Graft Polymer Growth by Tandem Photo-induced Photoinitiator-free CuAAC/ATRP

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ARTICLE

Graft Polymer Growth by Tandem Photo-induced Photoinitiator-free CuAAC/ATRP

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In this work we describe the use of the one-pot, photo-induced but photoinitiator-free combined copper-catalyzed azide-alkyne click reaction (CuAAC) and atom-transfer radical polymerization (ATRP) protocol to provide a graft copolymer of polystyrene-g-poly(methyl methacrylate) (PS-g-PMMA) to desirable conversion and polydispersity. Poly(styrene-co-4-chloromethylstyrene) (poly(S-co-4-CMS)) was prepared by nitroxide mediated polymerization (NMP). The benzylic chloride functional groups of poly(S-co-4-CMS) were substituted for azide functional groups by 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 photo-induced CuAAC while meanwhile in tandem initiating poly(methyl methacrylate) (PMMA) chain growth via the ATRP mechanism. The graft polymer was provided in good conversion and polydispersity and was characterized appropriately by ^{1}H NMR, FT-IR and GPC.

Introduction

Radical polymerization is used on an industrial scale for the manufacture of a host of polymeric materials.[1] Controlled/living radical polymerisation (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.[2-7] Transition metal catalysed atom transfer radical polymerization (ATRP) is most typically catalysed by a Cu(I)/ligand catalyst system and has almost become a standard operating procedure in polymer chemistry for obtaining uniform polymers of monomers such as styrenes, acrylates and methacrylates, among others.[8-10] Other CLRP methods worthy of mention of course are reversible addition-fragmentation chain transfer polymerization (RAFT) and nitroxide-mediated radical polymerization (NMRP) which have proved invaluable in producing well defined polymer structures.[2, 5]

Recently there has been a growing interest in the field in developing the external control of initiation and growth of the CLRP reaction.[11-13] The group of Matyjaszewski have described superbly 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 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[14-17].

Traditionally photochemical methods have been widely applied in polymerization processes in industry in the sectors of coatings, inks, adhesives. They are now gaining more popularity for their use in the production of more advanced technologies such as in optoelectronics and nanotechnology.[18] Most commonly the initiation of photopolymerization is carried out by the use of 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 are 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 photo-induced ATRP reaction has been researched extensively.[19-27] In our group we have reported pioneering work describing photoinitiator-free photo-induced ATRP systems. We showed that at room temperature under UV/VIS light irradiation the ATRP CuBr$_2$/PMDETA catalyst underwent a reduction to a Cu(I) complex system

which was able to initiate and propagate polymerization of acrylate monomers.[28, 29] During the process the deactivating $CuBr_2$ complex was shown to reform but could be continually reduced by the radiation applied 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 $CuBr_2/Me_6TREN$ catalyst.[30] The group of Rainer Jordan has shown that using a simple household fluorescent lamp the photo-induced ATRP polymerization of MMA can be implemented with good "living" nature. They proved this system's applicability towards the preparation of homogeneous, patterned and block copolymer brushes.[26]

The use of so-called click chemistry[31] has become widespread and indispensable as a tool for functionalization and preparation of complex architectures in the macromolecular and polymer sciences.[32-34] Some of the most known and potent examples of click chemistry include the Diels-Alder cycloaddition,[35] thiol-ene[36] and copper catalysed azide-alkyne click reactions (CuAAC).[37] The CuAAC, first described by Meldal and coworkers[38] is a highly implemented reaction system employed across all fields of biology and chemistry.[37] Like the ATRP system, CuAAC too takes advantage of a Cu(I) catalyst system in its case to yield substituted 1,2,3-triazoles most usually in excellent yields with little or no side products. The photo-induced CuAAC is now becoming a rigorously investigated transformation. Similar to the ATRP process, an air-stable Cu(II) complex such as $CuCl_2$ is employed in conjunction with or without a photo-sensitive reducing agent in the presence of an alkylamine ligand such as PMDETA and light.[39-43] The formation of a Cu(I) complex results which has been shown to carry out the CuAAC transformation to desirable yield and purity. There has been several different methods reported to date of affecting the reduction of Cu(II) to Cu(I) giving rise to effective CuAAC reactions. These methods have included the use of photochemically generated free radicals and excited polynuclear aromatic compounds which facilitate electron-transfer such as developed in our group.[44] And the use of Cu(II) complexes bearing acylphosphinate counter ions to initiate both ATRP and the CuAAC has been recently described by the group of Bowman.[45]

