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Visible Light Initiated Free Radical Promoted Cationic Polymerization Using Acylgermane Based Photoinitiator in the Presence of Onium Salts

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ABSTRACT: The cationic polymerization of cyclohexene oxide (CHO) was achieved by UV irradiation (λ = 350–420 nm) of methylene chloride solutions containing benzoyltrimethylgermane (BTG) and onium salts, such as diphenyliodonium hexafluorophosphate ($Ph_2I^+PF_6^-$) or *N*-ethoxy-2-methylpyridinium hexafluorophosphate ($EMP^+PF_6^-$). A feasible initiation mechanism involves the photogeneration of germyl radicals and benzoyl radicals in the first step. Subsequent oxidation of germyl radicals by onium salts yields germanium ions capable of initiating the polymerization of CHO. In agreement with the proposed mechanism, the polymerization was completely inhibited by a radical scavanger such as 2,2,6,6-tetramethylpiperidinyl-1-oxy, and polymerization efficiency was directly related to the reduction potential of the onium salts, i.e. $Ph_2I^+PF_6^-$ ($E_{red}^{1/2}$ = −0.2 V) was found to be more efficient than $EMP^+PF_6^-$ ($E_{red}^{1/2}$ = −0.7 V). The results were compared to the other photoinitiators generally used in free radical promoted cationic polymerizations. In addition to CHO, vinyl monomers such butyl vinyl ether and *N*-vinyl carbazole, and a bisepoxide such as 3,4-epoxycyclohexyl-3′,4′-epoxycyclohexene carboxylate, were polymerized in the presence of BTG and iodonium salt with high efficiency.

Introduction

Photoinitiated polymerization is a well-known technique exploited in many technologically important areas.[1,2] Both free radical and cationic polymerizations have been used, and the mechanisms of initiation have been studied in detail.[3–6] The free radical mode is in more advanced state due to its applicability to a wide range of formulations based on (meth)-acrylates, unsaturated polyesters, and polyurethanes and the availability of photoinitiators having spectral sensitivity in the near-UV and visible range. Photoinitiators for visible light[7,8] have found particular interest because of their use in many targeted applications such as dental filling materials,[9–11] photoresists, printing plates, integrated circuits, laser-induced 3D curing, holographic recordings, and nanoscale micromechanics. Both cleavable and bimolecular hydrogen abstracting type photoinitiating systems, acting in the visible range, are well-known. Titanocene[9] and camphorquinone[12] in conjunction with an amine are typical examples for the respective systems. Recently, organic ketones containing germanium were introduced as a new class of cleavable photoinitiators[13,14] for free radical polymerization under visible light irradiation. In a process analogous to acylphosphine oxides, these photoinitiators (upon irradiation) undergo α-clevage to produce free radicals capable of initiating polymerization of methacrylates. This is especially facile under aqueous acidic conditions (Scheme 1).

The long wavelength initiating systems for cationic polymerization[15] are based on the activation of the most prominent cationic photoinitiators, namely onium salts,[16,17] by light sensitive additives, which do not directly initiate the polymerization. One can adapt the initiating system to different wavelengths of irradiation in three ways: (i) oxidation of free radicals by onium salts[18–20] (also called free radical promoted cationic polymerization), (ii) electron transfer between photoexcited sensitizer and onium salt,[21–30] and (iii) electron transfer in photoexcited charge transfer complexes of certain onium salts.[31–33] Of these,

Scheme 1. Photoinduced α-Cleavage of Benzoyltrimethylgermane (BTG)
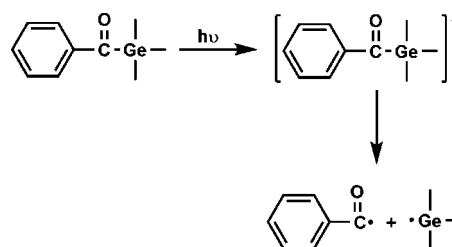
free radical promoted cationic polymerization is characterized as an elegant and relatively flexible type of initiation and, therefore, has been the subject of intense research. Benzoin derivatives are so far the most effective photoinitiators for the free radical promoted cationic polymerization, as they can be photolyzed with high quantum yields. The other suitable free radical promoters include benzyl ketals,[34] acylphosphine oxides,[35,36] benzaldehyde[37] and polysilanes.[38,39] The photochemical generation of oxidizable free radicals can be extended also
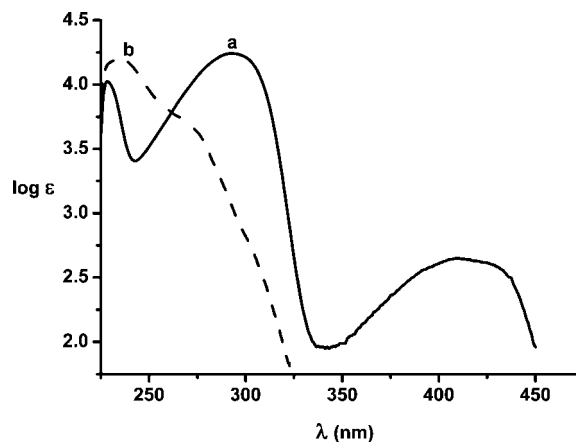

