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Dibenzoyldiethylgermane as a Visible Light Photo-reducing Agent for CuAAC Click Reactions

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The highly active, versatile and photoresponsive system for copper catalyzed azide-alkyne cycloaddition (CuAAC) click reaction has been developed using dibenzoyldiethylgermane (DBDEG) photoinitiator with copper (II) chloride ($CuCl_2$)-N,N,N′,N′′,N′′-pentamethyldiethylenetriamine (PMDETA) ligand under visible light. Selected azide and alkyne compounds with various functional groups are used to conduct the click reaction and almost quantitative yields are attained. The approach pertains to the visible light generation of germyl radicals capable of reducing Cu(II) ions to Cu(I) species to catalyze the CuAAC reactions. This strategy has been applied in the achievement of various macromolecular reactions including polymer end-group functionalization, block copolymer formation and step-growth polymerization.

Introduction

Click reactions are the most widely investigated class of organic reactions with superior features over the traditional routes such as rapidity, orthagonality, versatility and almost quantitative efficiency.[1] Nevertheless, equimolar concentrations of the substrates is enough to benefit from such advantages and the products are easy to purify since no by-products are formed.[2, 3] Due to these outstanding advantages, click chemistry has a wide-range of applications in organic chemistry, polymer chemistry, supramolecular chemistry, drug discovery and material design.[4, 5]

The most common examples of click reactions are the copper catalyzed azide-alkyne cycloaddition (CuAAC) and Diels-Alder (DA) reactions.[6-10] Lately, thiol-ene reactions, which are realized in the presence of a radical source is considered as a “click mode” despite not showing all features of click chemistry.[11-16] Nevertheless, all click reactions have both advantages and disadvantages over their sister modes and overcoming the major problems affiliated with each reactions is one of the most important topics for synthetic researchers.[17-20] For example, DA reactions, which occur between a diene and a conjugated diene (dienophille) generally take place in relatively higher temperatures compare to CuAAC.[9, 21-24] Lately, hetero DA reactions were improved, which show ultra-rapidity at room temperatures. However, syntheses of the reactants appropriate for hetero DA reactions require long steps of experimentation.[25] The limitation behind CuAAC reactions is the requirement of Cu(I) complexes in the reaction media, which are sensitive to the air oxygen. Thus, the reactions generally take place under vacuum or inert atmosphere. Several strategies have recently been developed to overcome such limitations. One approach considers using cyclooctyne derivatives as triple bond source, but the synthesis of such molecules is a synthetic cumbersome on its own. Alternative metal-free click reaction procedures, for instance, by thermal azide–alkyne cycloaddition appeared to overcome copper related problems particularly important for biomedical materials applications.[26-32]

Other approaches suggest the use of reducing agents together with Cu(II) compounds, which yield the Cu(I) species necessary for the reaction. Organic derivatives such as phenol, hydrazine and ascorbic acid and electrochemical processes[33-37] were shown to reduce Cu(II) complexes to realize Cu(I) requiring reactions, such as Atom Transfer Radical Polymerization (ATRP) as well as CuAAC.[38-42]

Photo-induced reductions were also developed for Cu(I)-requiring reactions providing spatial and temporal control over the processes. Direct irradiation of the Cu(II)/ligand complexes results in slower reduction, whereas use of an additional photolabile compound accelerates the process dramatically (indirect route). These photolabile compounds are the light absorbing species decomposing upon irradiation to give radicals. The radicals generated upon irradiation reduce the Cu(II) complexes to Cu(I), which mediate the click reactions.[38, 43-52]

In a previous study in our laboratory, we have shown the possibility of reducing Cu(II) complexes by *Type I* initiators such as 2, 2-dimethoxy-2-phenyl acetophenone, 2-benzyl-2-dimethylamino-4′-morpholino butyrophenone, (2,4,6 trimethylbenzoyl)diphenylphosphine oxide and

