New Photocleavable Structures. Diacylgermane-Based Photoinitiators for Visible Light Curing

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Received October 31, 2007; Revised Manuscript Received January 28, 2008

ABSTRACT: As bisacylphosphine oxides are highly efficient, cleavable photoinitiators for visible light curing, we were interested in preparing diacylgermane **2**. The UV–vis absorption maximum of the n−π* transition was red-shifted up to 50 nm. Photo-DSC results of **2** showed similar reactivity to bisacylphosphine oxides under broadband irradiation experiments. Irradiation with a dental LED lamp gave significantly improved initiation behavior compared to bisacylphosphine oxides and camphorquinone, especially in aqueous acidic primer formulations. Application-oriented tests in dental adhesive or composite formulations showed sufficient storage stability, high photocuring activity, excellent photobleaching behavior, and mechanical properties of the materials.

Introduction

Although photopolymerization is a rather old technique for the curing of acrylate-based formulations, numerous new applications are added regularly. Especially, visible light curing[1] is still a challenge due to the high demands in modern applications such as dental filling materials,[2] reprography (photoresists, printing plates, integrated circuits), laser-induced 3D curing, holographic recordings, and nanoscale micromechanics. Therefore, important components such as monomers and photoinitiators (PIs)[3,4] have to be adapted. A bimolecular PI system consisting of camphorquinone (CQ) and a tertiary amine, such as ethyl 4-dimethylaminobenzoate (DMAB), is the state of the art of PIs for dental filling materials. Beside some toxic effects and the tendency for discoloration of the amine based co-initiator, such bimolecular systems suffer from low reactivity, especially in water-based formulations.[5] Because CQ has an absorption maximum at 468 nm, nearly all dental lamps are designed to have their maximum emission at this wavelength. Cleavable titanocenes as alternative PIs absorb up to 560 nm, but unfortunately they suffer from a strong discoloration of the cured material and are not suitable for acidic water-based formulations.[3] Recently, we have developed a series of hydrophilic bisacylphosphine oxides as suitable alternative.[6] Since the absorption tails out at ~420 nm, these photoinitiating systems do not meet the requirements for some LED-based dental irradiation sources used today. Several efforts were undertaken in the past decade to red-shift the absorption of bisacylphosphine oxides, but only marginal success was achieved.[7,8] On the basis of our focus on new chromophores for PIs,[9–11] we were also interested to shift the absorption maximum of the important n−π* transition of these bisacylphosphine oxides toward the visible range of spectrum. While several derivatives are known from the literature,[6,12] sufficient spectroscopic data are not available. Therefore, we prepared acylphosphine oxides with hetero substituents. Substituents on the phosphorus-linked aromatic ring showed only increased extinction coefficient, and substituents on the benzoyl part gave an unwanted shift of π−π* transition that overlaps with the important n−π* transition. The latter modification led to both decreased reactivity and a significant sensitivity to decomposition by nucleophilic attack. As twisting of the carbonyl groups in diketones has shown a shift of the n−π* transition up to 500 nm,[13] we also tried to twist the CO−PO−CO system. Neither these efforts nor the substitution of the phosphine oxide group with a phosphine sulfide group[3,12] gave a significant red shift of the absorption. Therefore, the limitation in the longest wavelength of absorption of α-cleavable benzoyl-based PIs seemed to be given by bisacylphosphine oxides.

Very recently,[14] we have prepared benzoyltrimethylgermane (**1**) (Figure 1) due to the well-known interaction[15] of the lone pair of the carbonyl oxygen with the free d-orbitals of the germanium. The UV–vis absorption spectrum has been red-shifted about 30 nm compared to 2,4,6-trimethylbenzoyl diphenylphosphine oxide (MAPO). Beside excellent photobleaching behavior, good photoreactivity has been demonstrated. Additionally, low toxicity is known for organogermanium compounds[16] and has also been demonstrated for PI **1**.[17] Based on these investigations, the next step was to prepare a bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (BAPO) analogous compound based on germanium. UV–vis absorption characteristics, photobleaching behavior, and photoinitiating activity of dibenzoyldiethylgermane (**2**) under broadband irradiation experiments and with a special LED-based dental lamp were investigated. In addition, we prepared some dental composites based on **2** and determined their mechanical properties. As acidic dental primer formulations are also of interested due to the poor reactivity of bimolecular PIs,[5] the new compounds were also investigated under these conditions. The storage stability of such adhesives under aqueous conditions is of importance because acylphosphine oxides are known to suffer from decomposition reactions by nucleophilic reagents and therefore contain methyl groups for sterical shielding.

Experimental Section

Materials. All reagents were purchased from Sigma-Aldrich and ABCR and were used without further purification. BAPO was obtained from Ciba SC as a gift. The solvents were dried and purified by standard laboratory methods. Thin-layer chromatography (TLC) was carried out with Alugram Sil-G/UV 254 sheets (Macherey Nagel). Column chromatography was performed with conventional techniques on VWR silica gel 60 (0.040–0.063 mm particle size). The monomers 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]propane (Bis-GMA), tri(ethylene glycol) dimethacrylate (TEGDMA) (Esschem), 1,10-decanediol dimethacry-

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10.1021/ma702418q CCC: $40.75

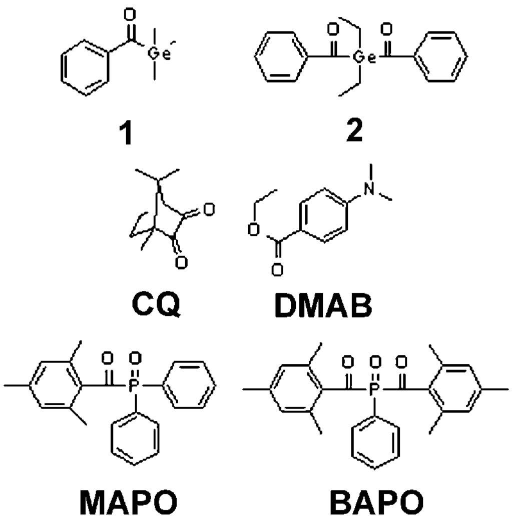


Figure 1. Diacylgermane **2** and reference PIs.

late (D_3MA), and 1,6-bis[2-methacryloyloxyethoxycarbonylamino]-2,4,4-trimethylhexane (UDMA) (Ivoclar Vivadent, Liechtenstein) were purchased from the above suppliers. DL-Camphorquinone (CQ, Rahn, Switzerland) and ethyl 4-(*N,N*-dimethylamino)benzoate (DMAB) (Fluka Chemie AG, Switzerland) were used without purification.

