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Highly Conjugated Thiophene Derivatives as New Visible Light Sensitive Photoinitiators for Cationic Polymerization

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ABSTRACT: A visible light sensitive photoinitiator system for the cationic polymerization of typical monomers, e.g. of oxiranes such as cyclohexene oxide, of vinyl ethers such as *n*-butyl vinyl ether, and of other vinyl monomers such as *N*-vinylcarbazole, using highly conjugated thiophene derivatives is described. The cationic polymerization of these monomers was initiated at room temperature upon irradiation in the visible region ($\lambda_{\text{inc}} = 480 \text{ nm}$) in CH_2Cl_2 solutions with 4,7-di(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)benzo-[1,2,5]thiadiazole (DTDT) or 5,8-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-2,3-di(thiophen-2-yl)quinoxaline (DTDQ) in the presence of diphenyliodonium hexafluorophosphate ($\text{Ph}_2\text{I}^+\text{PF}_6^-$). A feasible mechanism, as correlated with optical absorption and fluorescence spectroscopic measurements, free energy changes (ΔG), and proton scavenging studies, involves formation of exciplex by the absorption of light in the first step. Subsequent electron transfer from excited DTDT or DTDQ to iodonium ion yields radical cations of the thiophene derivatives. The resulting strong Brønsted acid derived from this process catalyzes the cationic polymerization of variety of monomers.

Introduction

Photopolymerizations that proceed under visible light^{1,2} have found particular interest because of their use in many targeted applications such as dental filling materials,^{3–5} photoresists, printing plates, highly pigmented coatings, integrated circuits, laser-induced 3D curing, holographic recordings, and nanoscale micromechanics. The possibility of conducting polymerizations at ambient sunlight offers further potential applications such as orthopedic casts, assembly of catheters, in-field repair of equipment, the construction of fiber reinforced composite boats, water storage and delivery systems, and for building panels. A number of photoinitiating systems for free radical polymerization, acting in the visible range, are well-known. Titanocene³ and camphorquinone⁶ in conjunction with an amine are typical examples for cleavage and H-abstraction type visible light photoinitiators, respectively. Recently, organic ketones containing germanium were introduced as new class of cleavable photoinitiators^{7,8} for free radical polymerization under visible light irradiation.

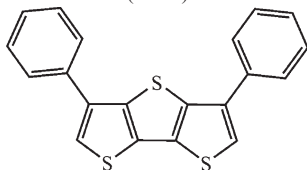
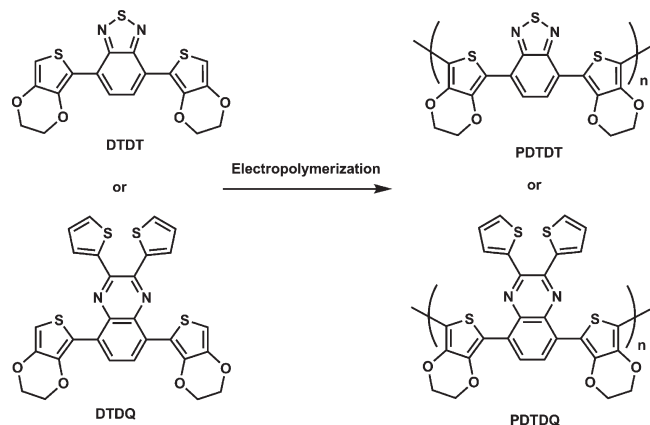
The long wavelength initiating systems for cationic polymerization⁹ also received drastically increased attention in the past several years. The existing strategies are based on the activation of the most prominent cationic photoinitiators, namely onium salts,^{10,11} by light sensitive additives, which do not directly initiate the polymerization. One can adapt the initiating system to different wavelengths of irradiation by three ways: (i) oxidation of free radicals by onium salts^{12–15} (also called as free radical promoted cationic polymerization), (ii) electron transfer between photoexcited sensitizer and onium salt,^{16–25} and (iii) electron transfer in photoexcited charge transfer complexes of certain onium salts.^{26–28} The suitable free radical promoters include benzoin derivatives, benzyl ketals,²⁹ acylphosphine oxides,^{30,31} benzaldehyde,³² and polysilanes.^{33,34} It was also demonstrated^{35,36} that silyl and germlyl radicals generated by the photolysis of

disilanes, and silanes and germanes, respectively, in the presence of aromatic carbonyl compounds can also participate in such electron transfer processes, resulting in efficient cationic polymerization.

