New Photoinitiating Systems for Cationic Polymerization Acting at Near UV and Visible Range

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Summary: New photoiniting systems for cationic polymerization acting at near UV and visible range are described. The applicability of acylgermanes as a new class of free radical promoters for photoinitiated cationic polymerization is demonstrated. Moreover, the use of substituted vinyl halides as source for readily oxidizable free radicals is presented. The polymerization of vinyl ethers can be initiated by the irradiation of substituted vinyl halides in the presence of Lewis acids such as zinc halide. Furthermore, possibilities for conducting cationic polymerization at visible range by using highly conjugated thiophene derivatives are demonstrated. Mechanistic aspects of all initiating systems are discussed.

Keywords: acyl german; cationic polymerization; dithienothiophene; photopolymerization; vinyl halides

Introduction

Although the majority of industrial applications of photoinitiated polymerizations for various techniques deal with free radical systems, the corresponding cationic mode is an important industrial process widely used in different applications such as coatings, inks, adhesives, varnishes, microelectronics, microlithography, and dyes due to the several advantages.[1–3] Like all photopolymerization processes, photoinitiated cationic polymerization minimizes energy consumption, and eliminates the need for solvents as diluents (i.e. it offers elimination of air and water pollution).[2,3] Moreover, photoinitiated cationic polymerization holds considerable promises in the future, particularly as a means of overcoming volatile emission, toxicity and molecular oxygen inhibition limitations.[4] Many cationic photoinitiators are known, and their photochemistry has been studied in detail. Among them, the onium-type photoinitiators such as iodonium,[5] sulfonium,[6] and alkoxypyridinium[7] salts are important due to their thermal stability, solubility in most of the cationically polymerizable monomers, and efficiency in generating reactive species upon photolysis.[8] 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 midwavelength UV regions (230–300 nm).[9] 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,[10–12] (ii) electron transfer[13–22] between a photoexcited molecule and an

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onium salt, and (iii) excitation of charge transfer complexes[23,24] of onium salts.

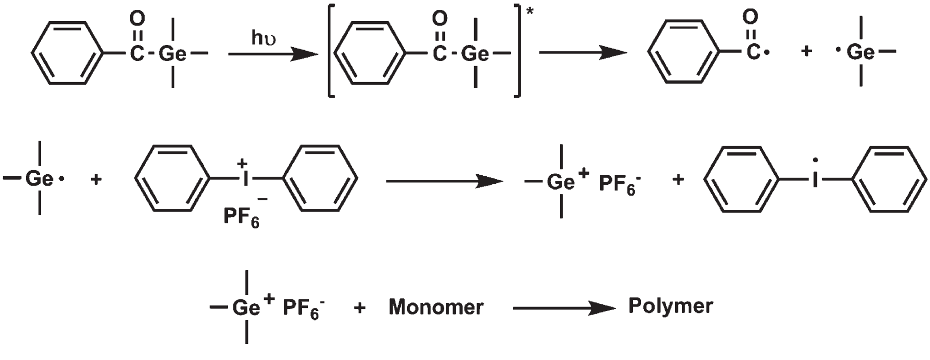
On the other hand, toxic effects of AsF_6^- and SbF_6^- anions of onium salts can be avoided by using these salts with highly nucleophilic counterions such as halides. Recently, iodonium halides have been employed in the controlled polymerization and cross-linking of vinyl ethers.[25,26] This controlled/living cationic photopolymerization of vinyl ethers has been originated from the thermal mode of cationic polymerization[27] developed by Higashimura and Sawamoto.[28] Diphenyliodonium halides were used as photoinitiator in the presence of zinc halide as a Lewis acid (Scheme 1).[25,26] Quite recently, a modified version of such photoinitiating was reported for photoinitiated cationic aqueous polymerization in which conventional Lewis acid is replaced with water-tolerant ytterbium triflate ($Yb(OTf)_3$) in the initiating system.[29] This novel initiation process will be used when proper cationic species are generated from any other compounds. Among them vinyl carbocations that are likely potential to initiate cationic polymerization can be produced simply photolysis of vinyl halides (i.e. 1-bromo-1,2,2-triphenylethene (PPPVB)). Upon irradiation vinyl halides give vinyl cations in a two-step process, in which vinyl radical and halogen radical are photochemically formed in primary process and vinyl cation and halide are generated by electron transfer in the second step.[30–33] In this circumstance, high nucleophilicity of the halide anion prevents polymerization of vinyl ethers; however, addition of a Lewis acid such as zinc halides probably stimulates the polymerization.[28]

