



## Light Induced Polyethylene Ligation

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Complete List of Authors:	Offenloch, Janin; Karlsruher Institut für Technologie, Norsic, Sébastien; CNRS, UMR5265 C2P2 - LCPP Team Mutlu, Hatice; Karlsruhe Institute of Technology (KIT), Soft Matter Synthesis Laboratory, Institut für Biologische Grenzflächen (IBG); Taam, Manel; CNRS, UMR5265 C2P2 - LCPP Team Boyron, Olivier; Chimie Catalyse Polymères et Procédés Boisson, Christophe; CNRS / University of Lyon, Chemistry D'Agosto, Franck; Chimie Catalyse Polymères et Procédés, Barner-Kowollik, Christopher; Queensland University of Technology, School of Chemistry, Physics and Mechanical Engineering; Karlsruhe Institute of Technology, Institut für Technische Chemie und Polymerchemie



# Polymer Chemistry

## COMMUNICATION

### Light Induced Polyethylene Ligation

Janin T. Offenloch,<sup>a,b</sup> Sébastien Norsic,<sup>c</sup> Hatice Mutlu,<sup>a,b</sup> Manel Taam,<sup>c</sup> Olivier Boyron,<sup>c</sup> Christophe Boisson,<sup>c</sup> Franck D'Agosto,<sup>\*c</sup> and Christopher Barner-Kowollik<sup>\*a,b,d</sup>

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**We introduce a photoreactive polyethylene (PE) derivative, which upon light irradiation ( $\lambda_{\text{max}} = 365 \text{ nm}$ ) can effectively react to form well-defined block copolymers with polystyrene and poly(methyl methacrylate). The herein introduced synthetic technology provides challenging to access polyethylene architectures based on a rapid and catalyst free photochemical ligation concept.**

Without any doubt, polyethylene (PE) is one of the most dominant thermoplastics in industrial chemistry. By virtue of its outstanding chemical and physical characteristics, e.g., chemical resistance, ductility and insulator properties, as well as low cost of manufacture in combination with facile processing characteristics, PE is found in many materials used in our daily life. Well-defined polyethylene chains are now accessible by ethylene catalytic polymerisation based on the development of a pseudo living polymerization of ethylene relying on the catalysed chain growth (CCG) concept. Similarly to the RAFT process for controlled radical polymerisation,<sup>1–3</sup> CCG is based on the establishment of reversible chain transfer reactions between an active metal centre and a main group metal centre.<sup>3–8</sup> One of the compelling benefits of CCG<sup>9</sup> is the efficient preparation of functional PEs,<sup>10</sup> which typically presents an extreme challenge: Due to the nucleophilicity of the carbon atom in  $\text{M(PE)}_x$  obtained in polyethylene CCG systems (M represents the main group metal used for polymerization, e.g. magnesium with  $x = 2$ ), a broad range of

various functional groups can be tethered to the termini of the PE chains, including e.g., iodo,<sup>11</sup> azido,<sup>11</sup> amino,<sup>11</sup> hydroxy,<sup>12</sup> thiol,<sup>13</sup> vinyl,<sup>14</sup> and recently phosphonic acid end groups,<sup>15</sup> directly after polymerization utilizing simple synthetic steps. Indeed, PE has already been equipped with functional end groups that can serve as control transfer agents, initiators or monomers for polymerizations,<sup>16</sup> and respective modular functionalities for block copolymer formation.<sup>17,18</sup> Thus, the long existing paradigm that PEs are non-functional entities is being effectively altered.

In soft matter science, it is critical for a wide range of applications to design hybrid materials which combine the macroscopic properties of covalently connected blocks (or segments) of polymers. The synthesis of block copolymers is often accomplished *via* the ligation of preformed homopolymers by coupling two polymeric chains at their respective ends *via* orthogonal and efficient coupling reactions.<sup>19–23</sup> Among them, photochemically driven reactions feature the advantages of often being fast and quantitative under equimolar reaction conditions at ambient temperature in the absence of any catalysts, sometimes even fulfilling the criteria of click reactions.<sup>24–26</sup> Polyethylene ligation can critically benefit from these advantages, too. Once shown that PE can be equipped with photoreactive functionalities as those exploited herein, the step to photochemical patterning onto solid substrates for interface design in arbitrary patterns using (laser) lithography techniques, is opened.<sup>27</sup> It may also become possible to exploit polyethylene strands in photoresist systems during 3D laser lithography.<sup>28</sup>