The CuAAC is also much lauded for its orthogonality whereby during the reaction, functional groups not pertaining to the intended process do not interfere. This is surely self-evident and intrinsic to the fact 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 N-acetyl-L-cysteine end functionalized poly (methylmethacrylate)-b-poly (caprolactone) block copolymer which was applied successfully as a matrix for cell culturing.[46] The photo-initiating systems for

the photo-induced CuAAC and ATRP reactions been have shown to be comparable and compatible.[47] And thus, our group has shown that a combined one-pot photo-induced ATRP and CuAAC protocol could be used to prepare AB block copolymers.[48] Here in the same line of research we expand the scope of the one-pot approach invoking combined photoinitiator-free, photo-induced 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,[49, 50] compatibilizers[51, 52] and surfactants.[53, 54] Previous work by Yoshida has described the preparation of polystyrene-g-poly (methyl methacrylate) (PS-g-PMMA) via photo-NMRP.[55] The work herein contributes to the expansion of methodology available to polymer chemists towards graft polymer preparation by demonstrating the synthesis of PS-g-PMMA via tandem photo-induced photoinitiator-free CuAAC/ATRP.

Experimental

Materials. Styrene (Sigma-Aldrich Corp, Munich, Germany 99%) and 4-chloromethylstyrene (Acros Organics Geel, Belgium, 90%), was 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 initiator was recrystallized from methanol. Propargyl alcohol (99%, Aldrich), triethylamine (99.5%, Fluka), 2-Bromoisobutyryl bromide (98%, Aldrich). N,N,N,N,N-pentamethyldiethylenetriamine (PMDETA; 99%, Aldrich), used as a ligand, was distilled before use. Sodium azide (99%, Aldrich), copper(II) chloride (98%, Aldrich) were used as received. Methyl methacrylate (MMA, 99%, Aldrich) was filtered over basic Al_2O_3 to remove inhibitor. Dichloromethane was distilled over CaH_2 before use. Toluene and dimethylformamide were dried over 4 Å sieves before use.

Characterization

^1H NMR and ^{13}C NMR of the intermediates and final polymers taken in $CDCl_3$ with $Si(CH_3)_4$ as an internal standard were recorded at room temperature at 500 MHz on a Agilent VNMRS 500 spectrometer. FT-IR spectra were recorded on Perkin–Elmer FT-IR spectrum one spectrometer with an ATR Accessory (ZnSe, PikeMiracle Accessory) and cadmium telluride (MCT) detector. Resolution was 4 cm^{-1} and 24 scans with 0.2 cm/s scan speed. Molecular weights and polydispersities of polymers and the block copolymer were measured by gel permeation chromatography (GPC) employing an Agilent 1100 instrument equipped with a differential refractometer by using THF as the eluent at a flow rate of 0.3 ml min^{-1} 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 mml) were stirred in a 50 mL flame-dried round-bottom flask dissolved in 5 mL of DCM under nitrogen at 0 °C. To the

