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Organocatalytic synthesis and post-polymerization functionalization of propargyl-functional poly(carbonate)s†

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The synthesis of well-defined propargyl-functional poly(carbonate)s was achieved *via* the organocatalytic ring-opening polymerization of 5-methyl-5-propargyloxycarbonyl-1,3-dioxan-2-one (MPC) using the dual catalyst system of 1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea (TU) and 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU). The resulting homopolymers showed low dispersities and high end-group fidelity, with the versatility of the system being demonstrated by the synthesis of telechelic copolymers and block copolymers. The synthesized homopolymers with varying degree of polymerization were functionalized with a range of azides *via* copper-catalyzed Huisgen-1,3-dipolar addition or thiols *via* radical thiylation, to produce functional aliphatic poly(carbonate)s from a single polymeric scaffold.

Introduction

The ability to readily tune the properties of synthetic biodegradable polymers makes them attractive materials for pharmaceutical applications.[1–7] Whilst the synthesis of functional poly(ester)s is a particularly challenging area,[8] a number of reported facile preparations of cyclic carbonate monomers from 1,3-diols have led to a poly(carbonate)s with a large range of pendant functionalities being reported.[9–15] With many synthetic routes available from which to prepare poly(carbonate)s with specific functional groups, the desire to apply post-polymerization functionalization chemistry presents an attractive method for producing materials with a wide range of properties from a limited monomer pool, as well as enabling the incorporation of reactive groups that are incompatible with the ROP process.

To date, there have been limited reports of the synthesis and post-polymerization functionalizations of such polymers, with allyl-,[16,17] maleimide-,[18] vinyl sulfone-[19] and (meth)acrylate-pendant polymers[20] being demonstrated to readily react with thiol-containing molecules. Other examples have reported the synthesis of azide-functional poly(carbonate)s and their modification using copper catalysed-(CuAAC) and strain-promoted (SPAAC) alkyne–azide cycloadditions.[21,22]

The alkyne functional group is utilized in many organic reactions as a consequence of its versatile reactivity. Alkynes have been widely studied in a range of coupling reactions (Sonogashira, Glaser and Eglinton),[23–25] cycloaddition reactions (Diels–Alder with 1,3-dienes, Huisgen 1,3-dipolar)[26,27] and in reactions such as hydrogenation, hydroboration, halogenation and the radical thiylation (or 'thiol-yne') in which two equivalents of the corresponding reagent can be added to one alkyne group as a result of its double unsaturation.[28] In particular the copper-catalyzed derivative Huisgen 1,3-dipolar cycloaddition of alkynes and azides (CuAAC) has been extensively applied in materials chemistry as a fast and quantitative 'click' method of functionalization.[29,30] The introduction of a pendant propargyl functionality in a poly(carbonate) backbone has previously been reported *via* the ring-opening polymerization of a propargyl ester functional cyclic carbonate, 5-methyl-5-propargyloxycarbonyl-1,3-dioxan-2-one (MPC).[31–34] Studies have focused on its copolymerization with lactide in toluene at 120 °C (ref. 34) or at 100 °C in bulk[31] using diethyl zinc as a catalyst, with the resulting statistical and block copolymers being used in the immobilization of proteins to biodegradable polymer fibres and in the preparation of protein-grafted polymer microspheres.[31–33] Surprisingly however, to date its homopolymerization and the investigation of the versatility of the resulting poly(MPC), (PMPC), for post-polymerization functionalization have not been previously reported.

Herein, the concept of synthesizing a single functional poly(carbonate) scaffold in a controlled manner is extended to those with a pendant propargyl functionality by the ring-opening polymerization of MPC as well as post-polymerization functionalization of the resulting homopolymers *via* the copper catalyzed addition of azides (CuAAC) or the radical addition of

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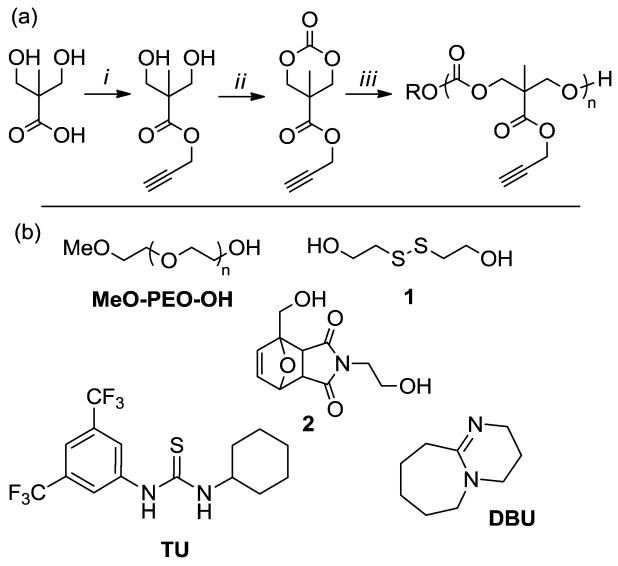
thiols ('thiol-yne') to the pendant propargyl groups, giving rise to a range of functional poly(carbonate)s.

Results and discussion

Monomer synthesis and polymerization

The monomer, 5-methyl-5-propargyloxycarbonyl-1,3-dioxan-2-one (MPC), was synthesized in a two-step procedure as previously reported (Scheme 1a).[31,32] Initial studies into the ring-opening polymerization (ROP) of MPC were carried out with the dual catalyst system of 1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea, TU, (10 mol%) in combination with (−)-sparteine (5 mol%) which had previously shown excellent control in the ROP of the analogous allyl-functional derivative, 5-methyl-5-allyloxycarbonyl-1,3-dioxan-2-one (MAC).[16] The resultant polymers revealed narrow, monomodal distributions by gel permeation chromatography (GPC) analysis (*e.g.*: $[M]_0/[I]_0 = 20$; $M_n = 6750$ g mol^{-1}, $Đ_M = 1.18$) however, the long polymerization times (*ca.* 24 h for a DP20 homopolymer) and the limited availability of (−)-sparteine presented significant drawbacks.[16,35] As such, our attention was turned to the dual catalyst system of TU in combination with 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU), which had previously shown good control and reduced reaction times in the ROP of other functional poly(carbonate)s.[7,36] Polymerizations with $[M]_0/[I]_0 = 100$ carried out in $CDCl_3$ ($[MPC]_0 = 0.5$ M) at 25 °C using 5 mol% TU and 1 mol% DBU with benzyl alcohol as initiator achieved >90% monomer conversion within 6 hours. Polymerizations were monitored using ^{1}H NMR spectroscopy by the disappearance of the methylene resonances in the carbonate ring at $\delta = 4.22$ and 4.72 ppm and the appearance of a multiplet at $\delta = 4.27$–4.40 ppm for the corresponding protons on the polymer backbone. Upon completion, pure polymers were obtained by precipitation into cold hexanes and removal of residual catalyst by column chromatography.