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dicyclopentadienyl bis[2,6-difluoro-3-(1-pyrrolyl)phenyl] titanium (titanocene) as well as camphorquinone (CQ) as *Type II* visible light photoinitiator.[44, 53] *Type I* initiators directly decompose upon irradiation to yield radicals capable of reducing Cu(II) to Cu(I). CQ, on the other hand, is excited to its triplet state under visible light irradiation to abstract hydrogen from a co-initiator (i.e. benzyl alcohol) to yield radicals, which act as the reductants. This photoreducing strategy was utilized for ATRP and synthesis of macromolecular structures such as telechelic polymers, block and graft copolymers and hydrogels and organogels through CuAAC reaction.[46, 54-66] In another study, we applied polynuclear aromatic compounds as photosensitivers for the reduction of Cu(II) complexes to realize CuAAC reactions.[46] Table 1 comprises the previously used photoinitiators and their operative wavelength regions for CuAAC reactions.

Table 1 Photoinitiators Used in Photo-induced CuAAC and Their Operative Wavelengths

Photoinitiators	λ (nm)	Ref.
2, 2-Dimethoxy-2-phenyl acetophenone	~350	40
2-Benzyl-2-dimethylamino-4'-morpholino butyrophenone	~350	40
2,4,6-(Trimethylbenzoyl)diphenylphosphine oxide	~400-500	40
Dicyclopentadienyl bis[2,6-difluoro-3-(1-pyrrolyl)phenyl] titanium	~400-500	40
Camphorquinone/benzyl alcohol	~400-500	40
Pyrene	~350	46
Anthracene	~350	46
Phenothiazine	~350	46

Among wide range of cleavage type free radical photoinitiators, acyl germanium compounds are efficient photoinitiators with favorable absorption characteristics.[67, 68] The absorptions in the visible spectral range and molar extinction coefficients of these photoinitiators were increased with the introduction of an additional acyl group.[69, 70] In a related work from the authors' laboratory, these photoinitiators were successfully used for the promotion of cationic polymerization,[39, 71] the bulk and emulsion polymerization of styrene,[72] and the preparation of block copolymers[73] and polygermanes.[73, 74]

As part of our continuous interest in investigating, designing, and developing novel photochemical processes for macromolecular synthesis, we herein report the use of a bisacylgermane photoinitiator, namely dibenzoyldiethylgermane for the visible light generation of active copper catalyst for CuAAC reactions. The applicability of the system was demonstrated on model organic compounds having different functionalities and macromolecular structures.

Experimental Part

Materials

Benzyl bromide (Aldrich, 98%), phenylacetylene (Aldrich, 98%), ethyl 2-bromopropionate (Aldrich, 99%), 3-bromo-2-methylpropene (Aldrich, 97%), 4-nitroaniline (Fluka, 98%), 1,4-bis(bromomethyl)benzene (Aldrich, 99%), 1,4-diethynylbenzene (Aldrich, 96%), 2-bromoethanol (Aldrich, 95%), 1,7-dibromoheptane (Aldrich, 97%), sodium azide (NaN_3, Panreac, 99%), 4-pentynoic acid (Aldrich, 95%), poly(ethylene glycol) methyl ether (Me-PEG) (M_n:2000 g·mol^{-1}, Aldrich), dibenzoyldiethylgermane, *N,N'*-dicyclohexylcarbodiimide (DCC, Aldrich, 99%), 4-dimethylaminopyridine (DMAP, 99%, Aldrich), and copper (II) chloride ($CuCl_2$, Acros Organics, 99%) were used as received without any further purification. Styrene (Aldrich, 99.9%) and *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%) was purified by passing through basic alumina (Al_2O_3) prior to use. All solvents were used as received. Dibenzoyldietylygermane (DBDEG) was kindly supplied by Ivoclar Vivadent, Liechtenstein.[75]

Characterizations

^{1}H-NMR measurements were recorded with $Si(CH_3)_4$ as internal standard, using an Agilent NMR System VNMRS 500 spectrometer. FT-IR spectra were recorded on a Perkin-Elmer FT-IR Spectrum One-B spectrometer. Molecular weights were determined by gel permeation chromatography (GPC) instrument, Viscotek GPCmax Autosampler system, consisting of a pump, three ViscoGEL GPC columns (G2000H_{HR}, G3000H_{HR} and G4000H_{HR}), and a Viscotek differential refractive index (RI) detector with a THF flow rate of 1.0 mL min^{-1} at 30°C. The RI detector was calibrated with PS standards having narrow molecular weight distribution. Data were analyzed using Viscotek OmniSEC Omni–01 software.

