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A Dithienothiophene Derivative as a Long-Wavelength Photosensitizer for Onium Salt Photoinitiated Cationic Polymerization

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ABSTRACT: The photosensitized cationic polymerization of typical monomers, e.g., of oxiranes such as cyclohexene oxide and 3,4-epoxycyclohexyl-3',4'-epoxycyclohexene carboxylate, of vinyl ethers such as *n*-butyl vinyl ether, and of other vinyl monomers such as styrene and *N*-vinylcarbazole by using a dithienothiophene derivative was studied. The cationic polymerization of these monomers was initiated at room temperature upon irradiation at $\lambda > 350$ nm either in bulk or CH₂Cl₂ solutions with 3,5-diphenyldithieno[3,2-*b*:2,3-*d'*]thiophene (DDT) in the presence of diphenyliodonium hexafluorophosphate (Ph₂I⁺PF₆[−]). Photophysical properties of DDT were studied in terms of optical absorption, fluorescence, and phosphorescence spectroscopy in order to provide information that would be useful in confirming the validity of the initiation mechanism. A mechanism involving formation of exciplex and subsequent electron transfer from excited DDT to iodonium ions is proposed.

Introduction

Although the majority of industrial applications of photoinitiated polymerizations for various techniques deal with free-radical systems, the corresponding cationic mode^{1–4} is an important industrial process widely used in different applications such as coatings, inks, adhesives, and photolithography. Moreover, UV-initiated cationic polymerization holds considerable promises in the future, particularly as a means of overcoming volatile emission, toxicity and molecular oxygen inhibition limitations.⁵ Many cationic photoinitiators are known, and their photochemistry has been studied in detail. Among them, the onium-type photoinitiators such as iodonium,⁶ sulfonium,⁷ and alkoxy pyridinium⁸ salts are important due to their thermal stability, solubility in most of the cationically polymerizable monomers, and efficiency in generating reactive species upon photolysis.⁹ Moreover, they possess high photolysis quantum yields and are efficient photoinitiators of cationic polymerization when irradiation is carried out using light in the short- to mid-wavelength UV regions (230–300 nm).¹⁰ A common strategy employed for improving the performance of these photoinitiators, particularly at long wavelengths, is the use of activators. The broader spectral sensitivity provided by an activator permits the capture of a higher fraction of the available light emitted from most common UV irradiation sources. This results in a more efficient photolysis of the photoinitiator and, consequently, generates a larger number of initiating species that produce an apparent acceleration of the rate of polymerization of the monomer. Regarding activation of onium salts, three modes of action concerning the formation of cationic species capable of reacting with monomers are distinguished: (i) oxidation of free radicals,^{11–13} (ii) electron transfer^{14–23} between a photoexcited molecule and an onium salt, and (iii) excitation of charge transfer complexes^{24,25} of onium salts.

(i) Many photolically formed radicals can be oxidized by onium salts. The cations thus generated are used as initiating species for cationic polymerization.

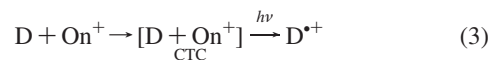


(ii) Certain aromatic hydrocarbons are able to sensitize the decomposition of onium salts via electron transfer in an excited

complex referred to as exciplex. In this complex, one electron is transferred from the sensitizer molecules to the onium salt, generating sensitizer radical cations.



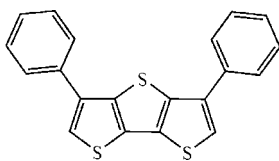
(iii) Excitation of charge transfer complexes (CTC) of onium salts results in the formation of aromatic radical cations.



The free radical oxidation process is limited to the photoinitiators capable of forming electron-donating radicals. For instance, except structurally specially designed, long wavelength absorbing acylphosphine oxide photoinitiators do not generate oxidizable radicals. Charge transfer complex activation is achieved only with alkoxy pyridinium type onium salts. Thus, electron-transfer photosensitization by using electron-rich polynuclear aromatic compounds such as anthracene, perylene, pyrene, and phenothiazine is the most efficient and generally applicable process.^{26,27} Despite the many potential applications, these photosensitizers also have several serious drawbacks that limit their use.^{28,29} For example, they are generally expensive, toxic, and poorly soluble in most reactive monomers and polymer systems. Moreover, they are easily lost from thin film coatings during polymerization and have high volatility at room temperatures. Therefore, there is a progressing need for long-wavelength-active photosensitizers are needed to overcome these limitations.

