Polymer Chemistry

Accepted Manuscript

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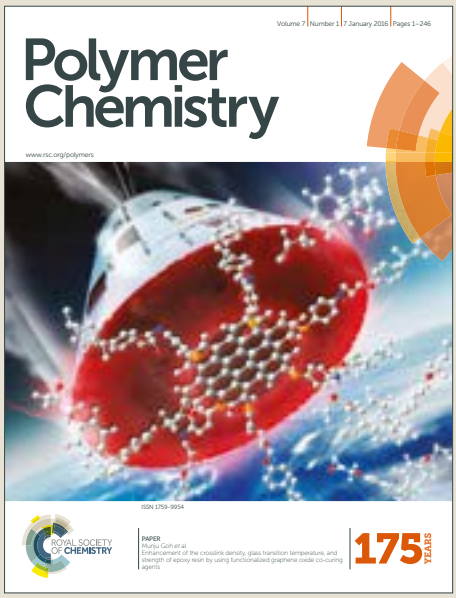

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DOI: 10.1039/C8PY00156A

Acrylate-macromonomers and telechelics of PBA by merging biphasic SET-LRP of BA, chain extension with MA and biphasic esterification

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ABSTRACT

Single electron transfer living radical polymerization (SET-LRP) provides excellent control on polymer chain-end functionality. The chain ends of poly(butyl acrylate) (PBA), prepared by biphasic SET-LRP in an acetone/water mixture using non-activated Cu(0) wire/TREN/Cu(II)X_2 catalytic system, could not be reacted quantitatively using a biphasic reaction mixture of potassium acrylate (KA) in acetonitrile at 75 ºC. This procedure was previously successfully applied to poly(methyl acrylate). The PBA chain ends showed lower reactivity due to its higher hydrophobicity and sterically hindered nature. However, the chain extension of α-bromo and α,ω-dibromo PBA with few monomeric units of MA was demonstrated to change dramatically the reactivity of PBA. Thus, acrylate-functionalizated macromonomers and telechelics based on PBA could be successfully prepared by merging biphasic SET-LRP, chain extension with MA and the heterogeneous esterification with KA in acetonitrile at 75 ºC. This three steps methodology, that can be simplified carrying out two or even three steps in one pot, is expected to become a general route for the preparation of acrylate-functionalizated polyacrylates derived from monomers with hydrophobic and sterically hindered substituents.

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Introduction

The recent developments on biphasic organic solvent/water single-electron transfer-living radical polymerization (SET-LRP) system represent a step toward expanding the scope of SET-LRP to complex macromolecular architectural concepts based on hydrophobic self-organizing dendronized monomers and polymers.[1,2, 3,4,5,6,7] SET-LRP demands polar solvents in combination with Cu(II)X_2-stabilizing N-ligands to mediate the disproportionation of the *in situ* generated Cu(I)X into Cu(0) activator and Cu(II)X_2 deactivator and establish control without making use of a persistent radical effect.[8,9,10] Favorite N-ligands to mediate the SET-LRP process are tris(2-dimethylaminoethyl)amine (Me_6-TREN) and tris(2-aminoethyl)amine (TREN) and branched poly(ethyleneimine) (PEI). SET-LRP has its origins in early studies on the use of copper[11,12,13,14] and Pd(0)[15]-catalyzed SET processes for the LRP of vinylic monomers as well as studies on condensation polymerization.

Organic solvent/water biphasic systems exploit the rapid disproportionation of Cu(I)X in water to free the organic solvents from their responsibility to mediate this mechanistically-required process.[16,17,18,19,20,21,22] These biphasic systems rely on the fact that water containing Cu(II)X_2 and a ligand is not miscible with water-miscible/immiscible organic solvents containing a monomer/polymer. Since water is the best solvent for both Cu(I)X and Cu(II)X_2, both copper salts are partitioned and reside in the water phase, where the ligand-mediated disproportionation of Cu(I)X takes place. Conversely, activation takes place in the organic phase while "self-controlled" reversible deactivation occurs at the interphase of both phases. Hence, biphasic systems eliminate the need of contemporary polar disproportionating solvents, [8,9,23,24,25] and will expand the scope of complex macromolecular architectures accessible by SET-LRP.[26,27,28,29,30]

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Acetone is an attractive solvent for technological applications because it serves as a good solvent for many polymers and is inexpensive. Last but not the least, it possesses a low boiling point that may be attractive to recover dissolved polymers without the need of using co-solvents. The non-activated Cu(0) wire-catalyzed SET-LRP of methyl and *n*-butyl acrylates (MA and BA, respectively) in acetone-water mixtures containing $Cu(II)Br_2$ and TREN provides an economical and efficient approach to well-defined PMA and PBA homopolymers.[21] The high bromine chain end functionality (f^{Br}) of these polymers can be exploited to introduce specific functional groups. In a back-to-back publication we disclosed that secondary α-bromoester end groups of relatively hydrophilic PMA can efficiently react with potassium acrylate (KA) in acetonitrile (75 ºC) or acetone (50 ºC).[31] Thus, acrylate macromonomers and telechelics of PMA were conveniently prepared by merging biphasic SET-LRP in an acetone-water mixture (8/2, v/v) with the esterification reaction of KA at the chain ends of ω-bromo and α,ω-bromo chain ends of PMA in acetonitrile (PMA-Br and Br-PMA-Br, respectively) (Scheme 1a and b). This combination of biphasic reactions furnished PMAs with high end-group fidelity. Here, we expand the scope of this strategy to a more challenging polymer, PBA. However, in this case, the access of the hydrophilic KA salt to the bromine chain ends of PBA is strongly reduced by the inherent higher hydrophobicity of the polymer as well as by the more sterically hindered nature of its end groups. In this work, the methodological solution to chain extend PBA, prior esterification, with few repeat units of MA to enhance the PBA chain end reactivity is reported.

Results and discussion

Analysis of the non-activated Cu(0) wire-catalyzed SET-LRP of BA in acetone-water (8/2, v/v) mixture mediated by TREN at $[BA]_0/[MBP]_0$ and $[MA]_0/[BPE]_0 = 30$

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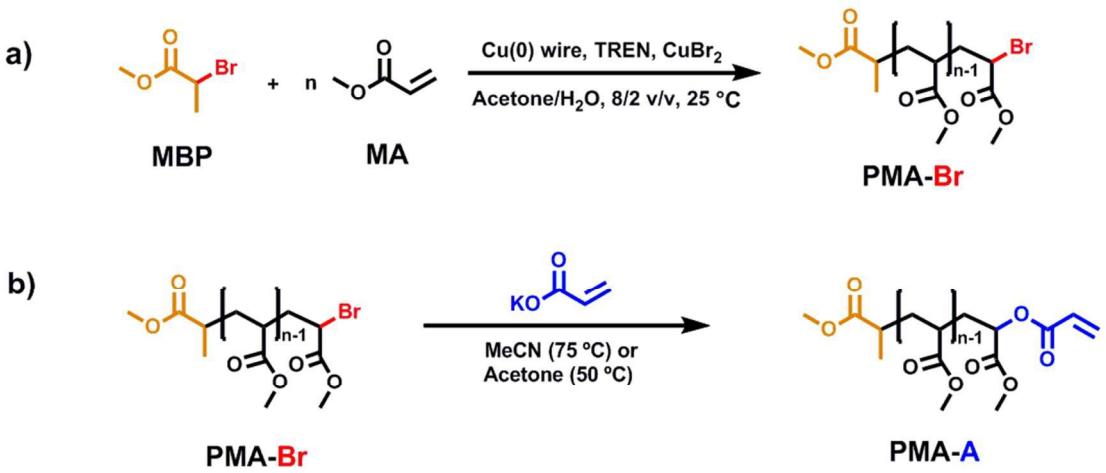
To study the biphasic esterification of KA with the α-bromoester chain ends of PBA, the non-activated Cu(0) wire/TREN catalyzed SET-LRP of BA was carried out in acetone-water (8/2, v/v) mixture to furnish an ω-bromo-terminated PBA (PBA-Br) by using methyl 2-bromopropionate (MBP) as a monofunctional initiator (Scheme 2a). The combination of non-activated Cu(0) wire, TREN and Cu(II)Br_2 was used as a catalytic system. It is important to mention that the SET-LRP of BA has been widely investigated using Cu(0) powder,[23,32] wire[21, 33,34,35,36,37] as well as Cu(0) generated *in situ,*[16,18,22] by reduction of Cu(II)Br_2 with $NaBH_4$.[38,39] The polymerization of BA became biphasic in solvents like DMSO[32,34,35] and dimethyl lactamide.[36] However, the highest molar mass PBA (M_n = 527,700 M_w/M_n = 1.21, 12 h) prepared by SET-LRP was obtained in an homogeneous system based on 2,2,3,3-tetrafluoropropanol (TFP) and DMSO.[40] A low $[MA]_0/[MBP]_0$=30 (M_n^{th} = 4,000 g/mol at 100% conversion) was used in this study to provide a low molar mass PBA-Br sample suitable for a precise analysis of chain-ends by 500 MHz ^{1}H NMR and MALDI-TOF before and after thio-bromo "click" and functionalization with KA.