The objective of this article is to present the new photoinitiating systems for cationic polymerization acting at near UV and visible range. Special emphasize will be placed on the use of long wavelength free radical photoinitiators and photosensitizers such as acylgermanes,[34] dithienothiophene derivatives[35] and substituted vinyl halides.[36]

Experimental Part

Materials and Characterization

Benzoyltrimethylgermane (BTG)[37] and 3,5-diphenyldithieno[3,2-*b*:2,3-*d*]thiophene (DDT)[38] were synthesized as described in the literature. Preparation of all substituted vinyl halides were described elsewhere.[39–41] Cyclohexene oxide (CHO, 98%, Aldrich), *n*-butyl vinyl ether (BVE, >97%, Fluka), isobutyl vinyl ether (IBVE, 99%, Aldrich) and styrene (S, 99%, Merck) were distillated over CaH_2 in vacuo. *N*-Vinyl carbazole (NVC, 98%, Aldrich) was crystallized from ethanol. Difunctional monomers, di(ethylene glycol) divinyl ether (DEGDVE, 99%, Aldrich), 1,4-butanediol divinyl ether (BDVE, 98%, Aldrich), and 1,6-hexanediol divinyl ether (HDVE, 97%, Aldrich) were used as



Scheme 1.
The oxidation of trimethyl germyl radicals by $Ph_2I^+PF_6^-$.

received. Benzophenone (BP, Merck) was recrystallized from heptane. 2,2-Dimethoxy-2-phenyl acetophenone (DMPA, Ciba Specialty Chemicals), (2, 4, 6-trimethylbenzoyl) diphenylphosphine oxide (TMDPO, Ciba), diphenyliodonium hexafluorophosphate ($Ph_2I^+PF_6^-$, 98%, Alfa Aesar), diphenyliodonium iodide ($Ph_2I^+I^-$, 98%, Alfa Aesar), zinc iodide (ZnI_2, anhydrous, Merck),), anthracene (99%, Acros) 3,4-epoxycyclohexyl-3′,4′-epoxycyclohexene carboxylate (EEC), commercial product of Ciba Specialty Chemicals, CY-179, poly(ethylene glycol) (PEG, $M_n = 1500$ g/mol, Fluka) were used as received. Dichloromethane (99.8%, Baker) was extracted first with sulfuric acid, 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.

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 (THF) 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 of polymers synthesized using vinyl halides were measured with a Viscotek GPCmax Autosampler system consisting of a pump, a Viscotek UV detector and Viscotek a differential refractive index (RI) detector. Three ViscoGEL GPC columns (G2000H_{HR}, G3000H_{HR} and G4000H_{HR}), (7.8 mm internal diameter, 300 mm length) were used in series. The effective molecular weight ranges were 456–42,800, 1050–107,000, and 10,200–2,890,000, respectively. THF was used as an eluent at flow rate of 0.5 mL min^{-1} at 30°C. Molecular weights were calculated with the aid of polystyrene standards.

UV spectra were recorded on a Shimadzu UV-1601 spectrometer or A Cary 3000-Bio (Varian) spectrometer. Fluorescence measurements were carried out using a Jobin Yvon-Horiba Fluoromax-P. All fluorescence measurements were performed at room temperature.