reaction mixture was slowly added 2-bromoisobutyryl bromide (1.000 mL, 8.090 mmol) over 10 mins. It was allowed to stir for 28 h slowly warming up, before water was added and it was extracted with DCM (2 X 20 mL). The organic fractions were combined, dried over MgSO$_4$ and solvents were removed in *vacuo*. Pure product (1.206 g, 80 %) was obtained as colourless non-viscous oil after purification by flash column chromatography (SiO$_2$, Hexanes/EtOAc, 80:20). ^{1}H NMR (CDCl$_3$, δ, ppm, TMS): 4.71 (2H, –CH$_2$O–), 2.47 (1H, C≡CH), and 1.90 (6H, (CH$_3$)$_2$C). IR (υ$_{max}$): 3296 ($_{≡C-H}$), 2132 ($_{C≡C}$), 1743 cm^{-1} ($_{C=O}$). ^{13}C NMR (CDCl$_3$, δ, ppm, TMS): 170.91 (C=O), 76.88 (–C≡CH), 75.42 (–C≡CH), 54.91 (–CH$_2$CO$_2$–), 53.43 (–C(CH$_3$)$_2$Br), 30.65 (–C(CH$_3$)$_2$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$_2$ by fluxing through N$_2$ 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$_2$ being blown over for a further 2 mins. 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 %). It was thereafter filtered and dried in *vacuo* to yield the polymer as a white solid (0.580 g, 16 % conversion, M_n = 13,600 g mol^{-1}, M_w/M_n = 1.7). ^{1}H NMR (CDCl3, δ, ppm, TMS): 7.23 – 6.24 (aromatic PS H), 4.52 (–CH$_2$Cl), 1.91 – 1.63 (–CH–), 1.58 – 1.25 (–CH$_2$–). IR (υ$_{max}$): 3075 – 2840 (Ar$_{C-H}$), 1516 – 1419 (Ar$_{C=C}$) cm^{-1}.). ^{13}C NMR (CDCl3, δ, ppm, TMS): 125 – 129 (aromatic C), 46.07–46.34 (–CH$_2$Cl), 44.72–42.00 (–CH$_2$–), 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 1 Pasteur-pipette aliquot of HCl (37 %) added. The polymer was then filtered and dried under vacuum over 24 h before it was isolated (0.492 g, 79 % conv., M_n = 14,200 g mol^{-1}, M_w/M_n = 1.7). ^{1}H NMR (CDCl$_3$, δ, ppm, TMS): 7.23 – 6.24 (aromatic H), 4.25 (–CH$_2$N$_3$), 1.91 – 1.63 (–CH–), 1.58 – 1.25 (–CH$_2$–). IR (υ$_{max}$): 3075 – 2840 (Ar$_{C-H}$), 2093 (large, N$_3$), 1516 – 1419 (Ar$_{C=C}$) cm^{-1}. ^{13}C NMR (CDCl3, δ, ppm, TMS): 125 – 129 (aromatic C), 54.60 (–CH$_2$N$_3$), 44.72–42.00 (–CH$_2$–), 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 was 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 fluxing through N$_2$ for 10 mins before CuCl$_2$ (0.054 g, 0.401 mmol) was added, N$_2$ was blown over the solution for a further 2 mins before it was sealed and irradiated. The mixture was

irradiated by a photoreactor (Rayonet) equipped with 16 lamps emitting light nominally at 350nm at room temperature.The light intensity was 3.0 mW·cm^{-2}. After the given irradiation time had 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. ^{1}H NMR (CDCl3, δ, ppm, TMS): 7.59 (–C$_2$HN$_3$–), 7.23 – 6.24 (aromatic PS H), 5.49 – 5.28 (ArCH$_2$C$_2$HN$_3$–), 5.16 (–CO$_2$CH$_2$C$_2$HN$_3$–), 3.61 (CH$_3$OC(O)–, PMMA), 2.10 – 1.82 (–CH–, PMMA), 1.75 (–CH–, PS) 1.44 (–CH$_2$–, PS) 1.03 (–CH$_2$C(CH$_3$)CH$_2$–, PMMA) 0.85 (–CH$_2$C(CH$_3$)CH$_2$–, PMMA). IR (υ$_{max}$): 3075 – 2840 (Ar$_{C-H}$), 1730 (C=O), 1516 – 1419 (Ar$_{C=C}$) cm^{-1}. ^{13}C NMR (CDCl3, δ, ppm, TMS): 176.82 – 178.07 (C=O), 142 (aromatic C$_q$) 125 – 129 (aromatic CH), 52.66 – 54.44 (–CH$_2$– (PMMA)), 51.81(–OCH$_3$), 44.35 – 45.56 (–C(CH$_3$)–), 16.29 –18.71 (–CH$_3$).