Dithienothiophenes have been receiving increasing attention due to their interesting electrochemical and optical properties. These compounds possess three fused thiophene rings, the orientations of which vary depending on the locations of the sulfur atoms of the peripheral thiophenes. With three S atoms, dithienothiophenes are electron-rich species, which makes them good electron donors and important building blocks of a wide variety of materials for electronic and optical applications such as electroluminescence, two-photon absorption, excited fluorescence, photochromism, nonlinear optical chromophores, transistors with high mobilities of on/off ratios, conducting polymers, and charge-transfer complexes. The possibility of favorable oxidation of the sulfur atom of the middle thiophene

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Chart 1. Structure of 3,5-Diphenyldithieno[3,2-*b*:2,3-*d*]thiophene (DDT)

ring gives the molecules property of fluorescence, which makes them good candidates for labeling, particularly important for biological systems.^{30–43}

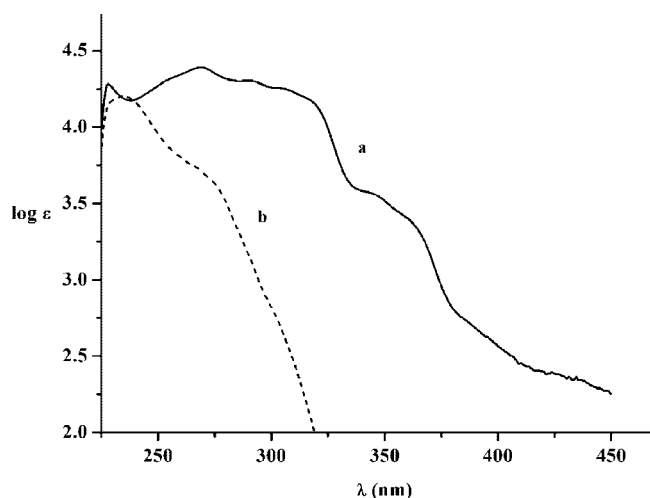
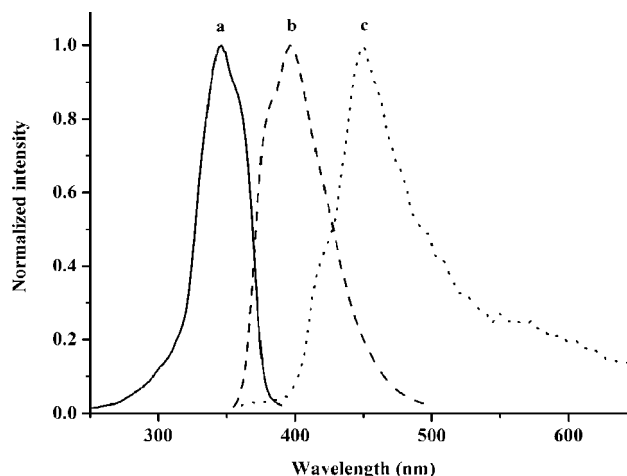
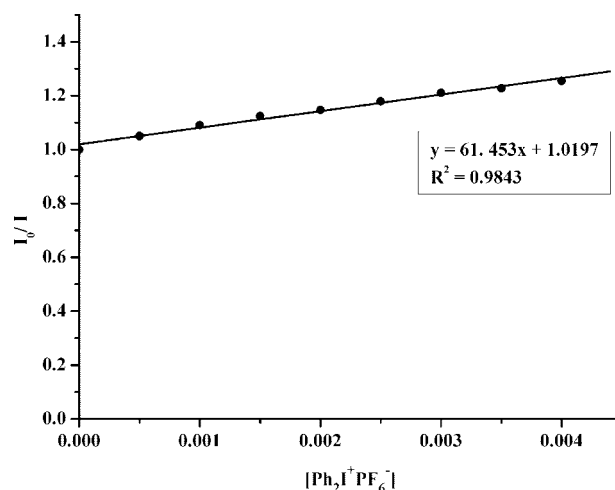
In this article, we describe the use of a dithienothiophene derivative, namely 3,5-diphenyldithieno[3,2-*b*:2,3-*d*]thiophene (DDT) (Chart 1) for the sensitization of onium salt decomposition and photopolymerization of several types of cationically polymerizable monomers.