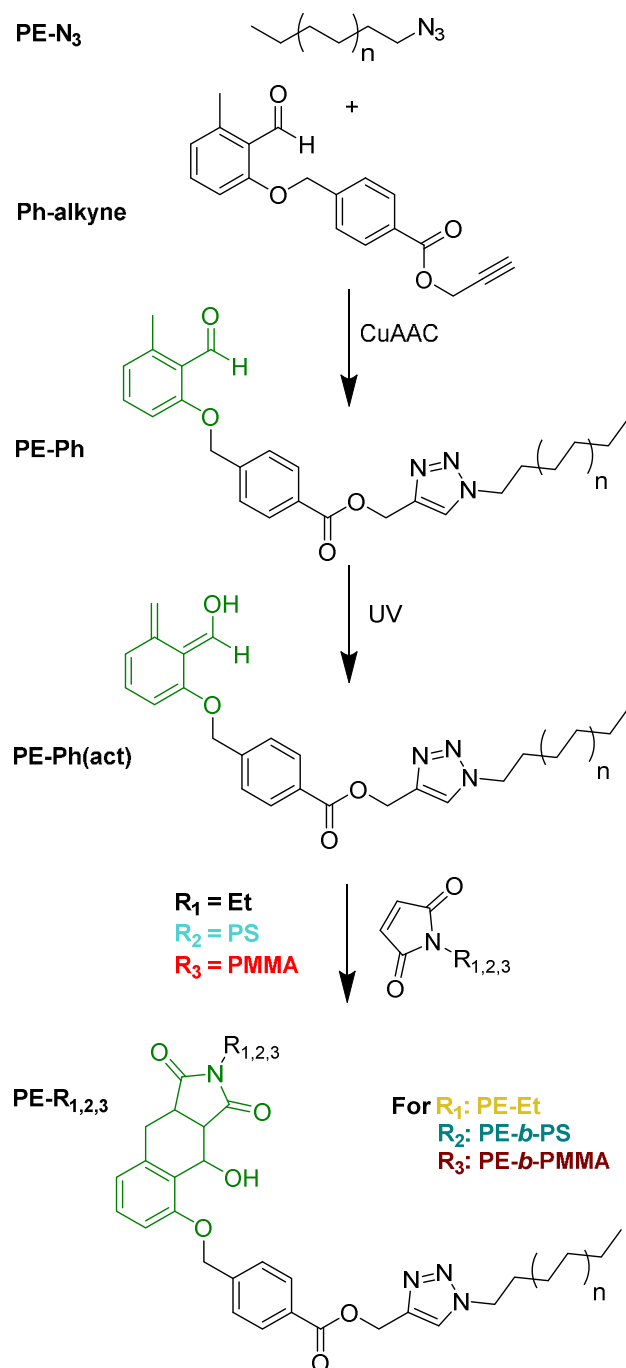
<sup>a</sup>Macromolecular Architectures, Institut für Technische Chemie und Polymerchemie, Karlsruhe Institute of Technology (KIT), Engesserstr. 18, 76128 Karlsruhe, Germany.

<sup>b</sup>Soft Matter Synthesis Laboratory, Institut für Biologische Grenzflächen, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Karlsruhe, Germany.

<sup>c</sup>Université de Lyon, Université Lyon 1, CPE Lyon, CNRS UMR 5265, Laboratoire C2P2, Equipe LCP2, 69616 Villeurbanne CEDEX, France. franck.dagosto@univ-lyon1.fr

<sup>d</sup>School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology (QUT), 2 George Street, QLD 4000, Brisbane, Australia. christopher.barnerkowollik@qut.edu.au

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In the current contribution, we move the synthesis of PE containing soft matter materials a critical step forward by fusing polyethylene synthesis with photochemistry, *via* the functionalization of a PE species with a photo-caged diene (i.e. *o*-methyl-benzaldehyde), a well-established photochemistry in polymer science,<sup>26,29,30</sup> by a copper(I) catalyzed azide alkyne cycloaddition (CuAAC). The photoreactive unit forms a highly reactive *cis*-diene (termed photoenol, see **PE-Ph(act)**) upon irradiation with UV light ( $\lambda_{\text{max}} = 365 \text{ nm}$ ) able to react with electron deficient double bonds in a Diels-Alder cycloaddition.<sup>29,31,32</sup> We establish the reactivity of the