GPC analysis of the resultant BnO-PMPC$_{100}$-OH polymers revealed a monomodal polymer chain distribution with a number-average molecular weight, $M_n = 16\,540$ g mol^{-1}, close to that predicted from the $[M]_0/[I]_0$ ratio, and a low dispersity (Fig. 1a). Further investigation of the living characteristics of the



Scheme 1 (a) Synthesis and ring-opening polymerization (ROP) of 5-methyl-5-propargyloxycarbonyl-1,3-dioxan-2-one, MPC. *Conditions*: (i) propargyl bromide, KOH, acetone, reflux, 16 h; (ii) ethyl chloroformate, NEt_3, THF, 0 °C; (iii) ROH, catalyst, $CDCl_3$, RT; (b) alcohol initiators and organic catalysts used in the ROP of MPC.

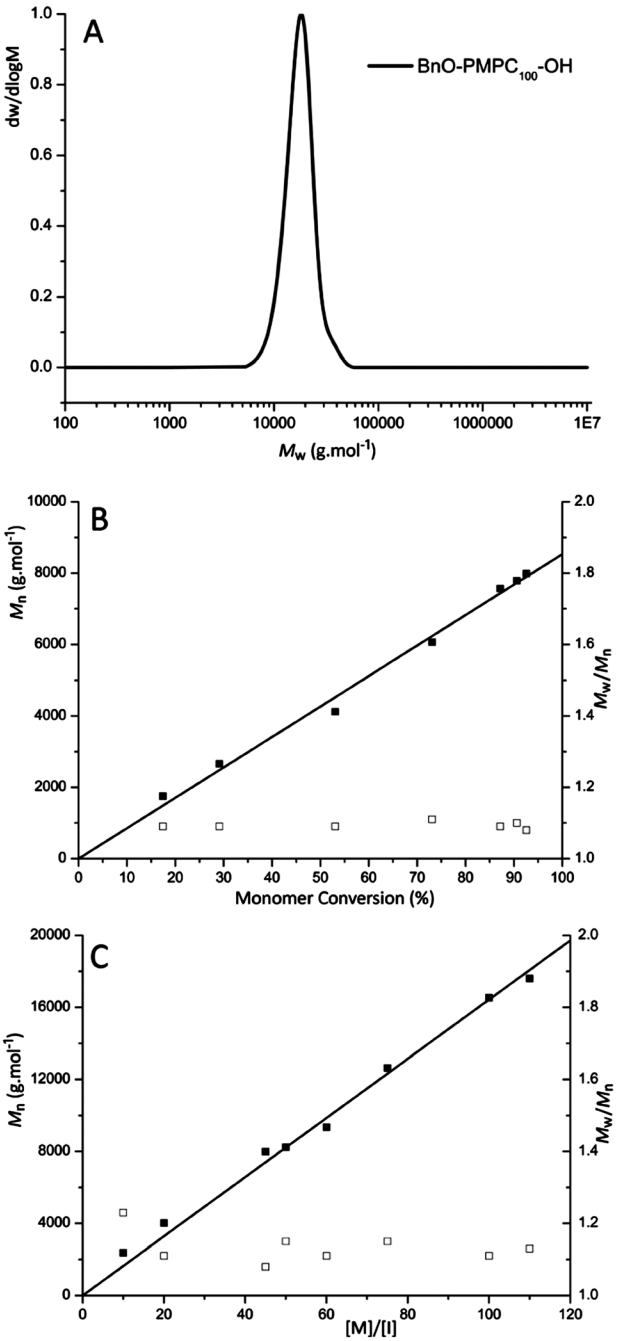


Fig. 1 (a) GPC chromatogram of BnO-PMPC$_{100}$-OH ($M_n = 16\,540$ g mol^{-1}, $Đ_M = 1.11$) prepared by the ROP of MPC; (b) Plot of number-average molecular weight (M_n; ■) and dispersity ($Đ_M = M_w/M_n$; □) against % monomer conversion in the ROP of MPC; $[M]_0/[I]_0 = 45$; (c) Plot of number-average molecular weight (M_n; ■) and dispersity ($Đ_M = M_w/M_n$; □) against initial monomer-to-initiator ratio, $[M]_0/[I]_0$, in the ROP of MPC. *Conditions:* $[MPC]_0 = 0.5$ M $CDCl_3$ at 25 °C, 1 mol% DBU, 5 mol% TU, using benzyl alcohol as initiator.

polymerization catalyzed by TU and DBU revealed linear correlations between M_n against monomer conversion (Fig. 1b) and initial monomer-to-initiator ratio ($[M]_0/[I]_0$) (Fig. 1c) while retaining low dispersity values throughout the polymerization. Analysis of the polymers by ^{1}H NMR spectroscopy revealed resonances expected for polymers with a benzyl alcohol end group ($\delta = 7.37$ (ArH) and 5.15 (CH_2) ppm) which demonstrates the end group fidelity of the polymerization (Fig. 2a). Further analysis of a low molecular weight polymer (DP = 12 by ^{1}H NMR spectroscopy) by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-ToF MS) revealed a single distribution with a spacing of 198 m/z, equal to that of a monomer unit, and a main peak at $m/z = 2715$ corresponding to a sodium charged polymer chain of DP13 with a benzyl alcohol end group; further confirming the living nature of the polymerization (Fig. 2b). Interestingly, ^{1}H NMR spectroscopic analysis of polymers that were synthesized in $CDCl_3$ showed a decrease in intensity of the propargyl proton resonance at $\delta =$ 2.50 ppm. MALDI-ToF MS analysis of the corresponding polymers revealed distributions with a repeat unit of ~199 m/z instead of the expected 198 m/z and an isotope pattern that is consistent with *ca.* 20% proton-deuterium exchange of the acidic acetylenic proton with the solvent during polymerization (see ESI, Fig. S1†).

Initiator versatility and block copolymers

To demonstrate the initiator versatility, the synthesis of telechelic PMPC and block copolymer structures from various hydroxyl-functional initiators was investigated (Scheme 1b). Initiation of ROP of MPC from 2-hydroxyethyl disulfide, **1**, and furan-protected maleimide functional diol, **2** ($[M]_0/[I]_0 = 20$ per alcohol group) enabled synthesis of telechelic copolymers with reductive- and thermally-cleavable chemical handles within the polymer chain.[37–39] Analysis of these polymers by ^{1}H NMR spectroscopy revealed resonances expected for the initiating alcohols with integration against the main chain polymer resonances being consistent with DP20 and DP24 polymers,