Scheme 1. (a) SET-LRP of MA initiated with MBP and catalyzed by non-activated Cu(0) wire, TREN and Cu(II)Br_2 in a mixture of acetone/water (8/2, v/v) at 25 ºC. (b) Chain end esterification of PMA-Br with KA in acetonitrile (75 ºC) or acetone (50 ºC).

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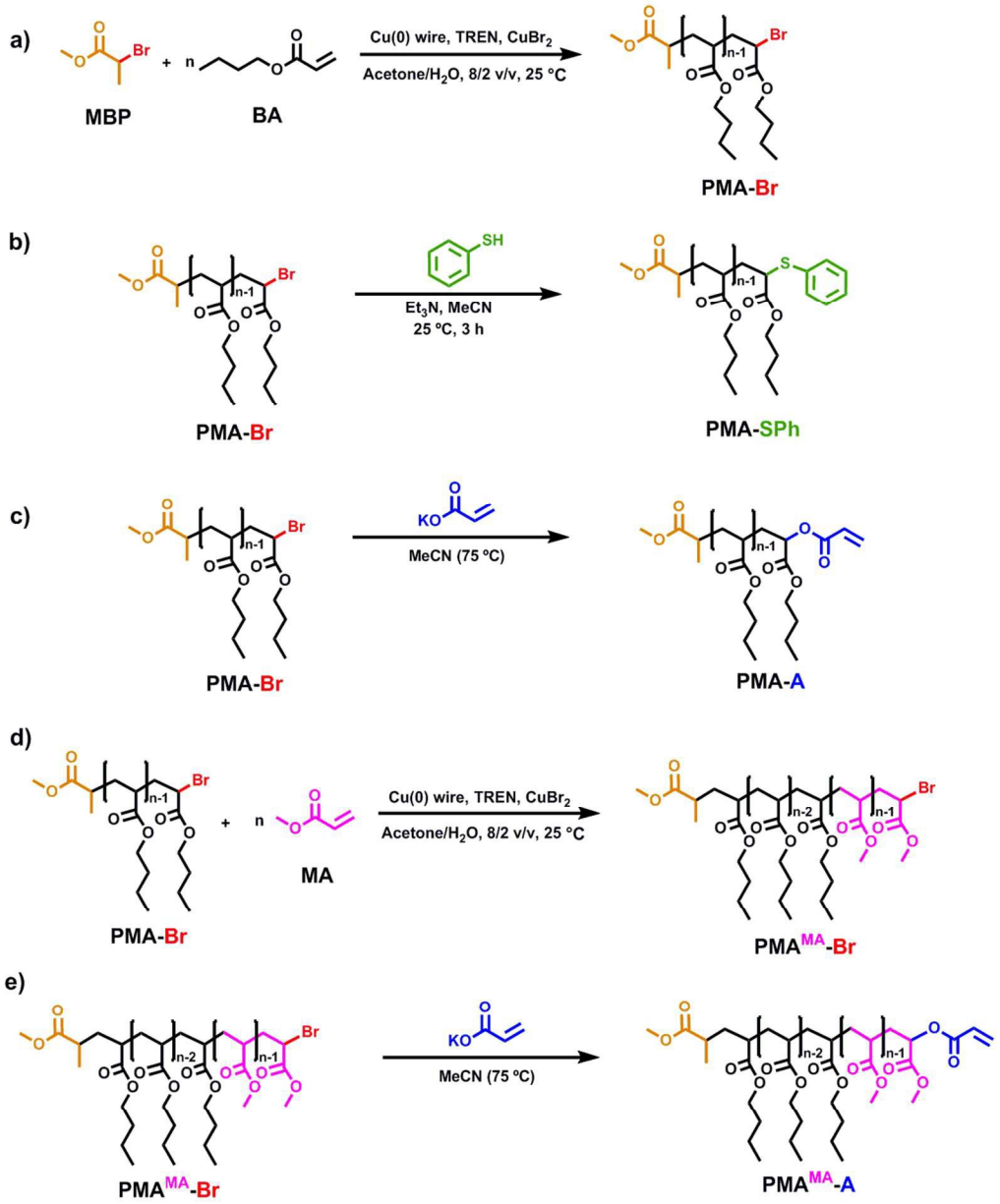

Scheme 2. (a) SET-LRP of BA initiated with MBP and catalyzed by 12.5 cm of 20 gauge Cu(0) wire/TREN/$CuBr_2$ in an acetone/H_2O mixture (8/2, v/v) at 25 ºC, (b) thio-bromo "click" reaction of monofunctional PBA-Br with thiophenol, (c) functionalization of the bromine-chain ends of PBA-Br with KA in MeCN at 75 ºC, (d) chain extension of PBA-Br with MA by a biphasic SET-LRP catalyzed by 12.5 cm of 20 gauge Cu(0) wire/Me_6-TREN in an acetone/H_2O mixture (8/2, v/v) at 25 ºC and (e) functionalization of the bromine-chain ends of PBA^{MA}-Br with KA in MeCN at 75 ºC.

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PBA-Br was prepared under the following conditions $[BA]_0/[MBP]_0/[TREN]_0/[CuBr_2]_0$ = 30/1/0.4/0.2 to exemplify the tolerance of the systems to high loadings of both activator and deactivator without undesired side reactions.[21] This is because, unlike homogeneous SET-LRP systems, in biphasic organic solvent/water systems the reversible deactivation occurs at the interface of aqueous and organic phase.[17] Fig. 1 shows the evolution of conversion and $\ln([M]_0/[M])$ *vs* time throughout this biphasic fast reaction. The polymerizations of BA under these conditions exhibit a linear first order kinetic plot suggesting a constant concentration of growing species up to high conversion. The linear evolution of molecular weight and the progressive decrease of dispersity also support the livingness of the system (see Fig. 1a, right panel).

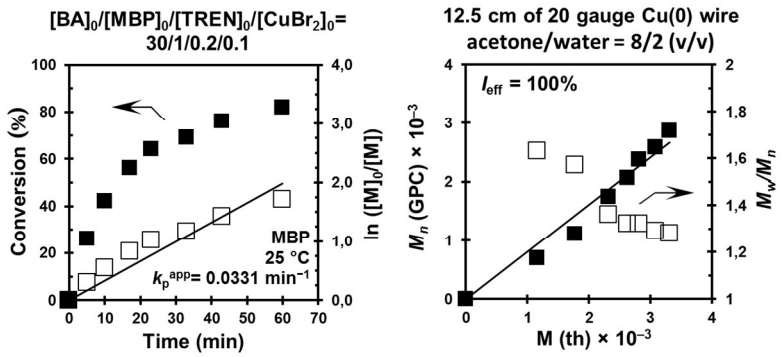

Fig. 1 Conversion and $\ln([M]_0/[M])$ *vs* time kinetic plots and experimental M_n (GPC) and M_w/M_n *vs* theoretical M(th) in SET-LRP of BA in a mixture acetone/water (8/2, v/v) initiated with MBP and catalyzed by non-activated Cu(0) wire at 25 ºC.

