

Photoinduced Decomposition of Dibenzyldiethylgermane: A Photochemical Route to Polygermanes

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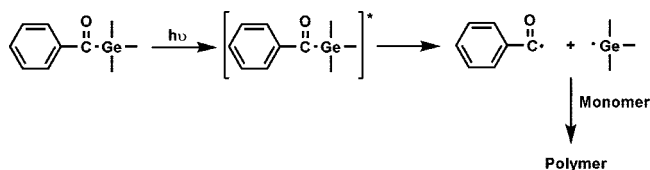
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Photopolymerizations that proceed under the influence of visible light have many targeted applications such as dental filling materials, photoresists, printing plates, integrated circuits, laser-induced 3D curing, holographic recordings, and nanoscale micromechanics.^{1–7} Various photoinitiating systems, acting in the visible range, are known, and their photochemistry has been studied in detail.^{8–14} Recently, organic ketones containing germanium were introduced as a new class of cleavable photoinitiators for free radical polymerization under visible light irradiation.^{15–18} In a process analogous to acylphosphine oxides, these photoinitiators (upon irradiation) undergo α -cleavage to produce free radicals capable of initiating polymerization of methacrylates (Scheme 1). This is especially facile under

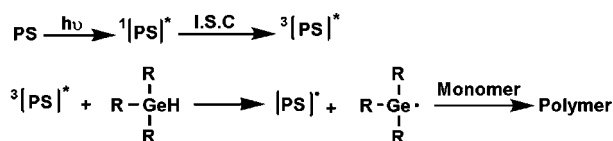
Scheme 1. Photoinduced α -Cleavage of Benzoyltrimethylgermane (BTG)



aqueous acidic conditions which is required etching and adhesion on the surface of (mine) in dental application.

This type of initiating germyl radical can also be generated indirectly by the hydrogen abstraction reaction of photoexcited aromatic carbonyl compounds such as benzophenone and thioxanthone (Scheme 2).¹⁷

Scheme 2. Photoexcited Free Radical Polymerization by Using Germanes as Co-initiator

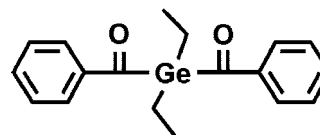


R : Phenyl

PS : Benzophenone or Thioxanthone

An analogous compound based on germanium, namely dibenzoyldiethylgermane (DBDEG, Chart 1), was shown to have better absorption characteristics and improved initiation behavior.¹⁹

Chart 1. Structure of Dibenzyldiethylgermane (DBDEG)



In addition to using the photoinitiating system in free radical polymerization, it was also demonstrated that germyl radicals can readily be oxidized to the corresponding cations by an iodonium salt, to then initiate cationic polymerization of epoxy monomers (Scheme 3).¹⁸

Similar to polysilanes, polygermanes have interesting electronic and optical properties related to σ -conjugation along the polymer backbone.^{20–23} The absorption maxima of these polymers shift to longer wavelengths with increasing molar mass (chain length) of the polymer. Polygermanes can be synthesized by various synthetic methods including Wurtz type coupling of dichlorogermanes and the reaction of germanium diiodide with Grignard or lithium reagents.^{23–27} However, these methods produced polymers either in low yields or with low molecular weight. Alternative ruthenium demethanative coupling method appeared to yield polymers with better yields and high molecular weight.²⁴

In the present paper, we report a novel and practical method for the preparation of polygermanes from DBDEG under visible light irradiation. The key for this method is the controlled scission of the photoinitiator and subsequent coupling of the radical species thus formed.

In the ground state, DBDEG strongly absorbs light between 350 and 450 nm (Supporting Information, Figure S1). The absorption at the visible range is attributed to the active $n-\pi^*$ transition which is well separated from the inactive $\pi-\pi^*$ transition. Figure 1 shows optical absorption spectral changes of DBDEG recorded in CH_3CN solutions before and after various periods of irradiation time. In a previous paper, it was reported that DBDEG underwent an irreversible photolysis leading to decomposition of the photoinitiator.¹⁹ Upon irradiation, beside decomposition, the maxima of the absorption spectra are shifted to lower wavelengths with increasing time, ca. 16 nm after 5 min irradiation. This behavior is typical indication