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

To a flame-dried glass tube fitted with stirrer bar was 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). It was sonicated to aid dissolution. It was purged of O$_2$ by fluxing through N$_2$ for 10 mins. CuCl$_2$ (0.018 g, 0.132 mmol) was then added to the reaction vessel and N$_2$ was blown over for a further 2 mins 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 before being allowed to stand overnight at – 20 °C. It was then filtered and isolated to yield the polymer as a white solid (0.494 g, 65 % conv., M_n = 56,700 g mol^{-1}, PDI = 1.7.).

Results and Discussion

Poly(styrene-*co*-4-chloromethylstyrene) (poly(S-*co*-4-CMS)) was prepared along standard NMP guidelines.[56] Chloromethyl styrene (CMS) and styrene in a 1:1 proportion were employed with 1,1′-azobis(cyclohexanecarbonitrile) VAZO as the radical source, mediated by TEMPO at a temperature of 120 °C, over 28 h to yield the copolymer in 16 % conversion with M_n = 14,200 g mol^{-1} M_w/M_n = 1.7. The obtained copolymer was also characterized by ^{1}H NMR and FT-IR. ^{1}H NMR revealed that the polymer had grown with CMS and styrene incorporating in a ratio of 1.16:1 respectively. This was deduced from comparing the integration of the aromatic region between 6.26 ppm and 7.37 ppm and that of the peak at 4.52 ppm corresponding to the CH$_2$ at the benzylic position which was 9:2.4 respectively.

Scheme 1. Preparation of poly(S-*co*-4-AMS) via NMP followed by azidation.
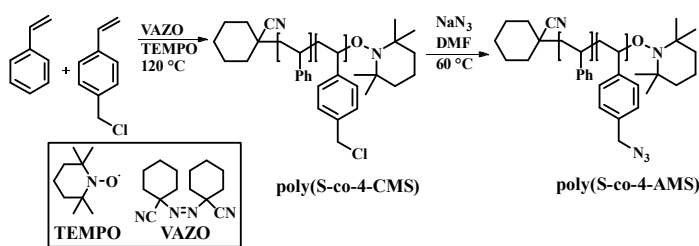
The benzylic chloride functionality was substituted for azide functionality by standard azidation procedure consisting of stirring the copolymer in DMF overnight at 60 °C with an excess of NaN$_3$ to yield the azidated copolymer poly(styrene-*co*-4-azidomethylstyrene) (poly(S-*co*-4-AMS)), as observed in Scheme 1. The azidation could be confirmed by analysis of the FT-IR whereby a great azide peak was observed at 2093 cm^{-1} as can be seen in Fig. 2. Also, the peak at 4.52 ppm corresponding to benzylic protons was entirely shifted upfield to 4.22 ppm when analysing the ^{1}H NMR spectrum.

The ATRP initiator PgBiB was prepared in good yield of 80 % after chromatography by stirring propargyl alcohol with α-bromoisobutyrylbromide in the presence of Et$_3$N, warming up from 0 °C overnight.[57] The prepared poly(S-*co*-4-AMS) was then used as the backbone for the growth of polystyrene-*g*-poly(methyl methacrylate) (PS-*g*-PMMA) graft polymer in a one-pot, photoinitiator-free, photo-induced, tandem CuAAC/ATRP procedure, as outlined in Scheme 2.

