have carbon-carbon double bonds, can be quenched by electron-deficient compounds, for example, unsaturated nitriles such as methacrylonitrile (MAN), acrylonitrile (AN), fumaronitrile (FN), and tetracyanoethylene (TCNE) and unsaturated esters such as methyl acrylate (MA) and methyl methacrylate (MMA), indicating that the acrylic carbon-carbon double bonds in these monomers possess a significant role for the fluorescence quenching of these monomers. This is not an accidental phenomenon but is commonly observed in a series of acrylic monomers bearing electron-donating chromophore moieties. Thus, we have termed this phenomenon based on the structural factor as the structural self-quenching effect, which is different from the well-known concentrational self-quenching effect. These monomers not only sensitize the photopolymerization of vinyl monomers such as AN, MMA, etc., via exciplex formation, but also incorporate into the polymer chains. We have also reported⁵ on the synthesis and photochemical behavior of acrylic monomers bearing phenothiazine moieties as electron-donating chromophores in which the sulfur atom of phenothiazine residues contributes the electron-donating nature. They display the same photochemical behavior as that of acrylic monomers bearing nitrogen-containing electron-donating chromophores. In this article, an acrylic monomer bearing phenoxazinyl moiety, that is, *N*-acryloylphenoxazine (APO), has been synthesized and polymerized in order to evaluate whether the oxygen atom in the oxygen-containing heterocyclic chromophore moiety displays the photochemical behavior as we have previously reported. The fluorescence behavior of APO and polymer P(APO) has been studied. In the study

of the fluorescence quenching of P(APO), besides the above-mentioned quenchers, C₆₀, a representative of the fullerene family, has been used as a quencher in order to widen the understanding of the electronic nature of fullerenes. The photopolymerization of AN sensitized by APO has also been undertaken.

EXPERIMENTAL

Materials

Phenoxazine (Aldrich), 3-chloropropionyl chloride (Aldrich), and 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU; Aldrich) were used without further purification. C₆₀ was prepared by an arcing method with a homemade apparatus according to the literature^{8,9}; the purity of C₆₀ is 99.9%. Toluene, absolute methanol, 1,2-dichloroethane (DCE), dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), MA, AN, MMA, and MAN were redistilled. TCNE and FN were purified by recrystallization before use. All solvents and reagents used for spectral measurements were confirmed to ensure no existence of interfering impurities.

Synthesis of *N*-3-Chloropropionylphenoxazine (I)

To a solution of 0.92 g of phenoxazine (5.0 mmol) in 15 mL of Na-dried toluene, 0.96 mL (10.0 mmol) of 3-chloropropionyl chloride in 2.0 mL of toluene was added dropwise with stirring. The reaction was kept refluxing for 24 h. After evaporation of the solvent, the residue was recrystallized twice from methanol. *N*-(3-chloropropionyl)phenoxazine (I) (1.11 g) was yielded (81.0%; melting point [m.p.], 126-8°C).

Synthesis of APO: Dehydrochlorination of (I) by Using DBU

A stirred mixture of 1.11 g (4.05 mmol) of *N*-(3-chloropropionyl)phenoxazine and 0.61 mL (4.05 mmol) of DBU in 6 mL of DMSO was heated at 80–90°C for 2 h. The mixture was allowed to cool and then poured into 10 mL of ice water, precipitating a light-brown solid powder. After recrystallization twice from hexane, 0.54 g (yield 56.3%) of pure product was obtained (m.p., 110-1°C).

Polymerization of APO

AIBN (1.1 mg) was added to the solution of 0.22 g of APO in 2.2 mL of toluene. The solution was

purged by N_2 and kept at 60°C for 48 h. The polymer was precipitated from methanol. The product was purified by dissolving in toluene and precipitating from methanol several times. P(APO) (0.045 g) was obtained with a polymerization conversion of 21%. The polymer was confirmed by following the disappearance of the carbon-carbon double bond with a $1,620\text{ cm}^{-1}$ absorbing peak of infrared (IR) spectrum.

