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# Graft polymer growth using tandem photoinduced photoinitiator-free CuAAC/ATRP†

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In this work, we describe the use of the one-pot, photoinduced but photoinitiator-free combined copper-catalyzed azide–alkyne click cycloaddition (CuAAC) and atom-transfer radical polymerization (ATRP) protocol to provide a graft copolymer of polystyrene-*g*-poly(methyl methacrylate) (PS-*g*-PMMA) in desirable conversion and polydispersity. Poly(styrene-*co*-4-chloromethylstyrene) (poly(S-*co*-4-CMS)) was prepared using nitroxide mediated polymerization (NMP). The benzylic chloride functional groups of poly(S-*co*-4-CMS) were substituted for azide functional groups using a conventional azidation procedure to provide poly(styrene-*co*-4-azidomethylstyrene) (poly(S-*co*-4-AMS)). Poly(S-*co*-4-AMS) was then used as the backbone of the graft copolymer. The alkyne-bearing ATRP initiator propargyl 2-bromoisobutyrate (PgBiB) could then be grafted to the backbone *via* photoinduced CuAAC, while meanwhile initiating in tandem the poly(methyl methacrylate) (PMMA) chain growth *via* the ATRP mechanism. The graft polymer was provided in good conversion and polydispersity and was characterized appropriately using <sup>1</sup>H NMR, FT-IR and GPC.

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## Introduction

Radical polymerization is used on an industrial scale for the manufacture of various polymeric materials.<sup>1</sup> Controlled/living radical polymerization (CLRP) has turned out to be one of the best approaches to provide polymers with low molecular weight dispersity, well defined polymer architecture and reliable end-group functionality.<sup>2–7</sup> Transition metal catalysed atom transfer radical polymerization (ATRP) is most typically catalysed by a Cu(I)/ligand catalytic system and has almost become a standard operating procedure in polymer chemistry for obtaining uniform polymers using monomers such as styrenes, acrylates and methacrylates, among others.<sup>8–10</sup> Other CLRP methods worthy of mention of course are reversible addition-fragmentation chain transfer polymerization (RAFT) and nitroxide-mediated radical polymerization (NMRP), which have proven invaluable in producing well defined polymer structures.<sup>2,5</sup>

Recently, there has been a growing interest in the field in developing external control of initiation and growth of the CLRP reaction.<sup>11–13</sup> The group of Matyjaszewski has superbly

described their approach of using electrochemistry in order to control the various parameters of a living radical polymerization. By applying an electrochemical potential across the polymerization process, they showed that the activation–deactivation process *via* the catalysing copper species could be controlled in real time. Apart from this excellent approach, the use of light has shown great promise towards the attainment of external control over the ATRP processes while providing excellent conversion and low polydispersity, with groups such as those of Hawker, Macmillan, Yoon and Stephenson providing vital contributions in this area.<sup>14–17</sup>

Traditionally, photochemical methods have been widely applied in polymerization processes in industry in the sectors of coatings, inks, and adhesives. They are now gaining more popularity for their use in the production of more advanced technologies such as optoelectronics and nanotechnology.<sup>18</sup> Most commonly, the initiation of photopolymerization is carried out using photoinitiators; light-absorbing small molecules that undergo a photochemical process upon light absorption which results in the initiation of the polymerization reaction. These photoinitiators are varied and divided into sub-classes according to the nature of how initiation takes place. The use of UV and visible light irradiation for the *in situ* generation of activators for the photoinduced ATRP reaction has been researched extensively.<sup>19–27</sup> In our group, we have reported pioneering work describing photoinitiator-free photoinduced ATRP systems. We have shown that at room temperature under UV/VIS light irradiation the ATRP CuBr<sub>2</sub>/PMDETA catalyst underwent reduction to a Cu(I) complex system which

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was able to initiate and propagate the polymerization of acrylate monomers.<sup>28,29</sup> During the process the deactivating CuBr<sub>2</sub>/PMDETA complex was shown to reform but could be continually reduced by the applied radiation to continue the polymerization. This process is in continual development and the group of Haddleton has most recently described excellent results with low polydispersity and high conversion when polymerizing acrylate monomers in a photoinitiator-free ATRP system, while employing a CuBr<sub>2</sub>/Me<sub>6</sub>TREN catalyst.<sup>30</sup> The group of Rainer Jordan has shown that using a simple household fluorescent lamp the photoinduced ATRP polymerization of MMA can be carried out with a good “living” nature. They proved this system’s applicability towards the preparation of homogeneous, patterned and block copolymer brushes.<sup>26</sup>

