A Facile Strategy for Synthesis of α,α′-Heterobifunctionalized Poly(ε-caprolactones) and Poly(methyl methacrylate)s Containing "Clickable" Aldehyde and Allyloxy Functional Groups Using Initiator Approach

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ABSTRACT: Two new initiators, namely, 4-(4-(2-(4-(allyloxy) phenyl)-5-hydroxypentane 2-yl) phenoxy)benzaldehyde and 4-(4-(allyloxy) phenyl)-4-(4-(4-formylphenoxy) phenyl) pentyl 2-bromo-2-methyl propanoate containing "clickable" hetero-functionalities namely aldehyde and allyloxy were synthesized starting from commercially available 4,4′-bis(4-hydroxyphenyl) pentanoic acid. These initiators were utilized, respectively, for ring opening polymerization of ε-caprolactone and atom transfer radical polymerization of methyl methacrylate. Well-defined α-aldehyde, α′-allyloxy heterobifunctionalized poly(ε-caprolactones) ($M_{n,GPC}$: 5900–29,000, PDI: 1.26–1.43) and poly(methyl methacrylate)s ($M_{n,GPC}$: 5300–28800, PDI: 1.19–1.25) were synthesized. The kinetic study of methyl methacrylate polymerization demonstrated controlled polymerization behavior. The presence of aldehyde and allyloxy functionality on polymers was confirmed by ^{1}H NMR spectroscopy. Aldehyde-aminooxy and thiol-ene metal-free double click strategy was used to demonstrate reactivity of functional groups on polymers. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 2091–2103

KEYWORDS: atom transfer radical polymerization; click chemistry; functional polymers; ring opening polymerization

INTRODUCTION The synthesis of well-defined functionally terminated polymers is an area of great contemporary interest due to the utility of such polymers as building blocks for the construction of complex polymer architectures.[1–5] As end-groups are retained, "living" polymerization processes are, by their nature, particularly suited for the synthesis of end-functional polymers. Thus, various "living" polymerization methods, including nitroxide-mediated polymerization,[6] atom transfer radical polymerization (ATRP),[7,8] reversible addition-fragmentation chain transfer[9,10] and ring opening polymerization (ROP)[11,12] have been successfully adapted for this purpose. Of the various available techniques, ATRP process is the most robust and promising. It tolerates traces of impurities, and is compatible with a broader range of monomers and reaction conditions.[13] Generally, three approaches are applied to prepare α-, ω- or α, ω-bifunctionalized polymers by ATRP. The first approach is to use a designed functional initiator, wherein functional group is tolerant to ATRP reaction conditions which results in the formation of α-functionalized polymers. Polymers with α- as well as α-,α′-homobifunctional groups such as dihydroxyl,[14,15] dicarboxylic acid,[16] bis(4-fluorobenzoyl),[17] bis(aromatic bromo),[18] and *tert*-amino[19] have been prepared successfully using initiator approach. The second approach is to transform the halogen end group of the polymer into different useful functional groups by post-polymerization modification. For example, dihydroxyl[20,21] and diamino[22] groups have been introduced onto the ω-chain end via nucleophilic substitution of bromine end group with appropriate amino-diols and triamine, respectively. The transformation of the terminal bromine into azido group followed by the click reaction with trialkyne leads to ω-dialkynyl polystyrene.[23] The same strategy was also used for the synthesis of ω-hydroxyl-ω′-alkynyl polystyrene via the click reaction of ω-azido polystyrene with 3,5-bis(propargyloxy)benzyl alcohol.[24] The third approach is to use functional initiator accompanied by post-polymerization functionalization of the halogen end group of the polymer into desired functional groups.[25] A survey of literature revealed that major attention has been paid to the synthesis of α,α′- or ω,ω′-homobifunctionalized polymers via ATRP process[14–18,20–23] with scant attention to the preparation of, α,α′ or ω,ω′-heterobifunctinalized polymers.[24,26] Notably, synthesis of α,α′-heterobifunctionalized polystyrenes with well-defined molecular weights via combination of ATRP and chemical modification of end-functional groups was reported by Bai and co workers.[27] To the best of our knowledge, synthesis of poly(-alkyl methacrylate)s or poly caprolactones with α,α′-heterobifunctional groups using initiator approach has not been reported in the literature.