Photopolymerization

Procedures for the photopolymerization of CHO, IBVE and other related mono and bifunctional monomers by using different initiating systems were described in detail previously.[34–36]

Results and Discussion

As stated in the introduction section, the photosensitivity of the cationic photoinitiators can be extended to the longer wavelengths by several routes. In the following section, we will report our recent findings on such tunability via oxidation of free radicals and photosensitization by electron transfer reaction.

Oxidation of Free Radicals

Recently, acyl germanes originally developed as visible light photoinitiators for free radical polymerization were also shown to activate cationic polymerization. As in the case of all free radical promoted cationic polymerizations, the photochemically formed electron donating radicals (germyl radicals) are readily oxidized to germanium ions capable of initiating cationic polymerization (Scheme 1).

Cyclohexene oxide (CHO) was selected as the typical model monomer for detailed mechanistic studies as it is unreactive towards free radicals, but readily polymerizes by cationic mechanism. This monomer undergoes efficient polymerization with a germane based photoinitiator such as benzoyltrimethylgermane (BTG) in the presence of diphenyl iodonium hexafluorophosphate ($Ph_2I^+PF_6^-$) at wavelengths where the salt is transparent. As can be seen in Figure 1, diphenyliodonium salt does not absorb at $\lambda > 340$ nm. The results of polymerizations conducted at different wavelengths are presented in Table 1. The highest conversion was attained at $\lambda_{inc.} = 420$ nm which is the wavelength of maximum absorption of BTG indicating

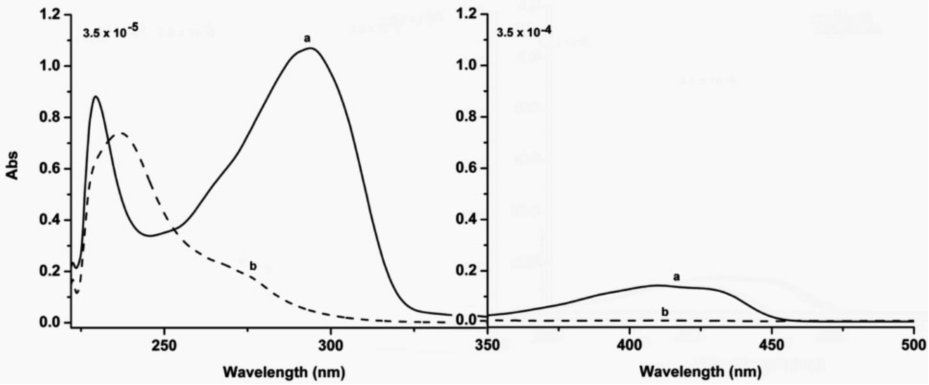


Figure 1.
Optical absorption spectra of BTG (a) and $Ph_2I^+PF_6^-$ (b) in CH_2Cl_2.

the crucial role of the acylgermane photoinitiator in the initiation process.

Detailed emission and quenching studies revealed that the polymerization is not initiated by direct energy transfer from the excited BTG to the iodonium ion. The most plausible mechanism involves the oxidation of trimethyl germyl radicals. While benzoyl radicals do not undergo significant redox reactions with even stronger oxidants, germyl radicals react with iodonium salt forming germanium cations. The lack of reactivity of benzoyl radicals towards iodonium salt was confirmed by ESR spin-trapping technique using benzylidene-*t*-butylamine-*N*-oxide as spin-trap in the absence and presence of Ph_2I^+ ions.[42] Thus, germanium cations would be capable of initiating cationic polymerizations (Scheme 1). Laleve et.al. also demonstrated that germyl radicals can readily be oxidized to the corresponding cations by iodonium salt, to then initiate cationic polymerization of epoxy monomers.[43]

Moreover, this mechanism was substantiated by performing polymerization experiments in the absence and presence of a radical scavenger, 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO). If the polymerization mechanism involves free radical species, the polymerization would be completely inhibited by the radical scavenger. The sample containing TEMPO yielded no polymer. It is therefore most probable that radical oxidation mechanism is responsible for the initiation.