Figure 1. Optical absorption spectra of benzoyltrimethylgermane (BTG) (a) and $Ph_2I^+PF_6^-$ (b) in CH_2Cl_2.

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Table 1. Photoinitiated Cationic Polymerization of CHO (0.97 mol L⁻¹) Using Benzoyltrimethylgermane (BTG) (4.8 × 10⁻³ mol L⁻¹) in the Presence of Ph₂I⁺PF₆⁻ (4.8 × 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 photoirradiations at monochromatic wavelength, an AMKO Ltd. photoreactor equipped with a HBO 100 W xenon lamp and monochromator was used. [b] Determined from gel permeation chromatography measurements based on polystyrene standarts. M_n: The number average molecular weight. M_w: The weight average molecular weight.

Scheme 2. Energy Transfer Mechanism between Photoexcited Benzoyltrimethylgermane (BTG*) and Ph₂I⁺PF₆⁻
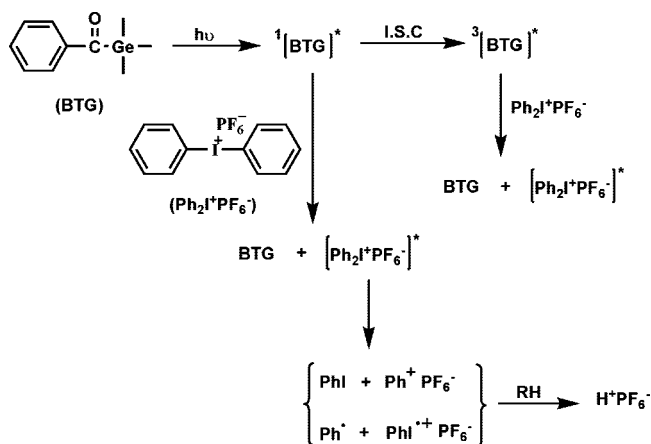
to the visible light. Certain dyes in conjunction with aromatic amines[40] and manganese decacarbonyl in the presence of alkyl halides[41] were shown to be suitable initiating systems to promote cationic polymerization at above 400 nm.

The aim of the present work was to test the reactivity of acylgermane based photoinitiators in free radical promoted cationic polymerization of appropriate monomers. Because of the fact that these photoinitiators exhibit long wavelength characteristics (due to the well-known interaction of the lone pair of the carbonyl oxygen with the free d-orbitals of the germanium), it was foreseen that the spectral sensitivity of cationic polymerization could be easily extended to the visible range.

Experimental Section

Materials. Benzoyltrimethylgermane (BTG) was synthesized as described in the literature.[13] Benzophenone (BP, Merck) was
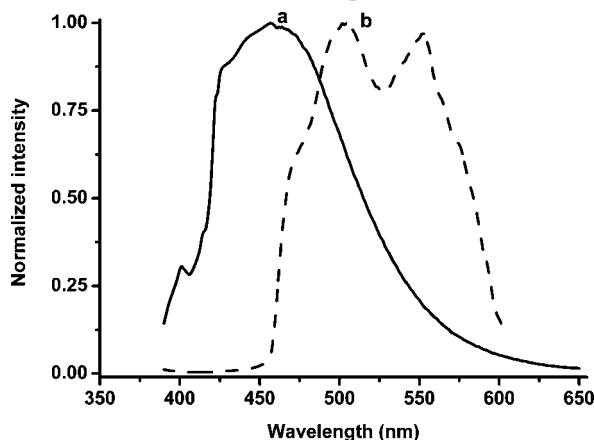

Figure 2. Normalized excitation (a) and emission (b) fluorescence spectra of benzoyltrimethylgermane (BTG) in CH₂C₂ at room temperature.