The photochemical generation of oxidable free radicals can be extended also to the visible light. Certain dyes in conjunction with aromatic amines³⁷ and manganese decacarbonyl in the presence of alkyl halides³⁸ were shown to be suitable initiating systems to promote cationic polymerization at above 400 nm. We have recently demonstrated that acylgermane-based α -cleavage free radical photoinitiators absorbing at the visible range can also induce cationic polymerization.³⁹ In this case, photochemically formed germlyl radicals are readily oxidized to the initiating germanium cations by onium salts. Recently, Crivello reported an efficient three component visible sensitive photoinitiator system for cationic ring-opening polymerization of epoxides and related monomers.⁴⁰ The photoinitiator system consists of camphorquinone in combination with a benzyl alcohol to generate free radicals by the absorption of visible light. The electron transfer reactions of resulting radicals with iodonium salt present in the system essentially leads to the formation of Brønsted acid capable of catalyzing the ring-opening polymerization of epoxy substrates. Although a broad range of spectral flexibility can be achieved, the free radical oxidation is limited to the photoinitiators capable of forming electron donor radicals. For instance, except structurally specially designed, long wavelength absorbing acylphosphine oxide photoinitiators do not generate oxidizable radicals. Thus, electron-transfer photosensitization by using electron-rich polynuclear aromatic compounds such as anthracene, perylene, pyrene, and phenothiazine appears to be an alternative efficient pathway to shift the absorption sensitivity to longer wavelengths.^{28,41}

More recently, we have reported⁴² the use of a polynuclear thiophene derivative, namely 3,5-diphenyldithieno[3,2-*b*:2',3'-*d'*]thiophene (DDT) of the following structure (Chart 1) as an electron-transfer photosensitizer for diaryliodonium salt cationic photoinitiators. Several types of cationically polymerizable

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Chart 1. Structure of 3,5-Diphenyldithieno[3,2-*b*:2,3-*d'*]thiophene (DDT)**Scheme 1.** Electropolymerization of 4,7-Di(2,3-dihydrothieno[3,4-*b*]-[1,4]dioxin-5-yl)benzo[1,2,5]thiadiazole (DTDT) and 5,8-Bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-2,3-di(thiophen-2-yl)quinoxaline (DTDQ)

monofunctional monomers, such as cyclohexene oxide, *n*-butyl vinyl ether, styrene, and *N*-vinylcarbazole, and bifunctional monomers such as 3,4-epoxycyclohexyl-3',4'-epoxycyclohexene carboxylate were readily polymerized in bulk or dichloromethane solutions upon irradiation at > 350 nm in the presence of DDT and diphenyliodonium hexafluorophosphate. Although DDT provides good sensitivity in the near-UV (350–400 nm) region, it possesses little appreciable absorption in the visible region above 400 nm; it is not useful for carrying out cationic photopolymerizations using visible light.

Conducting polymers have been extensively studied and used for different industrial applications.⁴³ Although a huge amount of efforts have been paid, the most of the electrochromic polymers reflect mainly in blue and red colors. Recently, Toppare and co-workers^{44,45} reported first green color electrochromic polymers with exceptional switching properties and remarkable stability. The polymers, obtained from the corresponding monomers, namely 4,7-di(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-benzo[1,2,5]thiadiazole (DTDT) and 5,8-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-2,3-di(thiophen-2-yl) quinoxaline (DTDQ) by electropolymerization (Scheme 1), exhibited two simultaneous absorption bands in the red and blue regions of the visible spectrum where these bands should be controlled with the same applied potential. The approach is based on the incorporation of both electron donor, 3,4-ethylenedioxythiophene (EDOT), and acceptor, thiadiazole and quinoxaline groups, for DTDT and DTDQ, respectively, into monomer and consequently polymer structure.

The present article describes the use of such highly conjugated thiophene derivatives in conjunction with iodonium salt as a new and efficient visible light cationic photoinitiator system and its application to the polymerization of several types of cationically polymerizable monomers.