Experimental Section

Materials. 3,5-Diphenyldithieno[3,2-*b*:2,3-*d*]thiophene (DDT) was synthesized as described in the literature.³¹ Diphenyliodonium hexafluorophosphate ($\text{Ph}_2\text{I}^+\text{PF}_6^-$, 98%, Alfa Aesar) and anthracene (99%, Acros Organics) were used as received. Dichloromethane (99.8%, Baker) was extracted first with sulfuric acid and then with 5% NaOH solutions. After washing with water, the dichloromethane was dried over anhydrous CaCl_2 and CaH_2 and finally distilled with a fractionation column. Cyclohexene oxide (CHO, 98%, Aldrich), *n*-butyl vinyl ether (BVE, >97%, Fluka), and styrene (S, $\geq 99\%$, Merck) were distilled over CaH_2 in vacuo. *N*-Vinylcarbazole (NVC, 98%, Aldrich) was crystallized from ethanol. 3,4-Epoxy-cyclohexyl-3', 4'-epoxycyclohexene carboxylate (EEC), commercial product of Ciba Specialty Chemicals, CY-179, was used as received.

Photopolymerization. Typical procedure: Cyclohexene oxide (0.5 mL, 4.9 mmol), DDT (1.7 mg, 5.0×10^{-3} mmol), and $\text{Ph}_2\text{I}^+\text{PF}_6^-$ (2.1 mg, 5.0×10^{-3} mmol) were put in a Pyrex tube and filled with dry nitrogen prior to irradiation from a Rayonet merry-go-round photoreactor equipped with 16 lamps emitting light nominally at 350 nm. Saturated cupric sulfate aqueous solution was used as the photofilter in order to avoid the absorption of onium salt. At the end of irradiation, polymer was precipitated in 10-fold excess methanol and dried in vacuum (yield: 58%; $M_n = 4450$ g mol^{-1}). All of the other polymerizations were performed under identical conditions except that CH_2Cl_2 was used as a solvent. Conversions for all samples were determined gravimetrically.

Characterization. Molecular weights were determined at room temperature by gel permeation chromatography (GPC) instrument equipped with a pump (Waters 600E) and three Waters styragel

**Figure 1.** Optical absorption spectra of 3,5-diphenyldithieno[3,2-*b*:2,3-*d*]thiophene (DDT) (a) and $\text{Ph}_2\text{I}^+\text{PF}_6^-$ (b) in CH_2Cl_2 .**Figure 2.** Normalized excitation (a) and emission (b) fluorescence spectra of 3,5-diphenyldithieno[3,2-*b*:2,3-*d*]thiophene (DDT) in CH_2Cl_2 at room temperature and emission phosphorescence spectra (c) at 77 K.**Figure 3.** Stern–Volmer plot of the quenching of 3,5-diphenyldithieno[3,2-*b*:2,3-*d*]thiophene (DDT) (1×10^{-5} mol L^{-1}) by $\text{Ph}_2\text{I}^+\text{PF}_6^-$ in CH_2Cl_2 (excitation wavelength = 350 nm). I_0 = fluorescence intensity of DDT, I = fluorescence intensity in the presence of $\text{Ph}_2\text{I}^+\text{PF}_6^-$.

columns HR5E (500 Å), HR3 (104 Å), and HR2 (100 Å). Tetrahydrofuran was used as the eluent (flow rate of 0.3 mL min^{-1}), and the detection was carried out with the aid of a Waters 410 differential refractometer. Molecular weights were calculated with the aid of polystyrene standards. UV spectra were recorded on a Shimadzu UV-1601 spectrometer. Fluorescence measurements were carried out using a Jobin Yvon-Horiba Fluoromax-P. All fluorescence measurements were performed at room temperature.

Results and Discussion

As shown in Figure 1, in the ground state, 3,5-diphenyldithieno[3,2-*b*:2,3-*d*]thiophene (DDT) strongly absorbs light between 350 and 450 nm where onium salts are transparent. Moreover, it has the advantage of being highly soluble in various monomers and solvents. For the potential use of DDT as a photosensitizer, the excited-state emission characteristics were investigated by means of fluorescence and phosphorescence spectroscopic measurements. Figure 2 depicts the normalized fluorescence—excitation and emission spectra of DDT in CH_2Cl_2 at room temperature. It is clear that a nearly mirror-image-like relation exists between absorption and emission of dithienothiophene compound.