General Procedures for the Syntheses of Azide Components

Corresponding bromide compound was dissolved (15 mmol, 1.0 eq) in 100 mL of DMSO and sodium azide was added in excess (1.5 eq). The solution was stirred for at least 5 h at room temperature. Water (100 mL) was added to the mixture and temperature of the solution increased. After cooling down to room temperature, the aqueous solution was extracted with diethyl ether (3 × 100 mL). The organic layers were combined and washed with water (2 × 100 mL), brine (100 mL) and dried over $MgSO_4$. The ether was removed under reduced pressure to yield azides (Table 1, azide compounds **1-4**). ^{1}H NMR (500 MHz, $CDCl_3$), (δ, ppm): **1)** 7.45-7.32 (m, 5H), 4.37 (s, 2H) **2)** (δ, ppm): 4.96 (s, 2H), 3.70 (s, 2H), 1.80 (s, 3H) **3)** (δ, ppm): 4.25 (q, 2H), 3.93 (q, 1H), 1.45 (d, 3H), 1.31 (t, 3H) **4)** (δ, ppm): 3.94-3.72 (q, 2H), 3.53-3.38 (t, 2H), 4.51 (s, 1H).

Synthesis of 1-Azido-4-Nitrobenzene

p-Nitroaniline (15 mmol, 1 eq.) was added to 60 mL of hydrochloric acid at room temperature followed by drop wise addition of ethanol. The solution was agitated to 0 °C and $NaNO_2$ (1.5 eq.) was added in small portions. After stirring at 0 °C for 40 minutes, NaN_3 (1.5 eq.) was slowly added and the mixture was stirred for further 3 h at room temperature. The reaction mixture was extracted with diethyl ether (3 × 75 mL) and the organic fractions were washed with saturated $NaHCO_3$ solution (3 × 40 mL) and with brine (50 mL). The organic layer was dried over $MgSO_4$, the ether was removed under reduced pressure to obtain azide. Orange solid. Yield 85%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25-8.21 (m, 2H), 7.14-7.12 (m, 2H).

General Procedure for Photoinduced CuAAC

General experimental procedure for the photo-induced copper(II)-catalyzed click reaction: DMSO-d_6 (0.5 mL) and azide compounds (1 mmol, 1eq) were added to an NMR tube containing Cu(II)Cl_2 (0.05 eq), PMDETA (0.10 eq) and DBDEG (0.05 eq). After 1−2 min, acetylene derivatives (1 eq) was added. The reaction tube was irradiated by a Ker-Vis blue photoreactor equipped with a circle of 6 lamps (Philips TL-D 18W) emitting light nominally at 400 −500 nm. ^{1}H NMR spectra were recorded 2 h later. Table 1, product **1-6**: ^{1}H NMR (500 MHz, $CDCl_3$), (*δ*, ppm): **1)** 7.81 (d, 2H), 7.68 (s, 1H), 7.41-7.25 (m, 8H), 5.58 (s, 2H); **2)** 8.52 (s, 1H), 7.54-7.29 (m, 5H), 4.97 (s, 2H), 4.80 (s, 2H) 1.65 (s, 3H); **3)** 8.73 (s, 1H), 7.88 (d, 2H), 7.49-7.42 (t, 2H), 7.40-7.30 (t, 1H), 5.65 (d, 1H), 4.15 (m, 2H), 1.82 (d, 3H), 1.22-1.10 (t, 3H); **4)** 8.20 (s, 1H), 7.48-7.42 (m, 4H), 7.39-7.32 (m, 3H), 7.29-7.25 (m, 2H); **5)** 8.90 (s, 1H), 7.95-7.15 (m, 5H), 0.40-0.03 (m, 9H); **6)** 8.53 (s, 1H), 7.90-7.80 (d, 2H), 7.50-7.27 (m, 3H), 4.60 (s, 1H), 3.85 (s, 2H), 3.69 (s, 2H).