Commercial products were used as fillers: fumed silica OX-50 (size of primary particles: 40 nm, Degussa, Germany), YbF_3 (mean particle size: 5 μm, Auer Remy, Germany), a SiO_2-ZrO_2 mixed oxide Sphärosil (mean particle size: 250 nm, Tokoyama Soda, Japan), and a barium−aluminum−borosilicate glass Ba−Al−B−SiO_2 (GM 27884, mean particle size: 1.5 μm, Schott, Germany). Before use, the silica, the mixed oxide, and the glass fillers were modified with the silane coupling agent 3-methacryloyloxypropyltrimethoxysilane (MPTS, Union Carbide). The fillers were silanized by mixing them with 1.0 wt % of water and 5.0 wt % of MPTS at room temperature over a period of 2 h and drying the modified fillers at 50 °C for 4 days.

Characterization. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-E-200 FT-NMR-spectrometer. Deuterated chloroform ($CDCl_3$) was used as solvent. IR spectra were recorded on a Biorad FTS 135 spectrophotometer equipped with a Golden Gate ATR unit. The UV–vis absorption was measured with a Hitachi U-2001 spectrometer with spectrophotometric-grade acetonitrile (MeCN) as solvent. Melting points were determined with a Kofler hot-stage-type microscope and are uncorrected. Elemental microanalysis was carried out with an EA 1108 CHNS-O analyzer from Carlo Erba at the microanalytical laboratory of the Institute for Physical Chemistry at the University of Vienna. A reversed-phase HP-1100 HPLC system with DAD detector was used to follow the reaction and to determine storage stability. All separations were carried out on a XTerra MS C_{18} column, particle size 5 μm, 150 × 3.9 mm i.d. (Waters). A linear gradient with a flow of 0.8 mL/min was formed from 97% water/3% MeCN to 97% MeCN/3% water over a period of 30 min. GC-MS measurements were performed with a HP 5890A gas chromatograph using a 5970 series mass selective detector and a SPB-5 column (Supelco, 60 m × 0.25 mm).

Synthesis. *Trimethyl(2-phenyl-1,3-dithian-2-yl)germane (**3**).* 2-Phenyl-1,3-dithiane (9.4 g, 47.9 mmol) was placed in a round-bottom flask under argon atmosphere and dissolved in dry THF (180 mL). The solution was cooled to –20 °C, and then a 2.36 M solution of *n*-BuLi in hexane (21.48 mL, 47.92 mmol) was added slowly. The mixture was stirred magnetically for 2 h at −20 °C. Trimethylchlorogermane (7.73 g, 47.92 mmol) was dissolved in dry THF (20 mL), and then the mixture was added dropwise to the lithiated dithian solution at 0 °C. The solution was stirred for 2 h at 0 °C and subsequently quenched with water (20 mL). The aqueous layer was extracted with ethyl acetate (2 × 15 mL), and the combined organic layers were extracted with water (2 × 20 mL) and brine (10 mL). After drying of the organic phases with Na_2SO_4, the solution was filtered and the solvent was evaporated. The crude product was recrystallized from ethyl acetate. **3** was obtained as a colorless powder (13 g, 86%); mp 92 °C. ^{1}H NMR ($CDCl_3$): δ (ppm): 7.89 (d, 2H, $J = 7.47$, Ar−$H^{2,6}$), 7.37 (t, 2H, $J = 7.99$, Ar−$H^{3,5}$), 7.16 (t, $J = 7.27$, Ar−H^4), 2.81 (m, S−CH_2), 2.40 (m, S−CH_2), 2.18–1.83 (m, $CH_2-CH_2-CH_2$), 0.18 (s, 9H, −CH_3). ^{13}C NMR ($CDCl_3$): δ (ppm): 140.64 (Ar−C^1), 128.82 (Ar−C^4), 128.44 (Ar−$C^{3,5}$), 125.19 (Ar−$C^{2,3}$), 25.64 (−S−CH_2−), 25.50 (−S−$CH_2-CH_2-CH_2$−S−), –3.94 (−CH_3). MS: m/z = 314, 195, 163, 121, 77. Elem. Anal. Calcd for $C_{13}H_{20}GeS_2$: C 49.88%, H 6.44%. Found: C 50.12%, H 6.48%.

*Benzoyltrimethylgermane (**1**).* Method A: **3** (12.0 g, 38.3 mmol) was dissolved in aqueous THF (THF:water = 10:1; 170 mL). After the addition of $CdCO_3$ (33.69 g, 195.4 mmol) and $HgCl_2$ (52.02 g, 191.6 mmol) under light protection, the suspension was stirred under reflux for 18 h. Afterward, the organic solvent was evaporated, and CCl_4 (50 mL) was added to the aqueous suspension. The precipitate was filtered off, and the filtrate was extracted with water (2 × 10 mL). After drying of the organic layer with Na_2SO_4, the solvent was evaporated. To remove all residues of mercury salts, the mixture was filtered over a short silica gel column. Then the crude product was purified by bulb tube distillation (130 °C, 10 mbar). **1** was obtained as a yellow liquid (5.3 g, 60%).

Method B: **3** (4.9 g, 15.7 mmol) was dissolved in aqueous THF (THF:water = 4:1; 240 mL). After the addition of $CaCO_3$ (12.4 g, 122.8 mmol), the suspension was stirred magnetically for 5 min at room temperature and then iodine (23.98 g, 94.5 mmol) was added in one portion under light protection. The reaction mixture was stirred at room temperature for 3 h. Afterward, the solution was diluted with ethyl acetate (50 mL), and the excess of iodine was decomposed with saturated $Na_2S_2O_4$ solution under vigorous stirring until the suspension turned yellow. The precipitate was filtered off over Celite and washed with ethyl acetate. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were extracted with water (2 × 40 mL) and brine (20 mL). After drying the organic layers with Na_2SO_4 the solution was filtered and the solvent was evaporated. The crude product was bulb tube distilled (130 °C, 10 mbar), and **1** was obtained as a yellow liquid (1.40 g, 40%). ^{1}H NMR ($CDCl_3$): δ (ppm): 7.78–7.82 (m, 2H, Ar−$H^{2,6}$), 7.48–7.58 (m, 3H, Ar−$H^{3,4,5}$), 0.51 (s, 9H, −CH_3). ^{13}C NMR ($CDCl_3$): δ (ppm): 234.39 (−C=O), 140.61 (Ar−C^1), 132.90 (Ar−C^4), 128.75 (Ar−$C^{2,6}$), 127.71 (Ar−$C^{3,5}$), –1.14 (−CH_3). IR (cm^{-1}): 2916, 2979, 1628 (C=O), 1582, 1448, 1310, 1239, 1207, 1172, 905, 827, 770, 732. MS: m/z = 223, 181, 151, 119, 105, 89, 77, 51. Elem Anal. Calcd for $C_{10}H_{14}GeO$: C 53.91%, H 6.33%. Found: C 54.03%, H 6.45%.