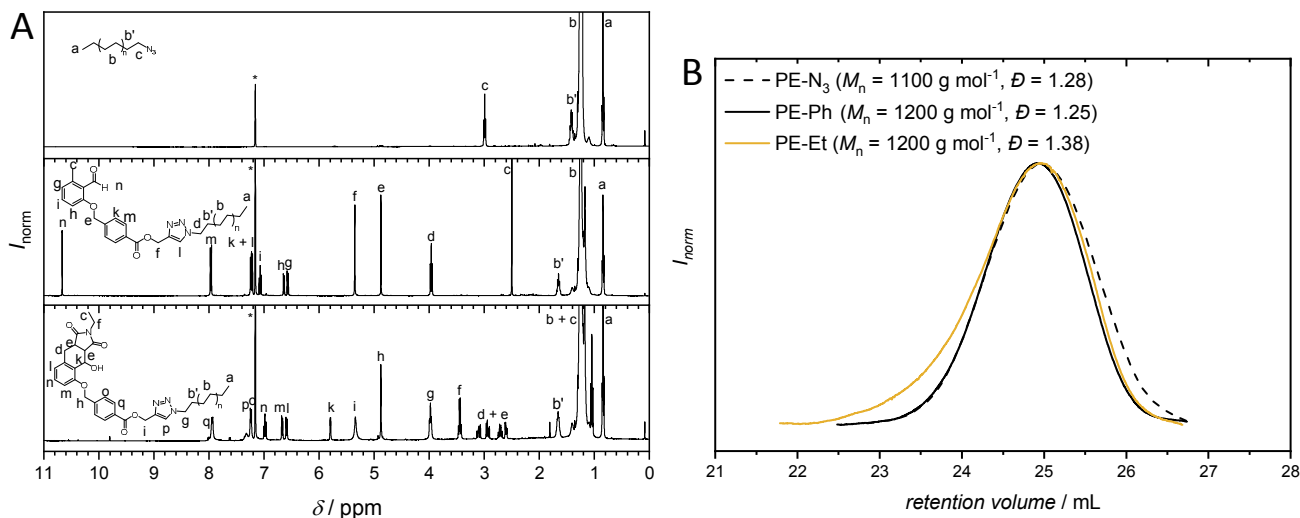
photoreactive PE species (**PE-Ph**) initially in a model reaction system, utilizing a small molecule maleimide species. Consequently, we synthesize one polystyrene (**PS**) and one poly(methyl methacrylate) (**PMMA**) polymer block capped with maleimide moieties *via* atom-transfer radical polymerization (ATRP). The respective polymer segments were subsequently reacted with the *o*-methyl-benzaldehyde capped PE derivative under UV light conditions to afford the targeted block copolymers (refer to **Scheme 1**). All synthetic steps were evidenced by detailed nuclear magnetic resonance (NMR) spectroscopy and high temperature size exclusion chromatography (SEC).

For the efficient modification of PE with the photoreactive group, a PE precursor equipped with an azide end group (**PE-N<sub>3</sub>**) was synthesized for subsequent conversion in a copper(I) catalyzed azide-alkyne cycloaddition (CuAAC). Specifically, ethylene was polymerized *via* Catalyzed Chain Growth (CCG) employing the complex  $[(\text{C}_5\text{Me}_5)_2\text{NdCl}_2\text{Li}(\text{OEt}_2)_2]$  in combination with BuMgOct.<sup>11</sup> The respective end group was introduced by adding iodine to the polymerization mixture leading to PE-I, which was consequently converted to **PE-N<sub>3</sub>** *via* a substitution reaction utilizing  $\text{NaN}_3$  (refer to the Experimental Procedures section in the Supporting Information for synthetic details).<sup>11</sup> The high-temperature (HT) SEC trace of **PE-N<sub>3</sub>** obtained using trichlorobenzene (TCB) as eluent at  $150^\circ\text{C}$  (refer to Figure 1B), indicates a monomodal distribution, and further evaluation on the basis of a PE calibration suggests a number-average molar mass ( $M_n$ ) of  $1100 \text{ g mol}^{-1}$  and a dispersity ( $\mathcal{D}$ ) of 1.28. In the HT  $^1\text{H}$  NMR spectrum of **PE-N<sub>3</sub>** in  $\text{C}_6\text{D}_6$ /tetrachloroethylene (TCE) at  $90^\circ\text{C}$  (refer to Figure 1A), magnetic resonances associated with the methylene group adjacent to the azide unit at 3.00 ppm and the methylene adjacent to the previous one at 1.47 ppm can be detected. The polymer backbone resonances can be identified in the range between 1.55 and 0.95 ppm. Furthermore, the  $\text{CH}_3$  end group is visible at 0.84 ppm. The in-depth analysis of the HT  $^1\text{H}$  NMR spectrum with regard to the  $\beta$ -H elimination reaction indicates only 5 % unsaturated, i.e. not functionalized polymer chains.