Scheme 2. One-pot photo-induced CuAAC/ATRP procedure for the synthesis of PS-*g*-PMMA.
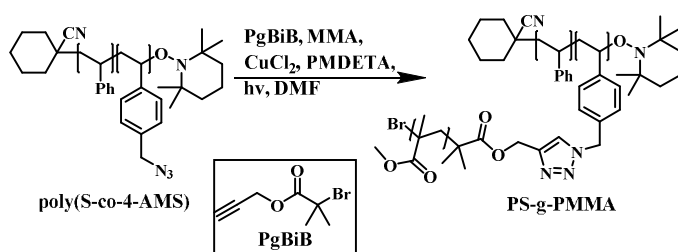
The air-stable CuCl$_2$ species when employed in conjunction with PMDETA forms a copper complex which is reduced to the CuAAC and ATRP active Cu(I) species under the irradiation of light of >350 nm. By employing this methodology it was possible to click the PgBiB ATRP initiator to the polystyrene backbone using the CuAAC reaction while simultaneously initiating poly(methyl methacrylate) (PMMA) ATRP chain growth.

Scheme 3. CuAAC coupling of PMMA chains growing via ATRP to polystyrene backbone.
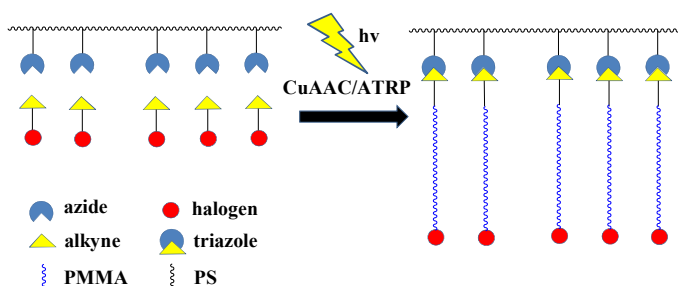
After 4 h of irradiation of the reaction system the PS-*g*-PMMA graft polymer was obtained in good 71 % conversion with M_n = 62,600 g mol^{-1} and M_w/M_n = 1.8. The polydispersity of the obtained graft polymer was slightly larger than that of the employed poly(S-*co*-4-AMS) backbone which was 1.7.

The formation of the bottle-brush graft polymer was confirmed by ^{1}H NMR as shown in fig 1. The aromatic triazole proton peak could be observed at 7.60 ppm as a broad signal. Broad signals pertaining to –CH$_2$– groups bonded directly to the triazole functional group were observed between 5.1 and 5.5 ppm. A broad signal corresponding to polystyrene aromatic protons was observed in the 6.2 to 7.1 ppm region and peaks corresponding to PMMA were distinguished further upfield. The characteristic PMMA methyl ester –OCH$_3$ peak was found at 3.6 ppm and PMMA –CH$_2$– and –CH$_3$ peaks were clearly distinguished in the 0.8 to 2.1 ppm region. Comparing the integration of the triazole adjacent –CH$_2$– peaks **c/d** with the aromatic peaks **a** as shown in fig. 1, it was found they correspond exactly as should be expected if the CuAAC was quantitative. This was inferred from the observed integration of 8. 31: 4 with respect to the peaks **a** and **c/d**. The aromatic region **a** integration of 8.31 was supposed 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).