Kinetic Study for the Polymerization of AN

The kinetics for the photopolymerization of AN sensitized by APO was performed by a dilatometric method in a thermostat. A 3-mL-volume dilatometer made of hard glass was used. The photopolymerization was performed in DMF under UV irradiation of a 300-W high-pressure mercury arc lamp which was filtered by potassium chromate solution. The distance between the centers of the dilatometer and the UV lamp was 6 cm. Oxygen in the polymerization system was purged out beforehand. The final polymer was obtained by precipitating in cold petroleum ether several times.

Apparatus and Spectral Measurement

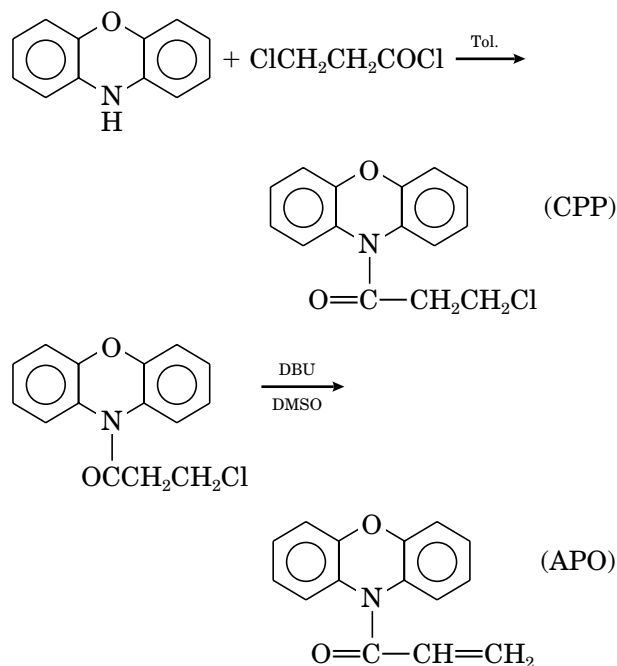
The determination of absorption spectra and fluorescence spectra was as follows. The absorption spectra were recorded on a Shimadzu UV-250 Spectrophotometer. The emission fluorescence spectra were recorded on a Hitachi M-850 Fluorescence Spectrophotometer at room temperature. The slit width of both monochromators was 10 nm. 1,2-Dichloroethane used as a solvent was purified to eliminate the interfering impurities for fluorescence. The fluorescence lifetime was determined by a multifrequency, phase-modulation method with an SLM Inc. 48000 Phase Fluorometer, equipped with a multifrequency modulation system.

RESULTS AND DISCUSSION

Synthesis of APO

Even though phenoxazine has an aromatic secondary amino group, like the preparation of *N*-acryloylcarbazole and *N*-acryloylphenothiazines, APO cannot be directly prepared by the reaction of phenoxazine with acryloyl chloride. A successful method is via the dehydrochlorination of *N*-3-chloropropionylphenoxazine with DBU as a dehydrochlorinating agent in DMSO. The synthetic route is shown below:

drochlorinating agent in DMSO. The synthetic route is shown below:



The structure of APO is confirmed by ^1H nuclear magnetic resonance (NMR), IR, MS, and elementary analysis as follows.

^1H NMR (δ , ppm, TMS, CDCl_3): 5.77–5.80 (m, 1H), 6.53–6.67 (m, 2H), 7.11–7.60 (m, 8H)
 IR (KBr, cm^{-1}): 753, 767, 785, 960, 1,621, 1,667
 MS (EI source): 237 (m/e)
 elementary analysis: CALCD (%) C: 75.85, H: 4.67, N: 5.90
 FOUND (%) C: 75.74, H: 4.55, N: 5.67

Absorption Spectra of APO and its Polymer P(APO)

Figure 1 shows the absorption spectra of APO and P(APO). The absorption wavelength maximum and corresponding molar extinction coefficients of APO and P(APO) in 1,2-dichloroethane ($6.0 \times 10^{-5}\text{ mol/L}$) are listed in Table I. It is seen that the absorption wavelength maximum of P(APO) possesses a little more blue shift than that of APO and the extinction coefficients of P(APO) are smaller than those of APO. These may be due to the disappearance of the carbon-carbon double bond in P(APO), which lessens the conjugation of the polymer.