Experimental Section

Materials. 4,7-Di(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-benzo[1,2,5]thiadiazole (DTDT) and 5,8-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-2,3-di(thiophen-2-yl)quinoxaline (DTDQ)

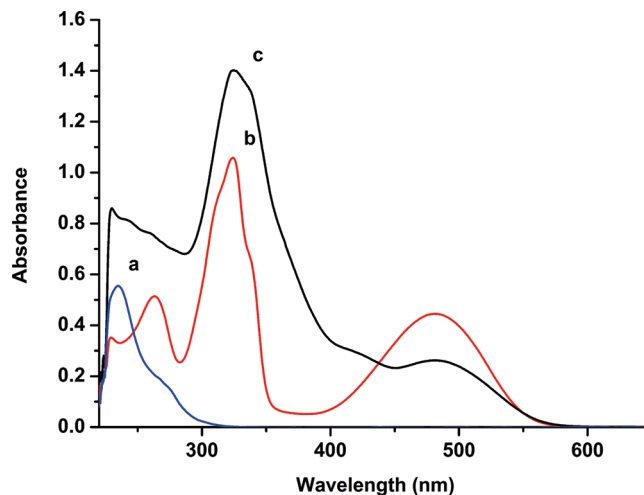


Figure 1. UV spectra of 3.5×10^{-3} mol L⁻¹ Ph₂I⁺PF₆⁻ (a), 3.5×10^{-3} mol L⁻¹ 4,7-di(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)benzo[1,2,5]-thiadiazole (DTDT) (b), and 3.5×10^{-3} mol L⁻¹ 5,8-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-2,3-di(thiophen-2-yl)quinoxaline (DTDQ) (c) in CH₂Cl₂.

were synthesized as described in the literature.^{45,46} Diphenyliodonium hexafluorophosphate (Ph₂I⁺PF₆⁻, 98%, Alfa Aesar) was 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 CaCl₂ and CaH₂ and finally distilled with a fractionation column. Cyclohexene oxide (CHO, 98%, Aldrich) and *n*-butyl vinyl ether (BVE, >97%, Fluka) were distilled over CaH₂ in vacuo. *N*-Vinylcarbazole (NVC, 98%, Aldrich) was crystallized from ethanol.

Photopolymerization. Typical procedure: Cyclohexene oxide (0.4 mL, 3.95 mmol), DTDQ (0.2 mL from 0.006 mol L⁻¹ stock solution in CH₂Cl₂), and Ph₂I⁺PF₆⁻ (0.1 mL from 0.012 mol L⁻¹ stock solution in CH₂Cl₂) were put in a Pyrex tube and filled with dry nitrogen prior to irradiation from a monochromatic light source equipped with a HBO 100 W lamp. At the end of irradiation, polymer was precipitated in 10-fold excess methanol and dried in vacuum. 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 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

Figure 1 shows the absorption spectra of highly conjugated thiophene derivatives and diphenyliodonium salt. The thiophene compounds, DTDT and DTDQ, absorb strongly above 400 nm presumably due to the extended conjugation of the thiophene groups through the central phenyl ring that makes them particularly useful for visible light applications.

For the potential use of DTDT and DTDQ, as photosensitizers, 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 DTDT and DTDQ, in CH₂Cl₂

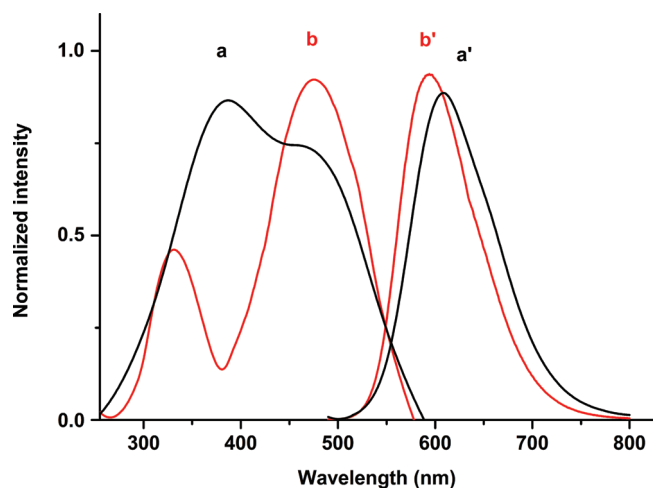


Figure 2. Normalized excitation fluorescence spectra of 5,8-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-2,3-di(thiophen-2-yl)quinoxaline (DTDQ) (a) and 4,7-di(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)benzo[1,2,5]thiadiazole (DTDT) (b) and normalized emission spectra of DTDQ (a') and DTDT (b') in CH_2Cl_2 at room temperature.