The use of so-called click chemistry<sup>31</sup> has become widespread and indispensable as a tool for the functionalization and preparation of complex architectures in the macromolecular and polymer sciences.<sup>32–34</sup> Some of the best known and most potent examples of click chemistry include the Diels–Alder cycloaddition,<sup>35</sup> thiol–ene<sup>36</sup> and the copper catalysed azide–alkyne cycloaddition (CuAAC).<sup>37</sup> CuAAC, first described by Meldal and coworkers,<sup>38</sup> is a highly applied reaction system employed across all fields of biology and chemistry.<sup>37</sup> Like the ATRP system, CuAAC also takes advantage of a Cu(I) catalytic system, in this case to yield substituted 1,2,3-triazoles most usually in excellent yields with little or no side products. The photoinduced CuAAC is now becoming a rigorously investigated transformation. Similar to the ATRP process, an air-stable Cu(II) complex such as CuCl<sub>2</sub> is employed in conjunction with or without a photosensitive reducing agent in the presence of an alkylamine ligand such as PMDETA and light,<sup>39–43</sup> which results in the formation of a Cu(I) complex, which has been shown to carry out the CuAAC transformation in desirable yield and purity. Several different methods have been reported to date that affect the reduction of Cu(II) to Cu(I) giving rise to effective CuAAC reactions. These methods include the use of photochemically generated free radicals and excited polynuclear aromatic compounds, which facilitate the electron-transfer, such as that developed in our group.<sup>44</sup> In addition, the use of Cu(II) complexes bearing acylphosphinate counter ions to initiate both ATRP and CuAAC has recently been described by the group of Bowman.<sup>45</sup>

CuAAC is also much praised for its orthogonality, wherein functional groups that do not pertain to the intended reaction process, do not interfere with the reaction. This is surely self-evident and inherent to the fact that few side reactions take place, but it also allows for one-pot systems involving two or more reactions to take place sequentially or simultaneously including the CuAAC. This allows for interesting and useful polymer architectures to be formed in a one step process. Recently, our group has published such work whereby the photoinduced CuAAC was combined in a sequential fashion with a photoinduced thiol–ene click reaction to provide an *N*-acetyl-L-cysteine end functionalized poly (methylmethacrylate)-*b*-poly(caprolactone) block copolymer, which was applied successfully as a matrix for cell culturing.<sup>46</sup> The photoinitiating

systems for the photoinduced CuAAC and ATRP reactions been have shown to be comparable and compatible.<sup>47</sup> And thus, our group has shown that a combined one-pot photoinduced ATRP and CuAAC protocol could be used to prepare AB block copolymers.<sup>48</sup> Here, in the same line of research, we expand the scope of the one-pot approach applying combined photoinitiator-free, photoinduced ATRP and CuAAC systems towards obtaining a graft polymer in good conversion and polydispersity. Graft polymers can be deemed useful for their roles as stabilizers,<sup>49,50</sup> compatibilizers<sup>51,52</sup> and surfactants.<sup>53,54</sup> Previous work by Yoshida has described the preparation of polystyrene-*g*-poly(methyl methacrylate) (PS-*g*-PMMA) using photo-NMRP.<sup>55</sup> The work herein contributes to the expansion of the methodology available to polymer chemists towards graft polymer preparation by demonstrating the synthesis of PS-*g*-PMMA using tandem photoinduced photoinitiator-free CuAAC/ATRP.