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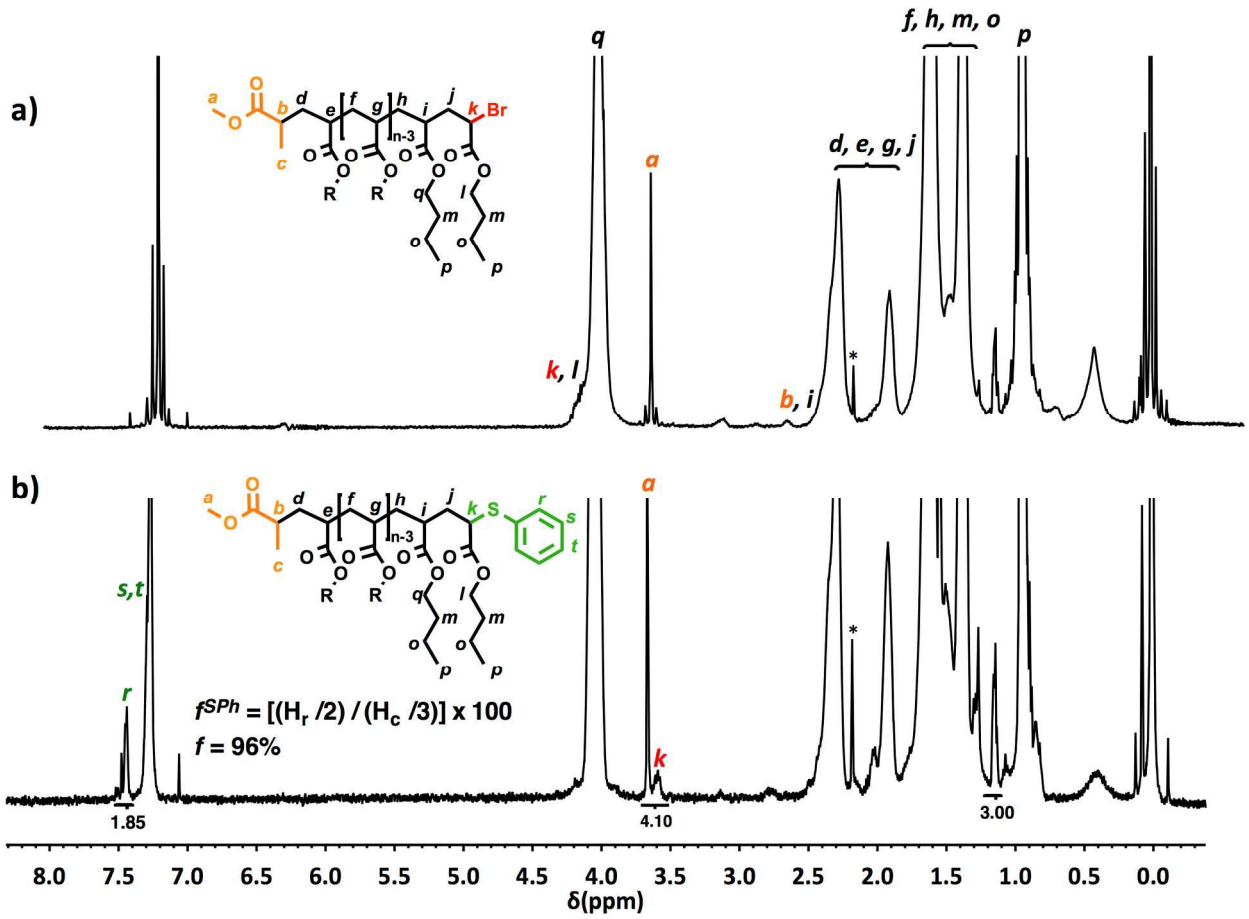

Fig. 2 ^{1}H-NMR (500 MHz) spectra recorded in $CDCl_3$ of (a) PBA-Br isolated at 89% conversion from biphasic SET-LRP of MA in an acetone/water (8/2, v/v) mixture initiated with MBP and catalyzed by non-activated Cu(0) wire at 25 ºC. (b) PMA-Br after thio-bromo "click" reaction with thiophenol. Reaction conditions for biphasic SET-LRP: $[BA]_0/[MBP]_0/[TREN]_0/[CuBr_2]_0$ = 30/1/0.4/0.2, BA = 1 mL, acetone + water = 0.5 mL, 12.5 cm of 20 gauge Cu(0) wire.

As can be seen in Fig. 2a, 500 MHz ^{1}H NMR analysis cannot be used to faithfully assess the f^{Br} of the produced PMA-Br due to the overlapping of signals. However, it can be done indirectly taking advantage of the efficient and quantitative thio-bromo "click" reaction (Scheme 2b).[41,42] It is important to mention that this functionalization reaction is usually carried out under homogeneous conditions in a solution of acetonitrile. As can be seen in Fig. 2b, the high-field shift of signal H_k after the thioetherification with thiophenol allows to determine the fraction of

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PBA chains capped with bromine atoms (f^{Br} = 96%). MALDI-TOF analyses performed before and after thio-bromo "click" reaction also confirm high end-group fidelity under these polymerization conditions (Fig. 3). This is a remarkable result considering the low targeted DP and the big surface area of Cu(0) wire (3.20 cm^2 for 1 mL reaction scale in 2/1 v/v monomer to solvent) and excess of externally added Cu(II)Br_2 (20 mol % with respect to initiator concentration) used in this experiment.

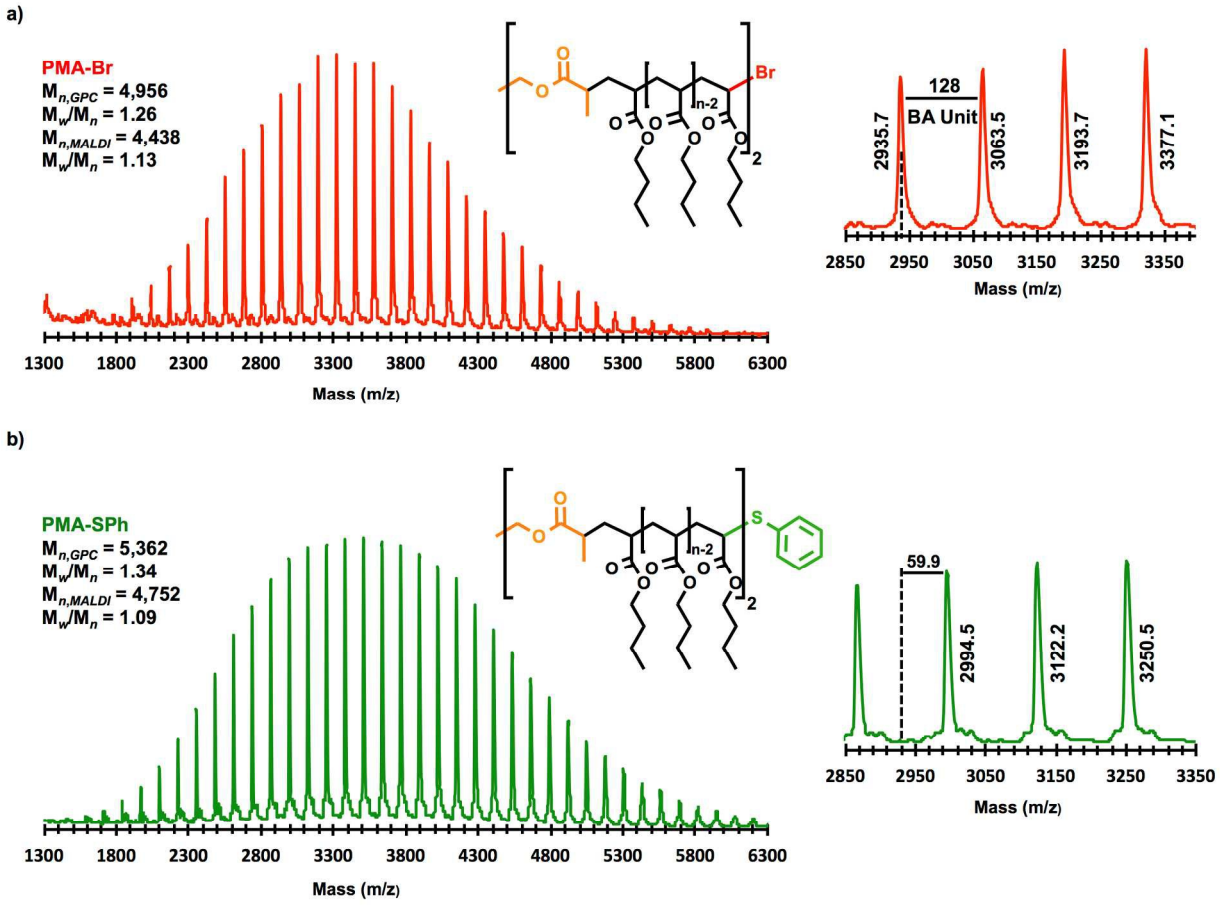

Fig. 3 MALDI-TOF of (a) PBA-Br isolated at 89% conv. from biphasic SET-LRP of BA in acetone/water (8/2, v/v) mixtures initiated with MBP and catalyzed by non-activated Cu(0) wire at 25 ºC (b) PBA-Br after thio-bromo "click" reaction. Reaction conditions: $[BA]_0/[MBP]_0/[TREN]_0/[CuBr_2]_0$ = 30/1/0.4/0.2, MA = 1 mL, acetone/water (8/2, v/v), acetone + water = 0.5 mL, 12.5 cm of 20 gauge Cu(0) wire at 25 ºC.