Herein, we present a facile strategy for synthesis of α,α′-heterobifunctionalized poly(ε-caprolactones) and poly(methyl methacrylate)s using functional initiator approach. Two new heterobifunctional initiators namely, 4-(4-(2-(4-(allyloxy) phenyl)-5-hydroxypentane 2-yl) phenoxy) benzaldehyde and 4-(4-(allyloxy) phenyl)-4-(4-(4-formylphenoxy)phenyl) pentyl 2-bromo-2-methyl propanoate having "clickable" functionalities such as aldehyde and allyloxy were synthesized starting from commercially available 4,4′-bis(4-hydroxyphenyl) pentanoic acid. These initiators were utilized for preparation of well-defined α,α′-heterobifunctionalized poly(ε-caprolactones) and poly(methyl methacrylate)s containing aldehyde and allyloxy groups. Furthermore, the possibilities provided by these functionalities for the preparation of new functionalized polymers by carrying out aldehyde-aminooxy and thiolene click reactions are explored.

EXPERIMENTAL

Materials

4,4′-Bis(4-hydroxyphenyl) pentanoic acid, lithium aluminum hydride, 4-fluoro benzaldehyde, *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA), 2-bromoisobutyryl bromide (98%), and stannous octoate (Aldrich) were used as received. Methyl ester of 4,4′-bis(4-hydroxyphenyl) pentanoate and 4,4′-(5-hydroxypentane-2,2-diyl) diphenol were prepared as reported by us earlier.[28] Styrene, ε-caprolactone and *N*,*N*-dimethylformamide (DMF) were stirred over calcium hydride for 4 h and distilled under reduced pressure. Copper (I) bromide (Aldrich, 99.9%) was washed with glacial acetic acid to remove any soluble oxidized species, filtered, washed with ethanol, and dried. Azobisisobutyronitrile was recrystalized from acetone. Triethyl amine was distilled prior to the use. Dichloromethane, tetrahydrofuran, sodium sulphate, potassium hydroxide, sodium hydrogen carbonate, methanol and chloroform, all received from S.D. Fine-Chem, India, were used as received.

Characterizations and Measurements

FT-IR spectra were recorded on a Perkin-Elmer *Spectrum GX* spectrophotometer in chloroform. NMR spectra were recorded on a Bruker 200 MHz spectrometer using $CDCl_3$, Acetone-d_6 or DMSO-d_6 as solvents. Molecular weight and molecular weight distribution of polymers were determined using GPC analysis at a flow rate of 1 mL min^{-1} in chloroform at 30 °C (Thermo separation products) equipped with spectra series UV 100 and spectra system RI 150 detectors. The sample concentration was 2 to 3 mg mL^{-1}. HPLC grade chloroform was used as an eluent. Polystyrene was used as the calibration standard.

Synthesis

Synthesis of 4-(2-(4-(Allyloxy) phenyl)5-hydroxy pentan-2-yl) phenol

Into a 500 mL two-necked round-bottom flask equipped with a reflux condenser were charged, 4,4′-(5-hydroxypentane-2,2-diyl) diphenol (16.3 g, 60 mmol), K_2CO_3 (8.1 g, 60 mmol) and dry acetone (150 mL) and the reaction mixture was stirred for 10 min. The solution of allyl bromide (7.20 g, 60 mmol) in acetone (50 mL) was added over a period of 30 min. The reaction mixture was refluxed for 8 h, cooled and filtered. Acetone was evaporated under reduced pressure and the reaction mixture was diluted with ethyl acetate (150 mL). The ethyl acetate solution was washed with saturated brine solution (3 × 50 mL), sodium bicarbonate solution (3 × 50 mL), and water (2 × 50 mL). The ethyl acetate solution was dried over sodium sulfate, filtered and evaporated under vacuum. The crude product was purified by column chromatography using ethyl acetate:pet ether (20:80, v/v) to yield 15.9 g (95%) of 4-(2-(4-(allyloxy) phenyl)5-hydroxy pentan-2-yl)phenol as a thick yellow liquid.