Apart from CHO, vinyl compounds such as butyl vinylether (BVE) and *N*-vinyl carbazole (NVC) and epoxy resin such as 3,4-epoxycyclohexyl-3′,4′-epoxycyclohexene carboxylate (EEC) were also studied in the photopolymerization reactions. All monomers were readily polymerized upon irradiation at >350 nm in bulk or methylene chloride solutions of containing BTG in the presence of iodonium salt (Table 2). The broader molecular weight distribution observed in the case of NVC can be attributed to concomitant participation of free radical and cationic mechanisms. NVC is known to undergo polymerization by both mechanisms.

Table 1.
Photoinitiated cationic polymerization of CHO ($0.97\ mol\ L^{-1}$) by using BTG ($4.8 \times 10^{-3}\ mol\ L^{-1}$) in the presence of $Ph_2I^+\ PF_6^-$ ($4.8 \times 10^{-3}\ mol\ L^{-1}$) at different wavelengths for 120 min.

Wavelengths[a] (nm)	Conversion (%)	M_n[b]	M_w/M_n[b]
350	13	8750	1.60
400	52	12050	1.80
420	62	9700	1.71

[a] For photo irradiations at monochromatic wavelength, AMKO Ltd. photoreactor equipped with a HBO 100 W xenon lamp and monochromator was used. [b] Determined from GPC measurements based on polystyrene standarts.

Table 2.
Photoinitiated cationic polymerization[a)] of different monomers in the presence of BTG (4.8×10^{-3} mol L^{-1}) and Ph_2I^+ PF_6^- (4.8×10^{-3} mol L^{-1}) at room temperature for 30 min at >350 nm.

Monomers (mol L^{-1})	Conversion (%)	M_n [b)]	M_w/M_n [b)]
CHO (9.1×10^{-1})	86	11650	1.89
BVE (7.5×10^{-1})	44	10420	1.60
NVC (5.0×10^{-1})	82	63400	4.80
EEC (3.5×10^{-1})	>95	–[c)]	–

[a)] An interference filter (aqueous cupric sulfate solution) was used in all experiments. [b)] Determined from GPC measurements based on polystyrene standards. [c)] Insoluble network formed.

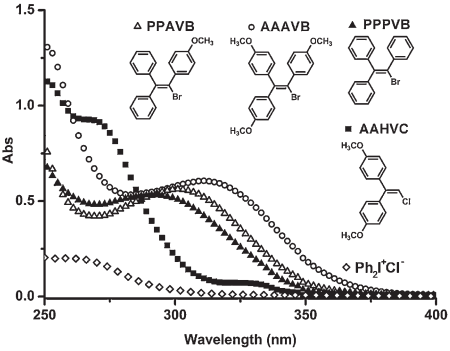


Figure 2.
UV-Vis spectra of AAAVB; PPAVB; PPPVB; AAHVC and $Ph_2I^+Cl^-$ in CH_2Cl_2 ($C = 3.3 \times 10^{-5}$ mol L^{-1}).

Bisacylgermanes such as dibenzoyldiethylgermane (DBDEG) were also shown to be active in promoting cationic polymerization. As these photoinitiators exhibit better absorption characteristics[44] and sequential decomposition behavior they can be used as precursors for polygermanes[45] and block copolymers[46] of monomers polymerizable by cationic and radical mechanisms.