## Experimental

### Materials

Styrene (Sigma-Aldrich Corp., Munich, Germany, 99%) and 4-chloromethylstyrene (Acros Organics, Geel, Belgium, 90%) were passed through a basic alumina column to remove the inhibitor. The 2,2,6,6-tetramethylpiperidine-*N*-oxyl free radical (TEMPO) (99%, Aldrich) was used as received. 1,1'-Azobis(cyclohexanecarbonitrile) (VAZO) as the initiator was recrystallized from methanol. Propargyl alcohol (99%, Aldrich), triethylamine (99.5%, Fluka), 2-bromoisobutryl bromide (98%, Aldrich) were used as received. *N,N,N,N,N*-Pentamethyldiethylenetriamine (PMDETA; 99%, Aldrich), used as a ligand, was distilled before use. Sodium azide (99%, Aldrich) and copper(II) chloride (98%, Aldrich) were used as received. Methyl methacrylate (MMA, 99%, Aldrich) was filtered over basic Al<sub>2</sub>O<sub>3</sub> to remove the inhibitor. Dichloromethane was distilled over CaH<sub>2</sub> before use. Toluene and dimethylformamide were dried over 4 Å sieves before use.

### Characterization

<sup>1</sup>H NMR and <sup>13</sup>C NMR of the intermediates and final polymers, dissolved in CDCl<sub>3</sub> with Si(CH<sub>3</sub>)<sub>4</sub> as an internal standard, were recorded at room temperature at 500 MHz on an Agilent VNMR5 500 spectrometer. FT-IR spectra were recorded on a Perkin-Elmer FT-IR Spectrum One spectrometer with an ATR Accessory (ZnSe, PikeMiracle Accessory) and a cadmium telluride (MCT) detector. The resolution was 4 cm<sup>-1</sup> and 24 scans were performed with a 0.2 cm s<sup>-1</sup> scan speed. Molecular weights and polydispersities of the polymers and the block copolymer were measured using gel permeation chromatography (GPC) employing an Agilent 1100 instrument equipped with a differential refractometer using THF as the eluent at a flow rate of 0.3 ml min<sup>-1</sup> at 30 °C. Molecular weights were determined using polystyrene standards.

### Synthesis of propargyl 2-bromoisobutyrate (PgBiB)

Propargyl alcohol (0.451 mL, 7.355 mmol) and triethylamine (1.230 mL, 8.826 mmol) were dissolved in 5 mL of DCM and stirred in a 50 mL flame-dried round-bottom flask under nitrogen at 0 °C. To the reaction mixture was slowly added 2-bromoisobutyryl bromide (1.000 mL, 8.090 mmol) over 10 min. It was allowed to stir for 28 h slowly warming up, before water was added and it was extracted with DCM (2 × 20 mL). The organic fractions were combined, dried over MgSO<sub>4</sub> and the solvents were removed *in vacuo*. Pure product (1.206 g, 80%) was obtained as a colourless non-viscous oil after purification using flash column chromatography (SiO<sub>2</sub>, hexane–EtOAc, 80:20). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm, TMS): 4.71 (2H, –CH<sub>2</sub>O–), 2.47 (1H, C≡CH), and 1.90 (6H, (CH<sub>3</sub>)<sub>2</sub>C). IR (ν<sub>max</sub>): 3296 (≡C–H), 2132 (C≡C), 1743 cm<sup>–1</sup> (C=O). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm, TMS): 170.91 (C=O), 76.88 (–C≡CH), 75.42 (–C≡CH), 54.91 (–CH<sub>2</sub>CO<sub>2</sub>–), 53.43 (–C(CH<sub>3</sub>)<sub>2</sub>Br), 30.65 (–C(CH<sub>3</sub>)<sub>2</sub>Br).

### Preparation of poly(styrene-*co*-4-chloromethylstyrene) (poly(S-*co*-4-CMS)).

Styrene (1.626 mL, 14.192 mmol) and 4-chloromethylstyrene (2.000 mL, 14.192 mmol), stirred in a flame-dried glass tube, were purged of O<sub>2</sub> by flushing with N<sub>2</sub> for 20 min. The vessel was opened for VAZO (0.005 g, 0.020 mmol) and TEMPO (0.008, 0.051 mmol) to be added before being sealed again with N<sub>2</sub> being blown over it for another 2 min. The vessel was heated to 120 °C and stirred for 28 h. It was removed from heat and allowed to cool before it was diluted with THF and precipitated into cold methanol, acidified with 1 glass Pasteur-pipette aliquot of HCl (37%). The precipitate was thereafter filtered and dried *in vacuo* to yield the polymer as a white solid (0.580 g, 16% conversion, *M*<sub>n</sub> = 13 600 g mol<sup>–1</sup>, *M*<sub>w</sub>/*M*<sub>n</sub> = 1.7). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm, TMS): 7.23–6.24 (aromatic PS H), 4.52 (–CH<sub>2</sub>Cl), 1.91–1.63 (–CH–), 1.58–1.25 (–CH<sub>2</sub>–). IR (ν<sub>max</sub>): 3075–2840 (Ar<sub>C–H</sub>), 1516–1419 (Ar<sub>C=C</sub>) cm<sup>–1</sup>. <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm, TMS): 125–129 (aromatic C), 46.07–46.34 (–CH<sub>2</sub>Cl), 44.72–42.00 (–CH<sub>2</sub>–), 40.36 (–CH–).