*Diethyldi(2-phenyl-1,3-dithian-2-yl)germane (**4**).* 2-Phenyl-1,3-dithiane (47.14 g, 0.24 mol) was placed in a round-bottom flask under argon atmosphere in dry THF (350 mL). The solution was cooled to 0 °C, and then a 2.5 M solution of *n*-BuLi in hexane (96 mL, 0.24 mmol) was added slowly. The mixture was stirred magnetically for 2 h at 0 °C. Dimethyldichlorogermane (20.16 g, 0.1 mol) was dissolved in dry THF (50 mL), and then the mixture was added dropwise to the lithiated dithian solution at 0 °C. The solution was stirred for 3 h at 0 °C. To complete the reaction, the flask was placed in the fridge at 4 °C overnight. The solution was quenched with water (30 mL), and then the organic layer was diluted with ethyl acetate (250 mL) and extracted with water (2 × 50 mL). The combined aqueous layers were extracted with ethyl acetate (100 mL), and the combined organic phases were washed with brine and then dried with Na_2SO_4. Then the solution was filtered, and the solvent was evaporated. The crude product was recrystallized from ethyl acetate. **4** was obtained as a colorless powder (38.11 g, 73%); mp 112–115 °C. ^{1}H NMR ($CDCl_3$): δ (ppm): 7.84 (d, 4H, $J = 7.27$, Ar−$H^{2,2',6,6'}$), 7.20 (t, 4H, $J = 7.58$, Ar−$H^{3,3',5,5'}$), 7.00 (t, 2H, $J = 7.06$, Ar−$H^{4,4'}$), 2.62 (m, 4H, −S−CH_2−), 2.17 (m, 4H, −S−CH_2−), 2.00−1.64 (m, 4H, −S−$CH_2-CH_2-CH_2$−S−), 1.18 (m, 4H, −Ge−CH_2−), 1.01 (t, 6H, $J = 7{,}58$, −CH_3). ^{13}C NMR ($CDCl_3$): δ (ppm): 140.59

(Ar$-$C$^{1,1'}$), 130.39 (Ar$-$C$^{4,4'}$), 128.18 (Ar$-$C$^{3,3',5,5'}$), 125.52 (Ar$-$C$^{2,2'6,6'}$), 51.91 ($-$S$-$C$-$S$-$), 25.89 ($-$S$-$CH$_2-$), 25.16 ($-$S$-$CH$_2-$*CH*$_2-$CH$_2-$S$-$), 10.26 ($-$Ge$-$CH$_2-$), 4.74 ($-$CH$_3$). Elem Anal. Calcd for $C_{24}H_{32}GeS_4$: C 55.29%, H 6.19%. Found: C 55.56%, H 6.22%.

Dibenzoyldiethylgermane (2). **2** was prepared in an analogous way to the preparation of **1** via method B with **4** (8.27 g, 15.9 mmol), $CaCO_3$ (25.0 g, 247.4 mmol), and iodine (48.3 g, 190.3 mmol). The crude product was purified by column chromatography (silica gel, hexane:ethyl acetate = 20:1). **2** was obtained as yellow oil (3.25 g, 60%) which crystallized after 2 days in the fridge; mp 47–49 °C. ^{1}H NMR ($CDCl_3$): δ (ppm): 7.73 (d, 4H, $J = 6.64$, Ar$-$H$^{2,6,2',6'}$), 7.39–7.51 (m, 8H, Ar$-$H$^{3,3',4,4',5,5'}$), 1.50 (q, 4H, $J = 7.89$, $-$Ge$-$CH$_2-$), 1.11 (t, 6H, $J = 7.79$, $-$Ge$-$CH$_2-$*CH*$_3$). ^{13}C NMR ($CDCl_3$): δ (ppm): 230.22 (C=O), 141.23 (Ar$-$C), 133.66 (Ar$-$C), 129.06 (Ar$-$C), 128.19 (Ar$-$C), 9.11 ($-$Ge$-$CH$_2-$), 6.61 ($-$Ge$-$CH$_2-$*CH*$_3$). IR (cm^{-1}): 2959, 2911, 1622 (C=O), 1579, 1447, 1308, 1207, 1169, 1022, 892, 767, 688; MS: m/z = 342, 314, 285, 237, 209, 181, 151, 123, 105, 91, 77, 51. Elem. Anal. Calcd for $C_{18}H_{20}GeO_2$: C 63.41%; H, 5.91%. Found: C 63.75%, H 5.94%.

Storage Stability. For storage stability experiments, monomer-free formulations based on 60% MeCN, 40% water, and a few drops of H_3PO_4 (pH = 1.7), with 1% (w/w) of PI and 0.5% (w/w) of an internal reference (1,2,4-trimethoxybenzene), were stored in the dark at 42 °C for 60 days. After 0, 1, 5, 14, 22, 42, and 60 days, the remaining PI concentration was determined by HPLC.

Steady-State Photolysis (SSP). Photolysis experiments for kinetic studies were carried out in a self-made glass flask ($l = 6$ cm, $d = 2.5$ cm) with two ground joints, one situated on the top and the other attached to the side wall. A self-made quick-fit (cone/screw thread adaptor) closed on the ground joint with a quartz window was connected to the ground joint on the top. The samples were magnetically stirred and were purged with argon before irradiation. A Novacure unit (Efos. 1000 mW cm^{-2}, 365 nm filter) was used as irradiation source with a light guide attached to the quartz quick-fit.

For visualization of the photobleaching effect, solutions of the PIs in MeCN were prepared with an initial absorption of 0.5 at 365 nm. After defined intervals samples were drawn and measured via UV–vis spectroscopy.