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Functionalization of ω-bromo end-groups of polyacrylates *via* heterogeneous esterification with KA: PMA *vs* PBA

In a back-to-back publication[31] we reported that the poor solubility of KA in common organic solvents is not an impediment to functionalize the α-bromoester chain ends of PMA synthesized by SET-LRP with acrylate moieties.[31] Both biphasic reactions were merged with the purpose to furnish well-defined acrylate macromonomers and telechelics of PMA. Despite KA is insoluble in acetonitrile, ^{1}H NMR analysis and MALDI-TOF was used to demonstrate that the reaction of KA with monofunctional PMA (M_n < 5,000 g/mol) was fast and quantitative in acetonitrile at 75 ºC using molar ratios CH-Br/KA = 1/5 (blue columns in Fig. 4). The same reaction was also successfully applied to a bifunctional PMA. In acetone, the modification of PMA-Br was much slower but also reached complete conversion (see green columns in Fig. 4). At this point, we already anticipated that the functionalization of PBA would be a more challenging task because of its sterically hindered and hydrophobic character. In fact, the functionalization of PBA-Br (M_n^{GPC} = 4,956 g/mol) with KA did not provide the same result as that obtained with PMA-Br (Scheme 2c). A direct comparison of the evolution of degree of acrylate functionalization (f^{A}) determined by ^{1}H NMR analysis *vs* time for PMA-Br (M_n^{GPC} = 4,956 g/mol) and PBA-Br (M_n^{GPC} = 3,346 g/mol) clearly supports different reactivity for the reaction of PMA-Br and PBA-Br with KA in acetonitrile at 75 ºC under heterogeneous biphasic conditions (compare blue and red columns in Fig. 4).

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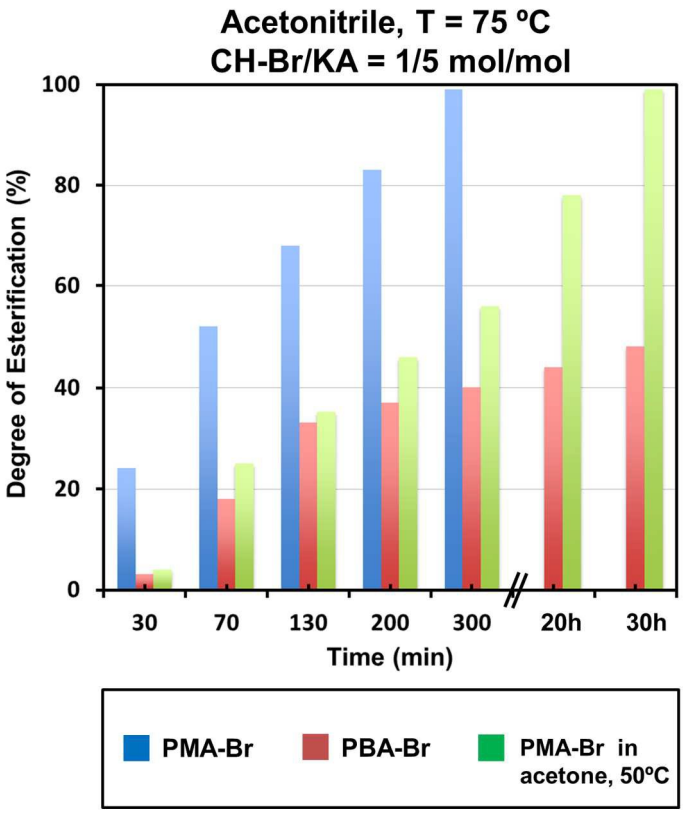

Fig. 4 Kinetics plots, degree of esterification *vs* time of PMA-Br, PBA-Br and PBA^{MA}-Br with KA in acetonitrile at 75 ºC. Blue columns (PMA-Br of M_n^{GPC} = 4,956 g/mol), red columns (PMA-Br of M_n^{GPC} = 4,956 g/mol) and green columns (PBA^{MA}-Br of M_n^{GPC} = 5,428 g/mol).

The esterification of KA with the chain ends of PBA-Br in acetonitrile at 75 ºC was significantly slower than in the case of PMA-Br. The f^A of PMA-A after 60 min was 50% and >99% after 5 h, but for the functionalization of PBA, the reaction reached a plateau at around 40%. MALDI-TOF analysis of the PBA after the reaction with KA confirmed that functionalization was not complete because the expected series of peaks for PBA-A coexisted with the original series of peaks of PBA-Br. Such differences in the reactivity of PBA *vs* PMA chain-ends were not reported previously because so far this interfacial reaction was applied only to bromine-terminated PMA.[31] The origin of the lower reactivity of PBA under these conditions can be related to the limited diffusion of the hydrophilic KA to the sterically hindered bromine chain-

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ends of the hydrophobic PBA. Conversely, although no kinetic experiments were reported for the thio-bromo "click" reaction at PMA and PBA chain ends and reaction times longer than required are commonly used to make sure for complete conversion, the α-bromoester chain ends of both polymers could be quantitatively reacted with thiols.[18,21,32,41,42,43,44] It is important to note, however, that although thio-bromo "click" reaction is usually also carried out in polar solvents such as acetonitrile, DMSO and DMF, it is done under homogeneous conditions using softer thiolate nucleophiles that are less hydrophilic than KA.

Synthesis and structural analysis of acrylate macromonomers and telechelics PBA by chain extension with MA and subsequent functionalization of ω-bromo end groups of PBA *via* heterogeneous esterification with KA: PMA *vs* PBA

The astonishingly dissimilar reactivity of the α-bromoester chain-ends of PMA and PBA inspired us to develop an alternative approach to furnish well-defined PBA macromonomers and telechelics with one or two acrylate chain ends by changing the nature of the last repeating units of the PBA. The high chain end fidelity retained in SET-LRP systems has widely been exploited for efficient preparation of complex architectures based on block and multiblock copolymers *via* the reinitiation of the bromine-capped chain-ends.[45,46,47,48,49] Thus, we envisioned that the subtle chain extension of PBA-Br with few monomer units of MA should change dramatically the reactivity of the chain ends, thus allowing the preparation of the targeted acrylate-functionalized polymers in a designed way (Scheme 2d and e). Monofunctional PBA-Br (M_n = 3,346 g/mol) and bifunctional Br-PBA-Br (M_n = 3,547 g/mol) synthesized as described above, but using the bifunctional initiator bis(2-bromopropniony)ethane (BPE) were used in the next series of experiments. First, we studied the chain extension of both polymers with MA under biphasic

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SET-LRP conditions. Fig. 5 shows the kinetic plots for the chain extension of polymers with MA under the following conditions: $[MA]_0/[PBA\text{-}Br]_0/[Me_6\text{-}TREN]_0$ = 60/1/0.1 and $[MA]_0/[Br\text{-}PBA\text{-}Br]_0/[Me_6\text{-}TREN]_0$ = 60/1/0.1 using 12.5 cm of Cu(0) wire 20 gauge in an acetone/water mixture (8/2, v/v).

