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Phenacyl Phenothiazinium Salt as a New Broad-wavelength-absorbing Photoinitiator for Cationic and Free Radical Polymerizations

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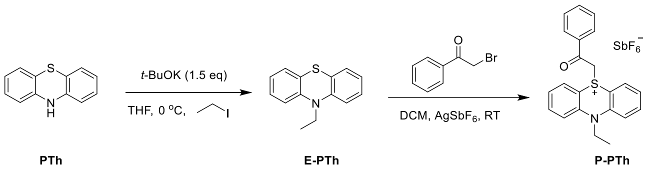
Abstract: A novel broad-wavelength-absorbing photoinitiator based on phenacyl phenothiazinium hexafluroantimonate (P-PTh) possessing both phenacyl and phenothiazine chromophoric groups was reported. P-PTh absorbs light at UV, Visible and Near-IR region. Photophysical, photochemical, and computational investigations revealed that P-PTh in solution decomposes at all wavelengths by homolytic and heterolytic cleavages and generates cationic and radical species, which could efficiently initiate cationic and free radical polymerizations. It is anticipated that the photoinitiator with such wavelength flexibility may open up new pathways in curing applications of formulations of pigment systems.

In recent years, photoinduced processes have received revitalized interest offering robust and versatile synthetic routes to form complex macromolecular structures in an energetically favorable and environmentally friendly fashion.[1] The developments in photoinduced electron transfer reactions (PET)[2] have led to a wide variety of new photoinitiating systems with tunable absorption characteristics. Different PET systems that can be activated at UV, visible and near-IR region of the electromagnetic spectrum have profusely been explored for chain polymerizations[3] involving radical and ionic species and step-growth polymerizations[4] as well as copper catalyzed azide alkyne click[5] processes. Controlled/living radical polymerizations, namely Photoinduced Atom Transfer Radical Polymerizations (PhotoATRP)[6] and Radical Addition Fragmentation Transfer (RAFT)[7] polymerization can be conducted by photochemical means, also referred to as PET reactions, yield polymers with various controlled architectures, narrow molecular weight distribution, and chain-end functionalities. Among various highly conjugated aromatic compounds, phenothiazine derivatives appeared [8] to be the most efficient organic catalysts in metal-free photoATRP. Detailed laser flash photolysis and spectroscopic investigations [9] revealed that the triplet-excited phenothiazines played a dominant role in the mechanism of metal free photoATRP.

Phenacyl salts are a class of onium salts that can be used as photoinitiators for cationic and free radical polymerizations.[10] Depending on the structure of the chromophore group containing heteroatom, the absorption of the salt can be shifted to longer wavelengths. Previously, phenacyl salts with sulphonium,[11] aniline,[12] pyridine,[13] carbazole,[14] and thioxathone[15] groups were synthesized and successfully used in cationic, free radical and step-growth[16] polymerizations. It was also shown that their charge transfer complexes further extend their absorption characteristics to longer wavelengths.[17]

Based on its spectral characteristics and excited state properties, it seemed appropriate to synthesize phenacyl salt with phenothiazine chromophore. Herein we report for the first time a new phenacyl phenothiazinium salt (P-PTh) that absorbs light over the UV–vis and near-IR region of the electromagnetic spectrum with relatively high absorption coefficient and initiates both radical and cationic photopolymerizatons at whole wavelength range. The structure and photophysical properties of the salt were evaluated by spectral and computational investigations.

As stated, phenothiazine is widely used in many photoinduced processes as a general chromophore and modified phenothiazine derivatives show outstanding absorption and high sensitizing efficiency.[8] As an efficient chromophore, phenacyl group has been incorporated into various heteroatom containing molecules to enhance spectral sensitivity.[11-15] We incorporated phenacyl group to photosensitive phenothiazine as an additional chromophore. P-PTh was prepared by direct phenacylation process of *N*-ethyl-phenothizine (E-PTh) in one step, one pot according to generally applied method.[16,18] (**Scheme 1**) However, unlike the previous work, there are two positions on phenothiazine, N and S, that can potentially react with 2-bromoacetophenone. DFT computational analysis, 1H-1H COSY and NOESY spectra were used to confirm that 2-oxo-2-phenylethyl group was substituted on S atom of phenothiazine (Supporting Information, **Figures S4 and S5**).