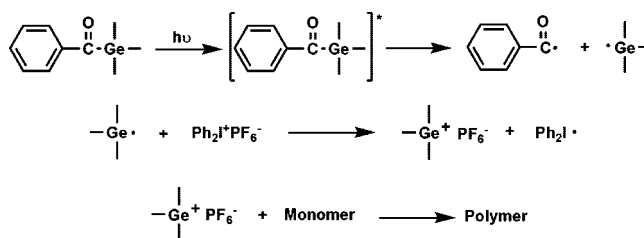**Scheme 3. The Oxidation of Trimethyl Germyl Radicals by Ph₂I⁺PF₆⁻**

Table 2. Photoinitiated Cationic Polymerization[a] of CHO (0.97 mol L⁻¹) in the Presence of Benzoyltrimethylgermane (BTG) (4.8 × 10⁻³ mol L⁻¹) and Ph₂I⁺PF₆⁻ (4.8 × 10⁻³ mol L⁻¹) at Room Temperature for 20 min at >350 nm

additive (mol L⁻¹)	conversion (%)	M_n[c]	M_w/M_n[c]
	85	14131	1.84
TEMPO[b] (2.4 × 10⁻²)			

[a] An interference filter (aqueous cupric sulfate solution) was used in all experiments. [b] TEMPO: 2,2,6,6-Tetramethylpiperidinyl-1-oxy was used as a radical scavenger. [c] Determined from gel permeation chromatography measurements. M_n: The number average molecular weight. M_w: The weight average molecular weight.
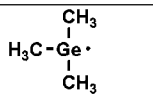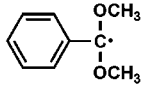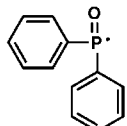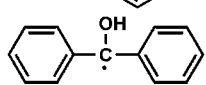
Scheme 4. Photoinduced Free Radical and Free Radical Promoted Cationic Polymerizations by Using Germanes as Co-Initiators
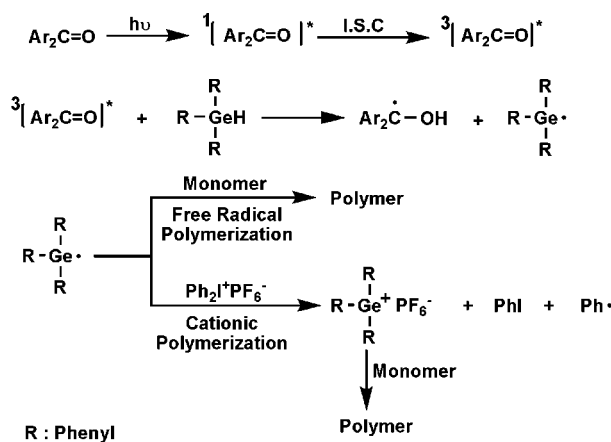
recrystallized from heptane. 2,2-Dimethoxy-2-phenyl acetophenone (DMPA, Ciba Specialty Chemicals), (2, 4, 6-trimethylbenzoyl) diphenylphosphine oxide (TMDPO, Ciba) and diphenyliodonium hexafluorophosphate (Ph₂I⁺PF₆⁻, 98%, Alfa Aesar), were used as received. Dichloromethane (99.8%, Baker) was extracted first with sulfuric acid, then with 5% NaOH solutions. After washing with water, the dichloromethane was dried over anhydrous CaCl₂ and CaH₂ and finally distilled with a fractionation column. Cyclohexene oxide (CHO, 98%, Aldrich) and *n*-butyl vinyl ether (BVE, >97%, Fluka) were distillated over CaH₂ in vacuo. *N*-Vinyl carbazole (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), 4.6 mL of CH₂Cl₂ stock solution of BTG (5.4 mg, 2.5 × 10⁻² mmol) and Ph₂I⁺PF₆⁻ (10.5 mg, 2.5 × 10⁻² 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: 85%; M_n = 14150 g mol⁻¹). All of the other polymerizations were performed under identical conditions. Conversions for all samples were determined gravimetrically.