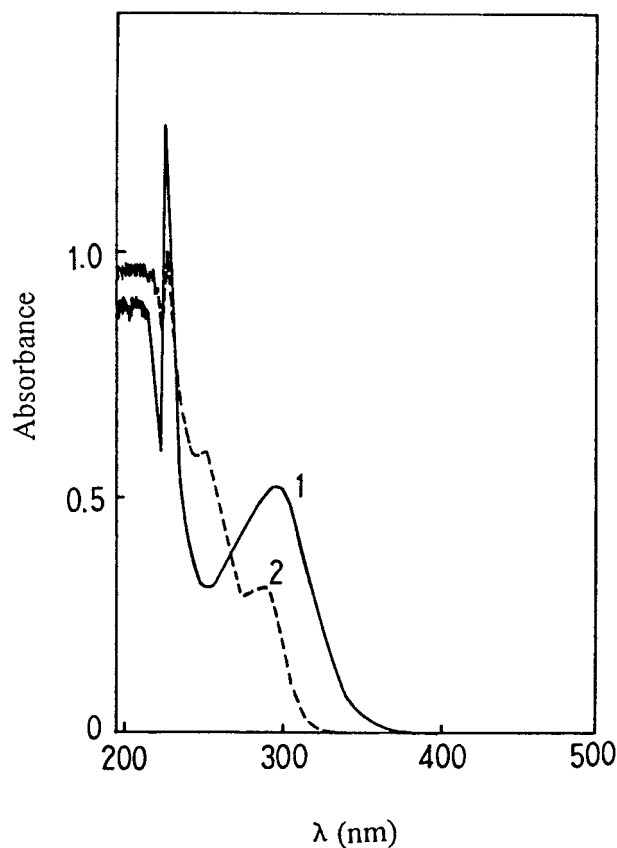


Figure 1 Absorption spectra of APO and P(APO) in DCE. Concentration (Conc.): 6.0×10^{-5} mol/L. (1) APO, (2) P(APO).

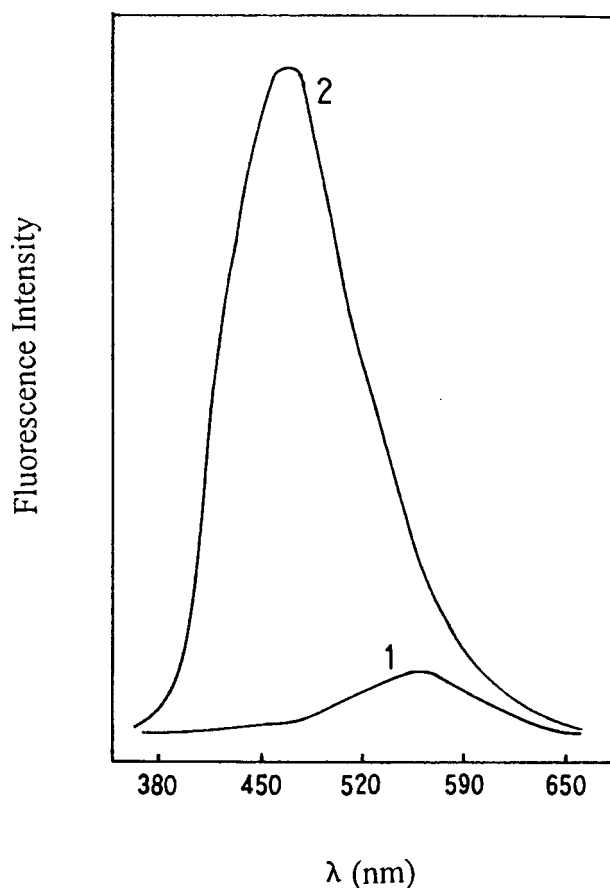


Figure 2 Fluorescence emission spectra of APO and P(APO) in DCE. Conc.: 4.2×10^{-3} mol/L; $\lambda_{\text{ex}} = 367$ nm. (1) APO, (2) P(APO).