Scheme 1. Synthesis of phenacyl phenothiazinium salt (P-PTh)

Optical absorption characteristic of the PTh-P photoinitiator was examined by UV spectroscopy (**Figure 1**) and the photophysical properties of PTh-P are displayed in **Table 1**. PTh-P showed high molar absorption coefficient and very weak fluorescence (fluorescence quantum yield: $\Phi_f \sim 0.002$). A strong red shift in the fluorescence spectrum (**Figure S3**) observed indicates that minimize energy point geometry of the excited state for PTh-P is quite different from that of the ground state. It also explains the reason of the observed low Φ_f. Internal conversion by the transfer of electronic energy to molecular vibration contributes mainly to the non-radiation process. Beyond our expectation, the UV−vis spectrum of PTh-P exhibits absorption at longer wavelengths with high molar absorption coefficients than common commercially available photoinitiators. In addition, it has broad-band absorption in different spectrum range, including UV, visible and near infrared (NIR) region. Best to our knowledge, such characteristic absorption in onium type photoinitiators has never been reported.

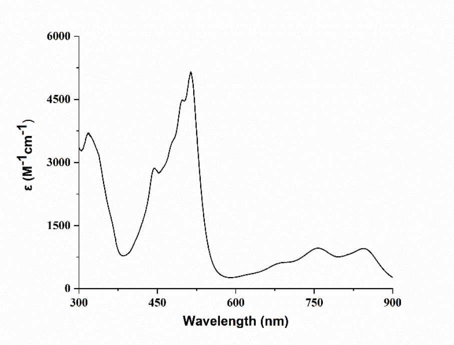


Figure 1. UV−vis spectrum of P-PTh (1.72×10^{-4} mol/L) in acetonitrile at room temperature

Table 1. Photophysical properties of PTh-P.

PI	λ_{max} (nm)	λ_{em} (nm)	ε_{max} (L mol^{-1} cm^{-1})	Φ_f
PTh-P	514	572	5151	0.002

Photolysis experiments were performed to investigate the photochemical behavior of the photoinitiator at different wavelengths. As can be seen from **Figure 2**, upon irradiation at all wavelengths, the absorbance in the near UV region increases, but decreases in the visible and NIR region indicating decomposition of the photoinitiatior and concomitant formation of new photoproducts absorbing at low wavelengths. The disappearance of the orange color of the solution upon irradiation further confirms the decomposition. The observed behavior clearly demonstrates that the photoinitiator provides immense wavelength flexibility and therefore, applicable to the wide range of pigmented formulations. Moreover, the activity at NIR region reflects potency in deep curing applications due to the weak photon energy and deep penetration depth of NIR light.[19]

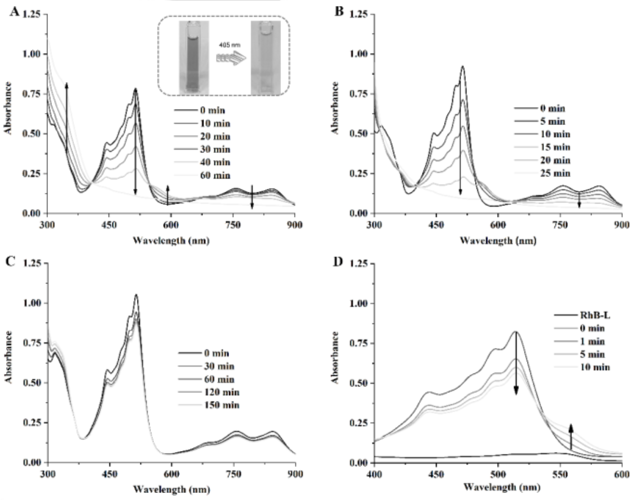


Figure 2. Steady-state photolysis of P-PTh (1.72×10^{-4} mol/L) in acetonitrile after (A) LED@405 nm (100 mW/cm^2), (B) LED@365 nm (100 mW/cm^2), (C) LED@850 nm (1.5 W/cm^2), (D) LED@405 nm (100 mW/cm^2) irradiation under air, RhB-L base (2.34×10^{-6} mol/L) is added as an acid indicator