Synthesis of PS with ω-Azide Functionality (PS-N_3)

ω-Bromo functional polystyrene (PS-Br) was synthesized by ATRP according to the previously reported procedure[76] ($M_{n,NMR}$: 4250 g/mol, $M_{n,GPC}$: 4190 g/mol, M_w/M_n: 1.08). In a flask equipped with a stirrer, PS-Br (1 eq), sodium azide (5 eq) and 15 mL DMF was added. The reaction mixture was stirred for 24 h at room temperature and precipitated in 10-fold excess of methanol to yield PS-N_3. The solid was collected after filtration and dried at room temperature under vacuum for overnight ($M_{n,NMR}$: 4100 g/mol, $M_{n,GPC}$: 4300 g/mol, M_w/M_n: 1.11).

Synthesis of ω-Alkyne Functionalized Poly(ethylene glycol) (PEG-Alkyne)

Me-PEG (M_n= 2000 g/mol) (1 eq) was dissolved in 25 mL of CH_2Cl_2. 4-Pentynoic acid (3 eq), 4-dimethylaminopyridine (3 eq) and *N, N′*-dicyclohexylcarbodiimide (3 eq) in 5 mL of dichloromethane were added to the solution in that order. The reaction mixture was stirred overnight at room temperature. It was filtered and evaporated, and the remaining product was purified by column chromatography over silica gel eluting first with CH_2Cl_2/ethylacetate (1:1), and then with methanol/CH_2Cl_2 (1:10). Finally, the organic phase was concentrated and precipitated in to diethyl ether to give PEG-Alkyne.

End-group Functionalization of Polystyrene and Poly(ethylene glycol) by Photo-induced CuAAC

To a Schlenk tube equipped with a magnetic stirrer, PS-N_3 (1 eq) or PEG-Alkyne, $CuCl_2$ (1 eq), PMDETA (1 eq) and DBDEG (1 eq) were added and dissolved in 10 mL DMSO. Corresponding click antagonists, (phenyl acetylene or benzyl azide, 1 eq) was finally introduced to the reaction media and the tube was sealed. The reaction tube was irradiated by a Ker-Vis blue photoreactor equipped with a circle of 6 lamps (Philips TL-D 18W) emitting light nominally at 400 −500 nm. At the end of 24 h, the mixture was diluted with CH_2Cl_2, passed through a neutral alumina to remove the copper complexes. Finally, CH_2Cl_2 was concentrated under reduced pressure and precipitated in appropriate solvents. The obtained polymers were collected after filtration and dried at room temperature under vacuum for overnight.

Synthesis of Polystyrene-*b*-Poly(ethylene glycol) by Photo-induced CuAAC

To a Schlenk tube equipped with a magnetic stirrer, PS-N_3 (0.15 mmol, 1eq), PEG-Alkyne (3 eq), Cu(II)Cl_2 (3 eq), PMDETA (3 eq) and DBDEG (3 eq) were added and dissolved in 10 mL DMSO. The tube was degassed by three freeze–pump–thaw cycles. The reaction tube was irradiated by the Ker-Vis blue photoreactor. At the end of 24 h, the mixture was diluted with CH_2Cl_2. Then, the copper complex was removed out by passing through a neutral alumina column, and CH_2Cl_2 was removed by rotary evaporation. The mixture was precipitated in cold methanol, and the solid was collected after filtration and dried at room temperature under vacuum for overnight. ($M_{n,NMR}$: 7080 g/mol, $M_{n,GPC}$: 5400 g/mol, M_w/M_n: 1.18).