### Preparation of poly(styrene-*co*-4-azidomethylstyrene) (poly(S-*co*-4-AMS))

Poly(S-*co*-4-CMS) (0.580 g, 0.043 mmol) was stirred with sodium azide (0.469 g, 7.224 mmol) in DMF (10 mL) in a 50 mL round-bottom flask at 60 °C for 20 h. It was then allowed to cool before being precipitated in 150 mL cold methanol with one Pasteur-pipette aliquot of HCl (37%) added. The polymer was then filtered and dried under vacuum for 24 h before it was isolated (0.492 g, 79% conv., *M*<sub>n</sub> = 14 200 g mol<sup>–1</sup>, *M*<sub>w</sub>/*M*<sub>n</sub> = 1.7). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm, TMS): 7.23–6.24 (aromatic H), 4.25 (–CH<sub>2</sub>N<sub>3</sub>), 1.91–1.63 (–CH–), 1.58–1.25 (–CH<sub>2</sub>–). IR (ν<sub>max</sub>): 3075–2840 (Ar<sub>C–H</sub>), 2093 (large, N<sub>3</sub>), 1516–1419 (Ar<sub>C=C</sub>) cm<sup>–1</sup>. <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm, TMS): 125–129 (aromatic C), 54.60 (–CH<sub>2</sub>N<sub>3</sub>), 44.72–42.00 (–CH<sub>2</sub>–), 40.36 (–CH–).

### One-pot CuAAC/ATRP preparation of polystyrene-*g*-poly(methyl methacrylate) (PS-*g*-PMMA)

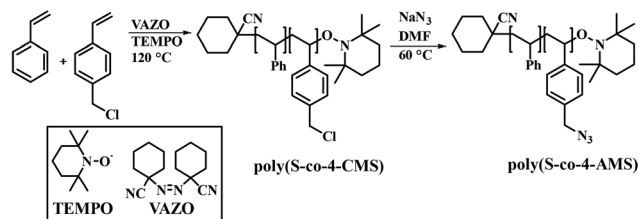
To a flame-dried glass tube under nitrogen were added poly-(S-*co*-4-AMS) (0.06 g, 0.004 mmol), PgBiB (0.034 mL, 0.0201 mmol), MMA (1.068 mL, 10.030 mmol), PMDETA (0.252 mL, 1.203 mmol) and DMF (1 mL). The contents of the glass tube were purged of oxygen by flushing with N<sub>2</sub> for 10 min, before CuCl<sub>2</sub> (0.054 g, 0.401 mmol) was added; then, N<sub>2</sub> was blown over the solution for another 2 min, before it was sealed and irradiated. The mixture was irradiated using a photoreactor (Rayonet) equipped with 16 lamps emitting light nominally at 350 nm at room temperature. The light intensity was 3.0 mW cm<sup>–2</sup>. After the given irradiation time was completed it was precipitated in excess cold MeOH and allowed to sit at –20 °C overnight. The following day, the graft polymer was filtered and isolated. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm, TMS): 7.59 (–C<sub>2</sub>H<sub>N<sub>3</sub></sub>–), 7.23–6.24 (aromatic PS H), 5.49–5.28 (ArCH<sub>2</sub>C<sub>2</sub>H<sub>N<sub>3</sub></sub>–), 5.16 (–CO<sub>2</sub>CH<sub>2</sub>C<sub>2</sub>H<sub>N<sub>3</sub></sub>–), 3.61 (CH<sub>3</sub>OC(O)–, PMMA), 2.10–1.82 (–CH<sub>2</sub>–, PMMA), 1.75 (–CH–, PS) 1.44 (–CH<sub>2</sub>–, PS) 1.03 (–CH<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>–, PMMA) 0.85 (–CH<sub>2</sub>C(CH<sub>3</sub>)CH<sub>2</sub>–, PMMA). IR (ν<sub>max</sub>): 3075–2840 (Ar<sub>C–H</sub>), 1730 (C=O), 1516–1419 (Ar<sub>C=C</sub>) cm<sup>–1</sup>. <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm, TMS): 176.82–178.07 (C=O), 142 (aromatic C<sub>q</sub>) 125–129 (aromatic CH), 52.66–54.44 (–CH<sub>2</sub>– (PMMA)), 51.81(–OCH<sub>3</sub>), 44.35–45.56 (–C(CH<sub>3</sub>)–), 16.29–18.71 (–CH<sub>3</sub>).