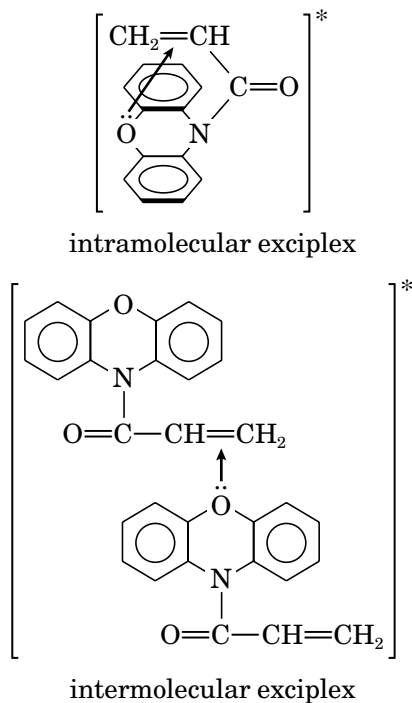
Fluorescence Behavior of APO and P(APO)

Both APO and P(APO) display fluorescence emission in solution. Figure 2 shows the fluorescence spectra of APO and P(APO) in DCE at the same chromophore concentration excited at 367 nm. It can be seen that the fluorescence emission intensity of APO is dramatically lower than that of its polymer P(APO), that is, APO possesses the structural self-quenching effect, as we have reported on the acrylic monomers having nitrogen-containing or sulfur-containing

electron-donating chromophore and their polymers. This may be due to the occurrence of charge transfer interacting between the coexisting electron-accepting acrylic carbon-carbon double bond and the electron-donating phenoxazinyl moiety in APO, intermolecularly under UV light irradiation. In the cases of acrylic monomers having nitrogen-containing and sulfur-containing electron-donating chromophore moieties, the electron-donating nature is contributed by the nitrogen atom and the sulfur atom, respectively. With regard to APO, instead of nitrogen and sulfur atoms, the electron-donating nature is contributed by the oxygen atom of the phenoxazine residue. This means that the structural self-quenching effect is not an accidental phenomenon but is commonly observed in the acrylic monomers having electron-donating moieties. The intramolecular or intermolecular exciplex is illustrated as follows:

Table I λ_{max} (nm) and Extinction Coefficient (ϵ , $\text{mol L}^{-1} \text{cm}^{-1}$)

Monomer/Polymer	λ_1	ϵ_1	λ_2	ϵ_2
APO	297	8.7×10^3	228	1.9×10^4
P(APO)	289	5.0×10^3	228	1.5×10^4



In the manifestation of the acrylic double bond is an important factor causing the structural self-quenching effect; a series of electron-deficient compounds, for example, unsaturated nitriles such as MAN, AN, FN, and TCNE and unsaturated esters such as MA and MMA, are added to the DCE solution of P(APO), at a concentration of 1.5×10^{-2} mol/L, which does not have a carbon-carbon double bond in the molecule. As a representative, Figure 3 shows the fluorescence quenching of P(APO) in DCE by adding MA as a quencher. The excitation wavelength for all of the experiments was 367 nm, and the emission was measured at 436 nm. The results were analyzed according to the Stern-Volmer equation by plotting F_0/F versus $[Q]$, as shown in Figures 4–6, where F_0 and F denote the fluorescence intensities in the absence and presence of quencher, respectively, and $[Q]$ denotes the concentration of quencher. Shown in Figure 4 is the Stern-Volmer plot for the fluorescence quenching of P(APO) in DCE by MAN, AN, FN, MA, and MAN. It is seen that all of the Stern-Volmer plots are straight lines but with different slopes. The Stern-Volmer quenching constant $k_q \cdot \tau_0$ is calculated as the tangential slope of the initial part of the curve. It is known that the quenching ability of quenchers is mainly represented by their degree of electron deficiency. Table II summarizes the correlation of “ e ” values of quenchers and Stern-Volmer constants for the fluorescence quenching of P(APO). In general, the “ e ” value represents the polarity