Step-growth Polymerization by Photo-induced CuAAC

1,4-Bis(azidomethyl)benzene (1 eq) or 1,7-diazidoheptan (1 eq), 1,4-diethynylbenzene (1 eq) are dissolved in a glass bottle containing DMSO. Then $CuCl_2$ (1 eq), PMDETA (1 eq), DBDEG (1 eq) were added to the solution under N_2 atmosphere. The reaction tube was irradiated for 24 h under visible light. The resulting mixture was filtered and precipitated in methanol. The solid was collected after filtration and dried at room temperature under vacuum for overnight.

Results and Discussion

In view of electron transfer reactions of germyl radicals with onium salts to initiate cationic polymerization of appropriate monomers[39, 73, 74], the similar redox reaction was envisaged to involve between copper which is member of semi-noble metal salt and generally tends to stay at lower oxidation states. Thus, the reduction of Cu(II) to Cu(I) is thermodynamically more favorable ($E_{red(Cu(II)-Cu(I))}$ = +0.15 V (SCE)) in comparision to the onium salts ($E_{red(onium)}$ = -0.12 V (SCE)). This paper deals with the visible light reduction of Cu(II) using a germyl radical source, DBDEG to trigger CuAAC reactions. The UV spectra of $CuCl_2$/PMDETA, CuCl/PMDETA and DBDEG are shown in Fig. 1. As can be seen, DBDEG is the only light absorbing component in the visible region where Cu(II) is completely transparent. Thus, we have photolysed the reaction media at this region of the electromagnetic spectrum so as to eliminate the possibility of direct reduction of Cu(II).

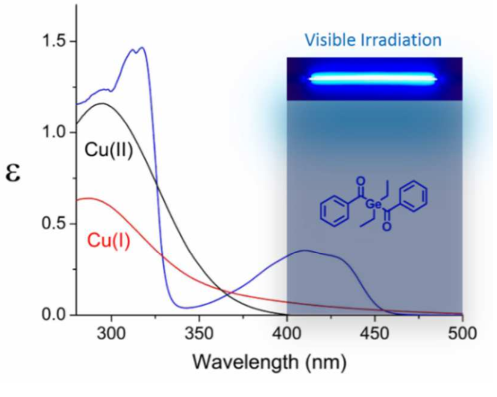
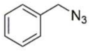
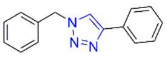
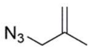
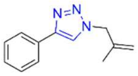
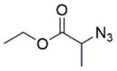
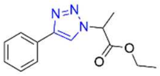
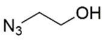
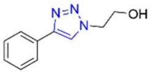
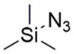
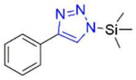
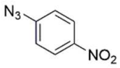
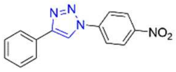


Fig. 1 UV–vis spectra of DBDEG, $CuCl_2$/PMDETA and CuCl/PMDETA.

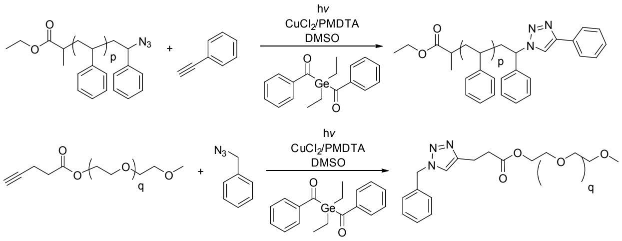
In a simple control experiment, a mixture of phenyl acetylene, benzyl azide and $CuCl_2$/PMDETA complex in d_6-DMSO was irradiated in an NMR tube in the absence of DBDEG. In this case, only trace amount of coupling product was formed since absorption of Cu(II) can be excluded in the irradiation region. However, when the same experiment was conducted in the presence of DBDEG, almost quantitative yield was obtained (Table 2). To demonstrate the tolerance of the reduction process to a variety of functional groups, selected low molar mass organic compounds were clicked under identical experimental conditions.