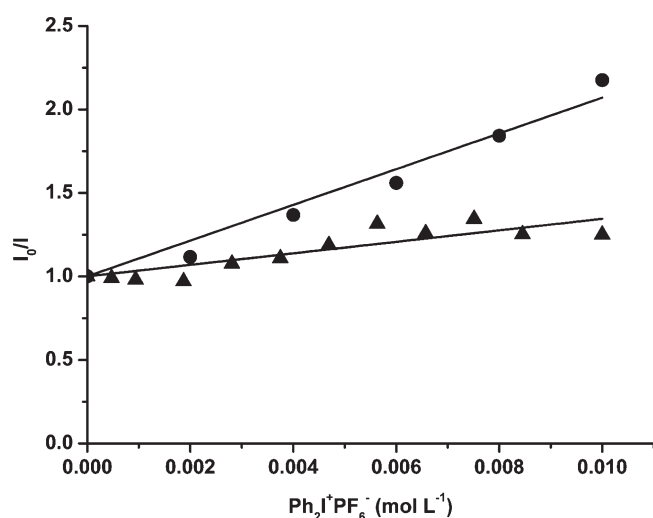


Figure 3. Stern–Volmer plot for the fluorescence quenching of 5,8-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-2,3-di(thiophen-2-yl)quinoxaline (DTDQ) ($1 \times 10^{-5} \text{ mol L}^{-1}$) (●) and 4,7-di(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)benzo[1,2,5]thiadiazole (DTDT) ($1 \times 10^{-5} \text{ mol L}^{-1}$) (▲) by $\text{Ph}_2\text{I}^+\text{PF}_6^-$ in CH_2Cl_2 (I_0 = fluorescence intensity of DTDT or DTDQ; I = fluorescence intensity in the presence of $\text{Ph}_2\text{I}^+\text{PF}_6^-$).

at room temperature. It is clear that structureless emissions were detected and a nearly mirror-image-like relation exists between absorption and emission of both compounds. Both compounds did not exhibit phosphorescence emission at 77 K, indicating rather low intersystem crossing efficiency between singlet and triplet excited states.

In the presence of diphenyliodonium salt, the fluorescence of the sensitizers is markedly quenched. Figure 3 shows a typical Stern–Volmer plot for the fluorescence quenching of DTDT and DTDQ as a function of the concentration of the diphenyliodonium salt. The linear correlation shown in the plot strongly confirms the reaction of excited states of both DTDT and DTDQ, with the iodonium salt.

In our studies the photopolymerization were performed under irradiation at 480 nm, e.g., at the wavelength where the light emission is well matched with absorption of sensitizers and iodonium salt is transparent. In Figure 4, the conversion of a

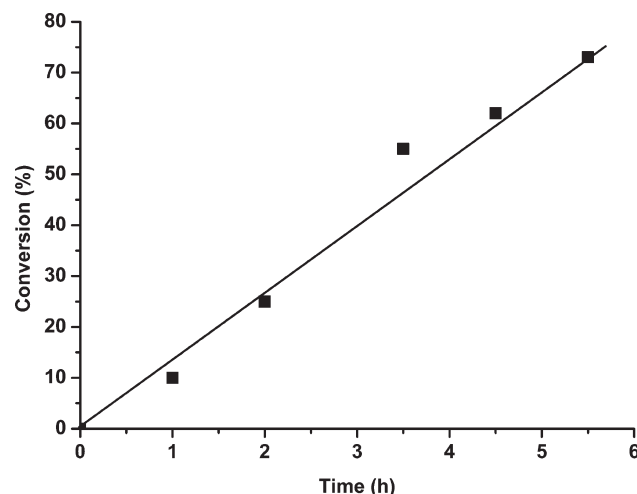


Figure 4. Time–conversion plot for photoinduced polymerization of CHO in the presence of 0.03% 5,8-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-2,3-di(thiophen-2-yl)quinoxaline (DTDQ) and 0.06% $\text{Ph}_2\text{I}^+\text{PF}_6^-$ (room temperature, $\lambda = 480 \text{ nm}$).

