Macromonomers, telechelics and more complex architectures of PMA by a combination of biphasic SET-LRP and biphasic esterification

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ABSTRACT

The high bromine chain end functionality of polyacrylates synthesized by single electron transfer living radical polymerization (SET-LRP) mediated by TREN in a biphasic acetone-water mixture containing Cu(II)Br_2 can be exploited to introduce specific functional groups to the chain-ends of these polymers. Here, the α-bromoester end groups of poly(methyl acrylate) (PMA) synthesized in this biphasic SET-LRP system using non-activated Cu(0) wire as catalyst were reacted also under heterogeneous biphasic conditions with potassium acrylate to yield PMA macromonomers and telechelics with α- and α,ω-acrylate chain ends. The reagents used in both steps are air insensitive and inexpensive. 500 MHz ^{1}H NMR, GPC and MALDI-TOF analyses in combination with the thio-bromo "click" reaction were used to confirm the high efficiency of this two-steps protocol. The reactive nature of these macromonomers was also demonstrated by the preparation of a PMA-g-PMA more complex architecture.

Introduction

The major role of living polymerization is to construct perfectly monofunctional, bifunctional or multifunctional chain-end polymers preferably with narrow dispersity and to employ them in the synthesis of complex macromolecular systems with new functions. Single-electron transfer-living radical polymerization (SET-LRP) has been demonstrated to be the method of choice for the synthesis of polymers with perfectly functional chain ends[1,2,3] and of polymers with more complex architecture at room temperature and below.[4,5,6,7,8,9,10,11,12] These unique characteristics opened up a great number of opportunities in biorelated fields.[13] The evolution and most fundamental aspects of SET-LRP were comprehensively reviewed elsewhere.[13,14,15,16,17,18,19] Briefly, the roots of SET-LRP are related to our early studies on the use of copper[20,21,22,23] and Pd(0)-catalyzed[24] SET processes for the LRP of acrylates, methacrylates, styrene, acrylonitrile, vinyl chloride (VC) and even for condensation polymerization. Despite of the fact that most of these studies were conducted in non-polar solvents using aryl and alkyl sulfonyl halides[25,26,27,28,29,30,31,32] and N-centered initiators,[33] symptoms of faster reactions were glimpsed under conditions favorable for the disproportionation of Cu(I)X into Cu(0) and Cu(II)X_2.[34] The discovery of the unexpected activity of Cu(0) to reinitiate the product generated by the monoaddition of iodine-containing initiators to VC constituted an important step forward to the development of SET-LRP.[22] Trying to develop an alternative methodology to control the polymerization of VC, because no bimolecular termination occurs during its radical polymerization and therefore no persistent radical effect (PRE) may be established, A.D. Asandei discovered that the very subtle disproportionation of Cu(I) into Cu(0) and Cu(II) in polar solvents (e.g. water, DMSO, DMF, alcohols) is dramatically enhanced in the presence of various N-ligands such as tris(2-aminoethyl)amine (TREN), tris(2-dimethylaminoethyl)amine

(Me_6-TREN), and branched poly(ethylene imine) (PEI). This fundamental discovery became the mechanistically-required step of SET-degenerative transfer living radical polymerization (SET-DTLRP) that was later shown to be in fact SET-LRP.[35,36,37,38] In this context, it was early thought that the use of water, protic, dipolar aprotic or polar disproportionating solvents would be a requirement to practice SET-LRP, and the polymerization of hydrophobic monomers/polymers the Achilles' heel of this LRP technique.[39,40] In fact, the loss of living character systematically observed in systems where disproportionation of Cu(I)X into Cu(0) and Cu(II)X_2 is insufficient and/or solubility of Cu(I)X and Cu(II)X_2 is poor,[41,42,43] and the loss of control experienced during the polymerization of hydrophobic monomers supports this initial belief.[44]

However, SET-LRP "self-generated" systems, in which polymer phase-separates from the homogeneous disproportionating reaction mixture above a certain molecular weight, served us as inspiration to solve this problem.[1,38,44,45,46,47,48] Nowadays, SET-LRP is already viable in polar non-disproportionating and non-polar solvents by using their mixtures with water in an approach named "programmed" biphasic systems.[49,50,51] This approach relies on the unexpected immiscibility between a solution of water containing Cu(II)Br_2 and a ligand with organic solvents, including water miscible organic solvents, containing monomer and polymer. Systems based on solvents with good disproportionation capabilities such as alcohols and dipolar aprotic solvents have also been developed.[52,53,54,55] Unlike homogeneous systems, when SET-LRP operates in a biphasic regime, activation, disproportionation and deactivation events occur in different compartments. The Cu(0) wire surface-mediated activation of dormant alkyl halide/polymer species takes place in the organic phase producing Cu(I)X species. The limited solubility of cuprous halides in organic solvents promote its partitioning into the aqueous phase,

containing ligand, where disproportionate into Cu(0) and Cu(II)X_2. In this scenario, deactivation of growing radicals into dormant species is mainly an interfacial process occurring at the interphase between organic and aqueous phases. Partition of reagents between two phases and the "self-controlled" interfacial activation/deactivation processes are advantageous to avoid side reactions encountered in homogeneous systems when an excess of externally added Cu(II)Br_2 is used.[2,42] Hence, biphasic SET-LRP systems tolerate excess of Cu(II)Br_2 and also of Cu(0) wire.

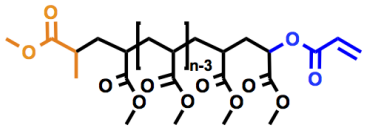
Fundamental examples in which relatively hydrophilic poly(methyl acrylate) (PMA) and hydrophobic poly(butyl acrylate) (PBA) polymers, with perfect or near perfect chain end functionality, evolved from biphasic mixtures of non-disproportionating solvents such as acetonitrile[50,51] and acetone[49] with water were previously reported. Here, acrylate macromonomers and telechelics of PMA, PMA-A and A-PMA-A (Scheme 1), with one and two acrylate functionalities were conveniently prepared by the coalescence of two interfacial reactions: (i) the biphasic SET-LRP in an acetone/water reaction mixture and (ii) the interfacial esterification of potassium acrylate (KA) with the α-bromoester chain ends of PMA in either acetone or acetonitrile. KA is not soluble in acetone or acetonitrile and therefore this chain end esterification occurs also at the interphase. Preliminary data on more complex architectures based on PMA will also be discussed.

Results and discussion

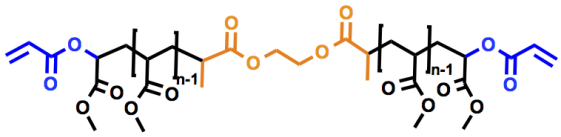
Synthetic strategy to acrylate macromonomers and telechelics of PMA

Our synthetic approach relies on the near perfect bromine chain-end functionality provided by the library of biphasic SET-LRP systems developed so far (Scheme 1).[49,50,51,52,53,54] Among them, here we selected the one based on a poor disproportionating solvent such as acetone. Non-

activated Cu(0) wire/TREN/Cu(II)Br_2 was selected as a catalytic system.[54] Acetone shows unique solubility properties toward many polymers. Indeed, it is the least expensive organic solvent after methanol and has an appealing low boiling point for recycling purposes.



PMA-A



A-PMA-A

Scheme 1. Chemical structure of macromonomers, PMA-A, and telechelics, A-PMA-A, synthesized by esterification of bromine-chain ends of PMA, synthesized by biphasic SET-LRP, with KA.

However, acetone had very limited possibilities as SET-LRP systems operating under homogeneous conditions[41,56,57] because its low disproportionation equilibrium constant, both without (K_{disp} = 0.03 M^{-1})[58,59] and in the presence of Me_6-TREN (K_{disp} = 4.12 x 10^2 M^{-1}).[43,60] In fact, previously reported control experiments for the Cu(0) wire-catalyzed SET-LRP of MA in pure acetone showed lack of first order kinetic and monomer conversion plateau at around 80%.[41,56] The loss of living character under these conditions was exemplified by progressive decrease of bromine chain-end functionality with conversion. However, biphasic SET-LRP systems in certain acetone/water mixtures expanded the scope of this attractive solvent. PMA and PBA of targeted molecular weight (DP=222, M_n^{th} = 19,300 g/mol at 100% conversion) and well-defined chain ends were conveniently prepared in less than 1 h at 25 ^oC.[49] Although "programmed" biphasic SET-LRP systems were originally developed using a methodology that generates Cu(0) catalyst *in situ* by the instantaneous reduction of Cu(II)Br_2 with $NaBH_4$,[16,61,62]

the possibility to use non-activated Cu(0) wire together with ligand was already demonstrated in the previous publication.[54] This simple methodology is equally effective both in the presence of Me_6-TREN and TREN. However, the use of TREN is industrially more attractive due to its low price, although it requires the presence of a small amount of externally added Cu(II)X_2 to mediate the SET-LRP process.