Table 2 Photoinduced CuAAC between various phenylacetylene and varios organic azides using dibenzoyldiethylgermane[a]

Run	R-N_3	Product	Conv.[b] (%)
1			99.1
2			99.0
3			98.2
4			98.3
5			99.0
6			98.1

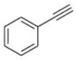
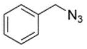
[a] All reactions were carried out under irradiation at 400–500 nm with a light intensity of 45 mW cm^{-2} at room temperature, in DMSO-d_6. The initial concentrations of azides and alkyne were 0.2 mM and the photoinitiator, $CuCl_2$ and PMDETA were 0.02 mM, reaction time: 2h. [b] Conversions were determined by ^{1}H-NMR spectroscopy.

In order to demonstrate applicability of the described process for the macromolecular syntheses, polymer end-group functionalization, blocking and step-growth polymerization experiments were conducted by photoinduced CuAAC using DBDEG as the photoiniator. Thus clickable polymers with controlled molecular weight and narrow polydispersities, namely azido functional polystyrene (PS-N_3) and alkyne functional poly(ethylene glycol) (PEG-alkyne) were prepared by well-established ATRP followed by azidation and esterification processes, respectively. Photoinduced click reactions with phenylacetylene and (azidomethyl)benzene gave their corresponding aromatic end-group functional polymers (Scheme 1, Table 3).



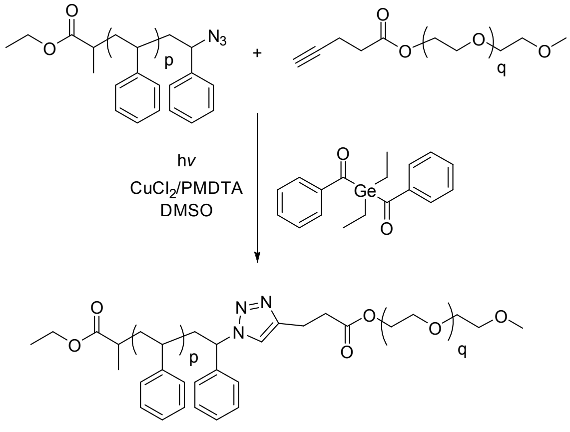
Scheme 1 End-group functionalization of polymers via photoinduced CuAAC click reaction.

Table 3 Polymer functionalization and blocking by photoinduced CuAAC using DBDEG[a].

Polymer ($M_{n,NMR}$ (g·mol^{-1}))[b]	Antagonist Compound	Yield (%)[b]	M_n (NMR)[b] (g·mol^{-1})	M_n (GPC)[c] (g·mol^{-1})	PDI[c]
PS-N_3 (4100)		98.5	4470	4520	1.15
PEG-Alkyne (3100)		91.0	3520	1890	1.10
PEG-Alkyne	PS-N_3	90.4	7080	5400	1.18

[a] All reactions were carried out in schlenk tube under irradiation at 400–500 nm with a light intensity of 45 mW cm^{-2} at room temperature in the presence of $CuCl_2$ and PMDETA. Reaction time: 2h. The polymers were precipitated in appropriate solvents. [b] Calculated by ^{1}H-NMR [c] Determined by GPC, according to polystyrene standards.

When the click process is accomplished between the polymers having antagonist click components, i.e. PS-N_3 and PEG-alkyne, the corresponding block copolymer is readily formed (Scheme 2).



Scheme 2 Synthesis of PS-b-PEG block copolymer via photoinduced CuAAC click reaction

The ^{1}H-NMR spectrum of the resulting PS-*b*-PEG block copolymer (Fig. 2) displays the characteristic signals of both macromolecular segments as well as the benzylic and triazole protons at 5.02 ppm and 7.46 ppm, respectively. Comparing the integrated area of these protons with that of the aromatic protons of the PS segment, the yield of the click process was estimated to be 90.4%.

The GPC traces of the precursors PS-N_3 and PEG-alkyne, and the block copolymer PS-*b*-PEG were demonstrated in Fig. 3. As can be seen, all polymers involved in the process show narrow molecular weight distributions suggesting that no significant side reactions occurred during the photoinduced click reaction. GPC analysis also displayed clear shifts to higher molecular weight regions indicating that an efficient click coupling process was achieved. To explore the suitability of the photoinduced click reaction, we further applied this method to the step-growth polymerization of bifunctional azide and alkyne monomers. Photoinduced polymerizations of commercially available 1,4-diethynylbenzene with aliphatic and aromatic azide compounds, namely 1,4-bis(azidomethyl)benzene and 1,7-(diazidoheptane) gave their corresponding triazole polymers (Scheme 3).