The post-polymerization functionalization reactions of PE usually require elevated temperatures, and the isolated products are typically characterized via HT SEC as well as HT NMR spectroscopy, making the thermostable *o*-methyl-benzaldehydes as photoreactive anchors an ideal choice for the functionalization of PE. The synthesis of the photoreactive group (**Ph-alkyne**), depicted in the Supporting Information section, was accomplished via multiple steps.

Subsequently, 1.0 eq. of **PE-N<sub>3</sub>** and 1.29 eq. of **Ph-alkyne** were reacted in a CuAAC employing a toluene-dimethylformamide mixture as solvent (toluene:DMF = 7:3) utilizing  $\text{CuSO}_4$ -sodium ascorbate as the catalytic system. After stirring at  $100^\circ\text{C}$  for three days, the modified polymer was isolated by adding methanol to the reaction mixture and subsequent filtration of the precipitate. The HT SEC analysis of the parent **PE-N<sub>3</sub>** and the resulting **PE-Ph** ( $M_n = 1200 \text{ g mol}^{-1}$ ,  $\mathcal{D}$  of 1.25, refer to Figure 1B) are similar, demonstrating the defined nature of the generated functionalized PE and the lack of detrimental effects

**Scheme 1** The photoreactive PE species PE-Ph was synthesized *via* CuAAC with PE-N<sub>3</sub>. By irradiation with UV light ( $\lambda_{\text{max}} = 365 \text{ nm}$ ), the *o*-methyl-benzaldehyde converts into a highly reactive diene species (PE-Ph(act)), which reacts with maleimides in a Diels-Alder cycloaddition resulting in PE block copolymer structures.



**Figure 1** A: HT  $^1\text{H}$  NMR spectra (400 MHz,  $\text{C}_6\text{D}_6/\text{TCE}$ , 90 °C) of **PE-N<sub>3</sub>** (top), **PE-Ph** (middle) and **PE-Et** (bottom) confirming the successful synthesis of the photoreactive PE species and its ability to react in Diels-Alder cycloadditions upon UV irradiation. B: SEC (TCB, 150 °C, RI) traces of the same polymer species.

associated with the end group modification at high temperature. The efficient tethering of the reactive moiety is additionally confirmed by HT  $^1\text{H}$  NMR analysis; the respective spectrum is depicted in Figure 1A. The magnetic resonance of the methylene group adjacent to the azide group is no longer detectable, while new resonances for the methylene group next to the triazole linkage at 3.96 ppm and next to this methylene at 1.66 ppm are identified. Further, the resonance of the aromatic proton of the triazole ring at 7.25 ppm confirms the successful product formation. Additional characteristic magnetic resonances associated with the skeleton of the *o*-methyl-benzaldehyde are present at 10.67 and 5.35 ppm, respectively for the aldehyde proton and the methylene group next to the ether bond.