Table 1. Photosensitized Cationic Polymerization^a of Various Monomers in the Presence of DTDT, DTDQ, CQ, and $\text{Ph}_2\text{I}^+\text{PF}_6^-$ in CH_2Cl_2 at Room Temperature ($\lambda = 480 \text{ nm}$)

monomer	[M] (mol L^{-1})	photo- sensitizer	$R_p \times 10^4$ ($\text{mol L}^{-1} \text{ s}^{-1}$)	conversion (%)	M_n	M_w/M_n
CHO	5.6	DTDT	2.02	26	10300	1.6
CHO	5.6	DTDQ	1.96	25	11900	1.5
BVE	5.3	DTDQ	4.75	78	51700	2.1
NVC	2.9	DTDQ	3.17	80	23000	2.6
NVC	2.9	DTDT	2.84	71	29500	3.2
CHO ^b	5.6	DTDT	56.0	59	5570	1.6
CHO ^{b,c}	5.6	DTDT	40.0	49	6060	1.7
CHO ^b	5.6	CQ	23.0	28	3510	1.5
CHO ^{b,d}	5.6	CQ	32.0	38	1620	1.3

^a Light intensity = 0.045 mW cm^{-2} , polymerization time = 2 h, [photosensitizer] = $1.7 \times 10^{-3} \text{ mol L}^{-1}$, $[\text{Ph}_2\text{I}^+\text{PF}_6^-] = 3.4 \times 10^{-3} \text{ mol L}^{-1}$, CHO = cyclohexene oxide, BVE = butyl vinyl ether, NVC = *N*-vinylcarbazole, DTDT = 4,7-di(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)benzo[1,2,5]thiadiazole, DTDQ = 5,8-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-2,3-di(thiophen-2-yl)quinoxaline, CQ = camphorquinone. ^b Light intensity = 25 mW cm^{-2} , polymerization time = 10 min. ^c The polymerization was performed in aerated media. ^d In the presence of benzyl alcohol as hydrogen donor.

typical epoxy monomer, cyclohexene oxide (CHO) into poly(cyclohexene oxide) is plotted versus time. As can be seen, the polymerization started without induction period and increased almost linearly with time.

The visible light photoinitiated polymerization of some representative monomers, namely *n*-butyl vinyl ether (BVE) and *N*-vinylcarbazole (NVC), with the thiophene derivatives in the presence of iodonium salt was also studied. As can be seen from Table 1, BVE and NVC were polymerized more effectively due to their strong electron donating nature. DTDT exhibited slightly better initiator efficiency for the polymerization of BVE than that of DTDQ which correlates well with their oxidation potentials (vide infra). It is also interesting to note that the thiophene derivatives activate cationic polymerization more efficiently than the well-known visible light photosensitizer, camphorquinone, even in the presence of a hydrogen donor such as benzyl alcohol. Although at reduced rate, polymerization also proceeds in the presence of air, indicating oxygen inhibition observed with the aromatic carbonyl sensitizers is not an important process. Notably, irradiations with increased light intensity resulted in much faster polymerizations.

As for the all polynuclear aromatic compounds, 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 photoinduced electron transfer process was estimated according to eq 1.⁴⁷

$$\Delta G = E_{\text{ox}}(\text{PS}) - E_{\text{red}}(\text{PI}) - E^*(\text{PS}) \quad (1)$$

Table 2. Free Energy Changes (ΔG_{S}) for the Electron Transfer from Singlet Excited States of DTD T and DTD Q to $\text{Ph}_2\text{I}^+\text{PF}_6^-$ ^a

photosensitizer	E_{ox} (kcal mol ⁻¹)	E^* (kcal mol ⁻¹)	ΔG_{S} (kcal mol ⁻¹)
DTD T	0.95	48.00	-21.48
DTD Q	0.70	47.13	-26.38

^a $E_{\text{red}} = -0.20$ (V) vs SCE, DTD T = 4,7-di(2,3-dihydrothieno[3,4-*b*]-[1,4]dioxin-5-yl)benzo[1,2,5]thiadiazole, DTD Q = 5,8-bis(2,3-dihydrothieno[3,4-*b*]-[1,4]dioxin-5-yl)-2,3-di(thiophen-2-yl)quinoxaline.