### PMMA chain extension of PS-*g*-PMMA

To a flame-dried glass tube fitted with a stirring bar were added PS-*g*-PMMA (0.1 g, 0.003 mmol), MMA (0.7 mL, 6.602 mmol), PMDETA (0.083 mL, 0.396 mmol) and DMF (0.7 mL). The mixture was sonicated to aid dissolution. It was purged of O<sub>2</sub> by flushing with N<sub>2</sub> for 10 min. CuCl<sub>2</sub> (0.018 g, 0.132 mmol) was then added to the reaction vessel and N<sub>2</sub> was blown over it for another 2 min, before the vessel was sealed and irradiated. It was irradiated for 3 h before it was precipitated in cold methanol. A glass Pasteur-pipette aliquot of HCl (aq. 37%) was added to the precipitation solution before being allowed to stand overnight at –20 °C. The precipitate was then filtered and isolated to yield the polymer as a white solid (0.494 g, 65% conv., *M*<sub>n</sub> = 56 700 g mol<sup>–1</sup>, PDI = 1.7).

## Results and discussion

Poly(styrene-*co*-4-chloromethylstyrene) (poly(S-*co*-4-CMS)) was prepared along standard NMP guidelines.<sup>56</sup> Chloromethyl styrene (CMS) and styrene in a 1 : 1 ratio were reacted with 1,1'-azobis(cyclohexanecarbonitrile) VAZO as the radical source, mediated by TEMPO, at a temperature of 120 °C for 28 h to yield the copolymer in 16% conversion with *M*<sub>n</sub> = 14 200 g mol<sup>–1</sup> and *M*<sub>w</sub>/*M*<sub>n</sub> = 1.7. The obtained copolymer was characterized using <sup>1</sup>H NMR and FT-IR. <sup>1</sup>H NMR revealed that the polymer had grown, with CMS and styrene incorporated in a ratio of 1.16 : 1. This was deduced by comparing the integration of the aromatic region between 6.26 and 7.37 ppm and



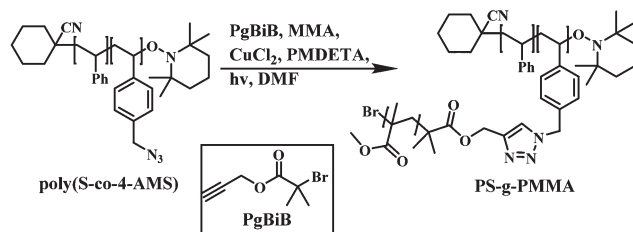
**Scheme 1** Preparation of poly(S-co-4-AMS) via NMP followed by azidation.

that of the peak at 4.52 ppm corresponding to the  $\text{CH}_2$  at the benzylic position of CMS, which was 9 : 2.4.

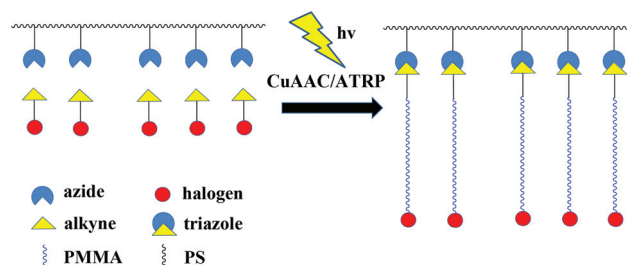
The benzylic chloride functionalities were substituted for azide functionalities using a standard azidation procedure, consisting of stirring the copolymer in DMF overnight at 60 °C with an excess of  $\text{NaN}_3$  to yield the azidated copolymer poly(styrene-co-4-azidomethylstyrene) (poly(S-co-4-AMS)), as shown in Scheme 1. Azidation could be confirmed by analysis of the FT-IR spectrum, whereby a great azide peak was observed at  $2093\text{ cm}^{-1}$ , as can be seen in Fig. 1. Also, the peak at 4.52 ppm, corresponding to benzylic protons, was entirely shifted upfield to 4.22 ppm, when analysing the  $^1\text{H}$  NMR spectrum.