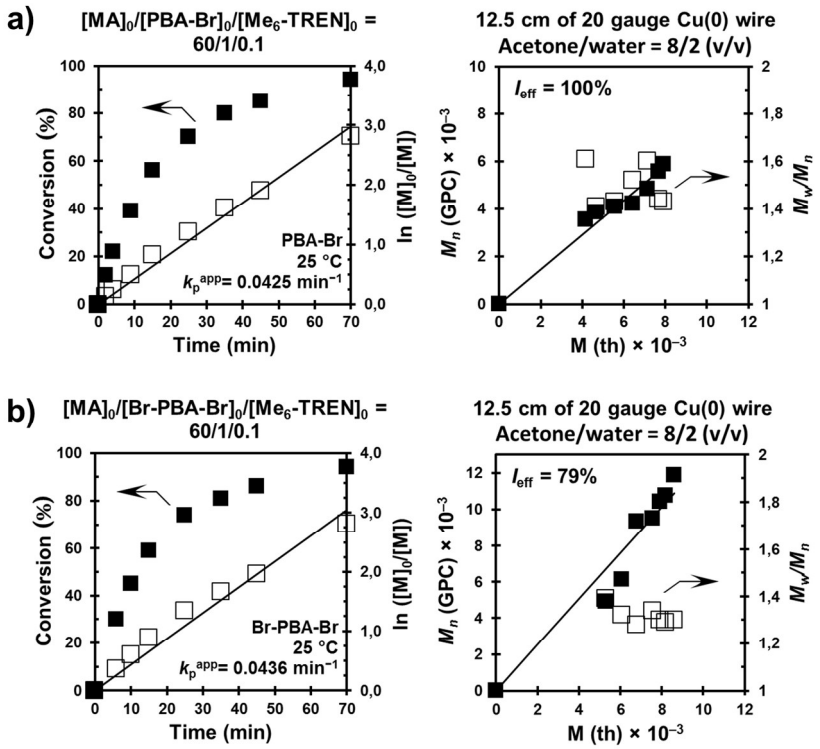

Fig. 5 Conversion and $\ln([M]_0/[M])$ *vs* time kinetic plots and experimental M_n (GPC) and M_w/M_n *vs* theoretical M(th) in SET-LRP of MA in a mixture acetone/water (8/2, v/v) initiated with (a) PBA-Br (M_n = 3,346 g/mol) and (b) Br-PBA-Br (M_n = 3,547 g/mol) catalyzed by non-activated Cu(0) wire at 25 ºC.

It is noteworthy to note that Me_6-TREN was used rather than TREN in these experiments to exemplify that both ligands may indistinctively be used to mediate the SET-LRP process.[16,21] Besides providing clear insights of the livingness, these experiments were used to determine the reaction time required to extend PBA-Br and Br-PMA-Br with few units of MA. In order to prove our concept, the chain extension of PBA-Br and Br-PBA-Br was stopped at 7% and 14% monomer conversion to introduce approximately 4 units of MA at the end of each PBA chain.

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The characterization of both chain-extended bifunctional PBA (Br-PBA^{MA}-Br) was carried out by MALDI-TOF. Fig. 6 shows the MALDI-TOF spectra of the original Br-PBA-Br (spectrum a), the chain-extended Br-PBA^{MA}-Br isolated at 16% MA conversion (spectrum c), as well as an intermediate sample, withdrawn from the reaction mixture at 9% MA conversion (spectrum b).

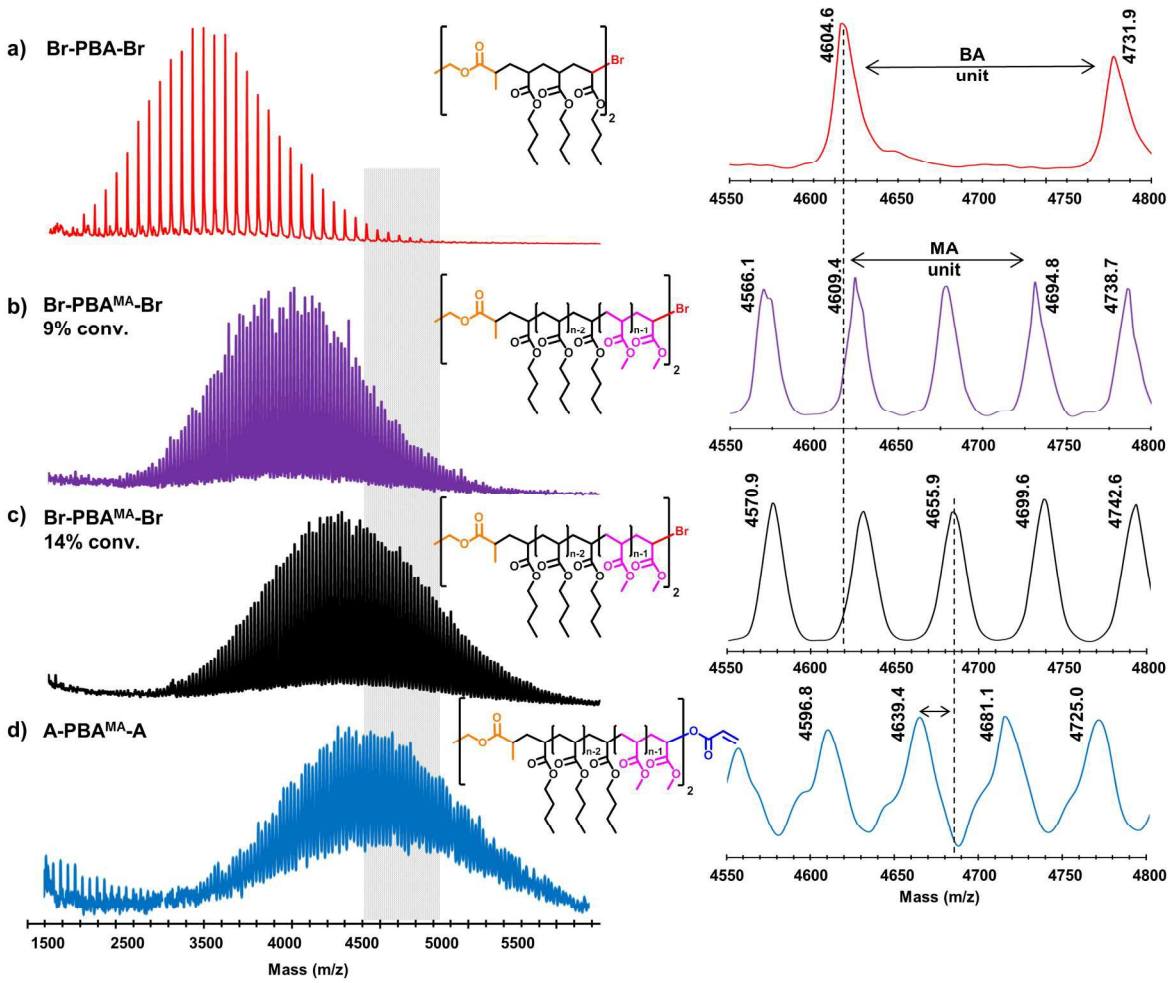

Fig. 6 MALDI-TOF of (a) Br-PBA-Br isolated at 88% conversion from biphasic SET-LRP of MA in an acetone/water (8/2, v/v) mixture initiated with MBP and catalyzed by non-activated Cu(0) wire at 25 ºC. Br-PBA^{MA}-Br isolated at (b) 9% and (c) 16% MA conversion from the chain extension experiment of Br-PBA-Br with MA under the following conditions: $[MA]_0/[$ Br-PBA-Br$]_0/[Me_6$-TREN$]_0$ = 60/1/0.4/0.2, 12.5 cm of 20 gauge Cu(0) wire). (d) A-PBA^{MA}-A isolated after the functionalization of Br-PBA^{MA}-Br with KA with acetonitrile at 75 ºC for 17 h.

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The MALDI-TOF analysis clearly show that molecular weight increases with conversion suggesting the success of the chain extension process. Thus, whereas Br-PMA-Br shows only one main series of peaks separated by 110 mass units, which corresponds to the molar mass of BA repeat units, new series of peaks appear 86 units above the original distribution appear once the chain extension starts. It is important to point out that the new series are located 86 mass units above the original one. This value corresponds to the MA repeating units incorporated at the both chain ends of Br-PBA-Br. The ^{1}H NMR spectrum of Br-PBA^{MA}-Br shows characteristic signals at approximately 3.5 ppm corresponding to the incorporated methyl ester groups of MA repeating units (-OCH_3 groups) (Fig. 7a).