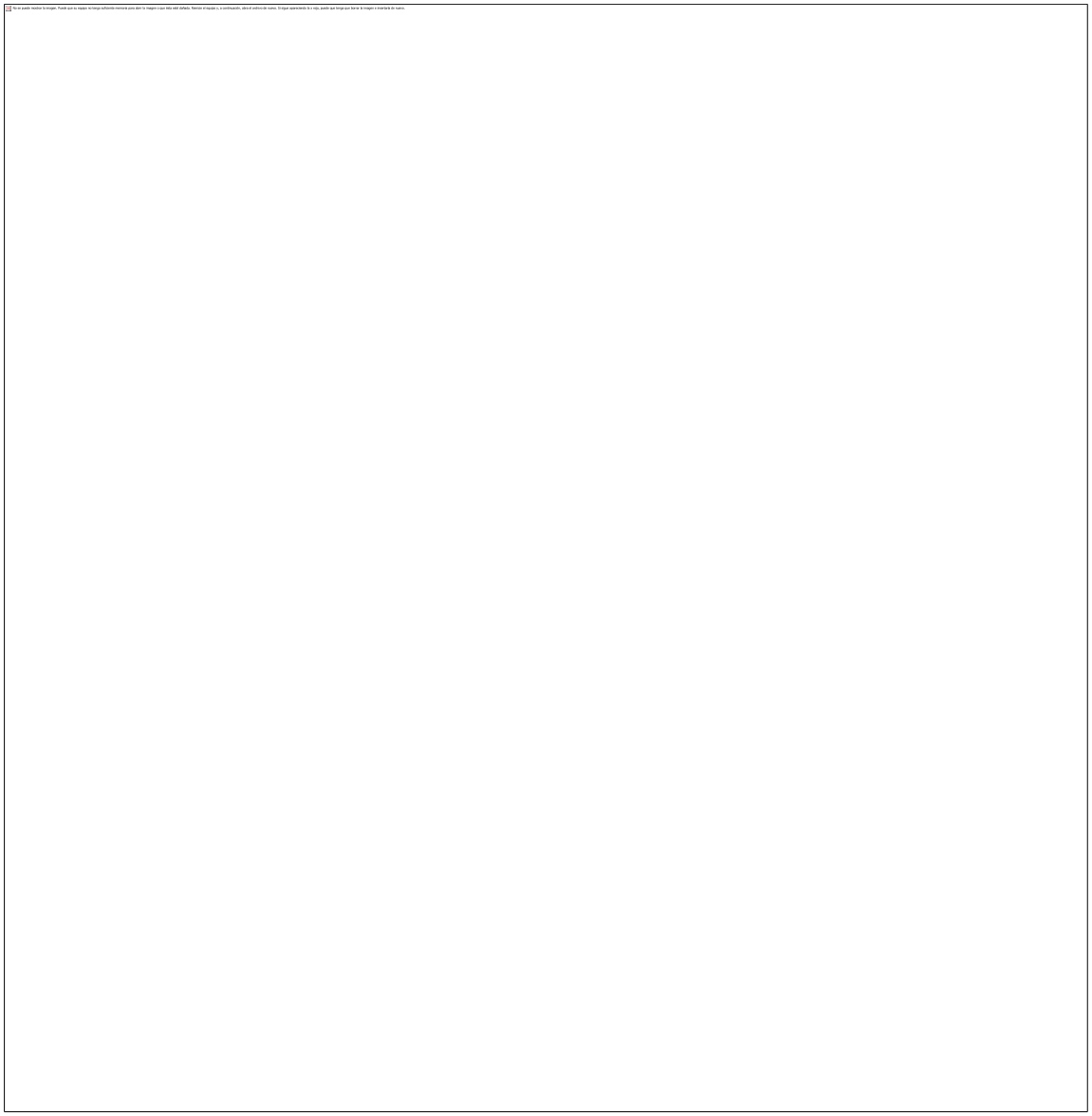
Here, we report a new approach for the preparation of polyacrylate macromonomers and telechelics by combining this biphasic SET-LRP process with the subsequent biphasic esterification of the α-bromoester groups of SET-LRP polymers with potassium acrylate (KA). The reagents used in both steps are air insensitive and inexpensive. Moreover, the use of Cu(0) wire as catalyst tolerates simple inert gas sparging deoxygenation protocols in disposable test tubes[63,64] and even no-degassing because the same Cu(0) catalyst consumes the oxygen from the reaction mixture.[65] In this publication, PMA will be used as a model polymer to later, in a back-to-back publication, expand the scope of this approach to hydrophobic and less reactive homologous structures based on poly(*n*-butyl acrylate), PBA.[66] In the first step towards PMA-A macromonomers, MA is polymerized at room temperature by SET-LRP in the above mentioned acetone/water biphasic SET-LRP system (8/2, v/v) using the monofunctional initiator methyl 2-bromopropionate (MBP) (Scheme 2a). Alternatively, the bifunctional bis(2-bromopropniony)ethane (BPE) is used to create the α,ω-dibromo telechelic Br-PMA-Br. (Scheme 3a). Next, the synthesis of the corresponding macromonomers and telechelics will be accomplished using the heterogeneous esterification, either in acetone or acetonitrile, of the secondary α-bromoester groups of PMA with KA at 50 ºC (acetone) or 75 ºC (acetonitrile) (Scheme 2b and 3b). It is important to emphasize that not only the polymerization, but also the

esterification is an interfacial process because KA is insoluble in both solvents. Note that KA was synthesized from acrylic acid (AA) and KOH in methanol (Scheme 2c).[67] A rigorous 500 MHz ^{1}H-NMR and MALDI-TOF structural analysis of the bromine-capped intermediates before and after thio-bromo "click" reaction with thiophenolate[14, 68] (Scheme 2d and 3c) and final polymers will be used to demonstrate that the coalescence of both heterogeneous reactions become an efficient synthetic approach for the functionalization of one or two PMA chain ends with reactive acrylate moieties and create well-defined acrylate macromonomers and telechelics that would aid to create more complex architectures. Pushing the limits of this SET-LRP biphasic system, the acrylate macromonomer of PMA-A will be copolymerized by biphasic SET-LRP with MA to furnish a complex PMA-g-PMA architecture (Scheme 2e), as a representative first example of the numerous possibilities of these well-defined structures in the construction of more complex macromolecular structures.

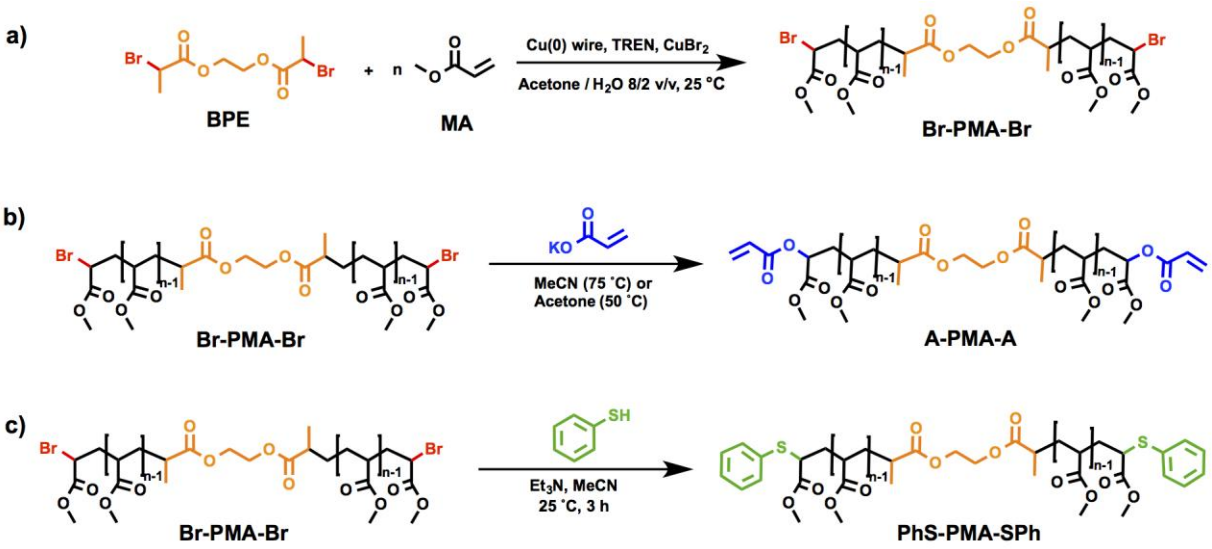
Synthesis and structural analysis of PMA-A macromonomers