The ATRP initiator PgBiB was prepared in a good yield (80%) after chromatography, by stirring propargyl alcohol with  $\alpha$ -bromoisobutyrylbromide in the presence of  $\text{Et}_3\text{N}$ , letting the solution warm up from 0 °C to room temperature overnight.<sup>57</sup> The prepared poly(S-co-4-AMS) was then used as the backbone for the growth of the polystyrene-g-poly(methyl methacrylate) (PS-g-PMMA) graft polymer in a one-pot, photoinitiator-free, photoinduced, tandem CuAAC/ATRP procedure, as outlined in Scheme 2.

The air-stable  $\text{CuCl}_2$  species, when employed in conjunction with PMDETA, forms a copper complex, wherein copper is



**Scheme 2** One-pot photoinduced CuAAC/ATRP procedure for the synthesis of PS-g-PMMA.

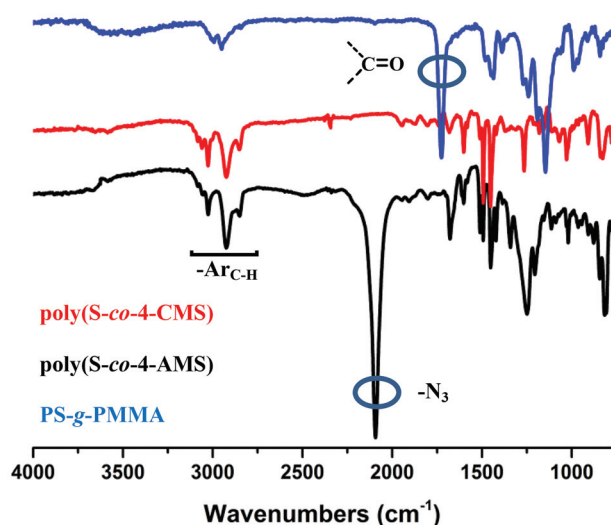


**Scheme 3** CuAAC coupling of PMMA chains, growing via ATRP, to the polystyrene backbone.

reduced to the CuAAC- and ATRP-active  $\text{Cu}(\text{I})$  species under light irradiation at  $>350\text{ nm}$ . By employing this methodology it was possible to click the PgBiB ATRP initiator to the polystyrene backbone using the CuAAC reaction while simultaneously initiating the poly(methyl methacrylate) (PMMA) ATRP chain growth (Scheme 3).

After 4 h of irradiation of the reaction system, the PS-g-PMMA graft polymer was obtained in good conversion (72%) with  $M_n = 62\,600\text{ g mol}^{-1}$  and  $M_w/M_n = 1.8$  (Table 1, entry 3). The polydispersity of the obtained graft polymer was slightly larger than that of the employed poly(S-co-4-AMS) backbone which was 1.7.

The formation of the bottle-brush graft polymer was confirmed using  $^1\text{H}$  NMR, as shown in Fig. 2. The aromatic triazole proton peak could be observed at 7.60 ppm as a broad signal. Broad signals belonging to the  $-\text{CH}_2-$  groups bound directly to the triazole functional groups, were observed between 5.1 and 5.5 ppm. A broad signal corresponding to the aromatic polystyrene protons was observed in the 6.2 to



**Fig. 1** FT-IR spectra of poly(S-co-4-CMS), poly(S-co-4-AMS) and PS-g-PMMA.

**Table 1** Conversions and molecular weight characteristics of PS-g-PMMA graft polymer with reaction time

Entry	Time (h)	Conversion (%)	$M_n^a$ ( $\text{g mol}^{-1}$ )	$\text{PDI}^a$
1	2	19	36 000	1.6
2	3	28	40 000	1.6
3	4	72	62 600	1.8
4 <sup>b</sup>	22	—	—	—
5 <sup>c</sup>	3	65	56 700	1.7

<sup>a</sup> Determined according to PS standards. <sup>b</sup> Polymer could not be recovered for analysis. <sup>c</sup> Chain extension test.