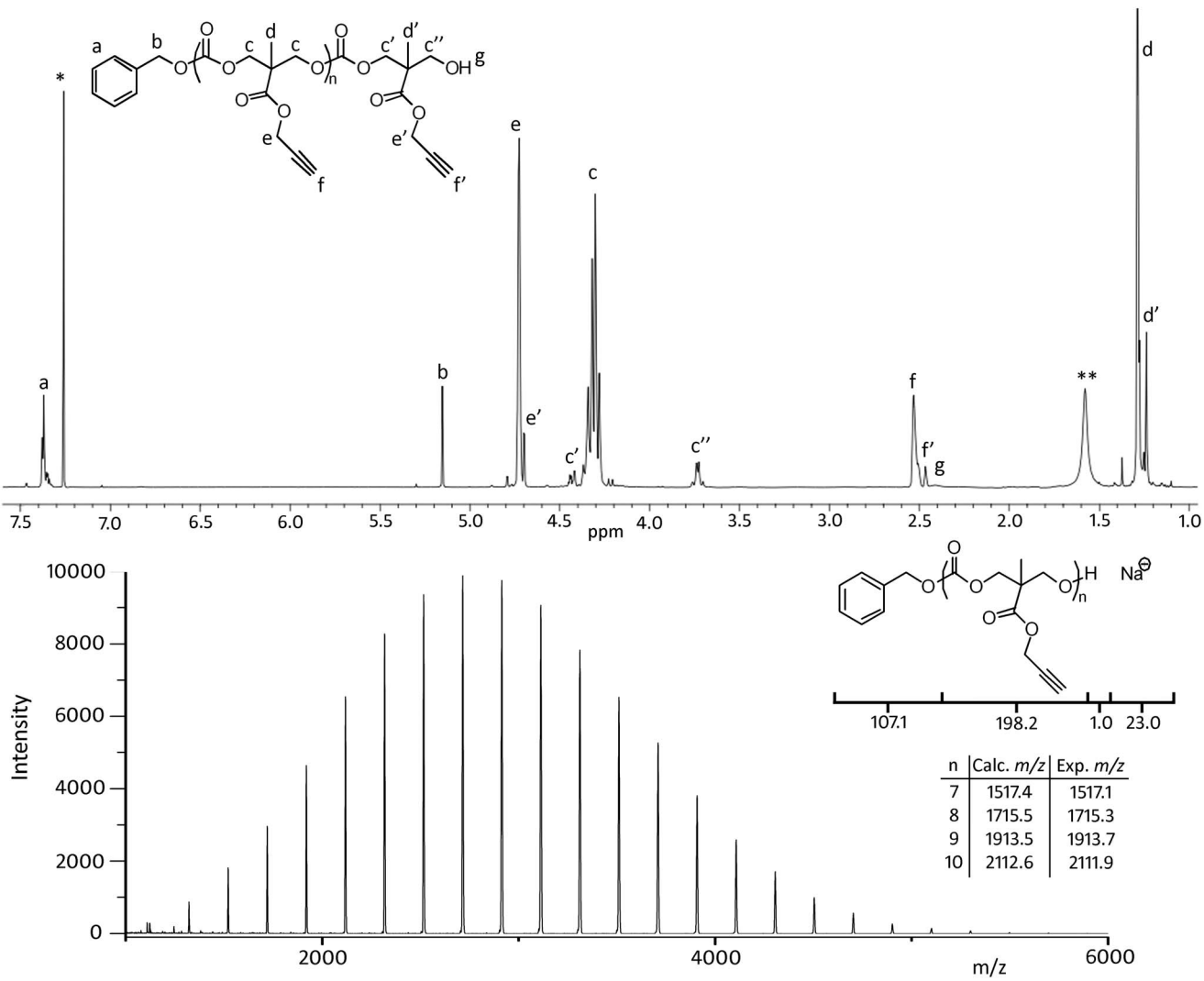


Fig. 2 (a) ^{1}H NMR spectrum ($CDCl_3$ 500 MHz, 298 K; * = residual $CHCl_3$, ** = H_2O) and (b) MALDI-ToF MS of PMPC (DP = 12) prepared by the ROP of MPC ($[MPC]_0 = 0.5$ M) catalyzed by 1 mol% DBU and 5 mol% TU.

Table 1 Block copolymers and telechelic polymers prepared by the ring-opening polymerization of MPC[a]

Entry	Polymer	DP[b]	M_n (NMR)[c] (g mol^{-1})	M_n (GPC)[d] (g mol^{-1})	$Đ_M$[d]
1	HO-PMPC-O-($C_{11}H_{10}NO_3$)-O-PMPC-OH	20[g]	8170	8100	1.08
2	HO-PMPC-O$(CH_2)_2$S-S$(CH_2)_2$O-PMPC-OH	24[g]	8480	8410	1.10
3	MeO-PEO_{114}-*b*-PMPC-OH[e]	18[g]	8610	11 020	1.06
4	MeO-PEO_{216}-*b*-PMPC-OH[f]	12[g]	11 930	17 870	1.06
5	BnO-$PLLA_{18}$-OH	18[h]	2700	4200	1.09
5a	BnO-$PLLA_{18}$-*b*-PMPC-OH	20[g]	6670	8740	1.08
6	BnO-$PMPC_{20}$-OH	20[g]	4070	4540	1.12
6a	BnO-$PMPC_{20}$-*b*-PLLA-OH	24[h]	7530	10 350	1.09
7	BnO-$PMPC_{17}$-OH	17[g]	3480	4010	1.11
7a	BnO-$PMPC_{17}$-*b*-PMAC-OH	19[i]	5280	8110	1.09

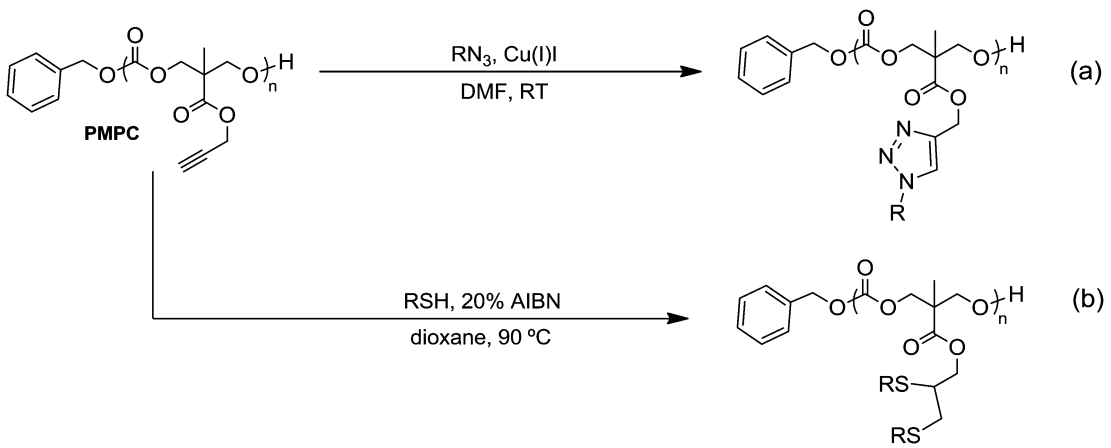
[a] Reactions were performed in $CDCl_3$ at 25 °C, [MPC]0 = 0.5 M, $[M]_0/[I]_0$ = 20 using 1 mol% DBU, 5 mol% TU. [b] Experimental degree of polymerization (DP) measured by ^{1}H NMR spectroscopy per OH group. [c] Determined by ^{1}H NMR spectroscopy. [d] Determined by GPC analysis in THF. [e] Poly(ethylene oxide) macroinitiator (DP = 114, determined as M_n = 6790 g mol^{-1}, $Đ_M$ = 1.03 by GPC analysis in THF against poly(styrene) standards). [f] Poly(ethylene oxide) macroinitiator (DP = 114, determined as M_n = 14820 g mol^{-1}, $Đ_M$ = 1.06 by GPC analysis in THF against poly(styrene) standards). [g] DP of PMPC block. [h] DP of PLLA block. [i] DP of PMAC block.