Once the synthetic route to the photoreactive **PE-Ph** was established, a UV light triggered model reaction with 5.0 eq. of *N*-ethyl maleimide was conducted. Specifically, after heating the reactants in a 1:1 mixture of toluene and acetonitrile to 100 °C, the solution was irradiated with a compact UV lamp for one hour (Philips PL-L cleo, 36 W, refer to the Supporting Information for the emission spectrum). In order to keep the reactants in solution, the mixture was again heated to 100 °C after one hour of irradiation. Following five heating-irradiation cycles, the modified polymer was obtained *via* precipitation in methanol. Whereas the HT SEC analysis ( $M_n = 1200 \text{ g mol}^{-1}$ ,  $\mathcal{D}$  of 1.38, refer to Figure 1B) does not show a clear increase in the apparent molecular mass, the HT  $^1\text{H}$  NMR spectrum (Figure 1A) confirms the successful formation of the cycloadduct. A magnetic resonance for the proton of the secondary alcohol of the cycloadduct is detectable at 5.80 ppm, while the other resonances of the protons associated with the formed cyclohexane ring are multiplets (due to isomers) in the range of 3.13 and 2.59 ppm. Importantly, the resonances associated

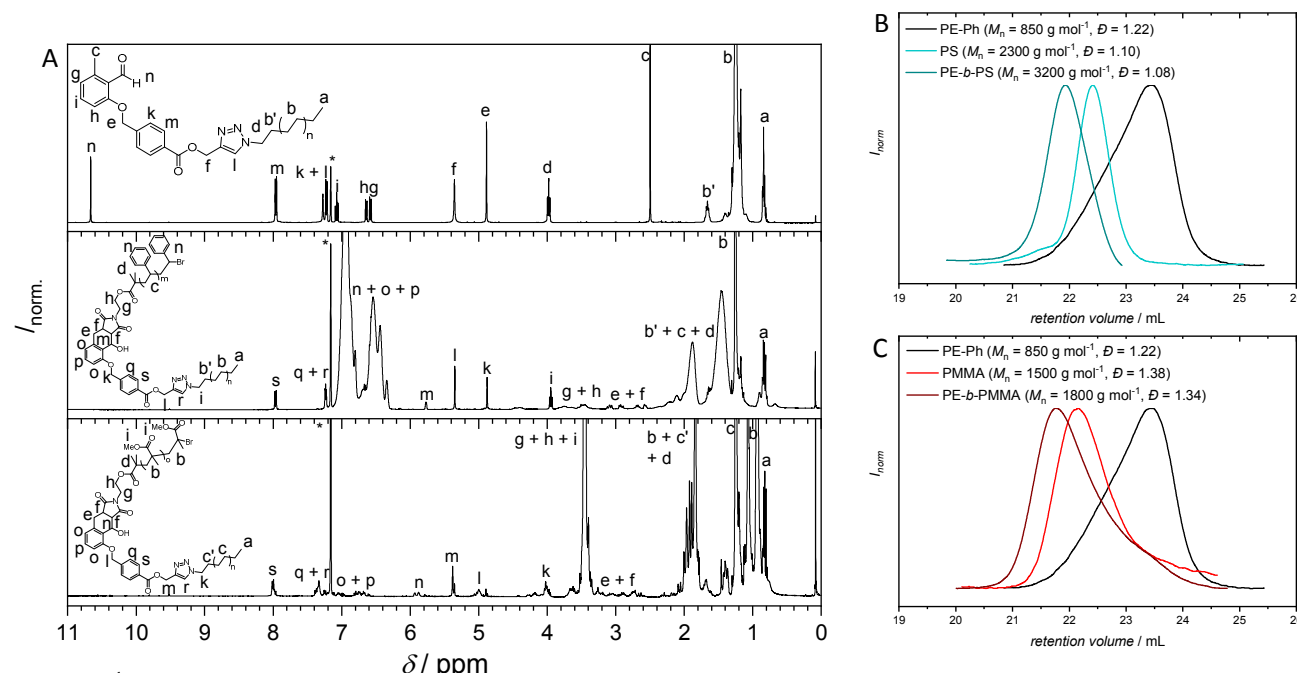
with the proton of the aldehyde functional group at 10.67 ppm vanished.

In order to establish the efficiency of the reaction conditions, block copolymer formation using **PE-Ph** in equimolar ratios was carried out. Two different counter blocks were synthesized employing atom-transfer radical polymerization (ATRP) with a furane-protected maleimide initiator, ensuring a high end group fidelity (for details of the polymerization, refer to the Experimental Procedures section in the Supporting Information).<sup>33</sup> After removal of the protecting group of the end group utilizing high temperature under high vacuum, one polystyrene species (HT SEC results: **PS**:  $M_n = 2300 \text{ g mol}^{-1}$ ,  $\mathcal{D} = 1.10$ , refer to Figures S5 and 2B for SEC traces) and one PMMA block were isolated (**PMMA**:  $M_n = 1500 \text{ g mol}^{-1}$ ,  $\mathcal{D} = 1.38$ , refer to Figure S5 and 2C for SEC trace), all featuring a reactive maleimide unit for the subsequent photoreaction.