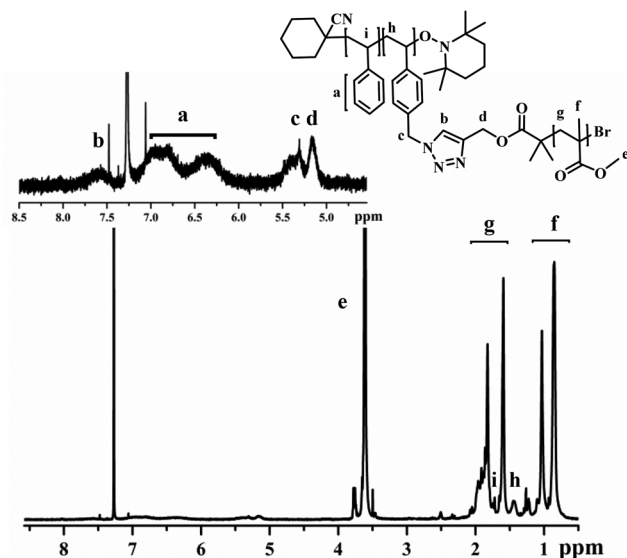


Fig. 2  $^1\text{H}$  NMR spectrum of PS-g-PMMA.

7.1 ppm region, and peaks corresponding to PMMA were distinguished further upfield. The characteristic PMMA methyl ester  $-\text{OCH}_3$  peak was found at 3.6 ppm, and the PMMA  $-\text{CH}_2-$  and  $-\text{CH}_3$  peaks were clearly distinguished in the 0.8 to 2.1 ppm region. Comparing the integration of the triazole-adjacent  $-\text{CH}_2-$  peaks (c/d) with the aromatic peaks (a), as shown in Fig. 2, it was found that they correspond exactly, as expected, to the quantitative CuAAC. This was inferred from the observed integration ratio of 8.31 : 4 with respect to the peaks a and c/d. The integration of the aromatic region a was supposed to be 8.31, due to the 1.16 : 1 incorporation of CMS with respect to styrene, which had been observed in the preparation of poly(S-co-4-CMS).

In the  $^{13}\text{C}$  NMR of PS-g-PMMA, the carbonyl peaks of the PMMA segments could be discerned between 176.82–178.07 ppm. The polystyrene backbone aromatic carbon peaks could be observed at 127–129 ppm and the quaternary aromatic carbons were found at 142 ppm. In the region of 52.66–54.44 ppm, methylene peaks, pertaining to PMMA, were detected. At 51.81 ppm, the methyl ester carbons of PMMA were observed. In the region of 44.35–45.56 ppm, the PMMA  $\text{CH}_3$ -adjacent quaternary carbon peaks and the PS methylene carbon peaks were discerned. Between 16.29–18.71 ppm, the PMMA methyl groups were detected.

Analysis of the FT-IR spectra of the PS-g-PMMA graft polymer gave evidence that no azide groups remained on the polymer backbone and also showed the presence of the expected polystyrene and PMMA moieties, as can be seen in Fig. 1.

Analysis of the GPC trace of the PS-g-PMMA graft polymer and comparison with its polystyrene backbone precursor poly(S-co-4-AMS) clearly revealed a shift to higher molecular weight (Fig. 3). It was noticed that the trace of the graft polymer was not completely smooth with slight ridges observed. These ridges can be attributed to sudden jumps to higher molecular

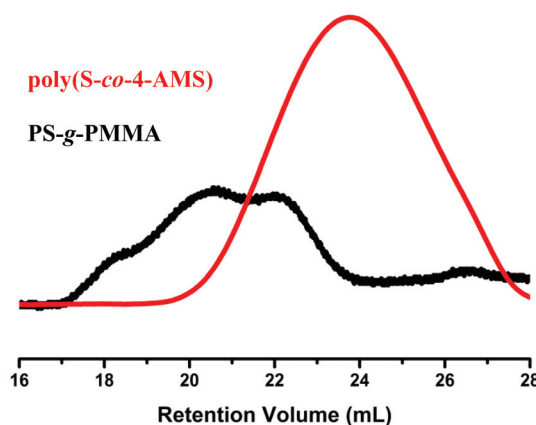


Fig. 3 GPC traces of PS-g-PMMA and its precursor backbone poly(S-co-4-AMS).

weights due to differences in the number of azide functional groups on the polystyrene backbone chains. The difference with respect to the number of azides in the backbone chains present, gives rise to graft polymer units that differ accordingly by the weight of one or more whole PMMA side chains.