respectively. MALDI-ToF MS analysis of the former showed a distribution with a spacing of 198–199 *m*/*z* and a main peak at *m*/*z* = 5928 (DP29) corresponding to the value expected for telechelic PMPC initiated from **1**. MALDI-ToF MS analysis of PMPC initiated from **2** revealed two distributions, both with a spacing of 198–199 *m*/*z*. These distributions with main peaks at *m*/*z* = 2542 (DP12) and *m*/*z* = 2687 (DP13) correspond to the polymer chains obtained after retro-Diels–Alder reaction of the initiator induced during ionization by the laser, comparable to that previously observed for related systems.[18,40]

Further initiator versatility was demonstrated by the synthesis of amphiphilic block copolymers by initiation of MPC polymerization from commercially available poly(ethylene oxide) monomethyl ethers (Table 1, entries 3 and 4). In each case, chain growth was confirmed by GPC analysis in THF against poly(styrene) standards with the block copolymers revealing shifts to shorter retention times in both cases with narrow dispersities maintained. Furthermore, the synthesis of block copolymers of PMPC with poly(L-lactide) (PLLA) and PMAC further supported that all initiating sites remain active after formation of the first block (Table 1, entries 5–7). For example, the synthesis of a dual functional poly(carbonate) block copolymer was prepared by chain growth of PMAC from a PMPC block. The presence of both functional groups in the BnO-$PMPC_{17}$-*b*-$PMAC_{19}$-OH block copolymer was confirmed by the observation of the resonances at δ = 5.89, 5.33–5.23 and 4.63 ppm corresponding to the pendant allyl ester and at δ = 2.54 ppm for the acetylenic proton. GPC analysis revealed a shift to lower retention from M_n = 4010 g mol^{-1} for PMPC to M_n = 8110 g mol^{-1} for the block copolymer (see ESI, Fig. S2†). Such a block copolymer may be further functionalized using orthogonal chemistries.

Functionalization of homopolymers by copper-catalyzed azido–alkyne dipolar cycloaddition (CuAAC)

Propargyl functional poly(carbonate)s were further functionalized by CuAAC (Scheme 2a) using conditions analogous to those reported for CuAAC functionalizations of (co)polymers from functional δ-valerolactone,[41–43] ε-caprolactone[44–46] and cyclic carbonate[22] monomers. Functionalization of DP10, DP20 and DP72 PMPC homopolymers with 1-azidooctane using 0.4 equivalent CuI and 0.8 eq. diisopropylethylamine (DIPEA), led to >99% conversion of the propargyl groups to the octyl triazole being observed by ^{1}H NMR spectroscopy as evidenced by the



Scheme 2 (a) Huisgen cycloaddition of azides (N_3R) to PMPC homopolymers; (b) radical addition of thiols (RSH) to PMPC homopolymers.

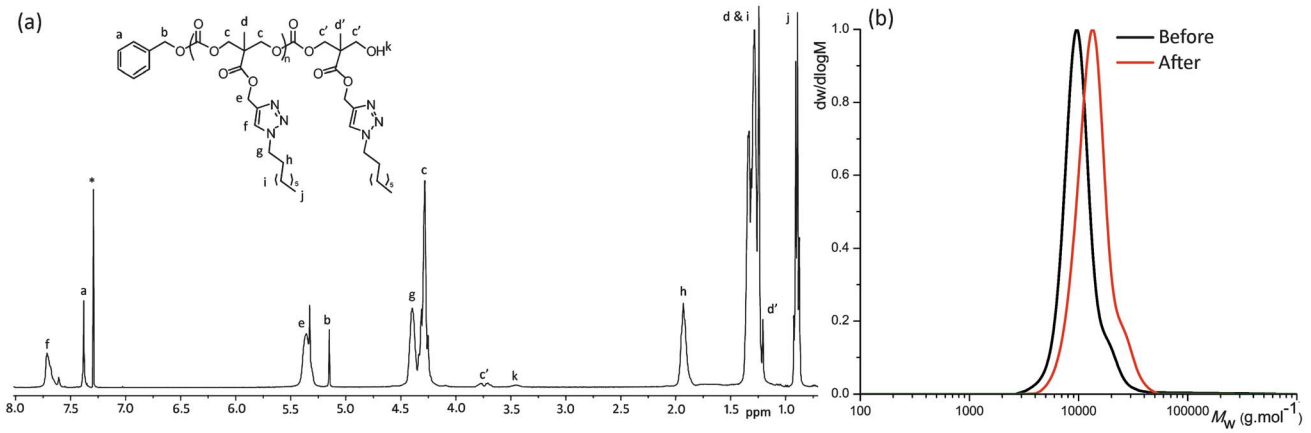


Fig. 3 (a) ^{1}H NMR in $CDCl_3$ of BnO-$PMPC_{10}$-OH after functionalization with 1-azidooctane (400 MHz, 298 K; * = residual $CHCl_3$); (b) GPC traces of BnO-$PMAC_{72}$-OH before (M_n = 9350 g mol^{-1}, $Đ_M$ = 1.11) and after post-polymerization functionalization with 1-azidooctane (M_n = 12740 g mol^{-1}, $Đ_M$ = 1.15).

disappearance of the resonance attributed to the acetylenic proton at $\delta = 2.53$ ppm and the appearance of new resonances consistent with the triazole proton at $\delta = 7.73$ ppm and the octyl resonances at $\delta = 4.38$, 1.92, 1.36–1.18 and 0.86 ppm (Fig. 3a). GPC analysis of the polymers revealed a shift to lower retention time while maintaining narrow distributions with dispersities similar to that of the unmodified PMPC (DP72, pre: $M_n = 9350$ g mol^{-1}, $Đ_M = 1.11$; post: $M_n = 12\,740$ g mol^{-1}, $Đ_M = 1.15$); Fig. 3b. Interestingly, analysis of the functionalized polymer by MALDI-ToF MS revealed two distributions, both with a repeat unit of 353 m/z. While the primary distribution displayed the expected $m/z = 4725$ that corresponds to a sodium charged, fully functionalized poly(carbonate) chain after the addition of 1-azidooctane with a DP of 13, the second distribution was observed with a copper counter ion in place of the expected sodium counter ion. This identification was confirmed by the preparation of the MALDI-ToF MS sample in the absence of added sodium trifluoroacetate as a cationization agent resulted in the observation of a single distribution with a repeat unit of 353 m/z and a main peak at $m/z = 4765$ corresponding to a copper charged, fully functionalized polymer chain of DP13 (see ESI, Fig. S3†).

Complete removal of copper from the polymers was facilitated by stirring a solution of the functionalized polymer with Cuprisorb™ beads. MALDI-ToF analysis of polymers after this process in the presence of NaTFA cationization agent only revealed peaks attributed to sodium charged, fully functionalized poly(carbonate) chains (Fig. 4 and ESI, Fig. S3†).