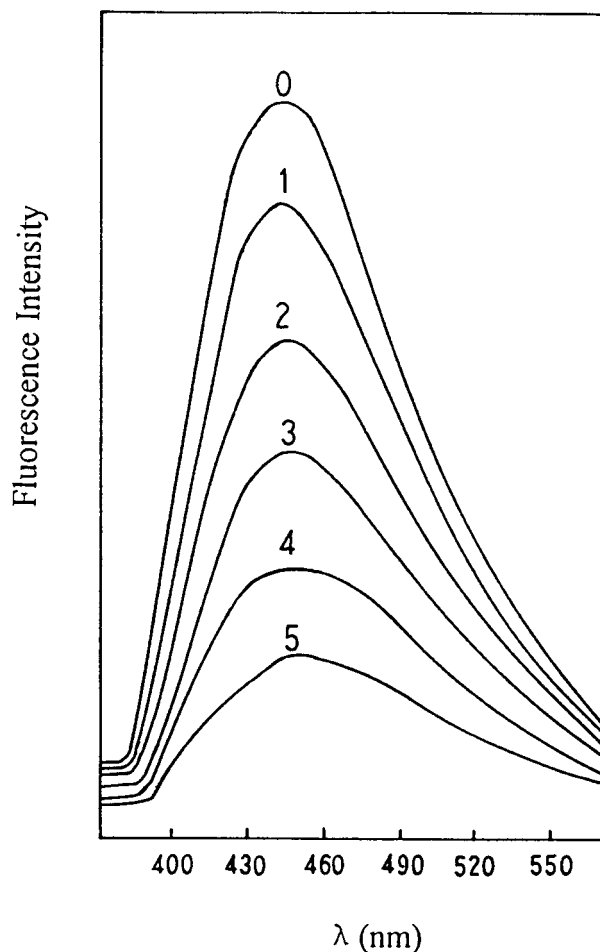


Figure 3 Fluorescence spectra of P(APO) quenched by MA in DCE. Conc. of MA ($\times 10^{-1}$ mol/L): (0) 0, (1) 0.41, (2) 1.33, (3) 2.53, (4) 4.34, (5) 6.01.

of the carbon-carbon double bond, that is, the scale of electron deficiency of quenchers. As shown in Table II, for unsaturated nitriles, the increasing of Stern-Volmer constants is consistent with the increase of “ e ” values; the order is FN > AN > MAN, and for unsaturated esters, the order is MA > MMA. It is interesting that the “ e ” value of MMA (0.60) is half and that of MA (0.40) is one-third of that of AN (1.20), but the Stern-Volmer constants are the same as and two times those of AN, respectively. This would be explained by structure compatibility, that is, P(APO) is a polymer of acrylate; MA and MMA are also acrylates, and they are similar in structure. Because “the like dissolves the like,” their structural similarity might make the quenching easy. Similar results are also found in our previous reports.^{3,5}

It is pointed out that the Stern-Volmer plot of P(APO) quenched by TCNE is an upward curvature, deviating from the linearity, as shown in

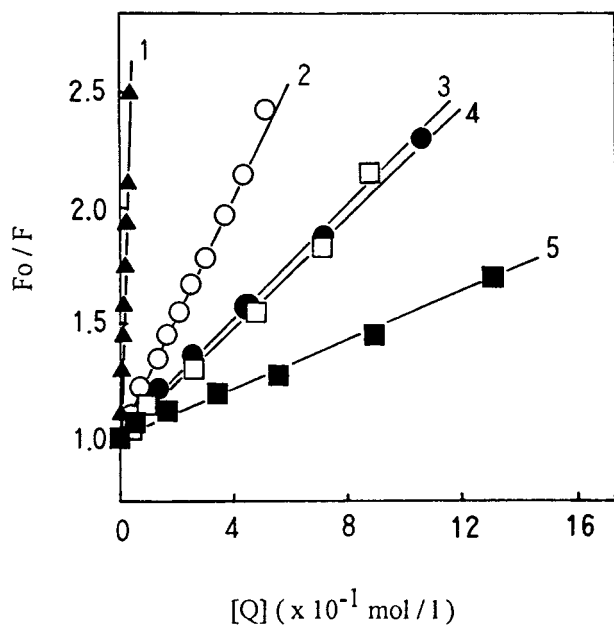


Figure 4 Stern-Volmer plots for the fluorescence quenching of P(APO) solution by different quenchers: (1) FN, (2) MA, (3) AN, (4) MMA, (5) MAN.

Figure 5. This indicates a significant contribution of static quenching besides dynamic quenching, that is, in addition to the exciplex formed by collision, a charge transfer complex is formed between the highly electron-deficient double bond of TCNE caused by four strongly electron-withdrawing cyano groups, with P(APO) in the ground state.