Previously reported kinetic studies on the SET-LRP of MA in acetone/water mixture 8/2, v/v demonstrated that the polymerization fulfills all the expected characteristics for a LRP process regardless of how Cu(0) is presented to the polymerization mixture (i.e. Cu(0) generated by reduction of Cu(II)X_2 with $NaBH_4$ and non-activated Cu(0) wire combined with Cu(II)Br_2).[49,54] In this study, the polymerization using MBP was performed over 30 min at 25 ºC under the following conditions: $[MA]_0/[MBP]_0/[TREN]_0/[Cu(II)Br_2]_0$ = 50/1/0.1, MA = 1 mL, acetone + water = 0.5 and 12.5 cm of non-activated Cu(0) wire of 20 gauge. As can be seen in Figure 1a (left image), the polymerization mixture is biphasic already at t=0 due to the insolubility of the aqueous phase containing Cu(II)Br_2 and TREN with the organic phase containing MA. The

heterogeneous nature of the reaction mixture is maintained throughout the entire polymerization process (Figure 1a, right image).



Scheme 2. (a) SET-LRP of MA 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) functionalization of the bromine-chain ends of PMA-Br with KA in acetonitrile or acetone, (c) synthesis of KA from acrylic acid (AA), (d) thio-bromo "click" reaction of monofunctional PMA-Br with thiophenol, (e) biphasic SET-LRP of MA with PMA-A macromonomer initiated with MBP and catalyzed by 12.5 cm of 20 gauge Cu(0) wire/TREN/$CuBr_2$ in an acetone/H_2O (8/2, v/v) mixtures at 25 ºC.



Scheme 3. (a) Biphasic SET-LRP of MA initiated with BPE 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) functionalization of the bromine-chain ends of Br-PMA-Br with KA in acetonitrile or acetone, (c) thio-bromo "click" reaction of bifunctional Br-PMA-Br with thiophenol.

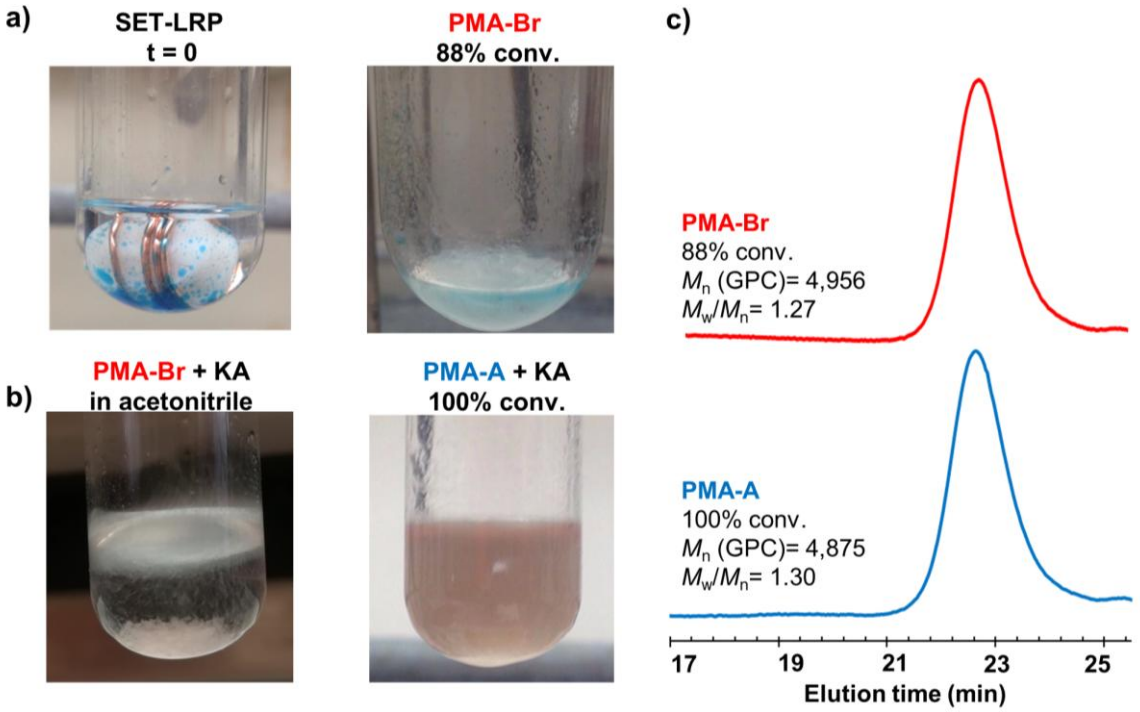


Figure 1. Visualization of the heterogeneous nature of (a) SET-LRP of MA in an acetone/water mixture (8/2, v/v) using non-activated Cu(0) wire/TREN/Cu(II)Br_2 as a catalytic system ($[MA]_0/[MBP]_0/[TREN]_0/[Cu(II)Br_2]_0$ = 50/1/0.1) and (b) esterification of KA with PMA-Br in acetonitrile. (c) GPC chromatograms of PMA-Br and PMA-A.

SET-LRP achieved 88% conversion under these conditions. GPC analysis revealed the formation of PMA-Br with M_n = 4,956 g/mol which is in good agreement with the theoretical value. Despite the low targeted $[M]_0/[I]_0$, the polymer was well defined as indicated by a symmetric GPC peak with narrow molar mass distribution (Figure 1c, red curve). The degree of control over polymer chain-end functionality was attained by the 500 MHz ^{1}H NMR analysis of the precipitated PMA-Br (Figure 2a). The ratio between signals H_c and H_k, characteristic of heterofunctional α and ω-polymer terminus revealed, within the experimental error of the measurement, near perfect bromine functionality (f^{Br}) for the synthesized PMA-Br ($f^{Br} = 99$ %). The analysis of this polymer after a thioetherification of the ω-end groups with thiophenolate using the rapid and efficient thio-bromo "click" reaction is in agreement with this result (see Figure 2b). Inspired by the success of thio-bromo "click" reaction at the polymer terminus of SET-LRP polymers, the esterification of KA with the α-bromoester groups of the halogen capped PMA was investigated as a means to prepare macromonomers of PMA consisting of a PMA chain with an acrylate moiety located at the ω-end group (Scheme 2b).