Table 3. Photoinitiated Cationic Polymerization^a of CHO (0.97 mol L^{-1}) at >350 nm with Various Free Radical Sources in the Presence of Ph$_2$I$^+$PF$_6^-$ at Room Temperature for 20 min

Photoinitiator[b] (mol L^{-1})	Radicals Produced	k_{ox}[c] (ref.) (mol^{-1} L s^{-1})	Conversion (%)	M_n[d]	M_w/M_n[d]
BTG (4.8 x 10^{-3})	H$_3$C–Ge· with CH$_3$, CH$_3$	5.6 x 10^7 [42]	85	14150	1.84
DMPA (1.7 x 10^{-3})	C· with OCH$_3$, OCH$_3$, phenyl	–[e]	88	13200	1.84
TMPDO (1.4 x 10^{-3})	P· with O and two phenyl	>1 x 10^6 [43]	<2	-	-
BP + DMA (3.8 x 10^{-3})	C· with OH and two phenyl	3.0 x 10^7 [44,45]	46	7050	1.65

^{a} Radical concentrations were adjusted to have the same absorption at 350 nm. An interference filter (aqueous cupric sulfate solution) was used in all experiments. The concentration of Ph$_2$I$^+$PF$_6^-$ was the same as the concentration of photoinitiators. ^{b}DMPA: 2,2-Dimethoxy-2-phenyl acetophenone. TMPDO: (2,4,6-Trimethylbenzoyl) diphenylphosphine oxide; BP: Benzophenone. N,N-DMA: N,N-Dimethylaniline.$^c k_{ox}$: Oxidation rate constants of the radicals. ^{d}Determined from gel permeation chromatography measurements based on polystyrene standards. M_n: The number average molecular weight. M_w: The weight average molecular weight. ^{e}Not determined.

Table 4. Photoinitiated Cationic Polymerization^a of CHO (0.97 mol L^{-1}) with Different Onium Salts in the Presence of Benzoyltrimethylgermane (BTG) (4.8 × 10^{-3} mol L^{-1}) at Room Temperature for 20 min at >350 nm^a

onium salts^b	conversion (%)	$E_{red}^{1/2c}$	M_n^d	M_w/M_n^d
Ph$_2$I$^+$PF$_6^-$	85	−0.2	15150	1.84
EMP$^+$PF$_6^-$	11	−0.7	4400	1.29

^{a} An interference filter (aqueous cupric sulfate solution) was used in all experiments. ^{b} Ph$_2$I$^+$PF$_6^-$: Diphenyliodonium hexafluorophosphate. EMP$^+$PF$_6^-$: 1-Ethoxy-2-methylpyridinium hexafluorophosphate. ^{c} Redox potentials of the cationic salts. ^{d} Determined from gel permeation chromatography measurements. M_n: The number average molecular weight. M_w: The weight average molecular weight.

Table 5. Photoinitiated Cationic Polymerization^a of Different Monomers in the Presence of Benzoyltrimethylgermane (BTG) (4.8 × 10^{-3} mol L^{-1}) and Ph$_2$I$^+$PF$_6^-$ (4.8 × 10^{-3} mol L^{-1}) at Room Temperature for 30 min at >350 nm

monomers^b (mol L^{-1})	conversion (%)	M_n^c	M_w/M_n^c
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	d	

^{a} An interference filter (aqueous cupric sulfate solution) was used in all experiments. ^{b} CHO: Cyclohexene oxide. BVE: Butyl vinyl ether. NVC: N-Vinyl carbazole. EEC: 3,4-Epoxycyclohexyl-3′,4′-epoxycyclohexene carboxylate. ^{c} Determined from gel permeation chromatography measurements based on polystyrene standards. M_n: The number average molecular weight. M_w: The weight average molecular weight. ^{d} Insoluble network formed.

Characterization. Molecular weights were determined at room temperature by a 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

This paper deals with the possibility of applying a germane based photoinitiator, namely, benzoyltrimethylgermane (BTG),

as an agent to reduce onium salts such as diphenyl iodonium hexafluorophosphate (Ph$_2$I$^+$PF$_6^-$) forming reactive species capable of initiating cationic polymerization. Figure 1 shows optical absorption spectra of BTG and Ph$_2$I$^+$PF$_6^-$. Since the iodonium ion does not absorb at λ > 340 nm, all irradiations were performed in the $\lambda_{inc.}$ = 350−420 nm range.

As can be seen from Table 1, cylohexene oxide (CHO) was readily polymerized with BTG in the presence of iodonium salt at wavelengths where the salt is transparent. In a comparative study at different wavelengths using a monochromatic light, the highest conversion was attained at $\lambda_{inc.}$ = 420 nm, which is the wavelength of maximum absorption of BTG, indicating the crucial role of the acylgermane photoinitiator in the initiation process.