Fig. 1. ^{1}H NMR spectra of PS-*g*-PMMA.
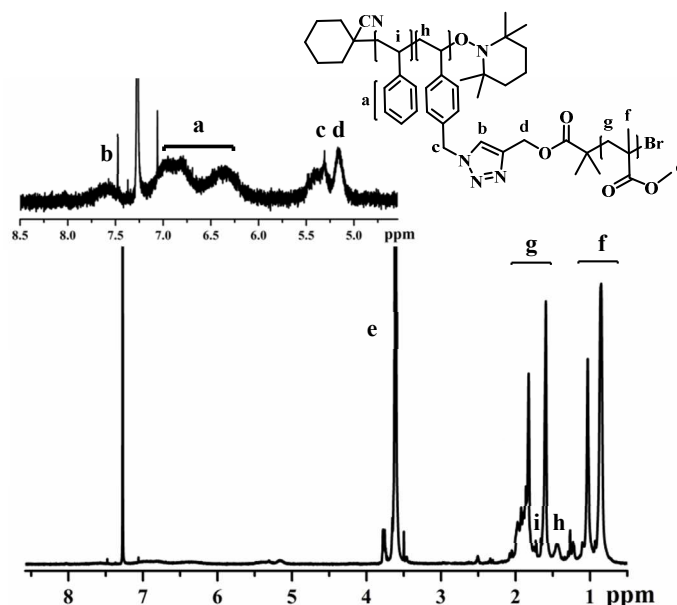
In the ^{13}C NMR of PS-*g*-PMMA the carbonyl peaks of the PMMA segments could be discerned between 176.82 – 178.07 ppm. The polystyrene backbone aromatic carbon peaks could be observed at 127 - 129 ppm and with the quaternary aromatic carbons lying at 142 ppm. In the region of 52.66 – 54.44 ppm methylene peaks pertaining to PMMA were evident. At 51.81 ppm the methyl ester carbon of PMMA was apparent. In the region of 44.35 – 45.56 ppm the PMMA CH$_3$– adjacent quaternary carbon peaks and PS methylene carbon peaks were present. Between 16.29 –18.71 ppm the PMMA methyl groups were apparent.

Analysis of the FT-IR spectra of the PS-*g*-PMMA graft polymer gave evidence that no azide remained on the polymer backbone and also showed the presence of expected polystyrene and PMMA moieties as can be seen fig. 2.

Fig 2. FT-IR spectra of poly(S-*co*-4-CMS), poly(S-*co*-4-AMS) and PS-*g*-PMMA.
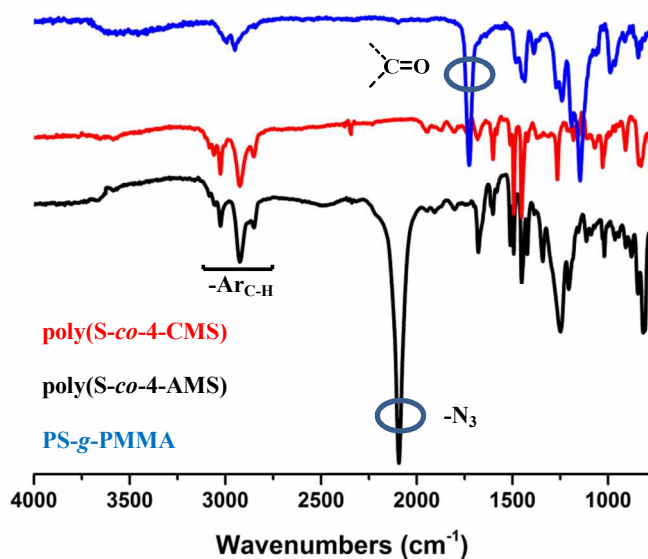
Analysis of the GPC trace of the PS-*g*-PMMA graft polymer and comparison with its polystyrene backbone precursor poly(S-*co*-4-AMS) clearly revealed the shift to higher molecular weight. It was noticed that the trace of the graft polymer was not completely smooth with slight ridges observed. These ridges can be attributed to sudden jumps to higher molecular weight due to differences in the number of azide functional groups lying on the polystyrene backbone chains. Backbone chains differing with respect to the number of azides present give rise to graft polymer units that differ according to the weight of a whole PMMA side chain.

Fig 3. GPC trace of PS-*g*-PMMA and its precursor backbone poly(S-*co*-4-AMS).
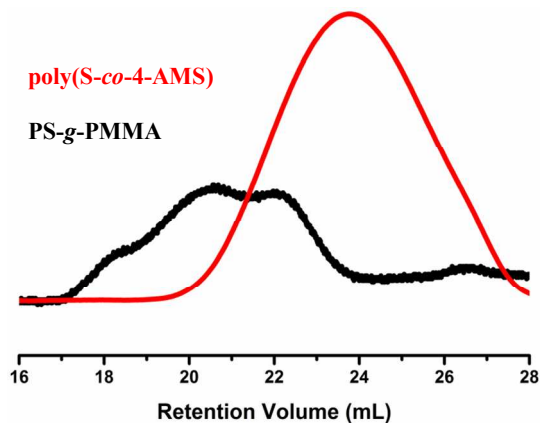
With good conversion of MMA to PMMA growing off the polystyrene backbone obtained in a short space of time of just 4 h, the graft polymer polymerization was investigated with respect to applying less time. The process was carried out as before but the polymerizations were halted by removing the vessel from the light source and precipitating in cold methanol 2 and 3 hours after the beginning of irradiation. A reaction time of only 2 h gave rise to 19

% conversion being obtained 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.