IR ($CHCl_3$, cm^{-1}): 3130, 1250

^{1}H NMR ($CDCl_3$, δ/ppm): 7.08–6.96 (m, 4H, Ar—H), 6.79–6.66 (m, 4H, Ar—H), 6.11–5.97 (m, 1H, CH=CH—), 5.43–5.23 (q, 2H, C=CH_2), 4.49 (d, 2H, O—CH_2), 3.58 (t, 2H, OCH_2), 2.12–2.05 (m, 2H, —CH_2—CH_2), 1.54 (s, 3H, —CH_3), 1.40–1.35 (m, 2H, —CH_2—CH_2).

Synthesis of 4-(4-(2-(4-(Allyloxy) phenyl)-5-hydroxy) pentan-2-yl)phenoxy)benzaldehyde

Into a 500 mL two necked round-bottom flask equipped with a reflux condenser were charged, 4-(2-(4-(allyloxy) phenyl) 5-hydroxy pentan-2-yl) phenol (12.5 g, 40 mmol), K_2CO_3 (5.44 g, 40 mmol) and dry DMF (150 mL) and the reaction mixture was stirred for 10 minutes. The solution of 4-fluoro benzaldehyde (4.96 g, 40 mmol) in DMF (50 mL) was added over a period of 30 minutes. The reaction mixture was heated at 100 °C for 8 h, cooled and filtered. DMF was evaporated under vacuum and the reaction mixture was diluted with ethyl acetate (150 mL). The ethyl acetate solution was washed with saturated brine solution (3 × 50 mL), sodium bicarbonate solution (3 × 50 mL), and water (2 × 50 mL). The ethyl acetate solution was dried over sodium sulfate, filtered and evaporated under vacuum. The crude product was purified by column chromatography using ethyl acetate:pet ether (20:80, v/v) to yield 14.80 g (92 %) of 4-(4-(2-(4-(allyloxy)phenyl)-5-hydroxy)pentan-2-yl)phenoxy) benzaldehyde as a thick yellow liquid.

IR ($CHCl_3$, cm^{-1}): 3200, 1715, 1250.

^{1}H NMR ($CDCl_3$, δ/ppm): 9.91 (s, 1H, CHO), 7.84 (d, 2H, Ar-H *ortho* to aldehyde), 7.25–6.82 (m, 10H, Ar-H), 6.13–5.97 (m, 1H, CH=CH—), 5.45–5.26 (q, 2H, C=CH_2), 4.52 (d, 2H, −OCH_2), 3.63 (t, 2H, OCH_2), 2.16–2.08 (m, 2H, —CH_2—CH_2), 1.64 (s, 3H, —CH_3), 1.46–1.39 (m, 2H, —CH_2—CH_2).

^{13}C NMR ($CDCl_3$, δ/ppm): 191.4, 162.3, 156.0, 155.6, 154.7, 140.2, 139.8, 139.2, 133.4, 131.4, 130.4, 129.7, 128.1, 126.9, 122.5, 118.3, 114.9, 114.5, 71.7, 63.8, 42.5, 42.2, 30.7, and 23.8

Synthesis of 4-(4-(Allyloxy)phenyl)-4-(4-(4-formylphenoxy)phenyl)pentyl 2-bromo-2-methyl propanoate

Into a 250 mL two-necked round-bottom flask equipped with a dropping funnel were charged, 4-(4-(2-(4-(allyloxy) phenyl)-5-hydroxy) pentan-2-yl)phenoxy)benzaldehyde (10.40 g, 25 mmol), triethylamine (3 g, 30 mmol), and dry chloroform (100 mL). The reaction mixture was cooled to 0 °C and the solution of 2-bromoisobutyryl bromide (6.80 g, 30 mmol) in

dry chloroform (30 mL) was added dropwise into the reaction mixture under stirring over a period of 30 min. The reaction mixture was stirred at 0 °C for 2 h, allowed to attain room temperature and was further stirred for 12 h. The reaction mixture was washed with 5% aqueous $NaHCO_3$ solution (3 × 100 mL) and de-ionized water (3 × 100 mL). The chloroform layer was dried over anhydrous sodium sulfate, filtered and was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using a mixture of ethyl acetate/pet ether (25:75, v/v) as an eluent. The removal of the solvent yielded 12.6 g (90%) of 4-4-(allyloxy) phenyl)-4-(4-(4-formylphenoxy) phenyl)pentyl 2-bromo-2-methylpropanoate as a pale yellow liquid.