With a good conversion of MMA to PMMA, growing off the polystyrene backbone, obtained in a short amount of time of just 4 h, the graft polymer polymerization was investigated with respect to applying less time (Table 1). The process was carried out as before but the polymerization was halted by removing the vessel from the light source and precipitating the product in cold methanol 2 and 3 hours after beginning the irradiation. A reaction time of only 2 h yielded 19% conversion with  $M_n = 36\,000$ , while 3 h allowed for 28% conversion and  $M_n = 40\,000$ . This would indicate that the polymerization of MMA begins slowly.

It is considered that the CuAAC and ATRP reactions occur side-by-side as an excess of  $\text{CuCl}_2$  is present, so there should be no competition between the reaction pathways. However, it is most likely the reactions occur and advance at different speeds. It has been shown by Bowman *et al.* that the photo-induced CuAAC can achieve close to complete conversion after only 80 min, with only 5 mol% of  $\text{Cu(II)}$  catalyst. The small molecule nature of the PgBiB moiety would also speed up the CuAAC process with respect to ATRP. And so it is assumed CuAAC is faster than ATRP in this case, but further studies are required to confirm this hypothesis.<sup>43</sup> When the reaction was carried out overnight and was irradiated for a total of 22 h under the outlined conditions, a completely insoluble product was obtained. To demonstrate the integrity of the PMMA end-chain bromide functionalization and the 'livingness' of the ATRP process, a chain extension test was carried out. The graft polymer PS-g-PMMA was used as a macroinitiator (MI) in a further photoinduced ATRP polymerization employing a reaction system of  $[\text{MI}] : [\text{CuCl}_2] : [\text{PMDETA}] : [\text{MMA}] = 0.021 : 1 : 3 : 50$ . It was found that after 3 h of irradiation using PS-g-PMMA ( $M_n = 40\,000\text{ g mol}^{-1}$ ) as the MI, the chains had grown to yield a graft polymer with  $M_n = 56\,700\text{ g mol}^{-1}$  and

PDI = 1.7. The ability to re-grow the PMMA chains of the PS-*g*-PMMA indicated good bromide end-group fidelity. The re-growth of the PMMA chains also demonstrated good 'livingness' of the ATRP process, as a linear relationship between time and  $M_n$  could be inferred from the increase in molecular weight after 3 h of the PMMA chain re-growth.

## Conclusions

In this article, we have reported the applicability of the one-pot, photoinduced combined ATRP and CuAAC protocol towards the preparation of a PS-*g*-PMMA graft copolymer. By using the polyazide poly(S-*co*-4-AMS) copolymer in conjunction with the alkyne bearing PgBiB initiator moiety in the described reaction system, the graft copolymer was achieved. The resulting graft copolymer showed comparable polydispersity with respect to the precursor polyazide species. The approach is noteworthy for its photoinduced nature under therefore mild reaction conditions, carried out at room temperature without the necessity of a photoinitiator. The protocol is also attractive for its reaction kinetics with only 4 hours needed to yield good conversion in both reactions, CuAAC and ATRP. The obtained graft polymer was characterized by appropriate means using  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, FT-IR and GPC. The fidelity of the PMMA chain end-group functionalities was confirmed using a chain extension test. And so this work stands to prove the versatility of this combined one-pot photoinduced CuAAC and ATRP approach towards the preparation of complex macromolecular structures in a one-step manner. In principal, the concept can be applied to other monomers since most of the vinyl monomers have no absorption at the irradiation wavelength to interfere with the system. This methodology is gaining popularity in the polymer chemistry field for the advantages it provides in synthesizing useful polymeric structures in a limited number of steps, and its scope shall be developed further by our group and surely other groups in the field.

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