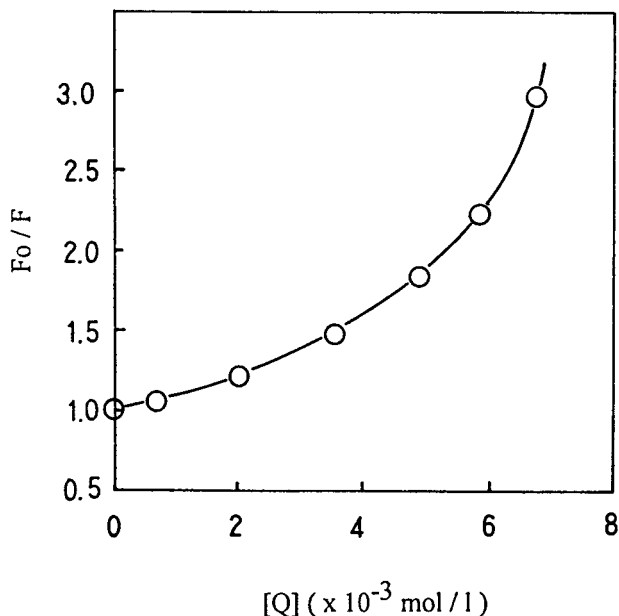


Figure 5 Stern-Volmer plot for the fluorescence quenching of P(APO) solution by TCNE.

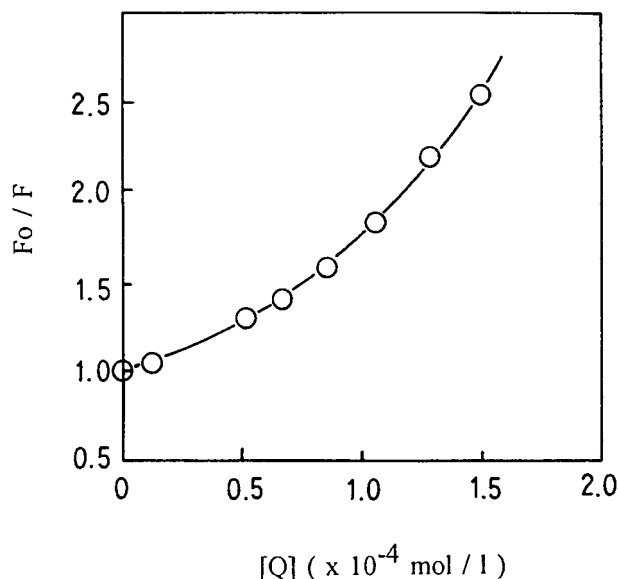


Figure 6 Stern-Volmer plot for the fluorescence quenching of P(APO) solution by C_{60} .

Recently, the study on the photophysics of C_{60} has attracted much interest. One of the intriguing properties of C_{60} is that it possesses both strongly electron-accepting and electron-donating natures. The ionizing potential and electron affinity of C_{60} are 7.61 and 2.56 eV, respectively. C_{60} does not display fluorescence in the ordinary experimental condition (in solution at room temperature), but it can quench the fluorescence of polymers bearing phenothiazine or phenoxazinyl residues as pendant groups. Figure 6 shows the Stern-Volmer plot for the fluorescence quenching of P(APO) by C_{60} . Similar to that of TCNE, an upward curvature is also obtained, indicating that charge transfer complexes are formed between strongly electron-accepting C_{60} with P(APO) in both the ground state and the excited state. Compared with TCNE, the electron affinity of which is 2.3 eV, C_{60} plays a more effective role as an electron acceptor, with a Stern-Volmer constant of $6.10 \times 10^3 \text{ mol L}^{-1}$. This result would widen the understanding of the electronic nature of fullerenes.

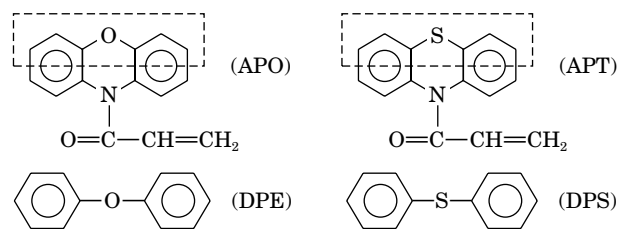
Table II The Correlation of "e" Values of Quenchers and Stern-Volmer Constant for P(APO)