Another long wavelength photoinitiating system based on the free radical oxidation involves the use of substituted vinyl halides. This initiating system can only be used for the polymerization of vinly ether based monomers and act even in the absence of onium salts. However, it utilizes Lewis acids such as zinc halides as co-initiator in the system. Comparison of absorption spectra of vinyl halides and a conventional iodonium salt can be seen in Figure 2. A typical diphenyliodonium chloride absorbs light below 300 nm; whereas, the vinyl halides with three aryl groups (i.e. AAAVB, PPAVB and PPPVB) absorb light strongly above 300 nm probably due to the conjugation of their three phenyl groups through the vinyl bond but 1-chloro-2,2-bis(*p*-methoxyphenyl)ethene (AAHVC) has much weaker absorption in this region because it only contains two phenyl units. Furthermore, electron donating groups (such as -OCH_3) on phenyl rings of the vinyl halides broaden their absorption wavelengths. Even, vinyl bromide substituted with three anisole moieties (AAAVB) has a quite broad spectral response which extends to near UV region (up to 380 nm) that makes AAAVB particularly useful for long-wavelength applications (see Figure 2).

All of the vinyl halides except AAHVC quite effectively polymerized IBVE, according to results listed in Table 3. The extent of polymerization and thus the photoinitiator efficiency increased in the order AAAVB > PPAVB > PPPVB > AAHVC, which correlates well with the absorbance of these photoinitiators at around 350 nm. Moreover, vinyl chloride instead of bromide decreases the possibility of formation of the carbocation and chloride during photolysis;[25] this leads to

Table 3.
Photopolymerization of IBVE (1.0 mL, 7.7×10^{-3} mol) induced by irradiation of various photoinitiators (1.5×10^{-3} mol L^{-1}) at 350 nm ($I = 3.0$ mW cm^{-2}) at 0 °C in the presence of ZnI_2 (6.3×10^{-3} mol L^{-1}) dissolved in CH_2Cl_2 (1.0 mL) by the aid of poly(ethylene glycol) (3.3×10^{-3} mol L^{-1}). Time of irradiation was 240 minutes.

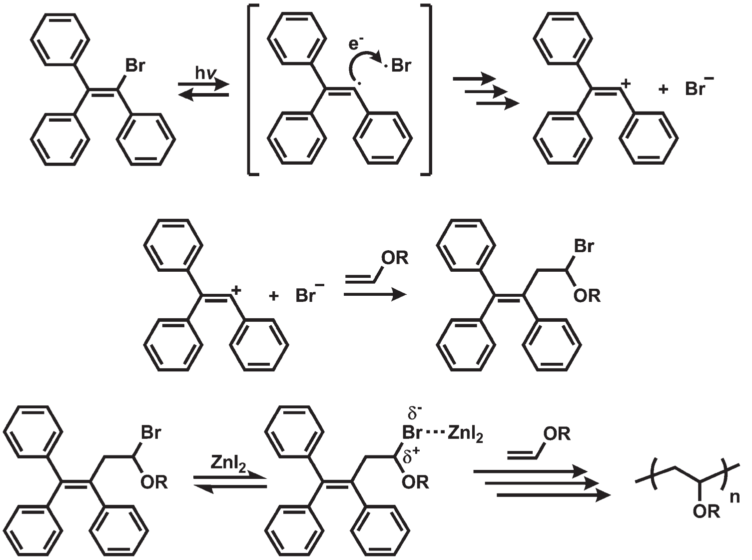
Run	Photoiniator	Conversion (%)[a)]	M_n [b)]	PDI[b)]
1	AAAVB	53.7	28660	1.77
2	PPAVB	29.9	22800	1.67
3	PPPVB	23.8	30900	1.47
4	$Ph_2I^+I^-$	5.2	9950	1.43

[a)] Monomer conversions were determined gravimetrically. [b)] Number average molecular weights (M_n) and polydispersities (PDIs) were determined using gel permeation chromatography.

poor performance of the vinyl chloride compared to the bromide derivatives. For comparison of the photoinitiation efficiency of the vinyl halides with that of the conventional photoinitiator (dipheniyliodonium salts), the photopolymerization of IBVE with $Ph_2I^+I^-$ was also performed (see Table 3). The observed low activity of $Ph_2I^+I^-$ may be due to its weak absorption at the wavelengths of the radiation source (350 nm), whereas all vinyl halides show fairly strong absorptions at wavelengths above 350 nm and therefore better photoinitiator activity.