IR ($CHCl_3$, cm^{-1}): 1735, 1710

^1H NMR ($CDCl_3$, δ/ppm): 9.92 (s, 1H, aldehyde), 7.84 (d, 2H, Ar-H *ortho* to aldehyde), 7.26–6.83 (m, 10H, Ar—H), 6.13–6.05 (m, 1H, CH=C—), 5.45–5.25 (q, 2H, C=CH_2), 4.52 (d, 2H, —OCH_2), 4.15 (t, 2H, CH_2OCO), 2.16–2.06 (m, 2H, —CH_2), 1.93 (s, 6H, $OCOC(CH_3)_2$) 1.64 (s, 3H, —CH_3), 1.53–1.47 (m, 2H, —CH_2)

^{13}C NMR ($CDCl_3$, δ/ppm): 191.3, 170.5, 162.8, 155.2, 154.4, 141.6, 140.6, 134.0, 131.4, 128.1, 122.2, 118.5, 114.3, 70.4, 65.7, 51.3, 41.6, 39.8, 30.7, and 24.1.

Synthesis of α-Aldehyde, α′-allyloxy heterobifunctionalized poly(ε-caprolactones)

In a typical experiment, Schlenk tube equipped with a magnetic stir bar was charged with, ε-caprolactone (5.68 g, 50 mmol), stannous (II) octoate (1 mg, 0.002 mmol), 4-(4-(2-(4-(allyloxy) phenyl)-5-hydroxy) pentan-2-yl)phenoxy)benzaldehyde (172 mg, 0.415 mmol) and toluene (30 mL) under nitrogen atmosphere. The reaction mixture was degassed three times by freeze-pump-thaw cycles. ε-Caprolactone polymerization was carried out at 110 °C. After a given time, the polymerization was terminated by cooling the reaction mixture to room temperature, diluted with dichloromethane (30 mL) and the solution was poured into cold methanol (300 mL). The polymer was collected by filtration and dried at room temperature in vacuum for 24 h. The monomer conversion was determined gravimetrically.

IR ($CHCl_3$, cm^{-1}): 1730, 1710

^1H NMR ($CDCl_3$, δ/ppm): 9.90 (s, —CHO), 7.84 (d, Ar—H *ortho* to aldehyde), 7.25–6.81 (m, Ar—H), 6.12–5.99 (m, —CH_2—CH=CH_2), 5.45–5.23 (q, —HC=CH_2), 4.50 (d, —OCH_2),4.04 (t, —CH_2OOC from poly(ε-caprolactone)), 2.29 (t, —CH_2CO from poly(ε-caprolactone)0, 1.58–1.53 (m, —CH_2CH_2 from poly(ε-caprolactone) + protons from initiator fragment), 1.34–1.31 (m, —CH_2CH_2 from poly(ε-caprolactone) + protons from initiator fragment)

Synthesis of α-Aldehyde, α′-Allyloxy heterobifunctionalized Poly(methyl methacrylate)s

In a typical experiment, Schlenk tube equipped with a magnetic stir bar was charged with, CuBr (120 mg, 0.85 mmol) and the tube was thoroughly flushed with argon. In a separate sample vial were taken, 4-4-(allyloxy) phenyl)-4-(4-(4-formylphenoxy) phenyl) pentyl 2-bromo-2-methylpropanoate (480 mg, 0.85 mmol), methyl methacrylate (4.25 g, 42.5 mmol) and anisole (5 mL). The solution was degassed and was transferred via argon-purged syringe into the Schlenk tube under argon atmosphere. The reaction mixture was degassed three times by freeze-pump-thaw cycles. Under argon atmosphere, the reaction mixture was opened and PMDETA (173 μL, 0.85 mmol) was added. The Schlenk tube was sealed with a stopper and was kept in an oil bath at 80 °C. Kinetic study was performed by taking aliquots at regular intervals. After appropriate time; polymerization was quenched by cooling reaction mixture in liquid nitrogen bath. The reaction mixture was diluted with tetrahydrofuran (50 mL) and the solution was passed through neutral alumina column to remove copper residue. The solution was concentrated and poured into cold methanol (500 mL) to precipitate the polymer. The polymer was filtered, dried under vacuum for 24 h and weighed. The monomer conversion was determined gravimetrically.