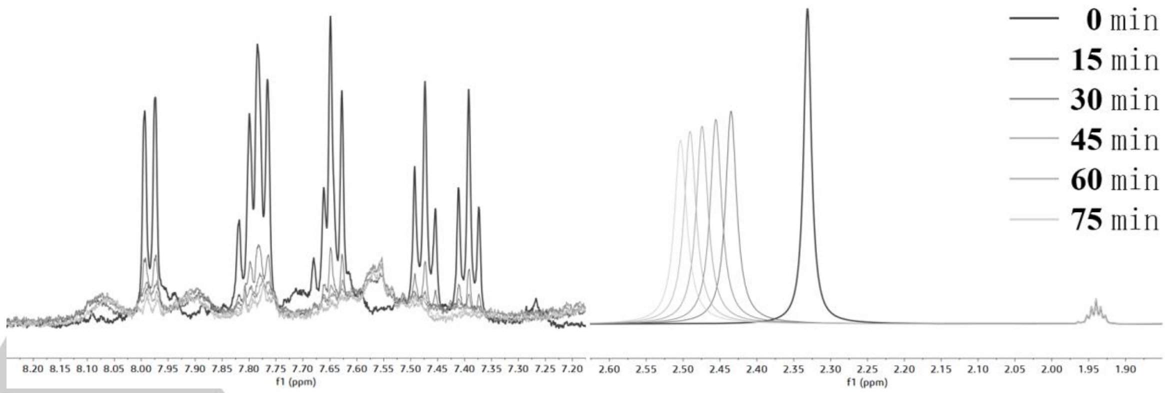


Figure 3. Real-time NMR spectral changes at 7.2-8.2 ppm and 1.9-2.6 ppm regions during photolysis process. The photolysis study of P-PTh (0.043 mol/L) was conducted in Acetonitrile-D3 irradiated by LED@365 nm (150 mW/cm^2) under Ar at room temperature. Curves represent NMR spectrum at 0 min, 15 min, 30 min, 45 min, 60 min and 75 min with irradiation. Photolysis were conducted in an NMR tube

Upon irradiation, in addition to phenacyl radicals and Brønsted super acids ($H^+SbF_6^-$) are expected to be formed by homolytic cleavage (*vide infra*). In order to confirm formation of Brønsted acid, photolysis of P-PTh was conducted in the presence of an acid indicator, Rhodmine B lactone (RhB-L). The observed increase of the absorption band at 550 nm corresponding to the acid form of RhB evidently confirms the formation of Brønsted acid[20] (**Figure 2D**). Since chain reactions do not occur, the acid formation may explain the low fluorescence quantum efficiency.

The photolysis process was also monitored by NMR spectroscopy. As can be seen from **Figure 3**, the signals of P-PTh disappears and new broad signals, which may correspond to the phenothiazine radical cations, appear with the irradiation time. These paramagnetic species result in the signal of water in solvent get an obvious change in chemical shift and broadening due to the impact on spin-spin relaxation times (T2).

The ESR experiment was conducted to further confirm the formation of radical species under light irradiation. As shown in **Figure 4**, under LED@365 nm for 15 min of P-PTh in solvent, one triplet signal (a_N = 13.39 G, a_H = 2.21 G) was observed, which was assumed to correspond to radical of phenothiazine radical cation. Spin density analysis confirmed that the phenothiazine radical cation is a decisive of N radical with high spin density localized on N atom.

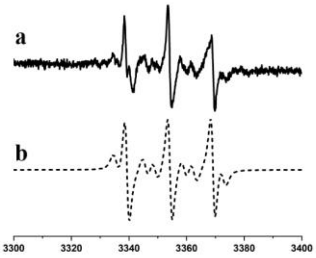
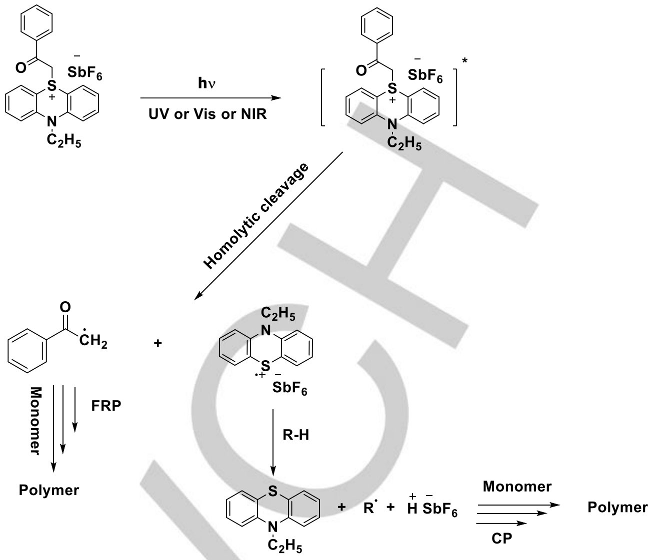


Figure 4. ESR spectra of the radicals generated in P-PTh upon light exposure and trapped by DMPO in tert-butylbenzene: a) experimental and b) simulated spectra. c) Spin density isosurface at 0.03 a.u.