Experiments were performed without either the vinyl halide or the zinc halide to further investigate the polymerization process. Exclusion of either of the two components failed to yield polymer, which is consistent with the proposed mechanism shown in Scheme 2. In this mechanism, vinyl cations, photochemically generated from the rupture of the carbon-halide bond followed by electron transfer, can directly react with the monomer.[47] The bromide ion reacts rapidly with this new cation leading to the formation of the monomer adduct with a structure resembling those used in conventional living cationic polymerization initiated by HI/ZnI_2 system.[48] The coordination effect of ZnI_2 stimulates the propagation, and affords the desired chain growth.

The crucial role of the vinyl halide in the initiation process was examined by ^{1}H-NMR analysis of the polymerization mixture in $CDCl_3$ in the absence of ZnI_2 where IBVE and AAAVB were used as monomer and photoinitiator, respectively. In this case, as expected the adduct is formed, but the subsequent chain growth does not occur since propagation cannot be stimulated when no Lewis acid is present in the system. The spectrum of the solution before irradiation consists of only proton resonances originated from IBVE and AAAVB. However, in addition to signals of IBVE and AAAVB, new peaks corresponding to the terminal CH-Br protons[49] at 5.58 ppm and CH_2 protons between 2.4 and 3.1 ppm were detected in the NMR spectrum of the irradiated sample. Additionally, protons of a series of side products occurring from different combination and coupling of active species were observed. Proposed photoinitiation mechanism where the adduct formation is the initial step is confirmed with these results.



Scheme 2.
Photoinitiated cationic polymerization of vinyl ethers by irradiation of PPPVB in the presence of ZnI_2.

Polymerization of several difunctional vinyl ether monomers was also examined. All monomers listed in Table 4 were polymerized readily in solutions containing AAAVB and ZnI_2. Comparison of the data runs 8 and 9 (Table 4) indicates again that $Ph_2I^+I^-$ is not an efficient photoinitiator when irradiated at 350 nm because it only absorbs strongly at shorter wavelengths,[26] and as a result, very small monomer conversion is found and no gelation is observed even after prolonged irradiation times.

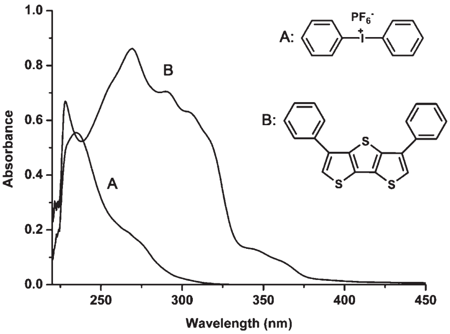


Figure 3.
Optical absorption spectra of A) $Ph_2I^+PF_6^-$ (3.5×10^{-5} mol L^{-1}) and B) DDT (3.5×10^{-5} mol L^{-1}) in CH_2Cl_2.

Photosensitization by Electron Transfer

Polynuclear aromatic compounds are known[13–21] to sensitize and consequently decompose onium salts via electron transfer in the exciplex. We have recently demonstrated that similar photosensitization action can be achieved by highly conjugated thiophene derivatives such as 3,5-diphenyldithieno[3,2-*b*:2,3-*d*]thiophene (DDT).[35] As it is shown in Figure 3, in the ground state, 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.

The potential use of DDT as a photosensitizer was verified by the existence of a nearly mirror-image like relation between its absorption and emission characteristics, investigated by means of fluorescence and phosphorescence spectroscopy. It was also found that in the presence of diphenyl iodonium salt, the fluorescence of DDT is markedly quenched.