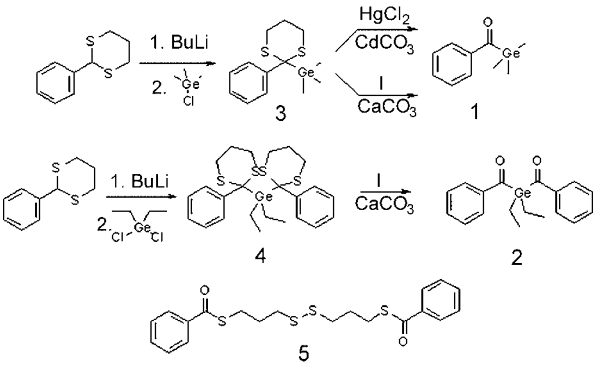
For the determination of quantum yields, quantitative analysis was carried out by HPLC with samples taken after 0, 30, 60, 90, and 120 s. The initial concentration of the PI solutions to ensure equal light absorption at 365 nm was as follows: MAPO and BAPO: 5×10^{-3} mol/L; **1**: 5×10^{-2} mol/L; **2**: 2×10^{-2} mol L^{-1} The *o*-nitrobenzaldehyde actinometer[18] was used to determine the total absorbed light intensity to be 2.16×10^{-4} einstein L^{-1} s^{-1}.

Photo-DSC. Photo-DSC was conducted with a modified Shimadzu DSC 50. Filtered UV–vis light was applied by a Omicure 2000 (Exfo, 320–500 nm, 1000 mW cm^{-2}) and a dental LED lamp (Bluephase C8; IVOCLAR VIVADENT; λ = 430–490 nm) attached to the top of a homemade aluminum cylinder[19] (h = 42 mm for Omnicure 2000 lamp, h = 32 mm for the dental lamp). The light intensity at the tip of the light guide was measured by an OPTILUX radiometer (model 100, P/N 10503, sds Kerr) to be 420 mW cm^{-2} for Bluephase C8. A dental formulation consisting of D$_3$MA:UDMA:Bis-GMA (1:1:1) with 22 μmol PI/g and a dental primer formulation consisting of EAEPA:DEBAAP:water (2:1:2) with 5.5 μmol PI/g were tested. In the case of CQ as bimolecular PI, an equimolar amount of DMAB was used as co-initiator. The photo-DSC measurements were carried out in an isothermal mode at room temperature under ambient atmosphere. The mass of the samples was 10 ± 0.5 mg. Important data for the determination of the time to reach the maximum polymerization heat ($t_{\max}$), double-bond conversion (DBC), and rate of polymerization (R_p) are shown in Table 1. The determination of the enthalpies ΔH_0 of each monomer was carried out using infrared spectroscopy and photo-DSC.[20] Monomers were mixed with 0.5% (w/w) BAPO, and then photo-DCS measurements were carried out with Omnicure 2000 under argon to determine the heat released during the photoreaction. Infrared spectra were recorded of the cured samples and of the monomers to determine the DBC. Thus, the enthalpies $\Delta H_0$for 100% DBC could be calculated.

Table 1. Molecular Weight (MW), Enthalpy (ΔH_0), and Density (δ) of the Monomers

monomers	MW [g/mol]	ΔH_0 [J/mol]	δ [g/mL]
D$_3$MA	310.43	110 000	950
UDMA	470.56	100 000	1110
Bis-GMA	512.59	101 000	1160
EAEPA	238.18	62 900	1300
DEBAAP	238.33	120 600	1030

Scheme 1. Preparation of 1, 2, and Byproduct 5



Preparation, Curing, and Characterization of the Mechanical Properties of Composites. The experimental composites were mixed in an LPM 0.1 SP kneading machine (Linden, Germany). The photopolymerization of the composites was carried out using **1** and **2** as photoinitiators or the photoinitiator system based on a mixture of CQ and DMAB. Flexural strength specimens (2 × 2 × 25 mm) were obtained by irradiating the resins or composites with the visible light source Spectramat (150 mW cm^{-2}, Ivoclar Vivadent AG, Liechtenstein) for 3 min per side of the specimens. The mechanical properties were determined according to the relevant ISO standard 4049[21] after immersing the cured specimens in water for 24 h at 37 °C. The flexural strength (FS) and flexural modulus of elasticity (E) were determined by using a BZ2.5/TS1S universal testing machine (Zwick, Germany).

Results and Discussion

Synthesis. Acylgermanes were designed according to the structures of acylphosphine oxide-based photoinitiators, e.g. MAPO and BAPO, but without methyl groups for sterical shielding at the benzoyl chromophore. The preparation of this class of compounds has been studied thoroughly in organic synthesis.[22] As the synthesis of alkylgermyllithium species cannot be easily achieved,[23–25] other synthetic routes had to be selected. The shortest way to obtain monoacylgermane derivatives is a palladium complex catalyzed reaction with hexamethyldigermane and benzoyl chloride.[14,26] But as in the course of this reaction half of the germane-containing reactant is lost after work-up, another synthetic route was now preferred (Scheme 1).

The classic preparation of acylgermanes by the dithian route was developed some 50 years ago by Brook et al.[27] In the first step of the reaction, 2-phenyl-1,3-dithiane can be metallated with n-BuLi at low temperature. The formed carbanion of the dithiane reacts efficiently with trimethylchlorogermane. Subsequently, **3** can be hydrolyzed via different routes. In our case the most effective way was treating **3** with an excess of mercuric chloride in the presence of a base like cadmium carbonate in aqueous THF[27] to give benzoyltrimethylgermane in 60% yield. As these PIs are to be used for medical application, slightest traces of toxic substances have to be avoided. The complete separation of mercuric and cadmium salts could be ensured by column

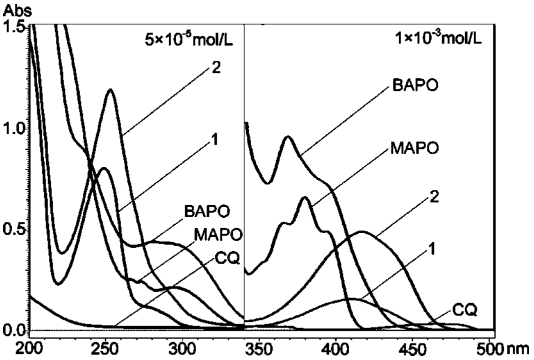


Figure 2. UV–vis spectra of the PIs in MeCN.