Quenchers	FN	AN	MA	MMA	MAN
"e" Value	1.96	1.20	0.60	0.40	0.68
kq. τ_0 (mol L ⁻¹)	39.1	1.27	2.84	1.24	0.51

Table III Stern-Volmer Constants $k_q \tau_0$ (mol L⁻¹) for P(APO) and P(APT) with C₆₀ and TCNE as Quenchers

Quenchers	C ₆₀	TCNE
P(APO)	6.10×10^3	1.36×10^2
P(APT)	6.93×10^3	2.30×10^2

We have also reported⁵ on the photochemical behavior of *N*-acryloylphenothiazine (APT). The structural similarity of APO and APT is shown as follows:



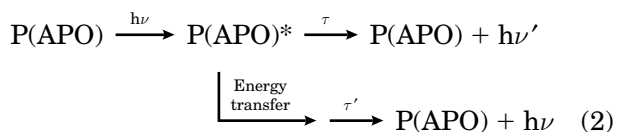
One can see clearly that the only difference between these two molecules is the electron-donating atom, O or S. The sulfur atom in phenothiazine is supposed to contribute mainly the electron-donating nature of APT. In the case of APO, the electron-donation nature is mainly contributed by the oxygen atom of the phenoxazine residue. Thus, the understanding of the fluorescence behavior of these two monomers, APO and APT, would be focused on the difference of the electron-donating nature between diphenyl ether (DPE) and diphenyl sulfide (DPS). Charge transfer complexes of substituted DPS as donors with TCNE and other electron-deficient compounds have been studied, and the reaction site is concluded to be the sulfur atom, even if the donor orbital is conjugated with π -system.¹¹ It is well known that the value of ionization potential reflects the degree of charge transfer interaction. Table III summarizes the Stern-Volmer constant of charge transfer complex formation for P(APO) and P(APT) with TCNE and C₆₀, respectively. It is obvious that the Stern-Volmer constant of the P(APT)-TCNE complex formation is greater than that of the P(APO)-TCNE complex formation and that P(APT)-C₆₀ is greater than P(APO)-C₆₀. The results are in agreement with the values of the ionization potentials, which are 8.82 and 7.90 eV for DPE and DPS, respectively. That is, the charge transfer energies decrease with an increase in electron-donating ability.

To get more understanding about the excited state of P(APO), its lifetime in DCE solution has been determined by a phase-modulation method. Multifrequency phase modulation data for P(APO) (excitation at 367 nm; emission at 436 nm) can be fitted to a biexponential decay with lifetimes, τ , of 3.97 and 141.1 nsec and fractional intensities, f_i , of 0.81 and 0.19, respectively. The average value of fluorescence lifetime is 30.2 nsec. In general, the monomer usually has one lifetime, and the excited state exhibits a single-exponential decay because the fluorophores of small molecules exist in almost the same circumstance. However, the circumstance of the fluorophores on the polymer chain is much more complicated, that is, some of the fluorophores are included on the inside of polymer coils and some of the fluorophores are exposed to the outside of the polymer coils in solution. This makes the fluorophores influenced differently by factors such as chain conformation and solvent relaxation, etc. Moreover, the movement of fluorophores on the polymer is also limited or hindered by the polymer backbone. All of these complications result in the double-exponential decay, illustrated as follows:

Single-exponential decay (monomer):



Double-exponential decay (polymer):



The Photosensitization Behavior of APO

As mentioned above, phenoxazinyl moiety can form charge transfer complexes with electron-deficient monomers such as AN, MMA, etc. This means that APO can act as a photosensitizer to initiate the polymerization of vinyl monomers on UV light irradiation. First, the variation of conversion with time for the photopolymerization of AN sensitized by APO was recorded by varying one of the concentrations of AN and APO and the polymerization temperature. All of the conversion time plots appear to be straight lines. The overall

rate of photopolymerization, R_p , was calculated from the slopes of the straight lines obtained. Shown in Figure 7 is the $\log R_p$ versus $\log[\text{APO}]$ and $\log[\text{AN}]$ plots. Figure 8 shows the $\log R_p$ versus $1/T$ plot for the photopolymerization of AN sensitized by APO in DMF. It is seen that the R_p is proportional to the 0.37th power of APO concentration and the 0.77th power of AN concentration, respectively. Therefore, the rate equation can be described as follows:

$$R_p \propto [\text{APO}]^{0.37} \times [\text{AN}]^{0.77} \quad (3)$$

The overall activation energy for the photopolymerization of AN sensitized by APO is 5.89 Kcal/mol.