As outlined in **Scheme 2**, the photolysis mechanism of P-PTh is based on homolytic cleavage of P-PTh[15a,16]. Homolytic cleavage leads to the formation of phenacyl radical and phenothiazine radical cation. The phenacyl radicals are able to initiate FRP in the presence of monomer. These radicals can undergo dimerization and hydrogen abstraction reactions in the absence of monomer. The product of the latter process was identified by GC-MS analysis (acetophenone m/z = 120, Supporting Information, **Figure S6**). As evidenced by ESR, GC-MS (phenothiazine, m/z = 227, Supporting Information, **Figure S7)** and photolysis studies in the presence of acid indicator, phenothiazine radical cation is formed simultaneously.

Thermal and storage stability of a photoinitiator is an important concern particularly for practical applications. The thermal stability experiments of P-PTh were conducted by TGA and DSC analyses in the absence and presence of monomers, respectively. The latter provides more conclusive information as the exothermic polymerization processes can readily be monitored (Supporting Information, **Figure S10**). As can be seen from **Table 2**, P-PTh has notable thermal and storage stability.



Scheme 2. Proposed Initiation mechanism for cationic and free radical photopolymerizations by using P-PTh

Table 2. TGA and DSC analyses of P-PTh-P/TMPTA, and P-PTh-P/EPOX formulations (1.72 × 10^{-5} mol/g resin)

photoinitiator	decomposition temperature (°C)	onset temperature (°C)		peak temperature (°C)	
		TMPTA	EPOX	TMPTA	EPOX
P-PTh	170	100	160	150	210

The viscosity of the formulations containing P-PTh and monomers polymerizable by free radical and cationic mechanism did not change significantly after keeping more than 100 days in the dark at 60 °C indicating excellent storage stability of P-PTh in the formulations (Supporting Information, **Figure S11**). Excellent thermal and storage stability indicate that P-PTh has important potential practical application value in the field of photocuring.

The kinetics of cationic polymerization bifunctional monomer, 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (EPOX) were studied by Real-time IR in thin samples (2 mm) in the presence of P-PTh salt using multi wavelength LED light irradiation sources. The related profiles are displayed in **Figure 5**. As can be seen, high conversions were attained in short irradiation times at the all wavelength range studied indicating high multi-band initiation efficiency.

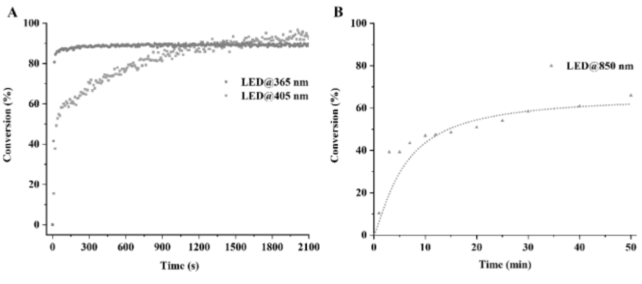


Figure 5. Kinetic profiles of EPOX in the presence of P-PTh salt under different irradiation sources. (A) LED@365 nm (30 mW/cm^2), LED@405 nm (30 mW/cm^2). (B) LED@850 nm (1.5 W/cm^2)

The free radical photopolymerizations of di- and tri-functional acrylates, namely tripropylene glycol diacrylate (TPGDA) and trimethylolpropane triacrylate (TMPTA) were studied on KBr tablet in the presence of P-PTh using different wavelength LED light sources. The photoiniatior shows almost similar activity with the monochromatic LED@365 nm or LED@405 light sources for both monomers (**Figure 6**). Notably, with broad-spectrum light source, much faster polymerization with quantitative conversion was attained.