Several types of cationically polymerizable mono functional monomers, such as CHO, BVE, styrene (S) and NVC were examined. Typical results are presented in Table 5. As can be seen, all monomers were readily polymerized upon irradiation at room temperature at $\lambda > 350$ nm either in bulk or CH_2Cl_2 solutions with DDT in the presence of iodonium salt. For comparison, polymerization sensitized with a typical polynuclear aromatic hydrocarbon, anthracene was also included (Table 5, Run 4). It should be noted that the two components of the initiating system are indispensable for the polymerization to occur; either no

Table 4.
Photo-induced crosslinking of various divinyl ethers (0.5 mL) initiated by irradiation of AAAVB or $Ph_2I^+I^-$ (2.0×10^{-3} mol L^{-1}) at 350 nm ($I = 3.0$ mW cm^{-2}) at room temperature in the presence of ZnI_2 (8.4×10^{-3} mol L^{-1}) dissolved in CH_2Cl_2 (1.0 mL) by the aid of poly(ethylene glycol) (4.4×10^{-3} mol L^{-1}).

Run	Monomer	Initiator	Irradiation wavelength (nm)	Gelation Time (min.)[b]	Monomer Conversion (%)[c]	Gel Content (%)[d]
5	BDVE	AAAVB	350	9	60.7	100
6	HDVE	AAAVB	350	8	52.3	95.1
7	DEDVE	AAAVB	350	8	50.4	95.6
8	BDVE	$Ph_2I^+I^-$	350	–	0	0
9	BDVE[a]	$Ph_2I^+I^-$	300	2	50.2	95.8

[a] Irradiation intensity was 1.0 mW cm^{-2}. [b] Gelation was followed qualitatively by simply inverting the tube, and the system was considered to have gelled when there was no flow of solution on inverting the tube. [c] Conversion of monomer to polymer was determined from weight of the precipitated cross-linked polymer in proportion to weight of the monomer. Note that for the divinyl ethers, this is not the same as the conversion of vinyl groups. [d] Gel content was determined by measuring the weight loss after 24 hours extraction with methylene chloride at room temperature.

Table 5.
Photoinitiated[a] cationic polymerization of various monomers in the presence of DDT and $Ph_2I^+PF_6^-$ at room temperature for 30 min at $\lambda > 350$ nm.

Run	Monomer (mol L^{-1})	[Photosensitizer] (mol L^{-1})	[Onium Salt] (mol L^{-1})	Conversion (%)	M_n[e]	M_w/M_n[e]
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 [c]	3450	2.56
5	BVE(3.84)[b]	0.5×10^{-2}	0.5×10^{-2}	66	14510	1.87
6	S (4.35)[b]	0.5×10^{-2}	0.5×10^{-2}	5	3700	2.26
7[d]	NVC(1.03)[b]	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] In CH_2Cl_2 solution. [c] Anthrecene is used instead of DDT. [d] Small portions of high molecular weight ($M_n = 98000$, PDI = 1.8) polymer was obtained. [e] Determined from GPC measurements.

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 EEC. Photopolymerizations of the bis-epoxide containing 5×10^{-3} mol L^{-1} $Ph_2I^+PF_6^-$ 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 min at $\lambda > 350$ nm at room temperature. Interestingly, anthracene did not function to promote the polymerization under identical experimental conditions.