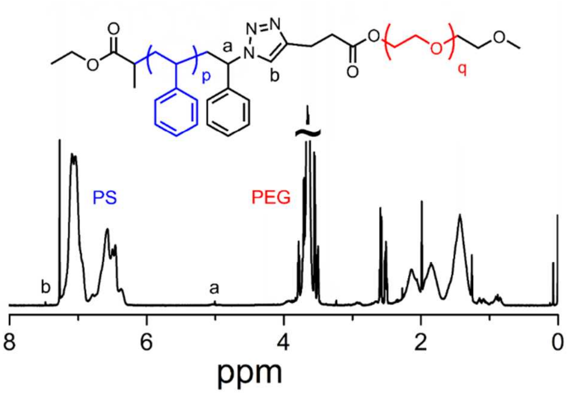


Fig. 2 ^{1}H NMR spectra of the PS-*b*-PEG copolymer prepared by photoinduced free radical promoted CuAAC click reaction.

The polymerizations proceeded homogeneously and gave quantitative monomer conversions within the 24 h polymerization time (Table 4). As can be seen, the polymerization with the aromatic azide monomer yielded polymers with relatively higher molecular weight and lower molecular weight distribution probably due to the structural similarity of the monomers involved.

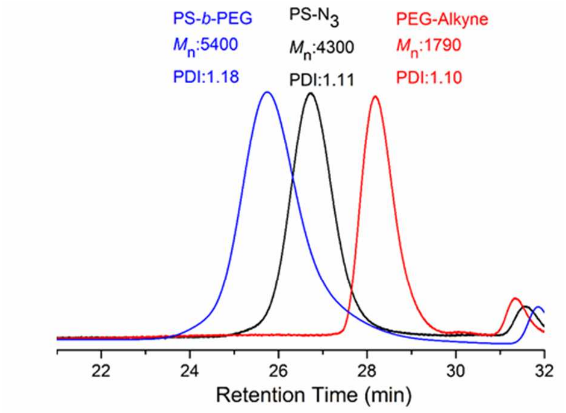
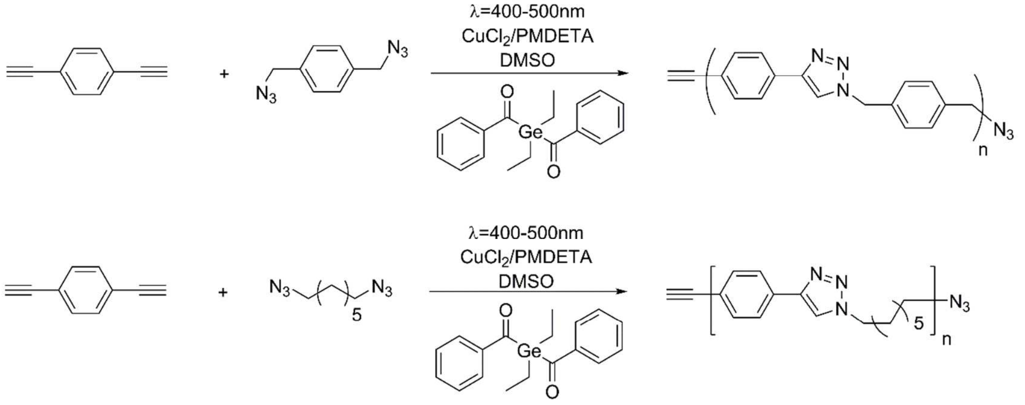


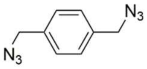
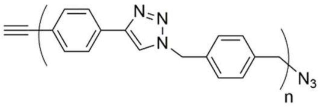
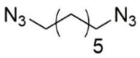
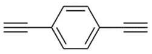
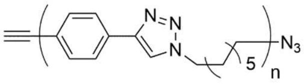
Fig. 3 GPC traces of PEG-Alkyne, PS-N_3 and PS-*b*-PEG.