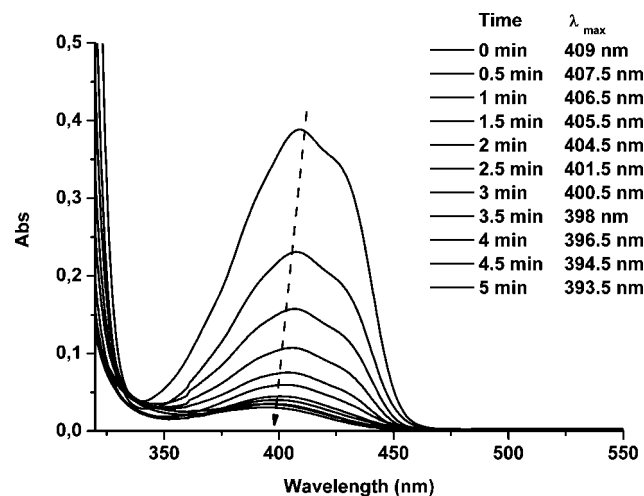
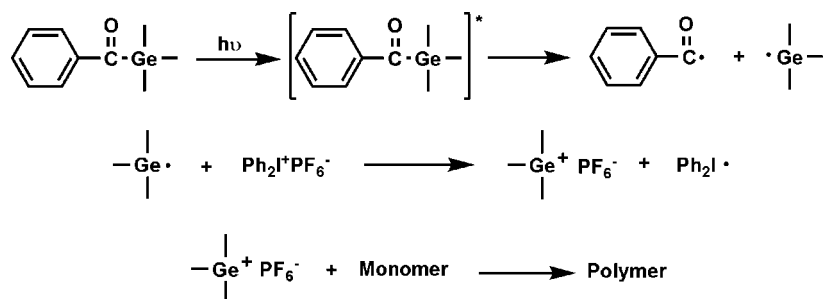


Figure 1. UV-vis spectral change of dibenzoyldiethylgermane (DBDEG) ($7.7 \times 10^{-3} \text{ mol L}^{-1}$) in CH_3CN solution.

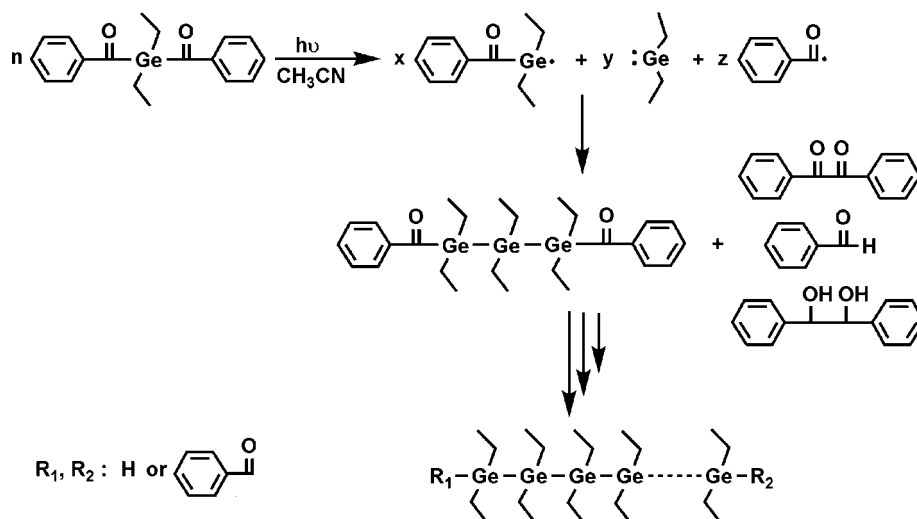
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Scheme 3. Oxidation of Trimethylgermyl Radicals by $\text{Ph}_2\text{I}^+\text{PF}_6^-$ 

Scheme 4. Possible Mechanism of Photoinduced Polygermane Formation

Table 1. Irradiation of Dibenzoyldiethylgermane (DBDEG) (0.3 mol L^{-1}) in CH_3CN in the Absence of Monomer with Different Light Sources

run	irradiation wavelength (nm)	relative light intensity ^d	time (h)	M_n^e (g/mol)	M_w/M_n^e
1 ^a	440	1	2.5	2750	1.11
2 ^a	440	1	5	1520	1.12
3 ^b	300–400	59	1	1500	1.05
4 ^a	410	6	2.5	1410	1.01
5 ^c	430–490	71428	0.25	290	1.04

^a AMKO Ltd. photoreactor equipped with a HBO 100 W xenon lamp and monochromator was used for the irradiation. ^b Rayonet merry-go-round photoreactor equipped with 16 lamps emitting light nominally at $\lambda > 300 \text{ nm}$. ^c Blue phase light source with 8 W LED light source was used for the irradiation. ^d Referans light intensity: $0.14 \times 10^{-1} \text{ (mW/cm}^2\text{)}$ ^e Determined from GPC measurements based on polystyrene standard. M_n : The number-average molecular weight, M_w : The weight-average molecular weight.