Table 1. Conversions and molecular weight characteristics of poly(S-*g*-PMMA) graft polymer with reaction time.

Entry	Time (h)	Conversion (%)	M_n (g mol^{-1})[a]	PDI[a]
1	2	19	36,000	1.6
2	3	28	40,000	1.6
3	4	72	62,600	1.8
5[b]	22	--	--	--
6[c]	3	65	56,700	1.7

[a]Determined according to PS standards. [b] Polymer could not be recovered for analysis.[c] Chain extension test.

It is considered that the CuAAC and ATRP reactions occur side-by-side as an excess of CuCl$_2$ is present so there should be no competition between 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 just 80 mins with only 5 mol % Cu(II) catalyst. The small molecule nature of the PgBiB moiety would also speed up the CuAAC process with respect to the ATRP. And so it is assumed the CuAAC is faster than the ATRP in this case, but further studies are required to confirm this hypothesis.[43]

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 functionality 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 photo-induced ATRP polymerization employing a reaction system of [MI]:[CuCl$_2$]:[PMDETA]:[MMA] = [0.021]:[1]:[3]:[50]. It was found that after 3 h of irradiation using PS-*g*-PMMA (M_n = 40,000 g mol^{-1}) as the MI it was found the chains had grown to yield a graft polymer with M_n = 56,700 g mol^{-1} and PDI = 1.7. The ability to regrow the PMMA chains of the poly(S-*g*-PMMA) indicated good bromide end-group fidelity. The regrowth of the PMMA chains also demonstrated good 'livingness' of the ATRP process as a linear relationship of time with respect to M_n could be inferred from the increase of molecular weight after 3 h of PMMA chain regrowth.

Conclusions

In this article we have reported the applicability of the one-pot, photo-induced combined ATRP and CuAAC protocol towards the preparation of 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 bore comparable polydispersity with

respect to the precursor polyazide species. The approach is noteworthy for its photo-induced nature with therefore mild reaction conditions carried out at room temperature without the necessity of photoinitiator. It is also attractive for its reaction kinetics with only 4 hours needed to yield good conversion in both CuAAC and ATRP reactions. The obtaining of the graft polymer was proved and characterized by the appropriate means of ^{1}H NMR, ^{13}C NMR, FT-IR and GPC trace. The fidelity of the PMMA chain end-group functionality was confirmed by a chain extension test. And so this work stands to prove the versatility of this combined one-pot photo-induced 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.

Acknowledgements

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Graphical and textual abstract

Graft Polymer Growth by Tandem Photo-induced Photoinitiator-free CuAAC/ATRP

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In this work we describe the use of the one-pot, photo-induced but photoinitiator-free combined copper-catalyzed azide-alkyne click reaction (CuAAC) and atom-transfer radical polymerization (ATRP) protocol to provide a graft copolymer of polystyrene-g-poly(methyl methacrylate) (PS-g-PMMA) to desirable conversion and polydispersity.   Poly(styrene-co-4-chloromethylstyrene) (poly(S-co-4-CMS)) was prepared by nitroxide mediated polymerization (NMP). The benzylic chloride functional groups of poly(S-co-4-CMS) were substituted for azide functional groups by 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 photo-induced CuAAC while meanwhile in tandem initiating poly(methyl methacrylate)

(PMMA) chain growth via the ATRP mechanism. The graft polymer was provided in good conversion and polydispersity and was characterized appropriately by 1H NMR, FT-IR and GPC.