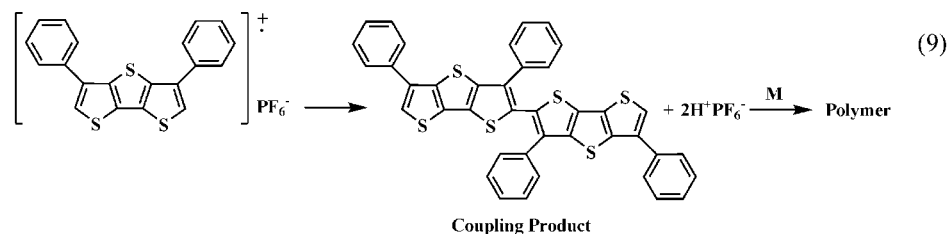
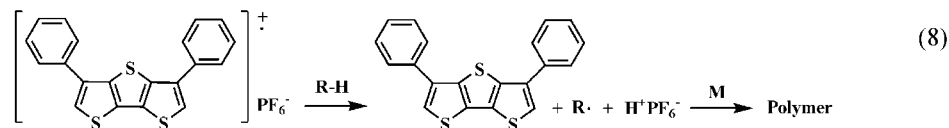
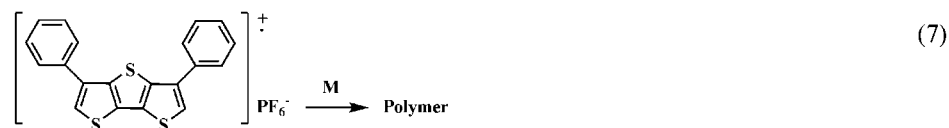
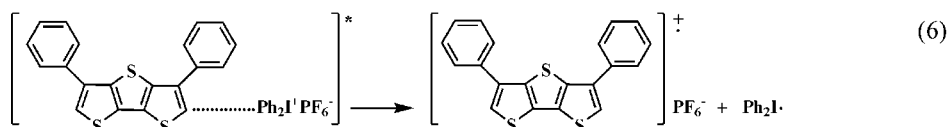
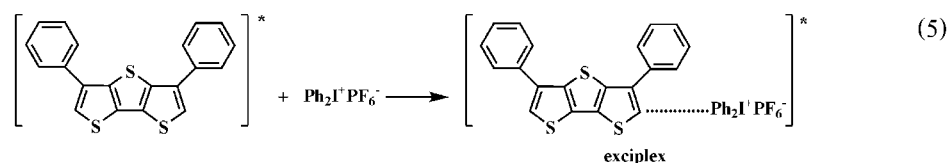
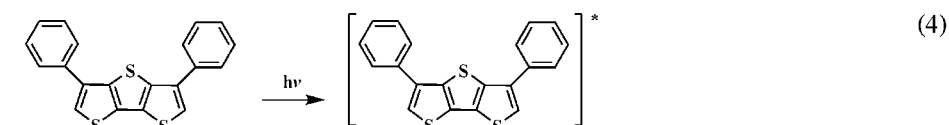
In the presence of diphenyliodonium salt, the fluorescence of DDT is markedly quenched. Figure 3 shows a typical

Table 1. Photoinitiated^a Cationic Polymerization of Various Monomers in the Presence of 3,5-Diphenyldithieno[3,2-*b*:2,3-*d*]thiophene (DDT) and Ph₂I⁺PF₆⁻ at Room Temperature for 30 min at λ > 350 nm

run	monomer ^b (mol L ⁻¹)	[photosensitizer] (mol L ⁻¹)	[onium salt] (mol L ⁻¹)	conversion (%)	<i>M</i> _n ^f	<i>M</i> _w / <i>M</i> _n ^f
1	CHO(9.88)	1 × 10 ⁻²	1 × 10 ⁻²	58	4450	1.97
2	CHO(9.88)		1 × 10 ⁻²	<1		
3	CHO(9.88)	1 × 10 ⁻²		<1		
4	CHO(9.88)	1 × 10 ⁻²	1 × 10 ⁻²	53 ^d	3450	2.56
5	BVE(3.84) ^c	0.5 × 10 ⁻²	0.5 × 10 ⁻²	66	14500	1.87
6	S(4.35) ^c	0.5 × 10 ⁻²	0.5 × 10 ⁻²	5	3700	2.26
7 ^e	NVC(1.03) ^c	0.5 × 10 ⁻²	0.5 × 10 ⁻²	98	1970	2.47

^a An interference filter (aqueous cupric sulfate solution) was used in all experiments. ^b CHO = cyclohexene oxide, BVE = butyl vinyl ether, St = styrene, NVC = *N*-vinylcarbazole. ^c In CH₂Cl₂ solution. ^d Anthracene is used instead of DDT. ^e Small portions of high molecular weight (*M*_n = 98 000, *M*_w/*M*_n = 1.8) polymer was obtained. ^f Determined from gel permeation chromatography measurements. *M*_n = number-average molecular weight; *M*_w = weight-average molecular weight.