Table 2. UV–vis Data of the PIs in MeCN

	$\pi-\pi^*$ transitions		$n-\pi^*$ transitions		
PI	λ_{max} [nm]	ϵ [L mol^{-1} cm^{-1}]	λ_{max} [nm]	ϵ [L mol^{-1} cm^{-1}]	ϵ (λ_{365}) [L mol^{-1} cm^{-1}]
MAPO	294	3778	365, 380, 394	437, 549, 405	532
1	249	16120	411.5	137	37
BAPO	281	8820	397, 369	698, 964	918
2	253	23920	418.5	490	95
CQ			468	41	

chromatography and distillation. Nevertheless, a more convenient way of hydrolysis to avoid the use of toxic catalysts was applied. Bouillon et al.[28] described the dethioketalization with iodine (Scheme 1). **3** was treated with a large excess of $CaCO_3$ and iodine in aqueous THF for 3 h at room temperature. The excess of iodine was decomposed with a saturated solution of $Na_2S_2O_4$, and **1** was obtained in a yield of 40%.

The synthesis of diacylgermanes was carried out according to the dithian route developed by Boillon et al. for the preparation of diacylsilanes.[28,29] In an optimized reaction procedure 2-phenyl-1,3-dithiane was metallated with *n*-BuLi and then converted with dimethyldichlorogermane to give **4** in 73% yield. The dithian was hydrolyzed with iodine, as this method of dethioketalization is described to work best for aromatic diacylsilanes.[28] In the course of the reaction the product might be cleaved under these conditions. The remaining benzoyl part forms the thio ester 3,3′-disulfanediylbis(propane-3,1-diyl)dibenzothioate (**5**), which can be monitored via HPLC but is difficult to separate from the product via column chromatography. When this thio ester was converted entirely by the excess of iodine, the reaction was terminated. To ensure complete conversion, cooling of the suspension shortly after the addition of iodine had to be avoided. In this way yields of about 60% of **2** were achieved.

UV–vis Spectroscopy. UV–vis absorption spectra (Figure 2) were measured from 1×10^{-3} and 5×10^{-5} mol/L solutions of the PIs in MeCN. The wavelength of maximum absorption (λ_{max}) and the extinction coefficient (ϵ) are summarized in Table 2. 1, BAPO, MAPO, and CQ were used as a reference.

In the benzoyl phosphine oxide-based PIs like MAPO and BAPO absorption below 350 nm can be generally assigned to the $\pi-\pi^*$ transition. The symmetry forbidden $n-\pi^*$ transitions (~360–400 nm) with therefore comparable low extinction coefficients are responsible for α-cleavage and formation of reactive radical sites in acylphosphine oxides. More than one maximum is generally found for this type of compounds due to the different angles between carbonyl group and the P=O group.

As could be seen in Table 2, it was possible to red-shift the long wavelength absorption maximum of **2** more than 20 and 50 nm compared to both $n-\pi^*$ transitions of BAPO. Compared to the monoacylgermanium compound **1**, a slight shift of about 7 nm to longer wavelength was obvious. In contrast to acylphosphine oxides, both germanium-based PIs **1** and **2** show an absorption of the $n-\pi^*$ transition, which does not overlap with the $\pi-\pi^*$ absorption. This might be of importance as in acylphosphine oxides both transitions overlap and therefore the inactive $\pi-\pi^*$ transition competes with the active $n-\pi^*$ transition. Similar to mono- and bisacylphosphine oxides, it was possible in germanium-based PIs to raise the extinction coefficient with the diacyl derivative **2**. Actually, the 3-fold value was measured. Compared to CQ, this value was more than 1 order of magnitude larger. The absorption peak of **2** tailed out at ~490 nm and overlaps with more than half the area of CQ. By comparing the extinction coefficient of CQ at its maximum of 468 nm with the absorption of **2** at the same wavelength, it can be seen that the extinction coefficients were in the same order of magnitude (CQ: $\epsilon_{468} = 41$ L mol^{-1} cm^{-1}; **2**: $\epsilon_{468} = 21$ L mol^{-1} cm^{-1}).

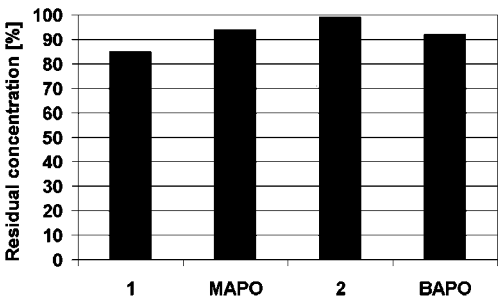


Figure 3. Storage stability of the different PIs in aqueous acidic solution (pH = 1.7); residual PI concentration after 60 days.

Storage Stability. To improve the poor stability of acylphosphine oxides against nucleophilic attack, they have been modified with sterically shielding groups.[30] Therefore, it was essential to investigate this behavior for our PIs as no methyl groups for sterical shielding are present. Storage stability (42 °C) of the PIs was determined in $MeCN/H_2O/H_3PO_4$, simulating an aqueous acidic primer formulation with a pH value of 1.7. This system was chosen, as the reactivity of CQ is dramatically reduced in these formulations.[5]

Although we have not introduced sterically demanding groups, sufficient storage stability for dental applications was proven (Figure 3). Within 60 days the residual concentration of the acylphosphine oxides in aqueous acidic solution decreased by 6–7%, whereas the decrease for **1** under the same conditions was only 2 times faster. Surprisingly, the storage stability of **2**, with a decrease of the residual concentration of only 2%, is even better than for acylphosphine oxides.

SSP Experiments. *Photobleaching.* For dental applications, it is of great importance that the cured samples are tooth-shaded and that the PI or decomposition products thereof do not show any discoloration. As CQ/DMAB containing samples do not always meet these requirements, the photobleaching effect of the new PIs **1** and **2** should be investigated. MAPO and BAPO were used as references, as they are known to show excellent photobleaching behavior. Samples of the PI's were prepared with an initial absorption of 0.5 at 365 nm in MeCN. The solutions were irradiated with monochromatic light at 365 nm (Efos Novacure) with an intensity of 1000 mW cm^{-2}. After defined intervals, samples were drawn and measured via UV–vis spectroscopy. In Figure 4 photobleaching through the successive destruction of the chromophore of the PIs could be demonstrated in an impressing way. In the case of MAPO, BAPO, and **2**, only 6–7 min was required for about 50% reduction of the $n-\pi^*$ absorption. It can also be seen that no photoproducts are formed that absorb in the visible range of spectrum. It is noteworthy