In the light of the successful model reaction, the block copolymer formation was conducted utilizing an equimolar ratio of **PE-Ph** and one of the maleimide functional polymer blocks. The HT SEC traces of the block copolymers compared to the starting **PE-Ph** are shifted to lower retention volumes indicating a clean increase of molecular weight. Employing a PE calibration, the apparent molecular weight increases by  $2300 \text{ g mol}^{-1}$  for **PE-*b*-PS** and  $900 \text{ g mol}^{-1}$  for **PE-*b*-PMMA**, respectively (**PE-*b*-PS**:  $M_n = 3200 \text{ g mol}^{-1}$ ,  $\mathcal{D} = 1.08$ , **PE-*b*-PMMA**:  $M_n = 1800 \text{ g mol}^{-1}$ ,  $\mathcal{D} = 1.34$ , refer to Figure 2B and 2C for SEC traces). The increase in the apparent molecular weight is in agreement with the HT SEC analysis of **PS** and **PMMA** based on the PE calibration. In-depth evaluation of the HT  $^1\text{H}$  NMR spectra of **PE-*b*-PS** and **PE-*b*-PMMA** (refer to Figure 2A) elucidates the structural composition of the respective blocks, which is in excellent agreement with the results of the model reaction with *N*-ethyl maleimide (refer to Figure 1A). The resonance of the proton of the aldehyde at 10.67 ppm is not

detected in the HT  $^1\text{H}$  NMR spectra of the block copolymers, while resonances of the proton of the secondary alcohol at 5.78 for **PE-*b*-PS** and at 5.90 ppm for **PE-*b*-PMMA** along with the residual resonances for the protons of the Diels-Alder cyclohexane adduct in the range of 3.14 to 2.54 ppm are visible. In addition, integration of the noted resonances is in good agreement with each other and with the integral of the individual backbone resonances (refer to Table S7 in the

different block copolymers (**PE-*b*-PS** and **PE-*b*-PMMA**) via the UV light triggered ligation of polymer strands. Our current study thus opens a unique avenue to photoreactive polyethylenes that cannot only be employed as building blocks for block copolymer formation but additionally hold promise for spatially resolved surface polyethylene surface design by photochemical means.



**Figure 2** A: HT  $^1\text{H}$  NMR spectra (400 MHz,  $\text{C}_6\text{D}_6/\text{TCE}$ , 90  $^\circ\text{C}$ ) of **PE-Ph** (top), **PE-*b*-PS** (middle) and **PE-*b*-PMMA** (bottom). B: SEC (TCB, 150  $^\circ\text{C}$ , RI) traces of **PE-Ph**, **PS** and **PE-*b*-PS** and C: SEC (TCB, 150  $^\circ\text{C}$ , RI) traces of **PE-Ph**, **PMMA** and **PE-*b*-PMMA** confirming the successful synthesis of the block copolymers due to a shift to lower retention volumes.

Supporting Information).

To further highlight the thermal stability of the resulting block copolymers, i.e. **PE-*b*-PS**, thermal stability studies were performed. HT SEC analyses of **PE-*b*-PS** were carried out after dissolution of the copolymer in TCB at 80 or 150  $^\circ\text{C}$  during different times (Figure S6). The traces obtained indicate monomodal distributions, the shape of which is not altered, indicating that the block copolymers are stable for analysis in TCB up to 24 h confirming all HT SEC results from **PE-Ph** and the block copolymers.

## Conclusions

In summary, we critically expanded the field of polyethylene chemistry by introducing photoreactive polyethylene building blocks. By exploiting the temperature stable nature of *o*-methyl-benzaldehydes a suitable photoreactive anchor was identified and tethered via CuAAC addition to low dispersity **PE-*N*<sub>3</sub>**. The reactivity of **PE-Ph** in the UV light triggered cycloaddition was initially established in a model reaction employing a small molecule, i.e. *N*-ethyl maleimide. The optimized conditions were adopted for the synthesis of two

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## Conflicts of interest

There are no conflicts to declare.

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