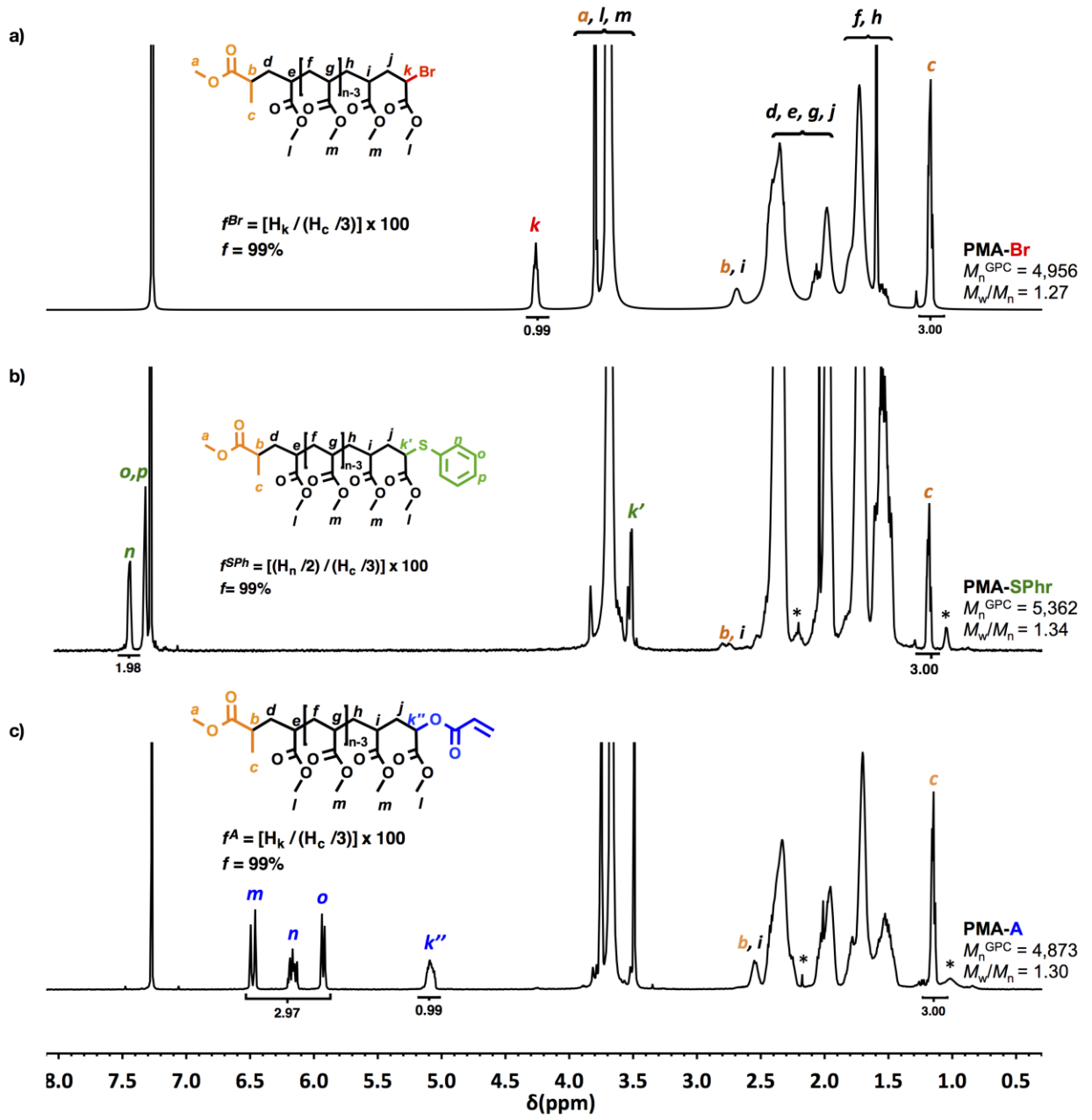


Figure 2. ^{1}H-NMR (500 MHz) spectra recorded in $CDCl_3$ of (a) PMA-Br isolated at 88% conversion from biphasic SET-LRP of MA in an acetone/water (8/2, v/v) mixture initiated with MBP and catalyzed by non-activated Cu(0) wire at 25 ºC. (b) PMA-Br after thio-bromo "click" reaction with thiophenol. (c) PMA-A synthesized by esterification of PMA-Br with KA. Reaction conditions for biphasic SET-LRP: $[MA]_0/[MBP]_0/[TREN]_0/[CuBr_2]_0$ = 50/1/0.4/0.2, MA = 1 mL, acetone + water = 0.5 mL, 12.5 cm of 20 gauge Cu(0) wire. *Residual solvent peak = grease, acetone.

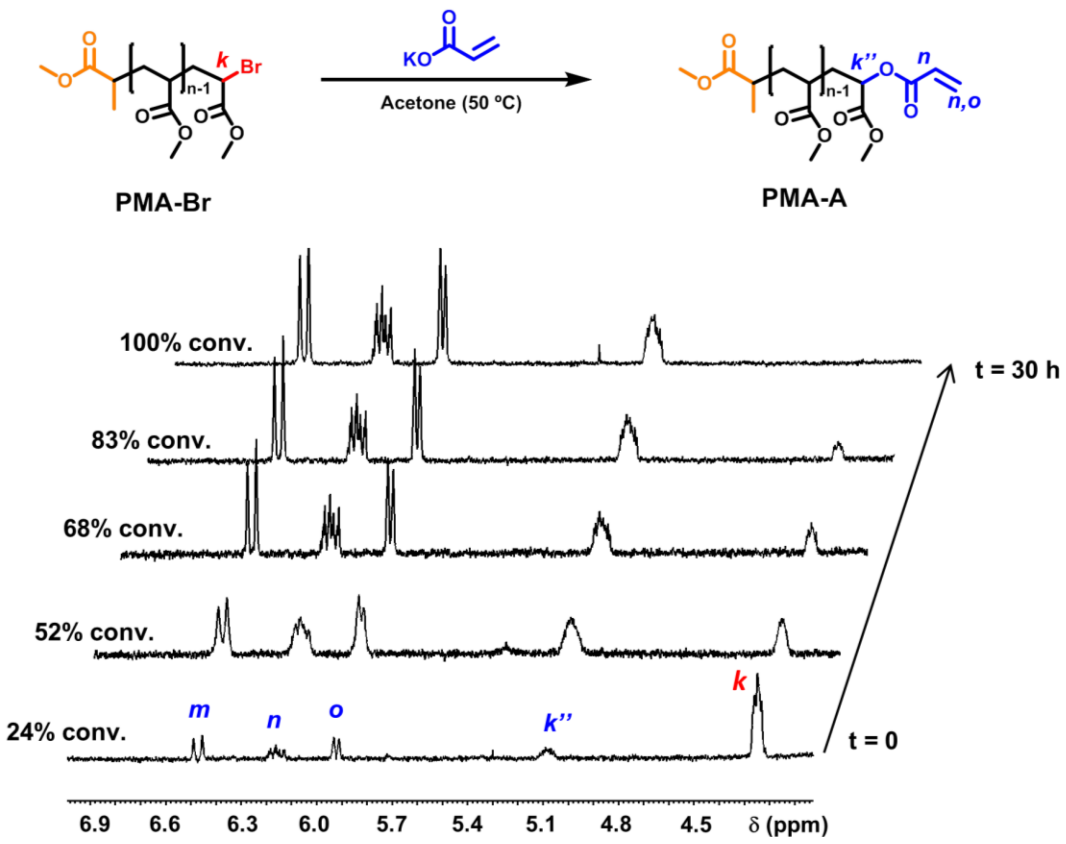


Figure. 3. ^{1}H-NMR evolution traces for the biphasic functionalization of PMA macromonomer (M_n = 4,596 g/mol) with KA in acetonitrile. Degree of esterification is shown at the left side of ^{1}H NMR traces.

The functionalization of the polymer chain end of PMA-Br was investigated at 50 ºC in acetone using a molar ratio CH-Br/KA = 1/5. This is exactly the same molar ratio used for the thioetherification reaction described above (CH-Br/SH = 1/5). As can be seen in Figure 3, the esterification reaction taking place at bromine chain ends of PMA-Br could be monitored by ^{1}H NMR spectroscopy by the disappearance of signal H_k characteristic of the PMA-Br and the appearance of $H_{k''}$ corresponding to PMA-A. Figure 4a shows that functionalization was complete after 30 h. This is a remarkable result considering that KA is insoluble in the reaction mixture and therefore this is an interfacial esterification process (see Figure 1b). This reaction could be dramatically accelerated using acetonitrile instead of acetone and increasing the

temperature to 75 ºC. In this case, esterification was quantitative after 5 h (Figure 4b, black squares). Targeting lower $[MA]_0/[MBP]_0$ ratios, PMA-Br with lower M_n were prepared and isolated to study their functionalization with KA. Thus, $[MA]_0/[MBP]_0$ ratios 20/1 and 6/1 (M_n^{th} = 1,920 g/mol and M_n^{th} = 711 g/mol at 100% conversion) were used to prepare PMA-Br of M_n^{GPC} = 2,680 g/mol (90% conv., M_w/M_n = 1.24) and M_n^{GPC} = 836 g/mol (96% conv., M_w/M_n = 1.32), respectively.