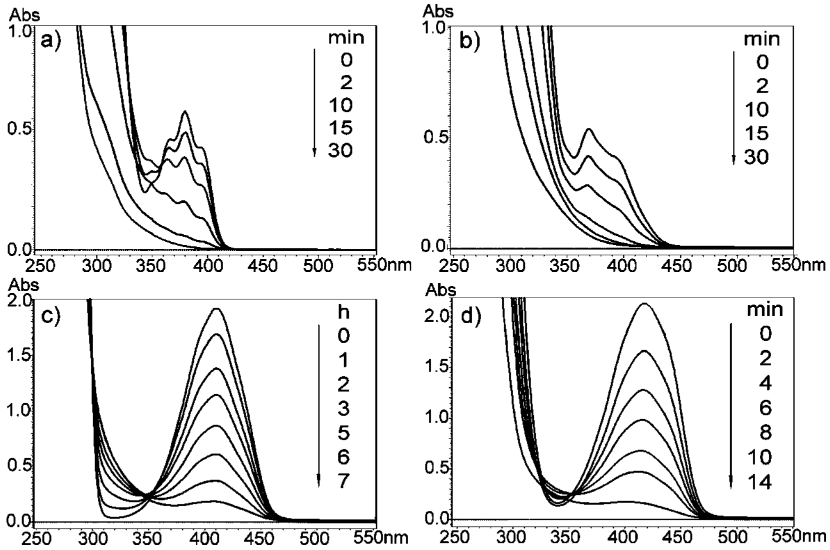


Figure 4. SSP of (a) MAPO, (b) BAPO, (c) **1**, and (d) **2** in MeCN.

Table 3. R_D **and** Φ_D **of the PIs in MeCN**

PI	$R_D \times 10^6$ [mol s^{-1} L^{-1}]	Φ_D [mol einstein^{-1}]
BAPO	12.8	0.59
MAPO	11.8	0.55
1	8.1	0.40
2	184	0.85

that the photolysis of **1** took significantly longer than for the other PIs.

Determination of Quantum Yields. Quantum yields of decomposition (Φ_D) were determined by chemical actinometry.[31] *o*-Nitrobenzaldehyde ($\Phi_D = 0.5$; 310–400 nm) was used as a chemical actimometer.[9] SSP experiments (365 nm) of solutions of the PIs were carried out in MeCN at a suitable concentration to ensure optical density. The kinetics were determined by HPLC. The data were fitted to second-order polynomials, from which initial rate constants (R_D) and Φ_D were calculated (Table 3).

Φ_D of acylphosphine oxides obtained through this method are well in agreement with values found in the literature ($\Phi =$ 0.5–0.7).[32] Φ_D of **1** is quite lower than that of acylphosphine oxides which corresponds to the first impression obtained at SSP experiments for the monitoring the photobleaching effect. Nevertheless, besides the Φ_D, additional effects must be responsible for the slow decomposition of **1** shown in Figure 3. In contrast, photodecomposition of **2** is quite effective, as Φ_D of **2** is twice as high as Φ_D of **1** and thus achieves a value that is about 40% higher than that determined for both acylphosphine oxides.

Photo-DSC. Photo-DSC is a unique method for obtaining a fast and accurate indication of the PI performance. With a single measurement, various important parameters are accessible. The t_{max} reveals information about the photoinitiator activity. From the height of the exothermic peak the R_p (mol L^{-1} s^{-1}) can be calculated as described earlier.[6] DBC was calculated from the overall enthalpy evolved [ΔH_p (J/g)]; ΔH_{0P} (J/g) is the theoretical enthalpy obtained for 100% conversion of the formulation. ATR-FTIR spectroscopy of samples cured in photo-DSC experiments was used to calculate the ΔH_{0P} of each single monomer based on the ΔH_p (photo-DSC) and the corresponding DBC (ATR-FTIR).

To investigate the reactivity in nonaqueous dental resins, 22 μmol/g of the PIs was mixed with the formulation consisting of D3MA:UDMA:Bis-GMA (1:1:1). The first set of experiments was carried out with broadband irradiation using a 320–500 nm filter. The results are shown in Figure 5, and data obtained are summarized in Table 4.

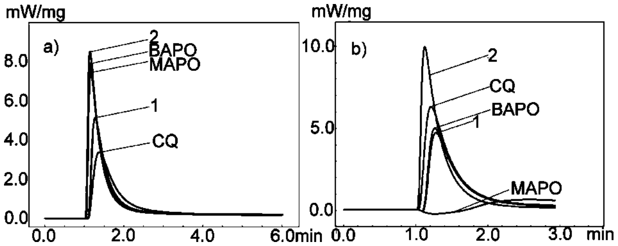


Figure 5. Photo-DSC plots of dental resin mixture using 22 μmol g^{-1} of the PIs CQ/DMAB, BAPO, MAPO, **1**, and **2** irradiated with (a) Omnicure 2000 and (b) Bluephase C8.

Table 4. Photo-DSC Data of Dental Resin Mixture with 22 μ**mol** g^{-1} **of the PIs**

	Omnicure 2000 (350–500 nm)			Bluephase C8 (430–490 nm)		
PI	t_{max} [s]	$R_p \times 10^3$ [mol L^{-1} s^{-1}]	DBC [%]	t_{max} [s]	$R_p \times 10^3$ [mol L^{-1} s^{-1}]	DBC [%]
CQ	22.8	66.4	55	13	126	66
MAPO	10.2	154	77	–[a]	–[a]	–[a]
1	16.2	103	59	16	99.0	51
BAPO	9.6	161	76	15	93.6	50
2	9	174	81	7.8	205	78

[a] Nearly no photopolymerisation activity was observed.

As has been expected, MAPO and BAPO gave significantly higher reactivity compared to CQ/DMAB in broadband irradiation experiments. Improvements by a factor larger than 2 were achieved for t_{max} and R_p. Also, the DBC could be raised from 55% to 77% under these conditions. It has been shown recently that **1** gave slightly improved performance compared to the state of the art in photopolymerizable dental materials.[14] The high performance of acylphosphine oxides has not been achieved. Surprisingly, the diacylgermanium compound **2** gave the best results. Compared to the highly reactive BAPO, all characteristic data were improved by nearly 10% under broadband irradiation.