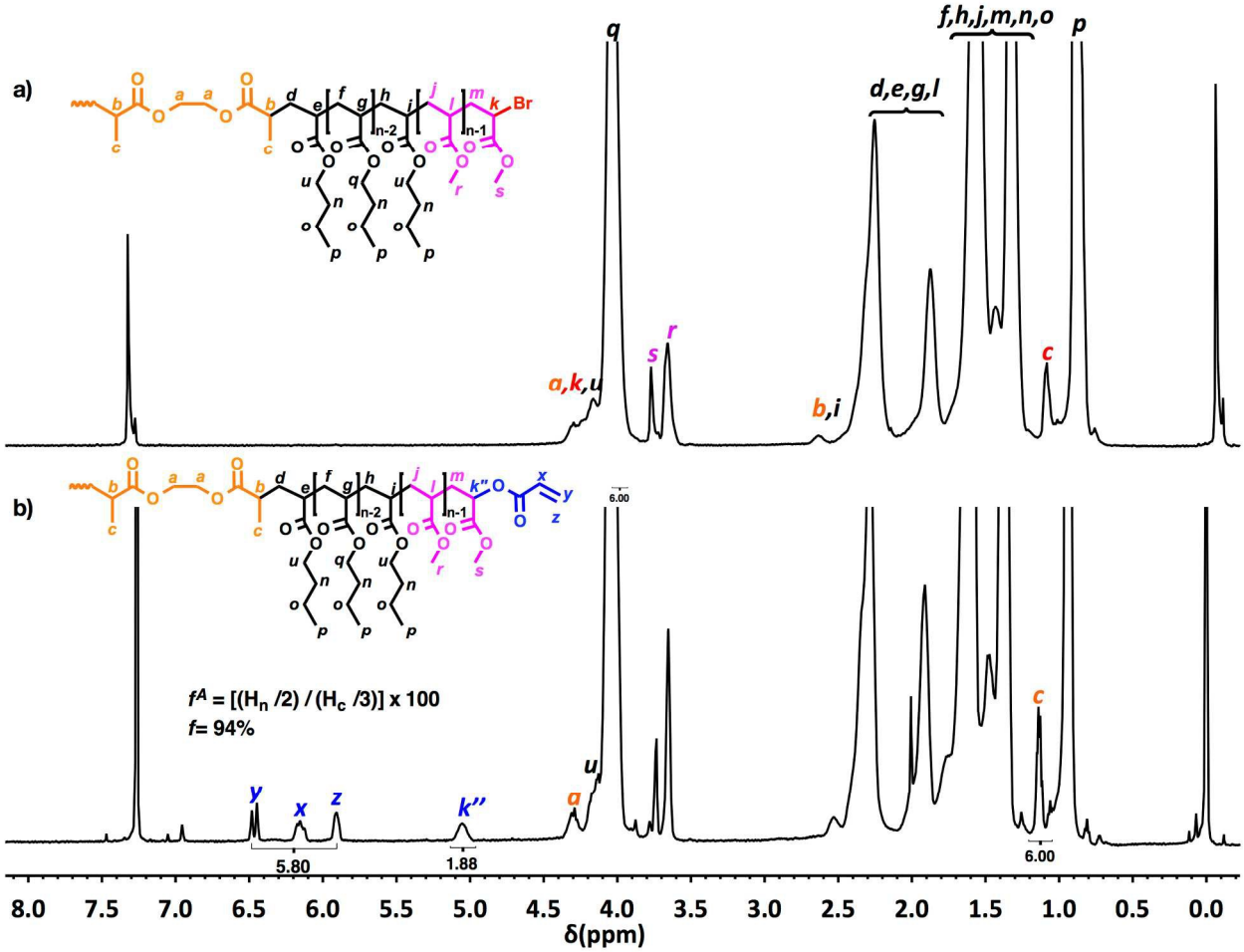

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Fig. 7 ^{1}H-NMR (500 MHz) spectra recorded in $CDCl_3$ of (a) Br-PBA^{MA}-Br isolated at 16% MA conversion from the chain extension experiment of Br-PBA-Br with MA under the following conditions: $[MA]_0/[$ Br-PBA-Br$]_0/[Me_6$-TREN$]_0$ = 60/1/0.4/0.2, 12.5 cm of 20 gauge Cu(0) wire). (b) A-PBA^{MA}-A isolated after the functionalization of Br-PBA^{MA}-Br with KA with acetonitrile at 75 ºC for 17 h.

Finally, to test the reactivity of both α-bromo and α,ω-dibromo chain extended PBA polymers with KA, they were reacted with KA under the conditions reported above. The functionalization could be monitored by ^{1}H NMR (Scheme 2e). Briefly, both polymers, dissolved in acetonitrile at 70 mg polymer/mL, were heated at 75 ºC in the presence of KA. The reaction mixture was heterogeneous due to the insolubility of KA in acetonitrile. Molar ratios CH-Br/KA = 1/5 and 1/10 were used for PBA^{MA}-Br and telechelic Br-PBA^{MA}-Br respectively. The evolution of the degree of esterification for PBA^{MA}-Br, which corresponds to its f^{A}, is shown in Fig. 8a (blue columns). In this case, the esterification of polymer chain ends of PBA^{MA}-Br with KA was complete after 300 min.

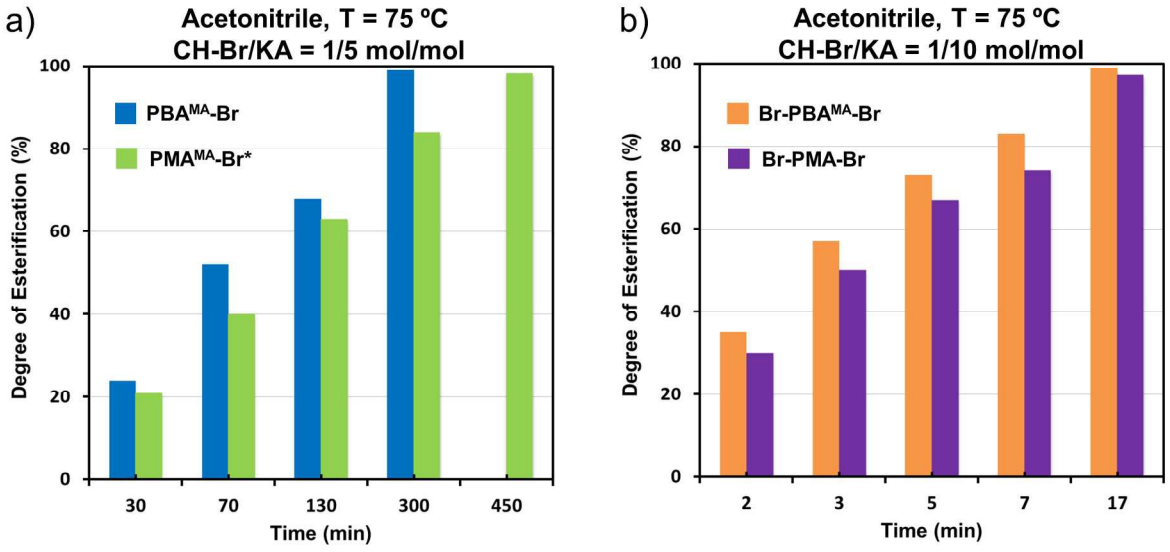

Fig. 8 Kinetics plots, degree of esterification *vs* time of a) PBA^{MA}-Br and PBA^{MA}-Br* and b) Br-PBA^{MA}-Br and Br-PMA-Br with KA in acetonitrile at 75 ºC. Blue columns (PBA^{MA}-Br of M_n^{GPC}

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= 5,428 g/mol), green columns (PBA^{MA}-Br* of M_n^{GPC} = 5,870 g/mol), orange columns (Br-PBA^{MA}-Br of M_n^{GPC} = 6,681 g/mol) and purple columns (Br-PMA-Br of M_n^{GPC} = 3,675 g/mol).

Similarly, the functionalization of the telechelic Br-PBA^{MA}-Br also was successful, but required approximately 17 h to reach quantitative functionalization (Fig. 7b, orange columns). These results are comparable with those reported elsewhere for the functionalization of the polymer chain ends of PMA (compare Fig. 7b, red and purple).[31] The successful of the functionalization of Br-PBA^{MA}-Br with acrylic moieties was finally confirmed by MALDI-TOF (Fig. 6d). In this case, after substitution of a bromine atom (79.9) with an acrylate moiety (71.06) at both polymer chain ends, a new series of peaks appear approximately 18 mass units below the bromine-terminated polymer i.e. Br (79.9) – $C_3H_3O_2$ (71.06) = 8.84 for each chain end. ^{1}H NMR analysis of the isolated polymer was used to determine a f^A >95% (Fig. 7b). Characteristic vinylic signals of the α,ω-acrylate end groups appear between 5.8 and 6.6 ppm.