Table 2 summarizes the ΔG_{S} values of the free energy changes for the electron transfer from the singlet states of the photosensitizers to the ground-state iodonium salt. E_{ox} and E_{S}^* for DTD T and DTD Q were determined by cyclic voltametry^{44,45} and fluorescence measurements, respectively. The free energy change (ΔG_{T}) for the electron transfer from the triplet states could not be estimated as phosphorescence studies of both sensitizer at 77 K failed to give any emission, and the possibility of the initiation from the triplet state was discarded. As can be seen from Table 2, electron transfer in singlet excited state of both thiophene compounds is thermodynamically favorable.

A mechanism based on electron transfer concerning the reaction of excited DTD T with iodonium ion is described in Scheme 2. The same mechanism may also be postulated for the other thiophene derivative DTD Q .

The radical cations formed by reaction 3 of Scheme 2 would be capable of initiating cationic polymerization since direct initiation by the species formed from polynuclear aromatic compounds is a well-known process,^{19,21,48,49} and because of the

Scheme 2. Photosensitized Cationic Polymerization by 4,7-Di(2,3-dihydrothieno[3,4-*b*]-[1,4]dioxin-5-yl)benzo[1,2,5]thiadiazole (DTD T) and Iodonium Salt

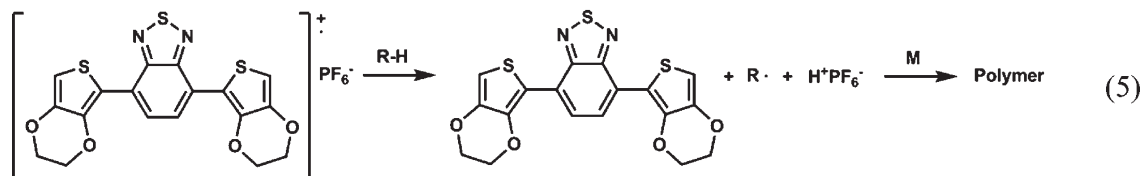
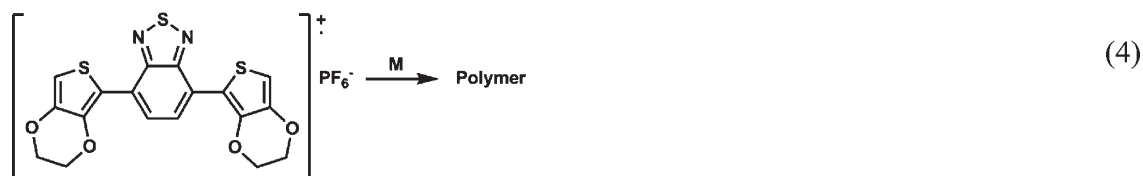
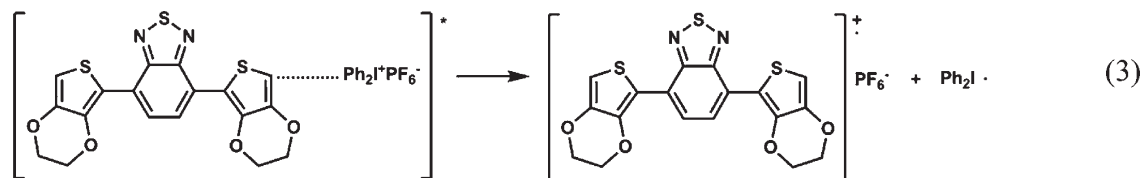
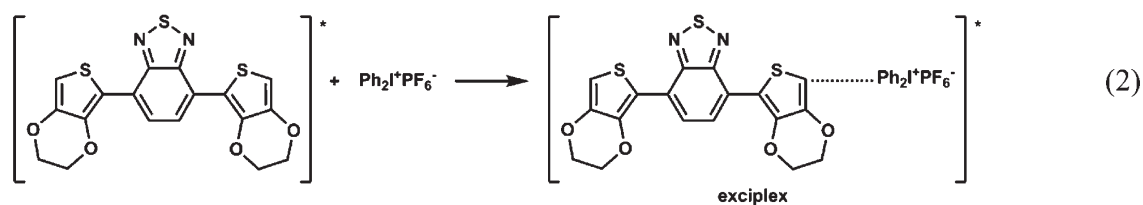
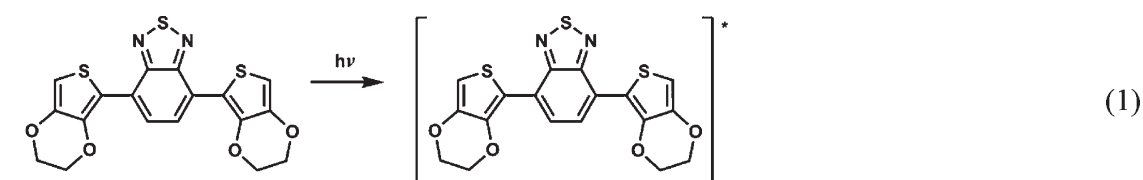