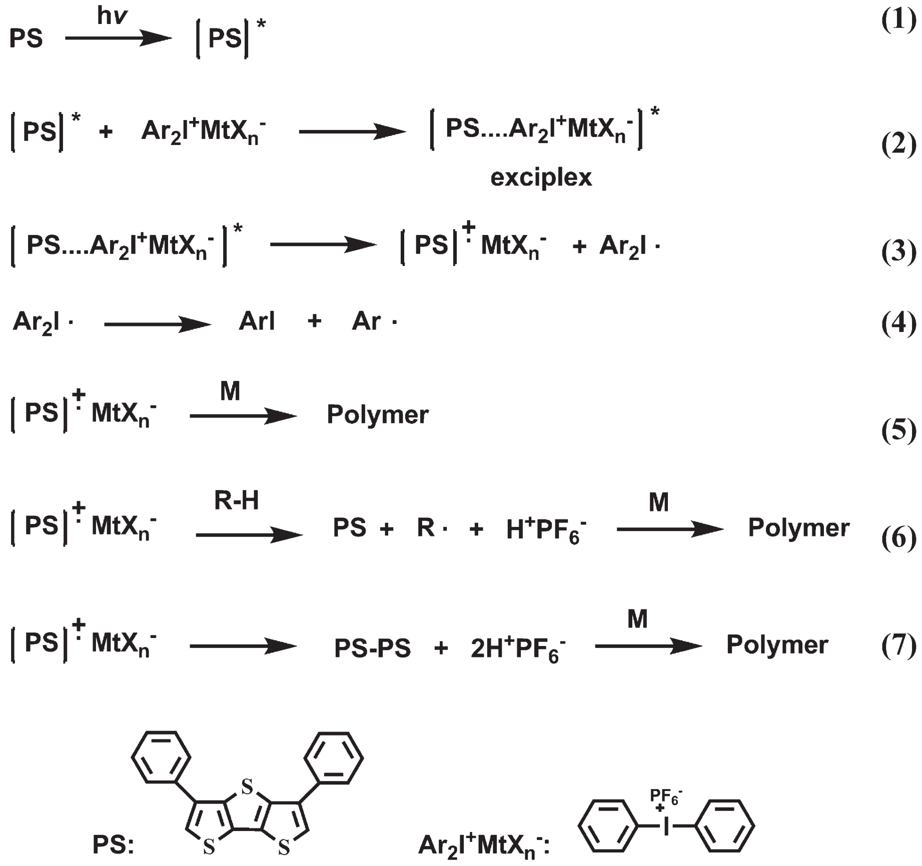
According to the Rehm-Weller equation (Equation 1) electron transfer from the excited sensitizer to onium salt is feasible if the change in free energy (ΔG) is negative. Based on the oxidation potential (E_{ox}) and active excitation energy (E^*) of the photosensitizer (PS) and the reduction potential (E_{red}) of the initiator (PI), the free energy change (ΔG) for the photoinduced electron transfer process was estimated.[50]

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

It was found that the electron between photoexcited DDT and ground state iodonium salt is thermodynamically favorable for both singlet and triplet excited states since the corresponding free energy changes (ΔG) were found to be -57.8 and -38.8 kcal mol^{-1}, respectively. Although the participation of the triplet state in the redox process can not be discarded, the more favorable ΔG value and fluorescence quenching of DDT with iodonium ion indicates that electron transfer from singlet state to the salt contributes strongly to the generation of radical cation.

Relatively low conversion of styrene polymerization indicates that triplet state also involves in the electron transfer process since styrene is known to be strong triplet quencher and reacts with triplet excited states with a high rate constant.[51]

A mechanism based on electron transfer reaction of excited DDT with iodonium ion was proposed as it is shown in Scheme 3. DDT radical cations formed by reaction (3) 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 6) or coupling reactions (reaction 7). We have recently presented evidences for such reactions of thiophene radical cations with the aid of laser flash photolysis studies.[52,53] However, further studies obtained by using 4,7-di(2,3-dihydro-thieno[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)-



Scheme 3.
Proposed mechanism for photosensitized cationic polymerization.

2,3-di(thiophen-2-yl)quinoxaline (DTDQ) as sensitizers revealed that radical cations do not contribute to the initiation of polymerization.[54] It was observed that polymerization of CHO was totally inhibited when a strong proton scavenger, 2,6-di-tbutyl-4-methylpyridine (DBMP) was present in the system. Such inhibition indicates that protons generated according to reactions (6 and 7) play important role regarding the initiation of cationic polymerization and direct initiation by the reaction of the radical cations with the monomer (reaction 5) can be neglected.

In conclusion, we have demonstrated that the photoinitiated cationic polymerization can be performed at near UV and visible range by using suitable radical sources and highly conjugated thiophene derivatives. The described initiating systems further extend the use of cationic polymerization in various practical applications particularly in pigmented coatings.

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