SET-LRP of BA and functionalization of the PBA chain-ends with KA *via* chain extension with MA in two steps

Finally, considering the potential technological application of the methodology reported here for the preparation of acrylate-functionalized macromonomers and telechelics of PBA and for other sterically hindered hydrophobic polymers, we decided to simplify it by performing the SET-LRP of BA and subsequent chain-extension with MA in a two steps one pot process i.e. no isolation of the bromine-terminated PBA before the chain extension with MA. Thus, the biphasic SET-LRP of BA was first performed under the following conditions: $[BA]_0/[MBP]_0/[TREN]_0/[Cu(II)Br_2]_0$ = 30/1/0.2/0.1 to high conversion (>90%). Next, an aliquot

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of deoxygenated MA (molar ratio BA/MA = 6/1) was added to the reaction mixture in order the complete the chain extension step. After 30 min, the produced PBA^{MA}-Br* (* is used to note that polymerization and chain extension steps were performed without isolation of the bromo-terminated PBA) was isolated by precipitation in cold methanol to carry out the subsequent functionalization with KA. Fig. 7a (green columns) shows the kinetic plots for the functionalization of PBA^{MA}-Br* with KA in acetonitrile at 75 ºC.

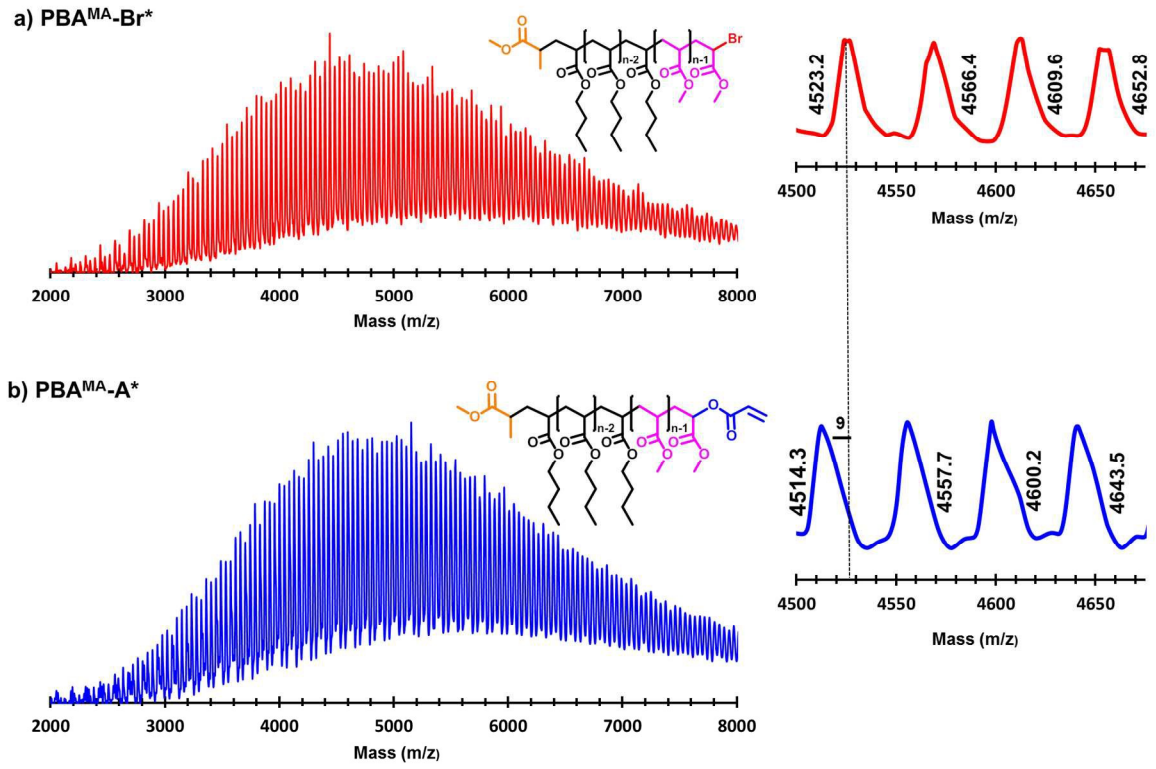

Fig 9 (a) MALDI-TOF of PBA^{MA}-Br* prepared in two steps one pot by SET-LRP of BA in an acetone/water mixture (8/2, v/v) and a subsequent chain extension with MA in the same reaction mixture. (b) MALDI-TOF of PBA^{MA}-A* prepared by the reaction of PBA^{MA}-Br* with KA in acetonitrile at 75 ºC for 7.5h.

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Under these conditions the functionalization proceeded similarly to that of PBA^{MA}-Br prepared in three separated steps (i.e. biphasic SET-LRP of BA, chain extension by biphasic SET-LRP of MA, and biphasic esterification with KA) (compare blue and green columns in Fig. 7a). Despite the reaction time required to achieve quantitative functionalization was a little longer (7.5 h), the MALDI-TOF analysis in this case also confirmed the end capping of bromine-terminated chains with acrylate moieties. As can be seen in Fig. 9, after the reaction with KA the series of peaks corresponding to PBA^{MA}-Br* vanished whereas a new series appeared 9 mass units below i.e. Br (79.9) – $C_3H_3O_2$ (71.06) = 8.84 for each chain end. These results demonstrate that the methodology reported here can be simplified performing the two first steps in one pot or even the three steps in one pot by carrying out the esterification step in the acetone/water biphasic SET-LRP reaction mixture. At the same time the esterification with KA can be performed also directly in the biphasic reaction mixture and the water phase can be reused in other biphasic SET-LRP experiments.

Conclusions

The functionalization of PBA chain ends with acrylate moieties by the reaction of KA under heterogeneous conditions is challenging due to the hydrophobic and sterically hindered nature of this polymer. The functionalization of PBA bromine end-groups is quantitative *via* thio-bromo "click" chemistry with thiophenol under homogeneous conditions at room temperature. However, this reaction was not successful with KA in acetonitrile at 75 ºC under heterogeneous conditions due to the reduced reactivity of PBA-Br vs that of PMA-Br. However, the subtle chain extension of both mono and bifunctional bromo-terminated PBA with few monomerunits

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of MA has been demonstrated to be a convenient approach to change drastically the reactivity profile of PBA chain ends. In this way, acrylate-functionalized PMA macromonomers and telechelics were prepared by merging biphasic SET-LRP of BA with biphasic chain extension with MA and subsequent biphasic esterification with KA. ^{1}H NMR and MALDI-TOF MS was used to demonstrate that the functionalization of both chain extended PBA^{MA}-Br and Br-PBA^{MA}-Br is quantitative using acetonitrile as solvent at 75 ºC in a heterogeneous biphasic reaction mixture. Moreover, it was demonstrated that this methodology can be simplified by performing the two first steps in one pot or even the three steps in one pot by carrying out the esterification step in the acetone/water biphasic SET-LRP reaction mixture. In all cased the water phase of the biphasic system can be reused in additional biphasic SET-LRP experiments. This methodology is expected to be general for other hydrophobic and bulky monomers and provide an accelerated route for the preparation of macromonomers and telechelics as well as other complex structures.