In order to demonstrate the versatility of this system, additional functionalizations of PMPC homopolymers (DP10 and DP72) were performed with benzyl azide, 2-(2-(2-azidoethoxy) ethoxy)ethanol (TEG azide) and pro-fluorophore 3-azido-7-hydroxylcoumarin (Table 2). ^{1}H NMR spectroscopic analysis of polymers modified with benzyl azide and TEG azide demonstrated that addition of the azide to the propargyl groups was occurring to >99% with data consistent with those expected for

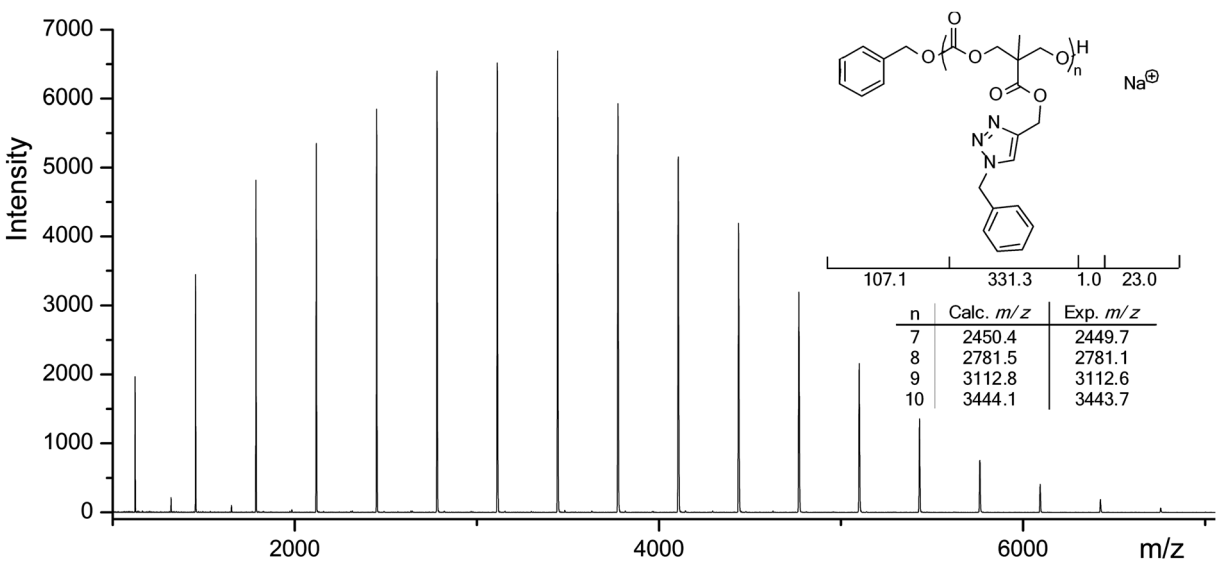


Fig. 4 MALDI-ToF MS of PMPC (DP = 12) after functionalization with benzyl azide.

Table 2 CuAAC functionalization of poly(carbonates)[a]

Azide	M_n[b] (g mol^{-1})	$Đ_M$[b]
—	9350[c]/15 700[d]	1.11[c]/1.13[d]
1-Azidooctane	12 740[c]	1.15[c]
Benzyl azide	9700[c]	1.12[c]
TEG azide	7000[c]	1.21[c]
3-Azido-7-hydroxylcoumarin	13 200[d]	1.30[d]

[a] $[PMPC]_{72}$ = *ca.* 0.34 M in THF or DMF, 1.1 eq. azide, 25 °C, 24 h. [b] Measured by GPC analysis using. [c] THF as eluent. [d] DMF as eluent.

the modified side chain groups as well as a resonance corresponding to the triazole proton at δ = 7.6–7.8 ppm. Functionalizations with the profluorophore 3-azido-7-hydroxylcoumarin revealed 85% functionalization of the propargyl groups by ^{1}H NMR spectroscopy and a shift to lower retention time by GPC. Incomplete conversion in this case was ascribed to the bulky nature of the functional group added, thereby sterically blocking the remaining propargyl groups. Interestingly, the GPC traces of polymers functionalized with benzyl azide and TEG azide showed only small shifts to lower retention time or a slight shift to higher retention time compared to that of PMPC (Table 2). These apparent small changes or decrease in M_n compared to the original polymers can be attributed to changes in their hydrodynamic volumes or Cu^{2+} complexation to the triazole upon functionalization *via* CuAAC.[22] The small change in apparent M_n observed in the addition of benzyl azide is consistent with the observed small change in apparent M_n of allyl-functional poly(carbonate)s upon functionalization with benzyl mercaptan as reported in our previous work,[16] and hence the effects of Cu^{2+} are considered to be minimal. MALDI-ToF MS analysis of the functionalized $PMPC_{10}$ provided further proof of polymer functionalization with both benzyl azide and 3-azido-7-hydroxylcoumarin with the former showing only a single distribution confirming full functionalization (Fig. 4 and ESI, Fig. S4 and S5†). Strong fluorescence was observed upon irradiation of polymer solutions of 3-azido-7-hydroxylcoumarin functionalized polymers with a UV lamp at 365 nm as a result of the inversion of the $^3(n,\pi^*)$–$^1(\pi$–$\pi^*)$ excited states upon triazole formation.[47] In contrast, solutions of the starting polymer, the azide or a mixture of both did not show any fluorescence upon irradiation (see ESI, Fig. S6†).

Functionalization of homopolymers by radical thiol-yne addition

Investigation of the post-polymerization functionalization of PMPC using radical 'thiol-yne' chemistry was undertaken as an alternative post-polymerization technique for the functionalization of the pendant propargyl esters in PMPC homopolymers (Scheme 2b).[48,49] Optimizations of a thermally initiated model system with propargyl acetate (AIBN, dioxane, 90 °C, 24 h, $[PMPC]_0$ = 0.15 M) revealed that 10 equivalents of thiol were required for full conversion to the doubly substituted product to occur. Under these conditions using 10 eq. of 1-dodecanethiol, polymer functionalizations led to complete disappearance of the acetylenic proton at δ = 2.53 ppm being observed by ^{1}H NMR spectroscopic analysis, suggesting full conversion to the new polymer with repeat units substituted with two thiol molecules (Fig. 5a). However, while GPC analysis (Fig. 5b) of the post-polymerization functionalized polymer displayed a shift to lower retention time upon polymer modification, a high molecular weight shoulder was observed that most likely resulted from either coupling of the polymer chains due to the reactive nature of the radical alkynes and alkenes formed during the reaction in combination with their high local concentration,[16,49] or from the amplification of water/self-initiated polymer chains that would be present at twice the molecular weight of the benzyl alcohol-initiated polymer. In order to eliminate the latter possibility, synthesis of a polymer initiated from 1,4-butanediol to yield a polymer possessing a homogeneous molecular weight distribution and its subsequent post-polymerization under 'thiol-yne' conditions with dodecanethiol was investigated. GPC analysis of the resulting polymeric species revealed the same high molecular weight shoulder,