^1H NMR ($CDCl_3$ δ/ppm): 9.93 (s, aldehyde from initiator), 7.85 (d, Ar—H *ortho* to aldehyde from initiator), 7.14–6.84 (m, Ar—H from initiator), 6.14–6.00 (m, —CH=C—), 5.46–5.26 (q, —C=CH_2), 4.53 (d, —OCH_2), 3.60 (s, —OCH_3 from poly (methyl methacrylate), 1.90–0.84 (m, CH_2, —CH from poly (methyl methacrylate + protons from initiator fragment))

Chemical Modification

Aldehyde-Aminooxy Click Reaction

Into a 50 mL two-necked round-bottom flask equipped with a dropping funnel were charged, α-aldehyde, α′-allyloxy heterobifunctionalized poly(ε-caprolactone) (1.94 g, 0.20 mmol, $M_{n,NMR}$ −9700)/poly(methyl methacrylate) (740 mg, 0.20 mmol, $M_{n,NMR}$ −3700), dichloromethane (20 mL) and a pinch of sodium sulfate. Then, solution of O-(2-azidoethyl) hydroxylamine (250 mg, 20 mmol) dissolved in dichloromethane (5 mL) was added and the reaction mixture was stirred at room temperature for 24 h. The reaction mixture was precipitated into cold hexane (200 mL). The obtained polymer was filtered and dried under vacuum at 50 °C for 8 h.

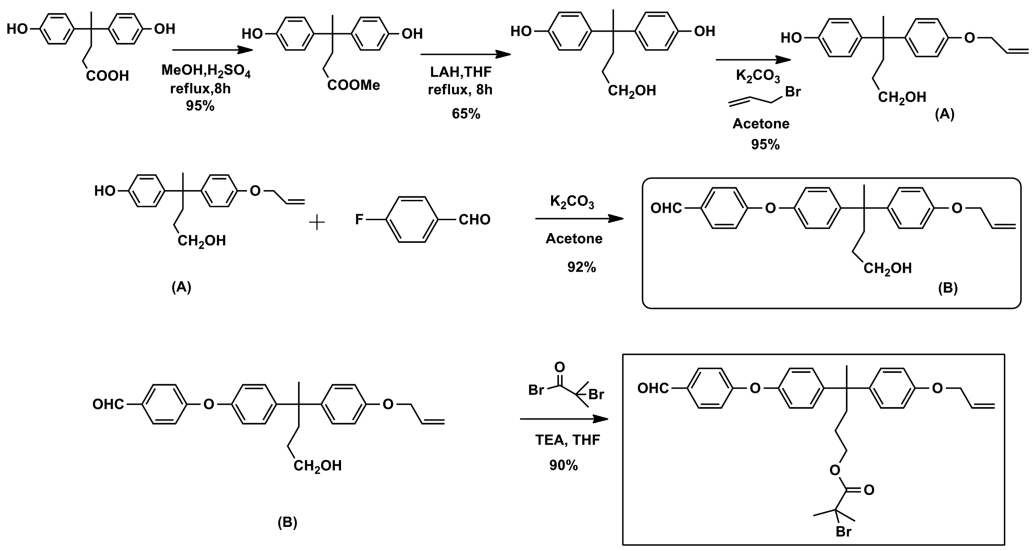
IR ($CHCl_3$, cm^{-1}): 2110, 1730

^1H NMR ($CDCl_3$, δ/ppm): 8.07 (s, —CH=N), 7.52 (d, Ar—H *ortho* to oxime), 7.11–6.80 (m, Ar—H), 6.12–6.00 (m, —CH=CH_2), 5.45–5.23 (q, —HC=CH_2), 4.50 (d, —OCH_2), 4.05 (t, —CH_2OOC from poly(ε-caprolactone)), 2.26 (t, —CH_2CO, from poly(ε-caprolactone)), 1.61–1.53 (m, —CH_2CH_2 from poly(ε-caprolactone) + protons from initiator fragment), 1.39–1.31 (m, —CH_2CH_2 from poly(ε-caprolactone))