Photo-DSC investigations with the dental LED lamp proved that the absorption spectrum of MAPO does not overlap with the emission spectrum of the lamp (~430–490 nm). Also, the reactivity of BAPO was reduced below the level of CQ in all important parameters. Nearly the same reactivity was obvious for monoacylgermane **1**. Under these conditions, the big

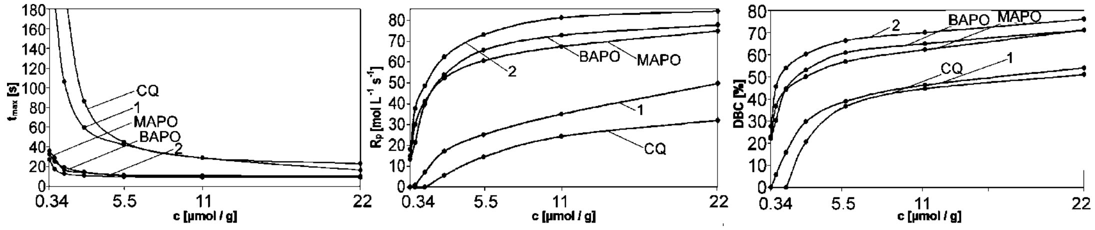


Figure 6. Concentration dependency of $t_{\max}$, R_P, and DBC of the PIs in dental resin.

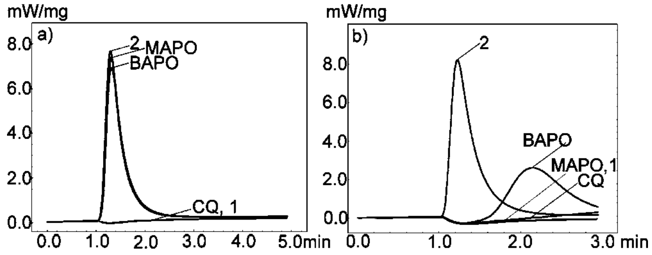


Figure 7. Photo-DSC plots of dental primer using 5.5 μmol g^{-1} of the PIs CQ/DMAB, BAPO, MAPO, **1**, and **2** irradiated with (a) Omnicure 2000 and (b) Bluephase C8.

Table 5. Photo-DSC Data of Dental Primer with 5.5 μmol g^{-1} of the PIs

	Omnicure 2000 (350–500 nm)			Bluephase C8 (430–490 nm)		
PI	$t_{\max}$ [s]	$R_p \times 10^3$ [mol L^{-1} s^{-1}]	DBC [%]	$t_{\max}$ [s]	$R_p \times 10^3$ [mol L^{-1} s^{-1}]	DBC [%]
CQ	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]
MAPO	19	83.5	85	—[a]	—[a]	—[a]
1	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]
BAPO	20	78.4	89	57	22.4	39
2	18	90.9	90	14	81.9	81

[a] Nearly no photopolymerisation activity observed.

advantage of diacylgermane **2** can be seen. Nearly half of the $t_{\max}$ of CQ could be achieved. Also, R_P and DBC were improved by 20–30%. Although only a restricted range of wavelength was applied, even slightly better performance of $t_{\max}$ and R_P as for broadband irradiation was found.

To determine the concentration dependency of the new PI, a series of photo-DSC experiments were performed under broadband irradiation (Figure 6). Generally, nearly the same effect of the PI concentration was obvious for all compounds. While CQ and **1** showed a very equal level for all parameters, bisacylphosphine oxides and **2** are significantly more reactive, especially at lower PI concentrations. Again, highest R_P and DBC were obtained by the new compound **2**.

It was of further interest to investigate the reactivity of the new germanium-based PIs **1** and **2** in a water-borne acidic primer formulation, as the type II PI system CQ/DMAB suffers from poor reactivity in this kind of resins.[5] 5.5 μmol g^{-1} of the PIs was mixed with the formulation consisting of EAEPA: DEBAAP:water (2:1:2). The PI concentration was much lower compared to the other experiments because of the known poor solubility of BAPO in aqueous formulations.[6] The first set of experiments was carried out with broadband irradiation using a 320–500 nm filter. The results are shown in Figure 7, and data obtained are summarized in Table 5.

As expected, the PI system CQ/DMAB was not reactive under these conditions. The performance of **2** is excellent and even slightly higher than for the acylphosphine oxide derivatives. Surprisingly, the formulation containing monoacylgermane **1** did not show any polymerization activity. This effect might be explained by a germoxycarbene formation in polar media as side reaction.[33]

Table 6. Mechanical Properties and Composition (wt %) of Experimental Composites Based on a Dimethacrylate Mixture of Bis-GMA/UDMA/TEGDMA = 4.23/3.75/2.02 (18.06) and a Mixture of Fillers (Ba−Al−B−SiO$_2$: 51.60; Sphärosil: 14.37; YbF$_3$: 14.89) Based on 1, 2, or of CQ/DMAB as PI (Standard Deviation in Parentheses)

components/properties	composite A	composite B	composite C
1	0.08		
2		0.11	
CQ/DMAB			0.05/0.09
OX-50	1.00	0.97	0.94
FS (MPa)[a]	150 (9.4)	170 (14)	168 (24)
FS (MPa)[b]	134 (15)	193 (16)	150 (16)
E (MPa)[a]	10540 (550)	13070 (940)	12190 (880)
E (MPa)[b]	10200 (760)	13500 (590)	11700 (420)

[a] FS or *E* measured of fresh prepared and cured composite pastes. [b] FS or *E* measured of specimens, which are cured after storage of the composites pastes for 3 months at 50 °C.

The second set of experiments was carried out with a dental LED lamp (~430–490 nm). Using lower PI concentrations, photopolymerization with BAPO could not be completed within the time of measurement. Furthermore, the emission spectrum of this lamp only slightly overlaps with the absorption spectrum of BAPO and does not overlap with the absorption spectrum of MAPO at all. Again, **1** did not show any reactivity, whereas very good performance could be achieved by using diacylgermane **2**. It is the only PI by far that is able to achieve outstanding polymerization results in aqueous acidic formulations using a dental LED lamp as irradiation source.

Dental Composites. Three dental model composites (A, B, and C) (Table 6) with a filler of about 82 wt % based on **1** (A), 2 (B), or the dental photoinitiating system CQ/DMAB (C) were prepared using a conventional dental resin based on the dimethacrylates Bis-GMA/UDMA/TEGDMA and dental fillers in order to evaluate the principal applicability of **1** or **2** as visible light PIs for restorative composites. These composites contained the same molar concentration of **1**, **2**, or CQ. The FS and *E* values of the composite A based on **1** as PI were somewhat lower compared to the corresponding composite C based on the PI CQ/DMAB. In contrast to this, **2** as PI resulted in a composite B with a similar FS values and significantly improved *E* values compared to the CQ/DMAB-based composite. For dental application the storage stability of the composite pastes is one basis requirement. Therefore, we measured the mechanical properties after storage of the composite pastes for 3 months at 50 °C. The results in Table 6 proved an excellent storage stability of the composite B, which is based on **2** as PI. Finally, it should be mentioned that composite based on **1** and **2** showed an excellent photobleaching behavior and UV light stability.