Experimental

Materials

n-Butyl acrylate (99%, from Acros) was passed over a short column of basic Al_2O_3 prior to use in order to remove the radical inhibitor. Tris(2-aminoethyl)amine (TREN) (99% Acros), Cu(0) wire (20 gauge wire, 0.812 mm diameter from Fischer), Cu(II)Br_2 (99%, Alfa Aesar), methyl 2-bromopropionate (MBP) (99% Acros), acetonitrile (99.5%, EMD Chemicals Inc.), acetone (99.8%, Certified ACS, Fischer), thiophenol (99%, Acros) and potassium hydroxide (99%, vmr) were used as received. Triethylamine (NEt_3, 99.9%, Chemimpex) was distilled under N_2 over CaH_2. Acrylic acid (97%, Alfa Aesar) was distilled under vacuum (bp. 59 ºC). Bis(2-bromopropionyl) ethane (BPE) was synthesized according to our previously reported procedure.[32]

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Techniques

500 MHz ^{1}H-NMR spectra were recorded on a Bruker drx500 NMR instrument at 25 ºC in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. For chain-end analysis of PBA macromonomers and telechelics, the delay time (D1) was set at 9 s and the number of scans was set as 120. Gel permeation chromatography (GPC) analysis of the polymer samples were performed using a Perkin Elmer Series LC column oven containing three AM gel columns (a guard column, 500 Å, 10μm column and a 10^4 Å, 10 μm column), a Shimadzu LC-20AD high performance liquid chromatograph pump, a PE Nelson Analytical 900 Series integration data station, a Shimadzu RID-10A refractive index (RI) detector and a Shimadzu SIL-10ADvp Autoinjector. THF (Fischer, HPLC grade) was used as eluent at a flow rate of 1 mL min^{-1}. The number-average (M_n) and weight-average (M_w) molecular weights of PBA samples were determined using a poly(methyl methacrylate) (PMMA) standards purchased from American Polymer Standards. MALDI-TOF analysis was performed in a Voyager DE (Applied Biosystems) equipped with a 337 nm nitrogen laser (3 ns pulse width). For all polymers, the accelerating potential was 25 kV, the grid was 88%, the laser power was 1950 arbitrary units, and a positive ionization mode was used. The sample analysis was performed with 2-(4-hydroxyphenylazo)benzoic acid as matrix. Solutions of the matrix (30 mg mL^{-1} in THF), NaCl (10 mg mL^{-1} in deionized water) and polymer (10 mg mL^{-1}) were prepared separately. The final solution for MALDI-TOF analysis was obtained by mixing the matrix, polymer and the salt solutions in a 5/1/1 volumetric ratio. Then 1μL of the solution mixture were deposited onto six wells of sample plate and dried in air at room temperature before being subjected to MALDI-TOF analysis.

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General procedure for TREN mediated SET-LRP in biphasic acetone-water mixtures

In a 25 mL Schlenk tube, organic solvent (acetone), monomer (BA), water (stock solution containing TREN and Cu(II)Br_2) and initiator (MBP or BPE) were added in the order mentioned. After six freeze-pump-thaw cycles, the Schlenk tube was opened under positive nitrogen pressure to add Cu(0) wire wrapped around a teflon-coated stirring bar. Then one more freeze-pump-thaw cycle was carried out while holding above the reaction mixture the Cu(0) wire using an external magnet. After that, the Schlenk tube was filled with nitrogen and the reaction mixture was placed in a water bath thermostated at 25 ºC. The stirring bar wrapped with the Cu(0) wire, was dropped gently into the reaction mixture. The introduction of the Cu(0) wire defines $t = 0$. Reactions were stopped at 30 min and the reaction mixture was then exposed to the air. The resulting PBA was precipitated in cold methanol, collected and dried under vacuum until constant weight to perform chain end analysis by ^{1}H-NMR and MALDI-TOF, before and after thioetherification by thio-bromo "click" reaction as well as functionalization of chain ends with KA.

General procedure for the chain end modification *via* thio-bromo "click" reaction

In a 10 mL test tube sealed with a rubber septum, thiophenol (0.05 equiv.) and distilled triethylamine (NEt_3, 0.05 equiv) were added into a solution of the corresponding polymer (0.01 equiv) in acetonitrile (1 mL) under nitrogen flow. The reaction mixture was stirred at room temperature for 3 h. Then, the resulting modified PMA was precipitated in cold methanol and washed with methanol several times. The thioetherificated polymers were dried under vacuum until constant weight.

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Synthesis of KA

KA was synthetized following a previously reported procedure.[50] Acrylic acid (AA) was purified by vacuum distillation (60 ºC, 5 mmHg). Distilled AA (1.1 equiv.) was added using an additional funnel to a solution of KOH (1.0 equiv.) and phenolphthalein (3 mg) in methanol (10 mL) at 12-15 ºC. The reaction was maintained at this temperature until the end-point of the indicator. KA was precipitated in 350 mL diethylether in a 500 mL Erlenmeyer flask. The formed crystals were filtered using a Büchner funnel, washed with diethylether and then placed under vacuum until constant weight. KA was obtained as a white powder (98% yield).

General procedure for the chain extension of PBA with MA in two steps.

In a 25 mL Schlenk tube, MA (0.5 mL, 5.55 mmol), acetone (0.4 mL), water (0.1 mL), Me_6-TREN and the macromonomer PBA-Br or Br-PBA-Br (200 mg, 0.09 mmol) were added in the order mentioned. The reaction mixture was deoxygenated following the previously described procedure by 6 freeze-pump thaw cycles and one extra cycle with the the Cu(0) wire (12,5 cm) wrapped around a teflon-coated stirring bar held above. The reaction mixure was placed into a water thermostated bath oil at 25 ºC with stirring. The SET-LRP was left until low conversions (12-14%) then, the reaction was stopped bubbling air for 1 minute into the reaction mixture. The resulting polymer was precipitated into cold methanol and placed into high vacuum until constant weight.

General procedure for the biphasic SET-LRP of BA and subsequent chain extension of with MA in one pot

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A solution of monomer (BA, 1mL, 6.97 mmol), acetone (0.4 mL) and water (0.1mL) (containing the ligand and Cu(II)Br_2) were added into a 25 mL Schelenk tube. The reaction mixture was deoxygenated as descrived previously by 6 freeze-pump thaw cycles. After that, the Cu(0) wire (12,5 cm) wrapped around a teflon-coated stirring bar was added and an extra freeze-pump thaw was carried out. The reaction flask was placed into a thermostated water bath at 25 ºC with stirring. The SET-LRP was left to proceed for 70 min, after that the conversion of the monomer was mesured by ^{1}H-NMR after sampling the reaction with an airtight syringe. Next, a previously deoxygenated solution (30 minutes at 0ºC) of MA (100 µl, 1.045 mmol) was injected and the reaction was left 30 minutes. The resulting polymer was precipitated in a cold solution of methanol/water (8/2, v,v). The obtained polymer was dried under vacuum until constant weight.

General procedure for the chain-end functionalization of PBA-Br, Br-PBA-Br, PBA^{MA}-Br and Br-PBA^{MA}-Br with KA

In a 10 mL test tube, PMA (0.01 equiv.) was dissolved in acetonitrile (1 mL) and KA (0.05 equiv.) was added. The test tube was then sealed with a rubber septum and placed into a 75 ºC thermostated bath oil (t=0). Samples were taken at different times and were purified by precipitation in water and washed three times in cold methanol. The degree of functionalization (f^A) was determined by ^{1}H-NMR.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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Financial support by the National Science Foundation (DMR-1066116 and DMR-1120901) and P. Roy Vagelos Chair at the University of Pennsylvania are greatly acknowledged. G. L. and M. G. acknowledge support from the Spanish Ministerio de Economía, Industria y Competitividad (MINECO) through project MAT2017-82669-R. G. L. also thanks the Serra Húnter Programme. A. M. was supported by an FPI grant (BES-2015-072662) and a mobility grant (BES-2015-072) from the MINECO. T. L. acknowledges financial support from Nankai University, China.

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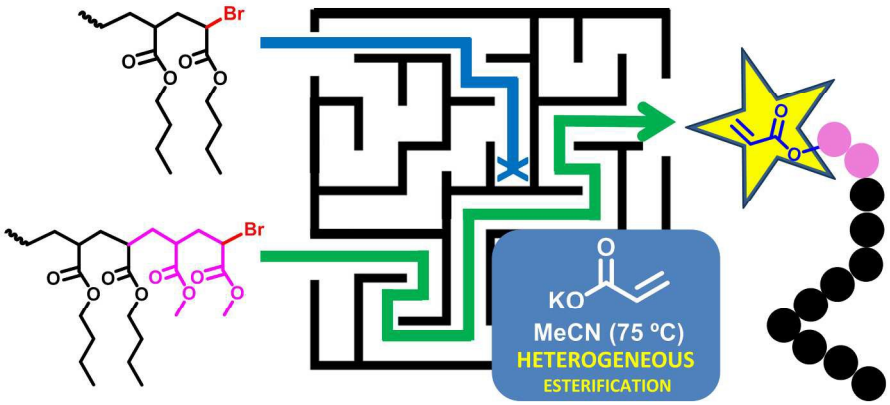

Chain extension of PBA with MA allows the preparation of acrylate-functional PBA.