Scheme 1. Photoinitiated Cationic Polymerization by 3,5-Diphenyldithieno[3,2-*b*:2,3-*d*]thiophene (DDT) and Iodonium Salt



Stern–Volmer plot for the fluorescence quenching of DDT as a function of the concentration of the diphenyliodonium salt. The linear correlation shown in the plot strongly confirms the reaction of excited state of DDT with the iodonium salt.

The polymerization of cyclohexene oxide (CHO), *n*-butyl vinyl ether (BVE), styrene (S), and *N*-vinylcarbazole (NVC) were examined. Typical results are presented in Table 1. As can be seen, all monomers were readily polymerized upon irradiation at room temperature at λ > 350 nm either in bulk or CH₂Cl₂ solutions with DDT in the presence of iodonium salt. For comparison, polymerization sensitized with a typical polynuclear aromatic hydrocarbon, anthracene, was also included (Table 1, run 4). The two components of the initiating system

are indispensable for the polymerization to occur; either no polymer or negligible amount of polymer is formed in the absence of DDT or iodonium salt at the irradiation wavelength. Notably, vinyl monomers with strong electron-donating groups, BVE and NVC, polymerized much more readily.

Even more convincing evidence for the sensitizing effect of DDT on cationic polymerization induced by iodonium salt was obtained from the cross-linking monomer 3,4-epoxycyclohexyl-3',4'-epoxycyclohexene carboxylate (EEC). Photopolymerizations of the bis-epoxide containing 5 × 10⁻³ mol L⁻¹ Ph₂I⁺PF₆⁻ were carried out. In the absence of DDT control experiments failed to produce a gel. In contrast, addition of 5 × 10⁻³ mol L⁻¹ DDT produced complete gelation after irradiation for 24

Table 2. Free Energy Changes (ΔG_S or ΔG_T) for the Electron Transfer from Either Singlet or Triplet Excited States of 3,5-Diphenyldithieno[3,2-*b*:2,3-*d*]thiophene (DDT) to $\text{Ph}_2\text{I}^+\text{PF}_6^-$

E_{red}^a (V) vs SCE	ΔG_S (kcal mol ⁻¹)	ΔG_T (kcal mol ⁻¹)
-0.20	-57.8	-38.8

^a Reference 20.

min at $\lambda > 350$ nm at room temperature. Interestingly, anthracene did not function to promote the polymerization under identical experimental conditions.

According to the Rehm–Weller equation (eq 10) electron transfer from the excited sensitizer to onium salt is feasible if the change in free energy (ΔG) is negative. On the basis of the oxidation potential (E_{ox}) and active excitation energy (E^*) of the photosensitizer (PS) and the reduction potential (E_{red}) of the initiator (PI), the free energy change (ΔG) for the photo-induced electron transfer process was estimated.⁴⁴

$$\Delta G = E_{\text{ox}}(\text{PS}) - E_{\text{red}}(\text{PI}) - E^*(\text{PS}) \quad (10)$$

Table 2 summarizes the ΔG_S and ΔG_T values of the free energy changes for the electron transfer from the singlet and triplet excited states, respectively, of the photosensitizer to the ground-state iodonium salt. E_{ox} for DDT determined by cyclic voltammetry is 0.88 V,³¹ whereas the singlet excitation energy E_S^* and triplet excitation energy E_T^* have been found to be 82.6 and 63.7 kcal mol⁻¹, respectively.

Although the electron transfer in both the singlet and triplet excited states of the dithienothiophene derivative is thermodynamically favorable, relatively low conversion of styrene polymerization indicates that triplet state also involves in the electron transfer process. Styrene is a strong triplet quencher and reacts with triplet excited states with a high rate constant.⁴⁵

A mechanism based on electron transfer concerning the reaction of excited DDT with iodonium ion is described in Scheme 1. DDT radical cations formed by reaction 6 would be capable of initiating cationic polymerization and, because of the non-nucleophilicity of PF_6^- ions, cationic chain propagation would not be prevented. Principally, polymerization could also be initiated by the protons formed via hydrogen abstraction (reaction 8) or coupling reactions (reaction 9). We recently presented evidence for such reactions of thiophene radical cations with the aid of laser flash photolysis studies.^{46,47} However, further studies are necessary to reveal which process substantially contributes to the initiation of polymerization.

In conclusion, although mechanistic details still remain to be evaluated, it is clear that DDT is an efficient electron-transfer photosensitizer for iodonium salt and cyclic ethers and vinyl monomers can efficiently be polymerized at wavelengths of $\lambda > 350$ nm with the aid of dithienothiophene compound. Further investigations concerning elucidation of initiation process by using laser flash photolysis are now in progress.

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