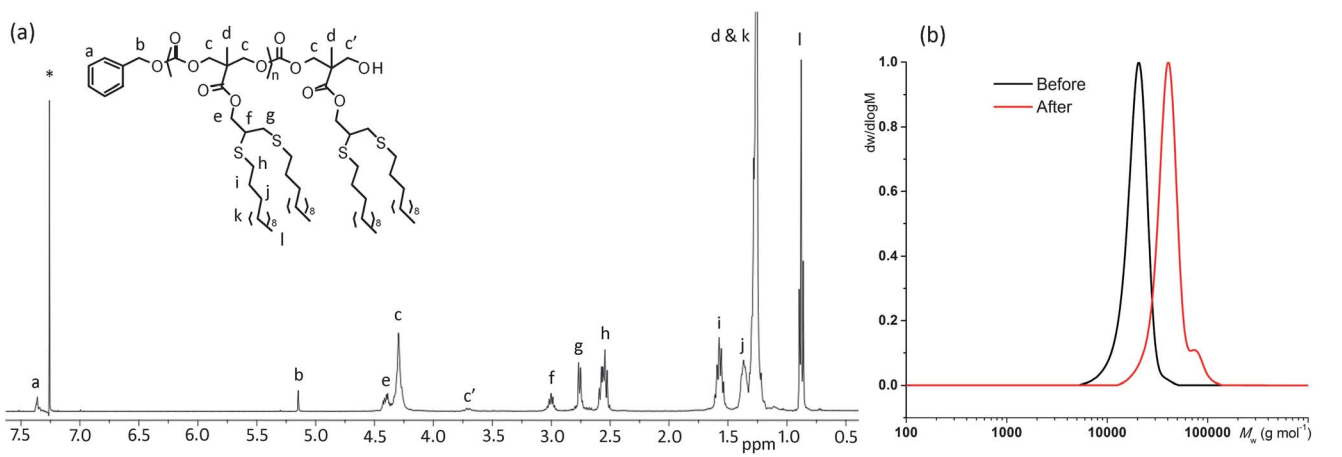


Fig. 5 (a) ^{1}H NMR spectrum of $PMPC_{12}$ after post-polymerization radical functionalization with 1-dodecanethiol in $CDCl_3$ (400 MHz, 298 K; * = residual $CDCl_3$); (b) GPC traces of $(CH_2CH_2O\text{-}PMAC_{45})_2$-OH before ($M_n$ = 18 360 g mol^{-1}, $Đ_M$ = 1.08) and after post-polymerization functionalization with 1-dodecanethiol (M_n = 38 620 g mol^{-1}, $Đ_M$ = 1.10).

Table 3 Radical 'thiol-yne' functionalization of BnO-PMPC$_{72}$-OH[a]

Thiol	M_n[b] (g mol^{-1})	$Đ_M$[b]
—	9350[c]/15 700[d]	1.11[c]/1.13[d]
1-Dodecanethiol	18 140[c]	1.17[c]
Benzyl mercaptan	14 020[c]	1.21[c]
1-Thioglycerol	11 550[d]	1.57[d]
Mercaptoethanol	24 830[d]	1.16[d]

[a] $[PMPC]_{72} = ca.$ 0.15 M in dioxane, 10 eq. thiol, 25 °C, 24 h. [b] Measured by GPC analysis using. [c] THF as eluent. [d] DMF as eluent.

which indicates that this high molecular weight shoulder is indeed the product of coupling between polymer chains that occurs in the reaction. Several attempts to overcome these coupling reactions were attempted including increased thiol equivalence (up to 20 eq.), decreased $[PMPC]_0$ (0.05 M) and milder UV-initiated functionalization using 1 wt% 2-benzyl-2-(dimethylamino)-4′-morpholinobutyrophenone photoinitiator however, consistent with the observations reported by Koo *et al.*,[50] suppression of the coupling was not possible.

Despite its limitations, the radical 'thiol-yne' process was repeated for a range of thiol-containing molecules including those with alcohol groups which are incompatible with the investigated ring-opening polymerization (Table 3). ^{1}H NMR spectroscopic analysis of the modified polymers all demonstrated that full conversion of the propargyl and allyl intermediates had occurred with data consistent with those expected for the modified side-chain groups. GPC analysis of the polymers revealed a shift to lower retention times with a shoulder due to cross-linking being observed in all cases. Further analysis using MALDI-ToF MS of DP10 polymers functionalized with 1-dodecanethiol and benzyl mercaptan revealed a main distribution consistent with full addition of two thiol molecules per repeat units in both cases. For example, functionalization with 1-dodecanethiol led to an increase of the repeat unit from 198 m/z to 603 m/z (+2 × 202 m/z) with a main peak corresponding to a sodium charged, fully functionalized polymer chain of DP4 at m/z = 2542 (Fig. 6). In both cases a second distribution was observed showing a difference of −135 Da in comparison to the main distribution; this is an apparent loss of a benzyl ester and was ascribed to mid-chain cleavage followed by loss of CO occurring during the ionization of the sample. The benzyl mercaptan-functional polymer displays a smaller third distribution corresponding to the loss of 4 benzyl mercaptan units from the polymer chain and is most likely due to reaction of two propargyl groups (see ESI, Fig. S8†).

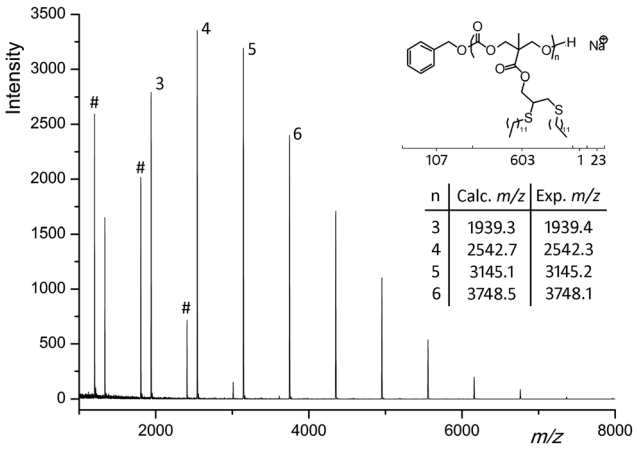


Fig. 6 MALDI-ToF-MS spectra of PMPC$_{12}$ after post-polymerization functionalization with 1-dodecanethiol (secondary distribution – #).

Conclusions

In conclusion, the controlled organocatalytic ring-opening polymerization of 5-methyl-5-propargyloxycarbonyl-1,3-dioxan-2-one, MPC, was achieved using the dual 1-(3,5-bis(trifluoromethyl) phenyl)-3-cyclohexylthiourea (TU)/1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) catalyst system. Polymers with predictable molecular weights (based on $[M]_0/[I]_0$) and narrow dispersities were able to be prepared with the polymerization occurring in a controlled manner. Notably, the post-polymerization functionalization of the pendant propargyl groups in the polymer backbone *via* CuAAC was shown to be highly efficient and occurring without observable polymer degradation leading to the synthesis of a range of new functional aliphatic poly(carbonate)s. Although the functionalization of pendant propargyl groups *via* the radical 'thiol-yne' reactions resulted in low levels of crosslinking being observed due to unavoidable side reactions of the reactive intermediates, reactions proceed with quantitative conversion of the propargyl groups and without degradation of the materials. The versatility of the functionalization of the pendant propargyl groups make these polymers scaffold essential materials for the facile preparation of new functional biodegradable and biocompatible materials and for the preparation of complex degradable materials for bioconjugation and drug delivery applications.