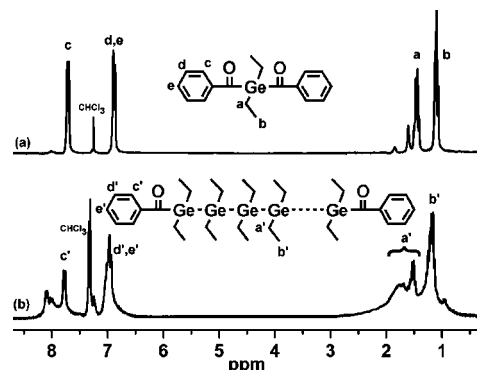
of the formation of new photoproducts absorbing at different wavelength.

Detailed investigations under different experimental conditions, i.e., at different wavelength and light intensity, revealed that photolysis of DBDEG in the absence of monomer causes scission and multiple coupling reactions forming polygermanes (Scheme 4).

As can be seen from Table 1, in all cases, oligogermanes with relatively low molecular weights were formed. Interestingly, the irradiations at high energy or prolonged irradiations caused oligomers with lower molecular weight. The structure of the polymers was confirmed by ^1H NMR analysis. ^1H NMR spectra of DBDEG and the photolysis product are shown in parts a and b of Figure 2, respectively. The broadening of all the aliphatic and end-group aromatic peaks together with the

slight shift of the aliphatic peaks appearing at 1.1–1.5 ppm, corresponding to the new vicinity (Ge–Ge bond) of the CH_2 and CH_3 protons, clearly indicates the polygermane formation. Additional aromatic peaks, which can be observed at 8.04–7.92 ppm, correspond to small organic products such as benzil and benzaldehyde (see Supporting Information).

Further evidence for the formation of oligogermane structure was provided by the ^{13}C NMR measurements. The ^{13}C NMR spectrum of DBDEG exhibits signals at $\delta = 230, 141.18\text{--}128.04$, and $8.94\text{--}6.53 \text{ ppm}$, corresponding to the carbonyl, aromatic, and aliphatic carbons, respectively (Figure 3a). After the photolysis, the resonance of the carbonyl carbon of terminal benzoyl group was observed at 220 ppm. The shifting of the peaks corresponding to aromatic and aliphatic carbons was also noted. Also, new carbonyl carbons at between 163.56 and 170.52

Figure 2. ^1H NMR spectra of DBDEG (a) and polygermane (Table 1, run 2) (b) in CDCl_3 .

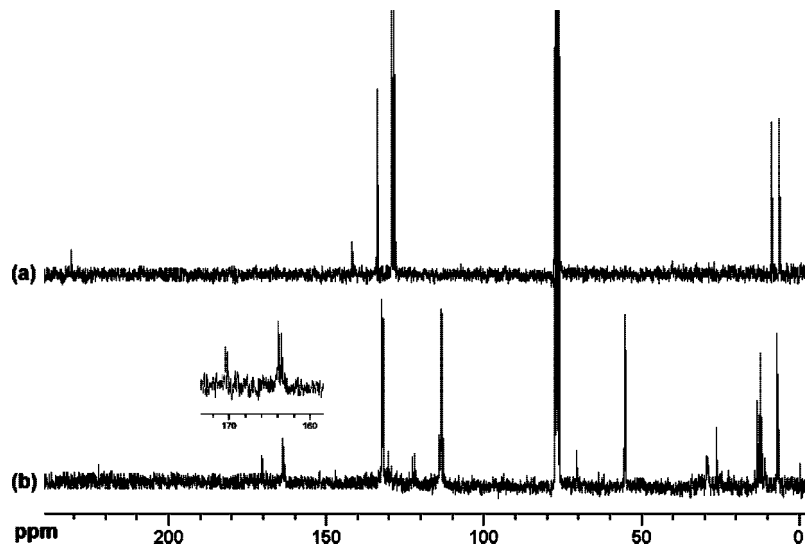
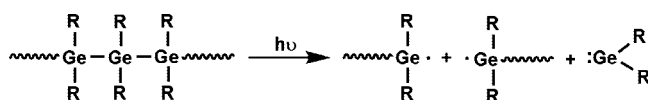


Figure 3. ^{13}C NMR spectra of DBDEG (a) and polygermane (Table 1, run 2) (b) in CDCl_3 .

Scheme 5. Photoscission of Oligogermenes under UV Light



ppm are attributed to the low molar mass carbonyl compounds formed concomitantly (Figure 3b).

Oligogermenes formed this way are also light-sensitive and undergo photoscission under UV light with the formation of germly radicals (Scheme 5).