Based on the related investigations dealing with organogermane compounds, Scheme 4 shows the photoinduced redox approach, in which DBDEG photoinitiator was used as an oxidant to activate the click reaction. The first step concerns the α-cleavage of the DBDEG to yield benzoyl and benzogermyl radicals. Because of the electron withdrawing nature of the carbonyl group, the possibility of the benzoyl radical to undergo a redox reaction with Cu(II) can be excluded.[39, 70, 73, 74] The benzogermyl radical on the other hand reduces the Cu(II) species to Cu (I), which is responsible for the CuAAC reaction. In addition, the benzogermyl radical formed is also known to undergo a further fragmentation to form diethylgermyl radical also capable of reducing Cu(II) to Cu(I).

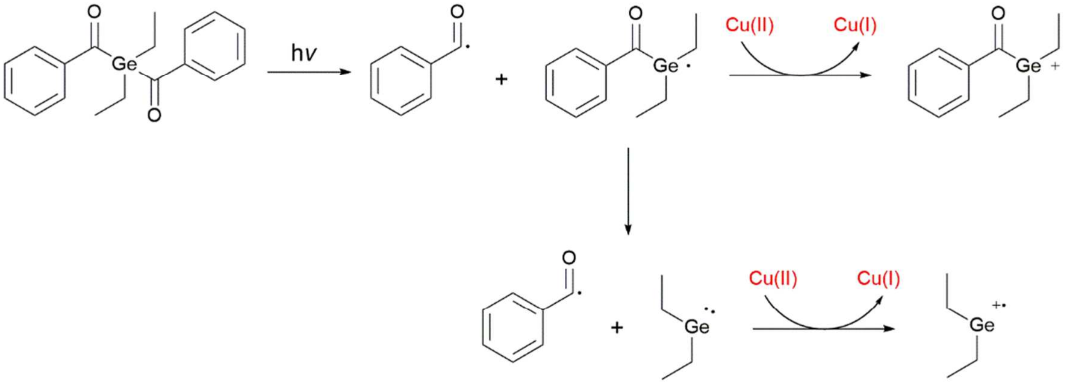


Scheme 3 Syntheses of step-growth polymers via photoinduced CuAAC click reaction.

Table 4 Photoinduced step-growth polymerizations[a] using DBDEG and the molecular weight characteristics of the polymers obtained.

Azide Compound	Alkyne Compound	Polymer	Conv (%)[b]	$M_{n,GPC}$[c] (g·mol^{-1})	PDI[c]
			~97	107000	1.45
			~96	83650	2.05

[a] All reactions were carried out in schlenk tube under irradiation at 400–500 nm with a light intensity of 45 mW cm^{-2} at room temperature in the presence of $CuCl_2$ and PMDETA. Reaction time: 24 h. The polymers were precipitated in methanol. [b] Determined gravimetrically [c] Determined by GPC, according to polystyrene standards.



Scheme 4 Photochemical generation of Cu(I) by DBDEG photoinitiator.

Conclusions

DBDEG photoinitiator was proven to be significantly efficient promoter for the photoinduced CuAAC click reactions of model organic compounds in the visible range. This system was also applicable to various macromolecular reactions including polymer end-group functionalization, block copolymer formation and step-growth polymerization with the use of appropriate azide and alkyne click components. All the DBDEG promoted reactions showed almost quantitative efficiency. The success of the click reactions is due to the visible light generation of germyl radicals capable of reducing Cu(II) species to Cu(I) species to catalyze the coupling of the azide and alkyne groups. This protocol can easily be implemented in the biological and material sciences particularly when surface patterning and incorporation of specific groups are required as visible light is used to induce the click reaction.

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For Graphical Abstract Only

The highly active, versatile and visible light-responsive system for CuAAC click reaction using dibenzoyldiethylgermane photoinitiator with Cu(II) has been developed.