Table 3. Photosensitized Cationic Polymerization of Cyclohexene Oxide (CHO) for 2 h at $\lambda = 480$ nm

CHO ^a	DTDQ ^b	Ph ₂ I ⁺ PF ₆ ^{-c}	conversion (%)
+	+	+	25
+	—	+	—
+	+	—	—
+ ^d	+	+	—

^a[CHO] = 5.6 mol L⁻¹. ^b[DTDQ] = 1.7 × 10⁻³ mol L⁻¹. ^c[Ph₂I⁺PF₆⁻] = 3.4 × 10⁻³ mol L⁻¹. ^dIn the presence of 2,6-di-*tert*-butyl-4-methylpyridine.

non-nucleophilicity of PF₆⁻ ions, cationic chain propagation would not be prevented. Principally, polymerization could also be initiated by the Brønsted acids formed via hydrogen abstraction (reaction 5, Scheme 2) or coupling reactions (reaction 6). We recently presented evidence for such reactions of thiophene radical cations with the aid of laser flash photolysis studies.^{50,51} Of particular importance is to evaluate if the Brønsted acids formed from the above reactions are the actual initiating species. Thus, photopolymerization experiments with CHO in the presence of a strong proton scavenger, 2,6-di-*tert*-butyl-4-methylpyridine (DBMP), were performed. It was observed that polymerization of CHO was totally inhibited when DBMP was present in the system (Table 3). Such inhibition indicates that protons generated according to reactions 5 and 6 play an important role regarding the initiation of cationic polymerization and direct initiation by the reaction of the radical cations with the monomer (reaction 4) can be neglected. In order to gain more insight into the polymerization process, experiments were performed where either the thiophene compound or iodonium ion was omitted. This omission of either of the two components failed to produce polymer, which is consistent with the proposed mechanism shown in Scheme 2.

Evidence for the practical value of the promoting effect of conjugated thiophene derivatives on cationic polymerization induced by onium salts was obtained from cross-linking monomer 1,3-bis(3,4-epoxycyclohexylethyl)tetramethyldisiloxane (EPOX). Bulk polymerizations of the bis-epoxide containing 3.4 × 10⁻³ mol L⁻¹ Ph₂I⁺PF₆⁻ were carried out. In the absence of the thiophene derivatives photoirradiations from a Bluephase light source emitting at 430–490 nm failed to produce a gel after 2 h irradiation. In contrast, addition of 1.7 × 10⁻³ mol L⁻¹ DTDQ produced complete gelation after 10 min irradiation at room temperature.

In conclusion, a new visible light sensitive cationic photoinitiator system consisting of highly conjugated thiophene derivatives and iodonium salt has been designed. Key features of this initiating system are (i) the use of visible light, e.g., $\lambda = 480$ nm, to excite thiophene derivatives which undergo electron transfer reactions with diaryliodonium salt, and (ii) the resulting radical cations rapidly couple and/or abstract hydrogen to yield Brønsted acid for initiation of cationic polymerization. New initiating systems for cationic polymerization acting at visible range such as this will play an important role in emerging fields such as highly pigmented coatings, rapid setting inject inks, coatings for wood preservation, and three-dimensional imaging processes that require visible light sensitization.

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