Experimental section

Materials

L-Lactide was purified from dry methylene chloride and sublimed twice before use and stored under inert atmosphere. Poly(ethylene oxide) methyl ethers were purchased from Sigma-Aldrich, dried in a desiccator over P_2O_5 and stored under inert atmosphere. $CDCl_3$, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and (−)-sparteine were dried over CaH_2, distilled, degassed, and stored under inert atmosphere. Benzyl alcohol was dried and stored over 4 Å molecular sieves under inert atmosphere. 2-Hydroxyethyl disulfide was purchased from Aldrich and dried and purified by distillation from CaH_2. Methylene chloride was purified over an Innovative Technology SPS alumina solvent column and degassed before use. 5-Methyl-5-propargyloxycarbonyl-1,3-dioxan-2-one (MPC) was synthesized as reported previously[31,32] recrystallized several times before use, and dried 4 Å molecular sieves under inert atmosphere in dry methylene chloride. Silica gel (pore size = 40 Å) was obtained from Fisher Scientific and used as received. The thiourea catalyst (TU), and maleimide diol (**2**) were synthesized as reported previously,[37,38,51] then dried over calcium hydride in dry tetrahydrofuran and recrystallized from dry methylene chloride. Azides were synthesized as previously reported.[47,52] All other solvents

and chemicals were obtained from Sigma-Aldrich or Fisher Scientific and used as received.

General considerations

Polymerizations were performed under inert atmosphere in a glovebox. Polymer functionalizations were carried out under oxygen-free conditions using standard Schlenk-line techniques. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX-300, DPX-400, DRX-500, AV II-600 or AV II-700 spectrometer at 293 K unless stated otherwise. Chemical shifts are reported as δ in parts per million (ppm) and referenced to the residual solvent signal ($CDCl_3$: ^{1}H, $\delta = 7.26$ ppm; ^{13}C, $\delta = 77.16$ ppm; $(CD_3)_2SO$: ^{1}H, $\delta = 2.50$ ppm; ^{13}C, $\delta = 39.52$ ppm). Mass spectra were acquired by MALDI-ToF (matrix-assisted laser desorption ionization-time of flight) mass spectrometry using a Bruker Daltonics Ultraflex II MALDI-ToF mass spectrometer, equipped with a nitrogen laser delivering 2 ns laser pulses at 337 nm with positive ion ToF detection performed using an accelerating voltage of 25 kV. Solutions of *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propylidene]malonitrile (DCTB) as a matrix (0.3 μL of a 10 g L^{-1} solution in methylene chloride or tetrahydrofuran), sodium trifluoroacetate as a cationisation agent (0.3 μL of a 10 g L^{-1} solution in methylene chloride or tetrahydrofuran), and analyte (0.3 μL of a 1 g L^{-1} solution in methylene chloride or tetrahydrofuran) were applied sequentially to the target followed by solvent evaporation to prepare a thin matrix/analyte film. The samples were measured in linear and reflectron ion mode and calibrated by comparison to 2×10^3 and 5×10^3 g mol^{-1} poly(ethylene oxide) monomethyl ether standards. Gel-permeation chromatography (GPC) was used to determine the molecular weights and polydispersities of the synthesized polymers. GPC in THF was conducted on a system composed of a Varian 390-LC-Multi detector suite fitted with differential refractive index (DRI), light scattering (LS), and ultraviolet (UV) detectors equipped with a guard column (Varian Polymer Laboratories PLGel 5 μM, 50 × 7.5 mm) and two mixed D columns (Varian Polymer Laboratories PLGel 5 μM, 300 × 7.5 mm). The mobile phase was either tetrahydrofuran eluent or tetrahydrofuran with 5% triethylamine eluent at a flow rate of 1.0 mL min^{-1}, and samples were calibrated against Varian Polymer Laboratories Easi-Vials linear poly(styrene) standards (162 to 3.7×10^5 g mol^{-1}) using Cirrus v3.3. GPC in DMF was conducted on a system composed of a Varian 390-LCMulti detector suite fitted with differential refractive index (DRI) and ultraviolet (UV) detectors equipped with a guard column (Varian Polymer PLGel 5 μM, 50 × 7.5 mm) and two mixed D columns (Varian Polymer Laboratories PLGel 5 μM, 300 × 7.5 mm). The mobile phase was DMF with 5% LiBr eluent at a flow rate of 1.0 mL min^{-1}, and samples were calibrated against Varian Polymer Laboratories Easi-Vials linear poly(methyl methacrylate) standards (690 to 1.9×10^6 g mol^{-1}) using Cirrus v3.3.

Typical procedure for the organocatalytic ROP of 5-methyl-5-propargyloxycarbonyl-1,3-dioxan-2-one (MPC)

A solution of MPC ($[MPC]_0 = 0.5$ M) in dry $CDCl_3$ or dry CH_2Cl_2 was added to a stirred solution of alcohol initiator, DBU (1 mol% to monomer), and 1-(3,5-bis(trifluoromethyl) phenyl)-3-cyclohexylthiourea (5 mol% to monomer) in the same solvent. After the desired time, the polymerizations were quenched by the addition of Amberlyst® 16 (acidic) ion exchange resin and precipitated into hexanes. Polymers with degrees of polymerization of 40 or higher were purified by repeated precipitation in hexanes, whereas 1-(3,5- bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea and DBU impurities were removed by column chromatography on silica gel in hexanes–ethyl acetate (4 : 1) for polymers with DP < 40. The polymer containing fractions were directly precipitated into hexanes. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ 7.37 (m, OBn–Ar*H*), 5.15 (s, OBn–CH_2), 4.73 (m, OCH_2C≡CH) 4.44–4.24 (m, OC(O)OCH_2), 3.73 (m, OC(O)OCH_2), 2.53 (s, CH_2C≡C*H*), 2.40 (br s, O*H*), 1.29 (s, CH_3), 1.24 (s, 3H, C(CH_3)CH_2OH). ^{13}C NMR (151 MHz, $CDCl_3$): δ 171.5 (C*C*(O)O), 154.4 (O*C*(O)O), 135.1, 128.8, 128.6 (Ar*C*), 75.7 (CH_2*C*≡CH), 70.1 (CH_2C≡*C*H), 68.6 (OC(O)O*C*H_2), 64.7 (C(O)O*C*H_2), 53.0 (*C*H_2C≡CH), 46.7 (*C*CH_3), 17.5 (*C*H_3). GPC (THF, RI, DP = 72): M_n ($Đ_M$) = 9350 g mol^{-1} (1.11). GPC (DMF, RI, DP = 72): M_n ($Đ_M$) = 15 700 g mol^{-1} (1.13).