Conclusion

The aim of these studies was the development of a benzoyl-based PI with significant red shift of the important n−π* transition. The new germanium-based PI **2** was prepared from dithioketal-protected benzaldehyde by coupling reaction with diethyldichlorogermane and subsequent cleavage of the protection group in 43% overall yield. UV–vis absorption spectroscopy revealed a red shift of up to 50 nm of the absorption maximum of the n−π* transition compared to the reference initiator BAPO. Nevertheless, excellent photobleaching effect was confirmed via SSP experiments. The quantum yield of decomposition of **2** ($\Phi_D = 0.85$) was found to be significantly higher than for corresponding acylphosphine oxides ($\Phi_D \sim 0.6$). It was also shown that even without any sterical hindrance in the molecule it was possible to get sufficient stability against nucleophilic attack for dental applications. Photo-DSC experiments proved similar reactivity and higher DBC as the bisacylphosphine oxides under broadband irradiation conditions. Experiments using a dental LED lamp generally showed much better performance of **2** compared to CQ/DMAB or BAPO. In aqueous acidic formulations, only the new PI **2** showed outstanding photoinitiation activity. In addition to it, **2** showed also excellent performance in dental composite formulations.

Acknowledgment. The generous financial support of a PhD student by Ivoclar Vivadent AG and samples of PIs from CIBA SC are gratefully acknowledged. Additionally, we thank Exfo for an Omnicure 2000 unit.

References and Notes

(1) Jakubiak, J.; Rabek, J. F. *Polymer* **1999**, *7–8*, 447–461.
(2) Moszner, N.; Salz, U. *Prog. Polym. Sci.* **2001**, *26*, 535–576.
(3) Dietliker, K. In *Chemistry & Technology of UV & EB Formulation for Coatings, Inks & Paints*, 2nd ed.; SITA Technology Ltd.: London, UK, 1998; Vol. *3*.
(4) Fouassier, J. P. *Photoinitiating Systems*; Elsevier Appl. Sci.: Amsterdam, 1993; Vol. II, p 717.
(5) Ullrich, G.; Burtscher, P.; Salz, U.; Moszner, N.; Liska, R. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 115–125.
(6) Ullrich, G.; Ganster, B.; Salz, U.; Moszner, N.; Liska, R. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 1686–1700.
(7) Henne, A.; Hesse, A.; Heil, G.; Schornick, G. DE 30 34 697, BASF AG, 1982.
(8) Wolf, J. P.; Hug, G. WO 03019295, CIBA SC Holding AG, 2003.
(9) Seidl, B.; Liska, R.; Grabner, G. *J. Photochem. Photobiol., A: Chem.* **2006**, *180*, 109–117.
(10) Liska, R.; Seidl, B. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 101–111.
(11) Liska, R.; Herzog, D. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 752–764.
(12) Rutsch, W.; Hug, G.; Köhler, M. CA 2059144, CIBA GEIGY AG, **1992**.
(13) Arnett, J. F.; Newkome, G.; Mattice, W. L.; McGlynn, S. P. *J. Am. Chem. Soc.* **1974**, *96* (14), 4385–4392.
(14) Ganster, B.; Moszner, N.; Liska, R. *Macromol. Chem. Phys., Rapid Commun.* **2008**, *29*, 57–62.
(15) Brook, A. G.; Peddle, G. J. D. *Can. J. Chem.* **1963**, *41*, 2351–2356.
(16) Mikhalil, G.; Voronkov, K.; Abzaveva, K. A. In *The Chemistry of Organic Germanium, Tin and Lead Compounds*; John Wiley & Sons: New York , 1992; Vol. *2*.
(17) Moszner, N. unpublished results.
(18) Willett, K.; Hites, R. *J. Chem. Educ.* **2000**, *77*, 900–902.
(19) Liska, R.; Herzog, D. *J. Polym. Sci., Part A* **2004**, *42*, 752–764.
(20) Fouassier J. P. In *Photochemistry and UV Curing: New Trends*; Research Signpost: 2006; pp 253–264.
(21) International standard ISO 4049:2000, Dentistry—Polymer-based filling restorative and luting materials.
(22) Spivey, A. C.; Diaper, C. M. *Science of Synthesis: Category 1 Organometallics*; Georg Thieme Verlag: 2003; Vol. *5*.
(23) Yamaguchi, J.; Tamada, Y.; Takeda, T. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 607–612.
(24) Vyazankin, N. S.; Razuvaev, G. A.; Gladyshev, E. N.; Korneva, S. P. *J. Organomet. Chem.* **1967**, *7*, 353–357.
(25) Bulton, E. J.; Noltes, J. G. *J. Organomet. Chem.* **1971**, *29*, 397–407.
(26) Yamamoto, K.; Hayashi, A.; Suzuki, S.; Tsuji, J. *Organometallics* **1987**, *6*, 974–979.
(27) Brook, A. G.; Duff, J. M.; Jones, P. F.; Davis, N. R. *J. Am. Chem. Soc.* **1967**, *89*, 431–434.
(28) Bouillon, J. P.; Portella, C. *Eur. J. Org. Chem.* **1999**, 1571–1580.
(29) Bouillon, J. P.; Huguenot, F.; Portella, C. *Synthesis* **2002**, *4*, 552–556.
(30) Baxter, J. B.; Davidson, R. S.; Hageman, H. J.; Hakvoort, G. T. M.; Overeem, T. *Polymer* **1988**, *29*, 1575.
(31) Kuhn, H.; Braslavsky, S. E. *Pure Appl. Chem.* **2004**, *76*, 2105–2146.
(32) Sumiyoshi, T.; Schnabel, W.; Henne, A. *Polymer* **1985**, *26*, 141–146.
(33) Taraban, M. B.; Volkova, O. S.; Kruppa, A. I.; Leshina, T. V. In *The Chemistry of Organic Germanium, Tin and Lead Compounds*; John Wiley & Sons: New York, 1992; Vol. *2*, p 589 ff.

MA702418Q