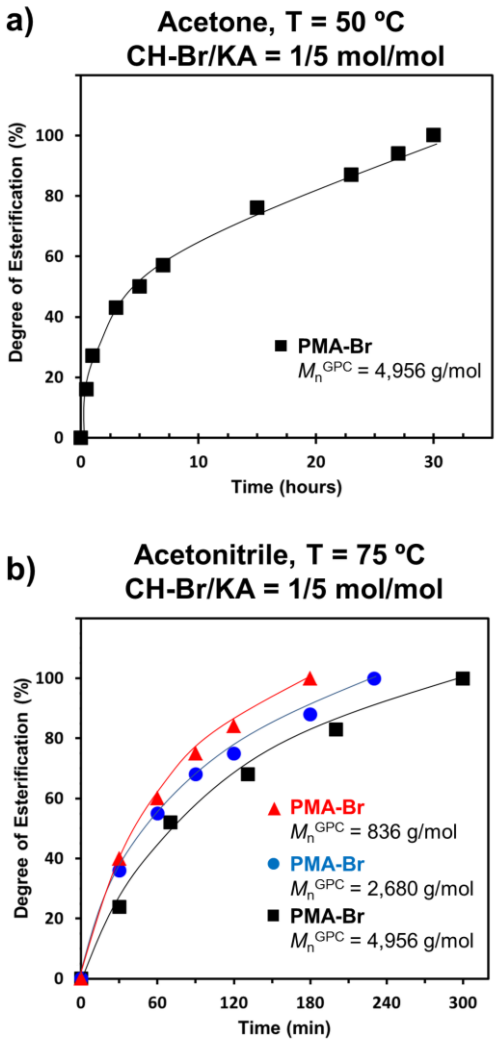


Figure 4. Kinetics plots, degree of esterification *vs* time of PMA-Br with KA in (a) acetone at 50 ºC and (b) acetonitrile at 75 ºC. Black squares (PMA-Br isolated at 88% conv. $[MA]_0/[MBP]_0/[TREN]_0/[CuBr_2]_0$ = 50/1/0.4/0.2), blue circles (PMA-Br isolated at 90% conv. $[MA]_0/[MBP]_0/[TREN]_0/[CuBr_2]_0$ = 20/1/0.4/0.2) and red triangles circles (PMA-Br isolated at 96% conv. $[MA]_0/[MBP]_0/[TREN]_0/[CuBr_2]_0$ = 6/1/0.4/0.2).

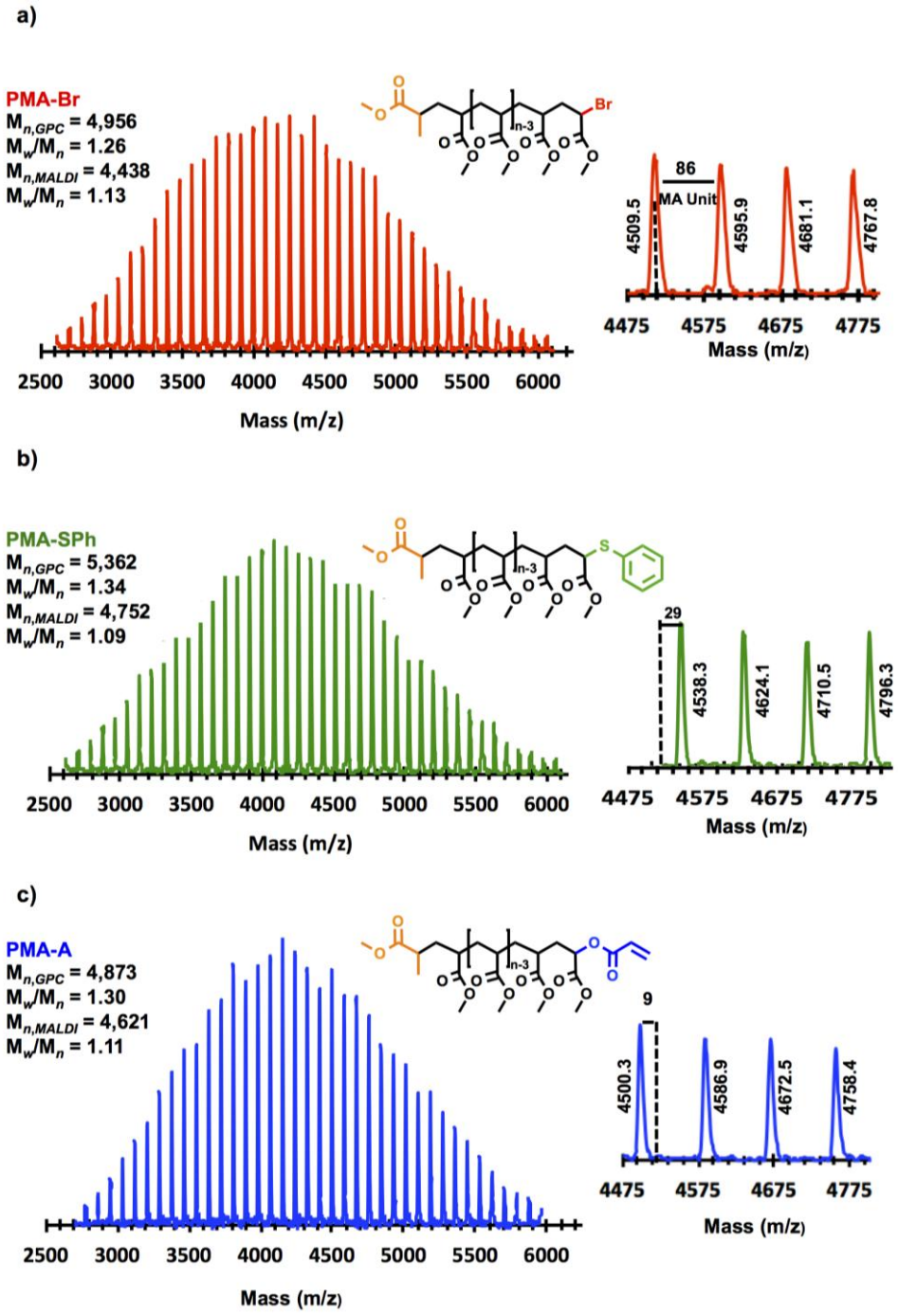


Figure. 5. MALDI-TOF of (a) PMA-Br isolated at 88% conversion from biphasic SET-LRP of MA in acetone/water (8/2, v/v) mixtures initiated with MBP and catalyzed by nonactivated Cu(0) wire at 25 ºC (b) PMA-Br after thio-bromo "click" reaction and (c) PMA-A synthesized by esterification of PMA-Br with potassium acrylate. Reaction conditions: $[MA]_0/[MBP]_0/[TREN]_0/[CuBr_2]_0$ = 50/1/0.4/0.2, 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.

As can be seen in Figure 4b, when using these low molecular weight bromine-terminated polymers (blue circles and red triangles) the esterification reaction proceeded even faster. The esterification was complete after approximately 3 h for the PMA-Br of M_n = 836 g/mol. A representative ^{1}H NMR spectrum of PMA-A macromonomer (M_n = 4,956 g/mol and M_w/M_n = 1.27) isolated after precipitation in cold methanol is shown in Figure 2c. A visual inspection of this spectrum indicates, within the experimental error, a near perfect acrylate functionality (f^{A}) for the corresponding PMA-A macromonomer. MALDI-TOF MS analysis confirmed perfect end group fidelity at each step of this synthetic strategy under the reported conditions. As can be seen in Figure 5a, PMA-Br (M_n = 4,956 g/mol and M_w/M_n = 1.27) isolated after biphasic SET-LRP process shows a single distribution of peaks attributable to PMA-Br species ionized with Na^+. The peak to peak separation (86 mass units) corresponds to the molar mass of the MA repeat unit of this polymer. The complete disappearance of this series of peaks after the thio-bromo "click" thioetherification with thiophenol supports the high f^{Br} determined previously by ^{1}H NMR. Meanwhile, only a new series of perfectly symmetric peaks appears 29 mass units above. Dotted line in the expansion shows the position of the original peak before thioetherification. The increase of 29 mass units in molar mass is consistent with the substitution of a bromine atom (79.9) by a thiophenolate group (109.2) at the polymer terminus i.e., SC_6H_5 (109.2) - Br (79.9) = 29.3. MALDI-TOF analysis supports quantitative functionalization of the ω-polymer chain end with the acrylate moiety (Figure 5c). In this case, the vanishment of the PMA-Br series of peaks is accompanied by the appearance of a new series 9 mass units below the original one. As can be seen in Figure 1c (blue curve), GPC analysis of PMA-A showed a symmetric chromatogram that together with the rigorous analysis discussed above supports the

structural perfection of the synthesized macromonomers. This is a remarkable result for a synthetic approach based on two interfacial reactions.