Typical procedures for the synthesis of PMPC block copolymers

PEO-*b*-PMPC block copolymers were synthesized using the abovementioned method using commercially available poly(ethylene oxide) monomethyl ethers as initiator ([M]/[I] = 20). For the synthesis of PMPC-*b*-PLLA and PMPC-*b*-PMAC block copolymers, benzyl alcohol, DBU, and 1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea were weighed and dissolved in dry $CDCl_3$. MPC (or L-Lactide) was dissolved separately in $CDCl_3$ and added to the initiator/catalyst solution. After 2 h (>90% conversion), a small aliquot was taken from the mixture and used for GPC analysis, and the reaction mixture was poured in a vial containing L-lactide (or MPC or MAC). The polymerization was carried out until >90% conversion was reached. The mixture was then quenched by addition of Amberlyst® 16 (acidic) ion exchange resin and precipitated in hexanes. *MeO-PEO$_{114}$-b-PMPC$_{18}$-OH.* ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.73 (OCH_2C≡CH), 4.39–4.27 (OC(O)OCH_2), 3.63 (OCH_2CH_2), 3.37 (OCH_3), 2.53 (m, C≡CH), 1.28 (s, CH_3). GPC (THF, RI): M_n ($Đ_M$) = 11 020 g mol^{-1} (1.06). *MeO-PEO$_{216}$-b-PMPC$_{12}$-OH.* ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.73 (OCH_2C≡CH), 4.40–4.25 (OC(O)OCH_2), 3.63 (OCH_2CH_2), 3.36 (OCH_3), 2.50 (m, C≡CH), 1.28 (s, CH_3). GPC (THF, RI): M_n ($Đ_M$) = 17 870 g mol^{-1} (1.06). *BnO-PLLA$_{18}$-b-PMPC$_{20}$-OH.* ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (OBn–Ar*H*), 5.21–5.11 (PLLA–C*H* and OBn–CH_2), 4.72 (OCH_2C≡CH), 4.45–4.24 (OC(O)OCH_2), 3.74 (OC(O)CH_2), 2.54 (C≡ C*H*), 1.57 (PLLA–CH_3), 1.29 (PMPC–CH_3), 1.24 (C(CH_3)CH_2OH). GPC (THF, RI): M_n ($Đ_M$) = 8740 g mol^{-1} (1.08). *BnO-PMPC$_{20}$-b-PLLA$_{24}$-OH.* ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (OBn–ArH), 5.22–5.11 (PLLA–C*H* and OBn–CH_2), 4.73 (OCH_2C≡CH), 4.38–4.25 (OC(O)OCH_2 and C*H*OH), 3.74 (OC(O)CH_2), 2.54 (C≡C*H*), 1.58 (PLLA–CH_3), 1.29 (PMPC–CH_3). GPC (THF, RI): M_n ($Đ_M$) = 10 350 g mol^{-1} (1.09). *BnO-PMPC$_{17}$-b-PMAC$_{19}$-OH.* ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (OBn–Ar*H*), 5.89 (CH_{vinyl}), 5.33–5.23 ($CH_{2\text{-vinyl}}$), 5.15 (OBn–CH_2), 4.73 (OCH_2C≡CH), 4.63 (OCH_2CHCH_2), 4.45–4.27 (OC(O)OCH_2), 3.72 (OC(O)CH_2), 2.54 (C≡C*H*), 1.29 (PMPC–CH_3), 1.27 (PMAC–CH_3). GPC (THF, RI): M_n ($Đ_M$) = 8110 g mol^{-1} (1.06).

Post-polymerisation functionalization of PMPC homopolymers *via* CuAAC

Stock solutions of polymer in dioxane (50 mg polymer mL^{-1}) and stock solutions of diisopropylamine in THF or DMF were prepared and degassed prior to the reactions. In a typical experiment, an ampoule was charged with of polymer stock solution (1 mL of a solution of 50 mg polymer, 3.5×10^{-3} mmol), before the dioxane was removed *in vacuo*. Under a nitrogen atmosphere, CuI (19.1 mg, 0.10 mmol), azide (0.28 mmol) and degassed diisopropylamine stock solution (0.4 M) were added, and the ampoule stirred for 24 h. Amberlyst® 16 (acidic) ion exchange resin and THF or DMF were added and the mixture was stirred vigorously, then passed over a neutral alumina plug. The mixture was then stirred for 16 h with Cuprisorb™ beads to remove residual copper, filtered and concentrated *in vacuo*; the residue was dissolved in a minimal amount of methylene chloride and precipitated into hexanes. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.71 (br s, N_3CHC), 7.35 (m, OBn–Ar*H*), 5.27 (s, C(O)OCH_2), 5.12 (s, OBn–CH_2), 4.37 (m, NCH_2), 4.30–4.22 (m, OC(O)OCH_2), 1.91 (m, N$CH_2CH_2(CH_2)_5CH_3$), 1.36–1.17 (m, $N(CH_2)_2(CH_2)_5CH_3$ and CCH_3), 0.86 (m, $(CH_2)_7CH_3$). ^{13}C NMR (151 MHz, $CDCl_3$): δ 172.1 (*C*C(O)O), 154.4 (O*C*(O)O), 142.0 (*C*=CHN_3), 131.7 (CH_{vinyl}), 68.7 (OC(O)O*C*H_2), 58.7 (O*C*H_2CCHN_3), 50.7 ($N_3CH_2(CH_2)_6CH_3$), 46.7 (*C*CH_3), 31.8, 30.4, 29.2, 29.1 and 26.6 ($(CH_2)_5CH_2CH_3$), 22.7 ($(CH_2)_5CH_2CH_3$), 17.5 (m, CH_3), 14.2 ($(CH_2)_7CH_3$)). GPC (THF, RI, DP = 72): M_n ($Đ_M$) = 12 690 g mol^{-1} (1.15).

Post-polymerization functionalization of PMPC homopolymers *via* radical 'thiol-yne'

Stock solutions of polymer and AIBN (20%) in dioxane (50 mg polymer mL^{-1}) and stock solutions of thiol in dioxane were prepared and degassed prior to the reactions. In a typical experiment, an ampoule was charged with 1 mL of polymer–AIBN stock solution, after which the dioxane was removed *in vacuo*. Under a nitrogen atmosphere, degassed 1-dodecanethiol stock solution was added, and the ampoule was placed in an oil bath at 90 °C and stirred for 24 h. The mixture was then concentrated *in vacuo*; the residue was dissolved in a minimal amount of methylene chloride and precipitated cold methanol. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 (m, OBn–Ar*H*), 5.15 (s, OBn–CH_2), 4.46–4.22 (m, OC(O)OCH_2 and O$CH_2CH_2CH_2$S), 3.70 (m, CH_2OH), 3.00 (m, OCH_2CHCH_2S), 2.76 (m, $OCH_2CH_2CH_2$S), 2.61–2.50 (m, $SCH_2(CH_2)_{10}CH_3$), 1.58 (m, $SCH_2CH_2(CH_2)_9CH_3$), 1.37 (m, $S(CH_2)_2CH_2(CH_2)_8CH_3$), 1.32–1.19 (m, CCH_3 and $(CH_2)_8CH_3$), 0.88 (m, $(CH_2)_8CH_3$). ^{13}C NMR (151 MHz, $CDCl_3$): δ 171.8 (*C*C(O)O), 154.5 (O*C*(O)O), 128.7, 128.5 (Ar*C*), 68.9 (OC(O)O*C*H_2), 65.9 (O*C*H_2CHCH_2S), 46.8 (*C*CH_3), 44.6 (OCH_2CHCH_2S), 34.9 (OCH_2CHCH_2S), 33.4 ($CHSCH_2(CH_2)_{10}CH_3$), 32.1 ($CH_2SCH_2(CH_2)_{10}CH_3$), 31.7 ($CH_2CH_2CH_3$), 30.0, 29.9, 29.8, 29.7, 29.5, 29.1, 29.0 ($CH_2)_8CH_2CH_2CH_3$), 22.8 ($CH_2CH_2CH_3$), 17.6 (C*C*H_3), 14.3 ($S(CH_2)_{11}CH_3$). GPC (THF, RI, DP = 72): M_n ($Đ_M$) = 18 140 g mol^{-1} (1.17).

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