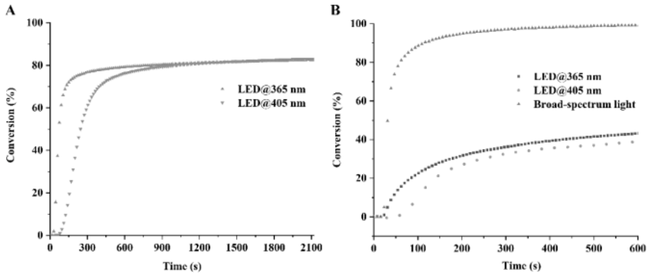


Figure 6. Kinetic profiles of double bond conversion under air in the presence of P-PTh salt under different light irradiation sources. (A) The conversion of double bond in TPGDA (LED@365 nm (30 mW/cm^2) and LED@405 nm (30 mW/cm^2)). (B) The conversion of double bond in TMPTA (LED@365 nm (30 mW/cm^2), LED@405 nm (30 mW/cm^2) and Broad-spectrum light (260 mW/cm^2))

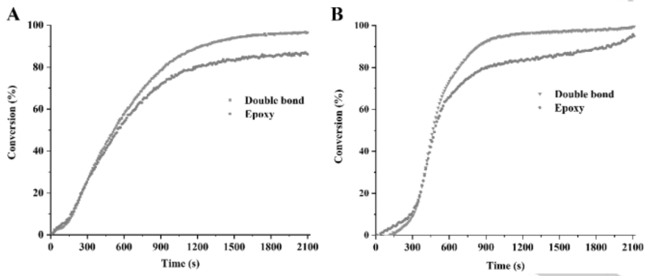


Figure 7. Kinetic profiles of double bond and epoxy conversions in photopolymerization of in the presence of P-PTh salt under different light irradiation sources; (A) LED@365 nm (30 mW/cm^2). (B) LED@405 nm (30 mW/cm^2).

Although at different rates, both FRP and CP proceeded efficiently in all cases, it, therefore, seemed appropriate to test if both types of polymerization proceed simultaneously. For this purpose, hybrid photopolymerization of a bifunctional monomer possessing both acrylate and epoxy functional groups, 7-oxabicyclo [4.1.0] heptan-3-yl) methyl methacrylate (TTA-15) in the presence of P-PTh using different wavelength LED light sources was studied. **Figure 7** clearly shows that both functions are consumed rapidly evidencing independent processes of FRP and CP.

In conclusion, a novel phenothiazine based phenacyl sulfonium (P-PTh) salt absorbing light over the UV–vis and near-IR region of the electromagnetic spectrum was synthesized and characterized by 2D NMR, MS analyses and DFT calculations. P-PTh demonstrates excellent initiating properties for cationic, free-radical and hybrid photopolymerizations at whole wavelength range and remarkable thermal stability and storage stability, which are extremely important for practical applications. The mechanism of initiation involves the photoinduced homolytic and heterolytic cleavages yielding initiating radical and ionic species responsible for the initiation of the respective polymerization reactions. The single component photoinitiator described here has the advantage of having broad-wavelength absorption characteristic particularly at NIR region and may provide new pathway for the curing applications of formulations of various pigmented systems.[19a, 21]. Although FRP dominates most of the applications comprising pigmented systems, CP has also gained importance in recent years.[22, 23]

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Conflict of interest

The authors declare no conflict of interest.

Keywords: broad-wavelength • photoinitiator •phenacyl• phenothiazine • photopolymerization

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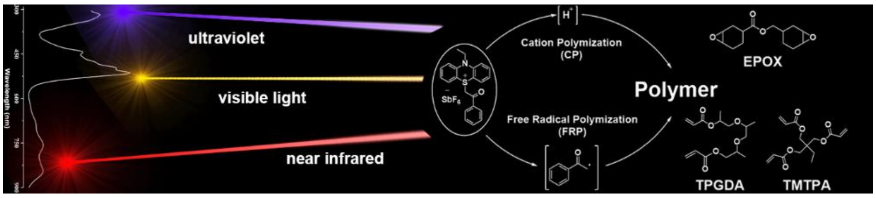

We report a new single component broad-band photoinitiator absorbing light at UV, Visible and Near-IR region for the initiation of free radical, cationic and hybrid polymerizations. This new photoinitiator may expand the curing application range of formulations of various pigmented systems.