Synthesis and structural analysis of A-PMA-A telechelics

Combining SET-LRP with the interfacial esterification of KA, bifunctional acrylate telechelics A-PMA-A were also conveniently prepared. In this case, the bifunctional initiator BPE was used to furnish a α,ω-bromine-terminated Br-PMA-Br using the conditions reported above (Scheme 2a). The biphasic SET-LRP of MA in acetone/water, 8/2, v/v furnished a telechelic Br-PMA-Br with M_n = 3,581 g/mol and M_w/M_n = 1.25 at 93% conversion (Reaction conditions: $[MA]_0/[BPE]_0/[TREN]_0/[Cu(II)Br_2]_0$ = 50/1/0.1, MA = 1 mL and 12.5 cm of non-activated Cu(0) wire of 20 gauge). Again, the functionalization of bromine-chain ends was much faster in acetonitrile than in acetone using a molar ratio CH-Br/KA = 1/10. As can be seen in Figure 6, the interfacial esterification at both chain ends of Br-PMA-Br is complete after approximately 17 h at 75ºC.

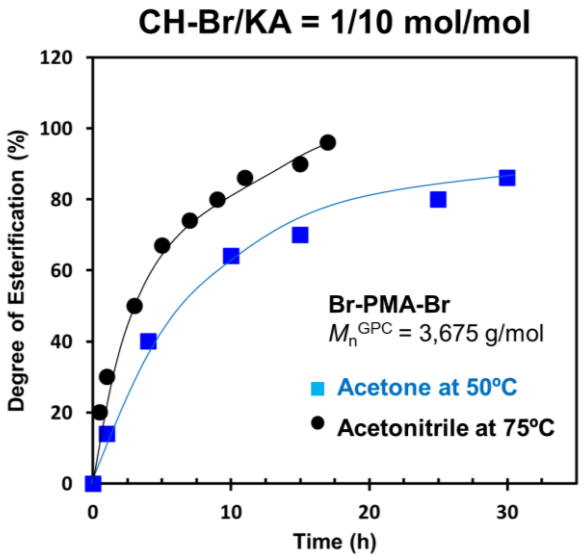


Figure 6. Kinetics plots, conversion for the esterification *vs* time of Br-PMA-Br with KA. Br-PMA-Br isolated at 93% conv. ($[MA]_0/[BPE]_0/[TREN]_0/[CuBr_2]_0$ = 30/1/0.4/0.2) from biphasic SET-LRP of MA in acetone/water (8/2, v/v) mixtures initiated with MBP and catalyzed by non-

activated Cu(0) wire at 25 ºC. Esterification reaction carried out in acetone at 50 ºC (blue squares) or acetonitrile at 75ºC (black circles).

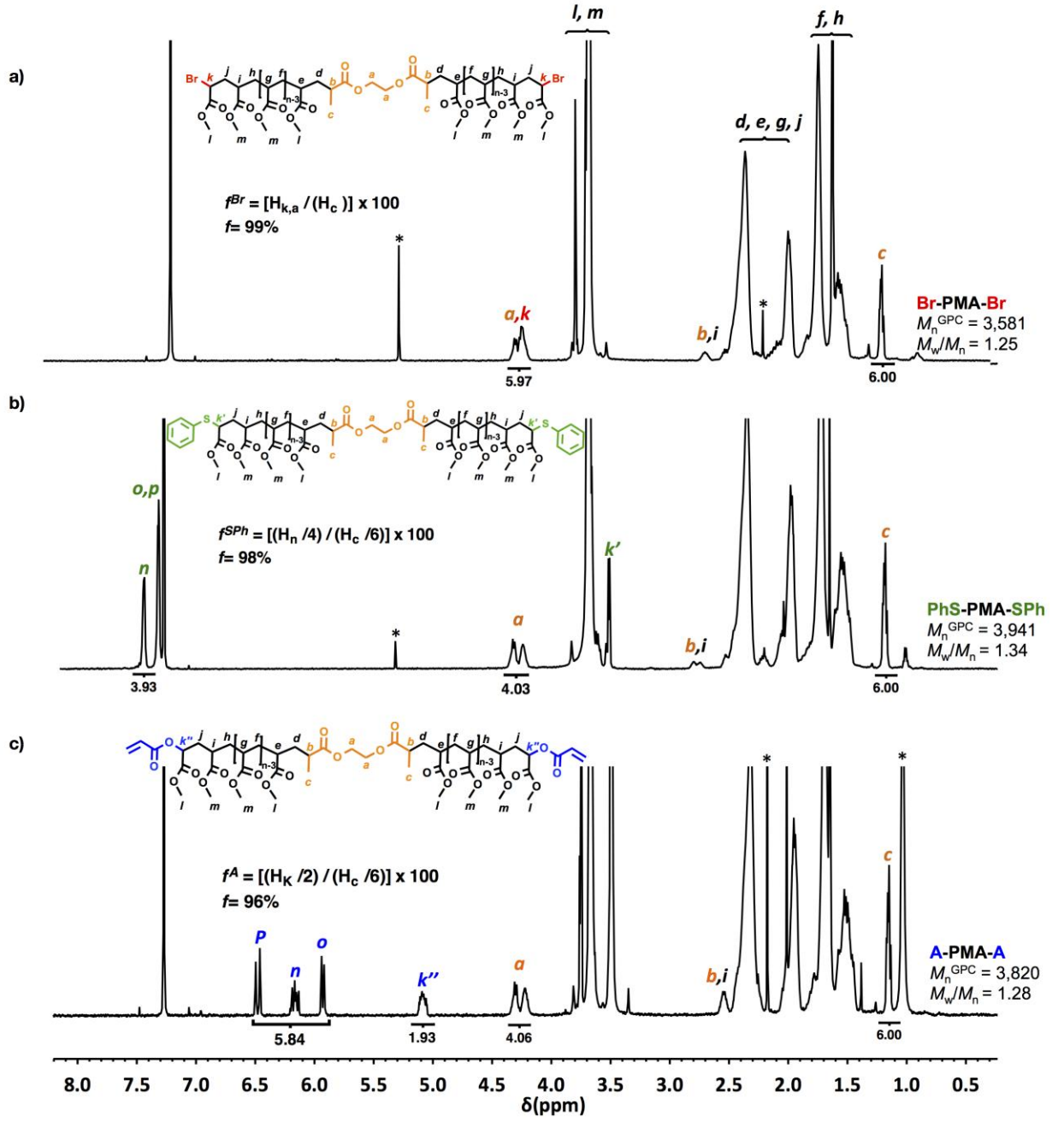


Figure 7. ^{1}H-NMR (500 MHz) spectra recorded in $CDCl_3$ of (a) Br-PMA-Br isolated at 93% conv. ($[MA]_0/[BPE]_0/[TREN]_0/[CuBr_2]_0$ = 50/1/0.4/0.2) from the biphasic SET-LRP of MA in an acetone/water (8/2, v/v) mixture initiated with BPE and catalyzed by non-activated Cu(0) wire at 25 ºC. (b) Br-PMA-Br after thio-bromo "click" reaction. (c) A-PMA-A synthesized by esterification of Br-PMA-Br with KA in acetonitrile at 75 ºC. *Residual solvent peaks: dichloromethane, hexane and acetone.