The UV absorption spectra of the oligogermane of solutions in CH_3CN before and after UV irradiation presented in Figure 4 clearly indicate rapid photoscission. Even more convincing evidence for the photodegradation behavior of polygermane was obtained from GPC measurements. As can be seen from Figure 5, the multimodal distribution of the irradiated sample at lower molecular weight indicates irregular scission of the polymer chain. It should be pointed out that a similar photodegradation pattern was also obtained with the polymers of the parent group 14 elements such as polysilanes.^{28–30}

As the germly radicals are highly reactive toward olefinic monomers, it seemed appropriate to test the use of polygermanes as macrophotoinitiators. As a simple demonstration of the

possible value of polygermanes as photoinitiators, several experiments were performed. In a typical experiment, photolysis of bulk styrene containing $1.3 \times 10^{-2} \text{ mol L}^{-1}$ polygermane at $\lambda > 300 \text{ nm}$ for 1 h produced polymer with 5.0% conversion and number-average molecular weight $M_n = 8800 \text{ g mol}^{-1}$. In the absence of the polygermane, control experiments failed to produce any precipitable polymer after the same irradiation time. Figure 6 shows the GPC chromatograms of the initial polygermane and the mixture obtained therefrom. The new peak at higher molecular weight is ascribed to polystyrene, and no trace for the polygermane was detected.

For the possibility of photoinitiation by the low molar compounds such as benzil also present in the product, a control experiment was performed. Photolysis of styrene in the presence of benzil under identical experimental conditions yielded a negligible amount of polymer (conversion $< 1.0\%$).

In conclusion, we have demonstrated for the first time that polygermanes formation can be achieved by photochemical means using a bisacylgermanes structurally equipped with photocleavable groups at both sides. Although the chain growth is limited and only oligomers are formed, it is clear that the process is highly efficient and the products also exhibit extremely high photoactivity and can be used as macrophotoinitiators for free radical polymerization. At this point, further studies are necessary to optimize conditions for obtaining

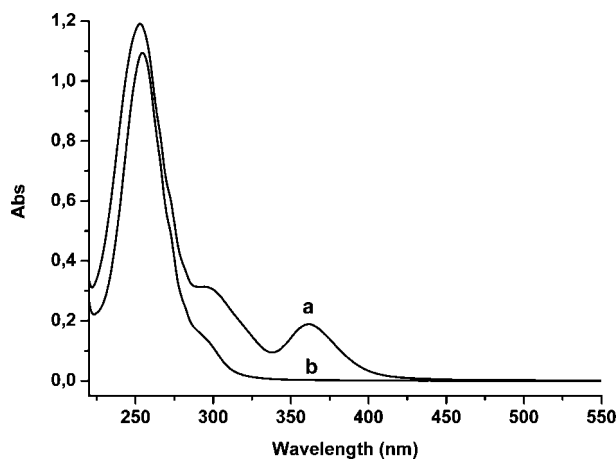


Figure 4. Optical absorption spectra of polygermane (Table 1, run 2) (a) and irradiated polygermane with UV light (b) for 15 min in CH_3CN .

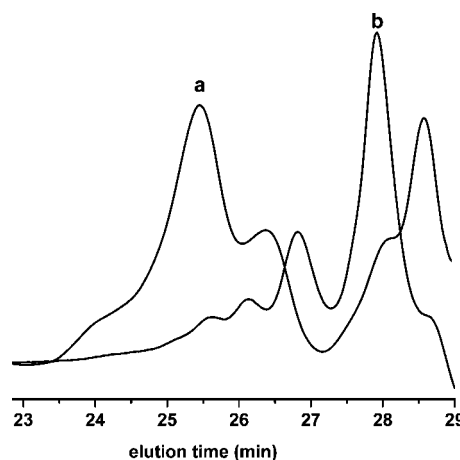


Figure 5. GPC traces of polygermane (Table 1, run 2) (a) and irradiated polygermane with UV light (b).

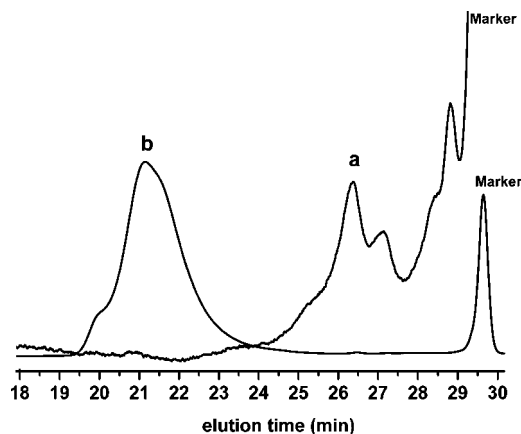


Figure 6. GPC traces of polygermane (Table 1, run 2) (a) and polystyrene obtained by using polygermane as a macrophotoinitiator (4.6×10^{-6} mol L $^{-1}$) (b).

polymers with higher chain length and photochemical stability by designing the initial bisacylgermane with more sterically hindered groups.

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Supporting Information Available: Details of experimental procedures, optical absorption spectra of DBDEG, FT-IR spectra of DBDEG and oligogermane, GPC traces of oligogermane and UV detector response, GC analyses of oligogermane formation, and excitation and emissions spectra of polygermane. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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