We first considered the possibility of the sensitization by classical energy transfer from the photoexcited BTG to the iodonium salt. This mechanism involves the electronic excitation of BTG to its excited state (BTG*). Energy may be transferred from BTG* to the iodonium salt by either resonance excitation or exchange energy transfer according to Scheme 2.

The energy transfer may proceed from either in the excited singlet state or in the triplet state. In consequence of the transfer process, the sensitizer returns to its ground state and excited iodonium salt is formed. Further reactions lead to the formation of cationic species as in the case of direct excitation of the iodonium salt. Figure 2 shows the excitation and emission fluorescence spectra of BTG. Interestingly, the extent of fluorescence intensity was not influenced upon adding Ph$_2$I$^+$PF$_6^-$ to the solutions at concentrations up to 1.8 × 10^{-1} mol L^{-1}. Thus, it appears that excited BTG in the singlet state does not react with the ground state iodonium salt. Phosphorescence measurements are useful to gain information on the triplet excited state. However, phophorescence studies of BTG at 77 K failed to give any emission. It appears either intersystem crossing efficiency is rather low or the short-lived triplet state is chemically deactivated by α-cleavage. Thus, classical energy transfer from both excited singlet and triplet BTG to the iodonium salt can be discarded. In general, although being a possible pathway for the decomposition of onium salts, the energy transfer sensitization has not been found a technically useful process. The next question concerns if the initiating species are formed from the electron transfer reaction within the exciplex formed between photoexcited BTG and iodonium

salt. At present it is not possible to estimate if such electron transfer is thermodynamically favorable since excitation energy of the short-lived excited state and oxidation potential of BTG are unknown. However, cleavage type photoinitiators do not undergo electron transfer reaction in their excited states and only polynuclear aromatic compounds such as anthracene, perylene and thiophene derivatives and certain abstraction type aromatic carbonyl compounds such as thioxanthone are successfully used as electron transfer sensitizers. As being an α-cleavage type photoinitiator, photoexcited BTG is not expected to undergo electron transfer reactions with iodonium salt. An alternative mechanism might be based on the oxidation of trimethyl germyl radicals by the iodonium salt. The photolysis of BTG involves in the primary step the homolysis of carbon–germane bonds, which leads to the formation trimethyl germyl and benzoyl 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 toward 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.[46] Thus, germanium cations would be capable of initiating cationic polymerizations (Scheme 3).

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. As can be seen from Table 2, sample containing TEMPO yielded no polymer. It is therefore most probable that radical oxidation mechanism is responsible for the initiation.

In this connection, it is worth mentioning the work of Laleve et al.,[42] who generated germyl radicals by hydrogen abstraction reaction of photoexcited aromatic carbonyl compounds such as benzophenone and thioxanthone. In addition to using of the photoinitiating system in free radical polymerization, these authors also demonstrated that germyl radicals can readily be oxidized to the corresponding cations by iodonium salt, to then initiate cationic polymerization of epoxy monomers (Scheme 4).

For comparison free radical promoted cationic polymerizations, using various other photoinitiators, were also performed. The results, together with the structure of the electron donor radicals generated, are collected in Table 3. Notably, high conversions were attained with the radicals having a high oxidation rate constant. Thus germyl radicals exhibit high ability to participate in free radical promoted cationic polymerization.

The efficiency of onium salts as oxidizing agents is related to their electron affinity. The higher the oxidation power of the onium salt, the higher (more positive) is the reduction potential $E_{red}^{1/2}$. As can be seen in Table 4, diphenyliodonium salt is more suitable then alkoxypyridinium salt for the oxidation of germyl radicals as reflected by their relatively high reduction potential. Therefore, these salts have been most frequently used for the oxidation of photogenerated free radicals.

Apart from CHO, vinyl compounds such as butyl vinyl ether (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 containing BTG in the presence of iodonium salt (Table 5). 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.

In conclusion, although mechanistic details still remain to be evaluated, it is clear that BTG (in combination with suitable onium salts such as iodonium and pyridinium salts) is an efficient photoinitiator for cationic polymerization. The proposed initiation mechanism involves the photogeneration of germyl and benzoyl radicals in the first step. Subsequent oxidation of germyl radicals by onium salts yields germanium ions capable of initiating the polymerization of monomers. The efficiency of the latter step is controlled by the redox potential of the onium salt. In this work we report, for the first time, that a cleavage type photoinitiator can act as sensitizer to shift the spectral response of onium salts to the visible light region. This possibility may provide interesting new perspectives in the field of visible light cationic polymerization.

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