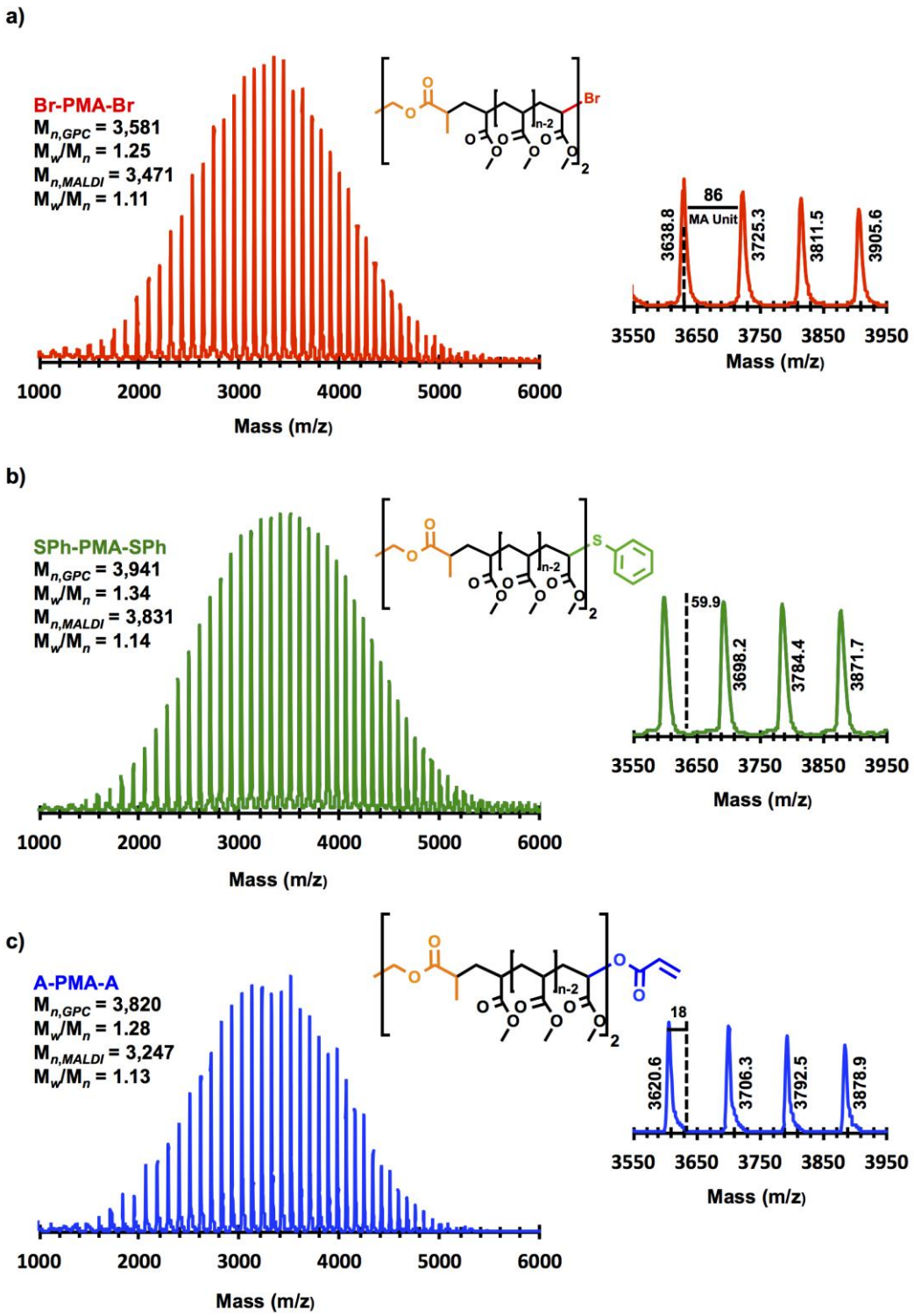


Figure. 8. MALDI-TOF of (a) Br-PMA-Br isolated at 93% conversion ($[MA]_0/[BPE]_0/[TREN]_0/[CuBr2]_0$ = 50/1/0.4/0.2) from SET-LRP of MA in acetone/water (8/2, v/v) mixtures initiated with BPE and catalyzed by non-activated Cu(0) wire at 25 ºC, (b) Br-PMA-Br after thio-bromo "click" reaction and (c) A-PMA-A synthesized by esterification of Br-PMA-Br with KA in acetonitrile at 75 ºC.

The powerful combination of analytical techniques used in the previous subchapter together with the thio-bromo "click" reaction was used to assess the high efficiency of this two-steps protocol when acrylate PMA telechelics are targeted (see Figures 7 and 8). In this case, H_k of Br-PMA-Br is overlapped with signal H_a corresponding to methylene protons at the core of this telechelic polymer. However, the ratios between signals $H_c/H_{a,k}$ and H_c/H_n before and after thioetherifcation proved the near perfect f^{Br} (>98%, see Figure 7a and b). This is also supported by an unique series of symmetric peaks in the MALDI-TOF spectra before and after thio-bromo "click" modification and the appearance of PhS-PMA-SPh/Na+ series 59.9 unites above than that corresponding to Br-PMA-Br/Na^+. The subsequent esterification showed the same level of perfection (compare Figure 8b and c). In this case, the new series of peaks corresponding to A-PMA-A/Na^+, appears 18 mass units below the original bromine-capped telechelic species. This is in agreement with the complete functionalization of both polymer end groups with acrylate moieties. Dotted line in the expansion of Figure 8c, shows the original Br-PMA-Br series. The new series A-PMA-A appears 18 mass units below according to the mass difference between a bromine atom and the acrylate moiety i.e., Br (79. 9) – $C_3H_3O_2$ (71.06) = 8.84 for each chain end. Within the experimental error, this is in agreement with f^{A} = 96% determined by ^{1}H NMR spectroscopy. Both PMA macromonomers and telechelics reported here may be used as building blocks for the synthesis of various polymers with different architectures by SET-LRP. Preliminary results in this line are shown in the following subchapter.

Synthesis of a PMA-g-PMA by biphasic SET-LRP

The recent developments on biphasic SET-LRP systems are expected to facilitate synthesis of hydrophobic self-organizing polymers with complex architectures by SET-LRP. The developments reported here are preliminary steps in this direction. As a representative example of the possibilities offered by biphasic SET-LRP systems, a more complex PMA-g-PMA architecture was targeted a PMA-A macromonomer of M_n = 1,230 g/mol and M_w/M_n = 1.34. PMA-A was copolymerized with MA using MBP as a initiator in a biphasic reaction mixture comprised of acetone/water, 8/2 v/v using the following conditions: $[MA]_0/[MBP]_0/[TREN]_0/[CuBr_2]_0$ = 333/1/0.4/0.2, MA=2 mL, PMA-acrylate = 0.4 g, acetone + water = 0.5 mL, 12.5 cm of 20 gauge Cu(0) wire at 25 ^oC. The preparation of this PMA-g-PMA architecture was monitored by GPC (Figure 9). The reactivity of the PMA-A macromonomer and the success in the preparation of this PMA-g-PMA homopolymer is supported by the displacement of the GPC curve corresponding to the PMA-A macromonomer to lower elution times. A remarkable result is that the dispersity of the graft copolymers is lower than that of the macromonomer. This preliminary result envision great possibilities for the design and preparation of more complex macromolecular architectures based on self-organizing dendronized polymers and other by other concepts.[69,70,71,72,73,74,75,76,77,78,79,80,81] For example chain end functionalization of PMA-g-PMA with acrylate followed by its SET-LRP copolymerization with MA can make the structure of the newly obtained PMA-g-(PMA-g-PMA) unprecedented. How many generations of this structure can be obtained is unknown and was never asked before. Biphasic SET-LRP copolymerization of various ratios of PMA-A with A-PMA-A can lead to either hyperbranched PMA or by photo SET-LRP to networks with well-defined properties.[82]