PAN obtained this way displayed the same fluorescence emission peak as that of P(APO). After the removal of P(APO) by reprecipitation from chloroform several times, the fluorescence intensity at 436 nm remained almost unchanged. It is confirmed that APO not only initiates the polymerization but also incorporates into the AN polymer chain, that is, APO acts as a polymerizable photosensitizer. Thus, if an acrylic monomer bears chromophore moiety with an electron-donating nature mainly contributed by nitrogen, sulfur, or oxygen and possesses fluorescence structural self-quenching effect in solution, it can be used as a polymerizable sensitizer due to the exciplex formation in itself

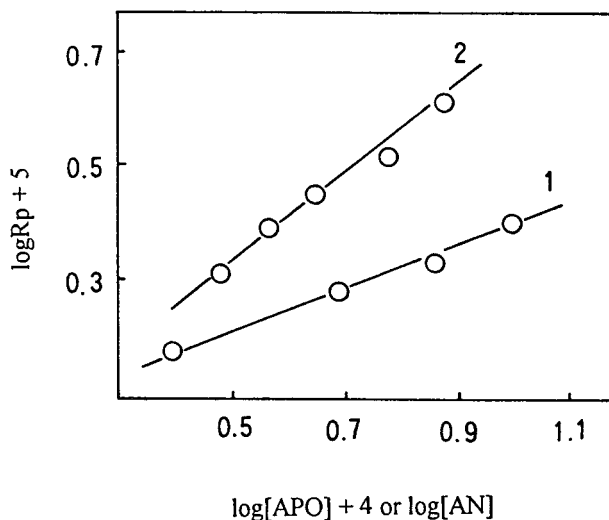


Figure 7 (1) $\log R_p$ versus $\log[\text{APO}]$ and (2) $\log R_p$ versus $\log[\text{AN}]$ plots for the polymerization of AN sensitized by APO in DMF at 25°C.

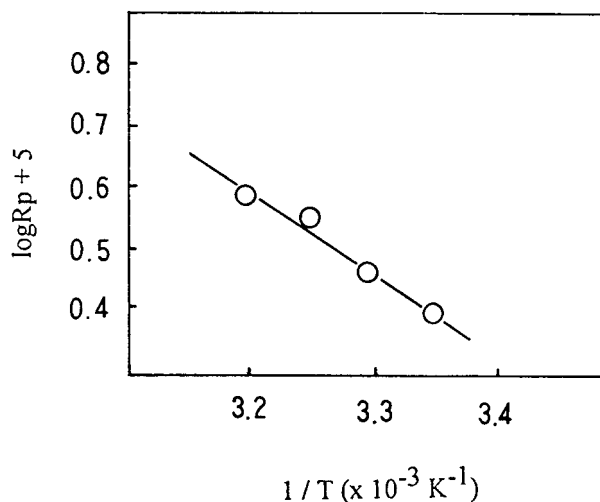


Figure 8 $\log R_p$ versus $1/T$ plots for the polymerization of AN sensitized by APO.

or with other electron-deficient vinyl monomers such as AN.

CONCLUSIONS

An acrylic monomer bearing phenoxazinyl moiety, APO, and its polymer have been prepared. The fluorescence emission intensity of APO is dramatically lower than that of its polymer in the same chromophore concentration. This firmly proves that the structural self-quenching effect is commonly observed in a series of acrylic monomers having electron-donating chromophores including nitrogen-, sulfur-, and oxygen-containing heterocyclics.

The fluorescence of P(APO) can be quenched by electron-deficient compounds such as MAN, AN, FN, TCNE, MA, MMA, and C_{60} . The quenching efficiency of the quenchers depends on their electron negativities and their structural compatibilities with P(APO). TCNE and C_{60} can form charge transfer complexes with P(APO) in both the ground state and the excited state. APO can act as a polymerizable photosensitizer to initiate the photopolymerization of vinyl monomers, that is, APO not only initiates the polymerization but also incorporates into the AN polymer chain.

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