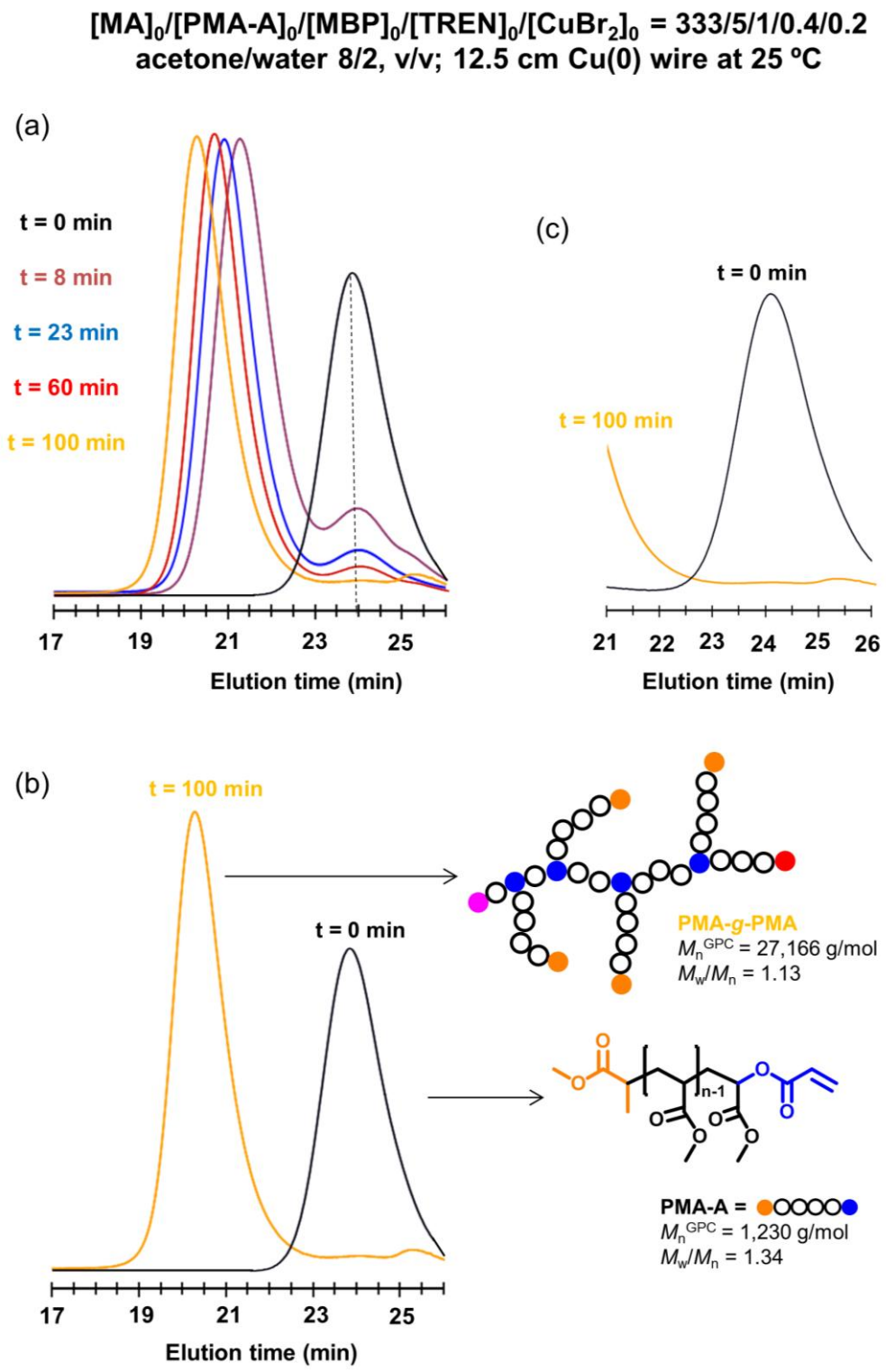


Figure. 9 (a) GPC evolution and (b,c) initial and final GPC curves for the Cu(0) wire-catalyzed SET-LRP copolymerization of MA with PMA-A macromonomer in an acetone/water (8/2, v/v) mixture initiated with MBP. Reaction conditions: $[MA]_0/[PMA\text{-}A]_0/[MBP]_0/[TREN]_0/[CuBr_2]_0$ = 333/5/1/0.4/0.2, MA=2 mL, PMA-acrylate = 0.4 g, acetone + water = 0.5 mL, 12.5 cm of 20 gauge Cu(0) wire.

Unlimited new architectural concepts can be generated from these macromonomers and telechelics. This was hardly accessible so far by the classic SET-LRP in homogeneous systems,[83] due to the mechanistically required disproportionation of Cu(I)X into Cu(0) and Cu(II)X_2 that takes place only in water and polar solvents in the presence of ligands that stabilize Cu(II)X_2 rather than Cu(I)X. Results on this line will be reported in due course.

Conclusions

The unexpected immiscibility of an aqueous solution containing TREN and Cu(II)Br_2 with a water-miscible solvent such as acetone containing MA provides excellent conditions for biphasic SET-LRP at 25 ºC. The partition of reagents between both phases throughout the entire process has been exploited to synthesize PMA with ω-bromo and α,ω-dibromo chain end functionality close to perfection (f^{Br} >98%) using MBP and BPE as initiators and non-activated Cu(0) wire as a catalyst. The analysis of these polymers by 500 MHz ^{1}H NMR before and after chain-end functionalization *via* thio-bromo "click" chemistry proved this statement. Despite KA is not soluble in acetone and acetonitrile, it can react with the α-bromoester chain ends of PMA in both solvents. ^{1}H NMR and MALDI-TOF MS was used to demonstrate that the functionalization of PMA-Br (M_n^{GPC} = 4,956 g/mol, M_w/M_n = 1.27) in acetone is quantitative after 30 h at 50 ºC. However, this interfacial esterification reaction is complete after 5 h in acetonitrile at 75 ºC. The merging of both interfacial reactions has been used to create well-defined PMA macromonomers and telechelics with α- and α,ω-acrylate chain ends. These results provide important information toward the functionalization of more hydrophobic and less reactive polyacrylates. This will be the topic of a manuscript ready to be submitted. We also demonstrate the reactive nature of these macromonomers by the preparation of a more complex PMA-g-PMA architecture using the same

biphasic SET-LRP. Finally, functionalization of the PMA chain-ends with KA can be performed directly in the polymerization reaction mixture as a two steps one pot reaction and the aqueous phase of the reaction mixture containing KBr and $CuBr_2$ can be subsequently be reused for additional biphasic SET-LRP experiments. The resulting polymer prepared by this methodology will not require any additional purification.

Experimental

Materials

MA (99%) (from Acros) was passed over a short column of basic Al_2O_3 before use in order to remove the radical scavenger. 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% Across), 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.[1]

Techniques

500 MHz ^{1}H-NMR spectra were recorded on Bruker drx500 NMR instrument at 25 ºC in $CDCl_3$ containing tretamethylsilane (TMS) as internal standard. For the chain end analysis of PMA macromonomers and telechelics the delay time (D1) applied was 9 s and the number of scans (nt) were 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 PMA samples were determined using a poly(methyl methacrylate) (PMMA) standards purchased from American Polymer Standards. MALDI-TOF analysis was performed with a Voyager DE (Applied Biosystems) equipped with a 337 nm nitrogen laser (3 ns pulse width). The accelerating potential was 25 kV, the grid was 88%, the laser power was 1950 arbitrary units, and a positive mode was employed. The sample analysis was carried out with 2-(4-hydroxyphenylazo)benzoic acid as matrix. THF solutions of the matrix (30 mg mL^{-1}), NaCl (10 mg mL^{-1}) 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 cationization agent solution in a 9/1/1 volumetric ratio. Then 1μL of the solution mixture were deposited onto five wells of sample plate and dried in air at room temperature before being subjected to MALDI-TOF analysis.

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

Organic solvent (acetone), monomer (MA), water (stock solution containing the TREN and Cu(II)Br_2) and initiator (MBP or BPE) were as indicated to a 25 mL Schlenk tube. The reaction mixture was then deoxygenated by six freeze-pump (~1 min)-thaw cycles and filled with nitrogen. Next, the Schlenk tube was opened under a positive flow of nitrogen to add Cu(0) wire wrapped around a teflon-coated stirring bar. One more freeze-pump (~1 min)-thaw cycle was carried out while holding above the reaction mixture the Cu(0) wrapped in the stir bar 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. Then, 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 expossed to the air. The resulting PMA was precipitated in cold methanol and dried under vacuum until constant weight to perform chain end analysis by ^{1}H-NMR and MALDI-TOF, before and after the thio-bromo "click" thioetherification 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 polymers with thiophenol chain-ends were dried under vacuum until constant weight.

Synthesis of KA

KA was synthetized following a previously reported procedure.[67] 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. 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-end functionalization of PMA-Br and Br-PMA-Br with KA

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

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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 projects 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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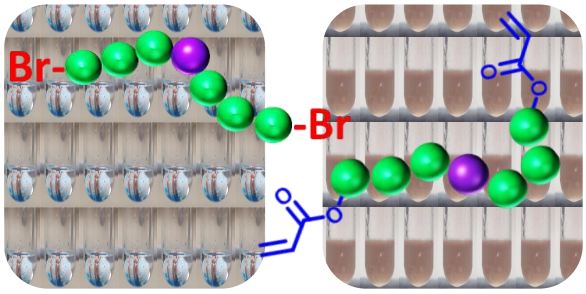

Macromonomers and telechelics of PMA *via* biphasic SET-LRP and biphasic esterification with potassium acrylate.