^1H NMR ($CDCl_3$, δ/ppm): 8.11 (s, —CH=N), 7.55 (d, Ar—H *ortho* to oxime), 7.14–6.82 (m, Ar—H from initiator fragment), 6.19–6.02 (m, —CH=C—), 5.46–5.31 (q, —C=CH_2), 4.54 (d, —OCH_2), 4.30 (t, OCH_2), 3.60 (s,-OCH_3 from poly (methyl methacrylate)), 1.91–0.81 [m, —CH_2, —CH from poly (methyl methacrylate + protons from initiator fragment)].

Thiol-Ene Thermal Click Reaction

Into a clean and dry Schlenk tube were charged, allyloxy functionalized poly(ε-caprolactone) (490 mg, 0.05 mmol)/poly (methyl methacrylate) (185 mg, 0.05 mmol), 3-maracptopropionic acid (53 mg, 0.5 mmol), AIBN (82 mg, 0.5 mmol), and



SCHEME 1 Synthesis of 4-(4-(2-(4-(allyloxy)phenyl)-5-hydroxy)pentan-2-yl)phenoxy)benzaldehyde and 4-(4-(allyloxy)phenyl)-4-(4-(4-formylphenoxy)phenyl)pentyl 2-bromo-2-methyl propanoate.

chlorobezene (20 mL). The mixture was degassed via three freeze-pump-thaw cycles and subsequently sealed under vacuum. The Schlenk tube was heated at 80 °C for 6 h. The reaction mixture was cooled at 0 °C. Chlorobenzene was removed under reduced pressure. The polymer was dissolved in dichloromethane (20 mL) and precipitated into cold methanol (200 mL) and purified by carrying out precipitation for another two times into cold methanol. The polymer was filtered and was dried under vacuum at 50 °C for 8 h.

^{1}H NMR ($CDCl_3$, δ/ppm): 8.05 (s, —CH=N), 7.51 (d, Ar—H *ortho* to oxime), 7.11–6.78 (m, Ar—H), 4.01 (t, —CH_2OOC from poly(ε-caprolactone)), 2.89 (t, S—CH_2), 2.75 (t, S—CH_2), 2.63 (t, CH_2—COOH), 2.31 (t, —CH_2CO, from poly(ε-caprolactone)), 1.69–1.63 (m, —CH_2CH_2 from poly(ε-caprolactone) + protons from initiator fragment), 1.41–1.35 (m, —CH_2CH_2 from poly(ε-caprolactone))

^{1}H NMR ($CDCl_3$, δ/ppm): 8.11 (s, —CH=N), 7.55 (d, Ar—H *ortho* to oxime), 7.14–6.82 (m, Ar—H from initiator), 4.54 (d, —OCH_2), 4.30 (t, OCH_2), 3.60 (s, —OCH_3 from poly(methyl methacrylate), 2.89 (t, S—CH_2), 2.75 (t, S—CH_2), 2.63 (t, CH_2—COOH), 1.87–0.81 (m, CH_2, —CH from poly(methyl methacrylate).

RESULTS AND DISCUSSION

Synthesis of 4-(4-(2-(4-(Allyloxy)phenyl)-5-hydroxy)pentan-2-yl)phenoxy)benzaldehyde and 4-(4-(allyloxy)phenyl)-4-(4-(4-formylphenoxy)phenyl)pentyl 2-bromo-2-methyl propanoate

α,α'-Bifunctionalized polymers possessing "clickable" functional groups represent valuable precursors for synthesis of different types of end functionalized polymers and Y-shaped miktoarm star copolymers. In the present work, we report synthesis of α,α'-hetero bifunctionalized polymers using initiator approach. The construction of heterobifunctional initiators for ROP and ATRP was envisaged by considering the fact that orthogonality of functional groups should remain intact and functional groups could be further used for chemical modifications. The selection of allyloxy and aldehyde functional groups was made by considering the fact that both these functional groups are compatible with reaction conditions of ROP as well as ATRP[29–34] and both the functional groups could further undergo metal-free click reactions such as thiol-ene and aldehyde-aminooxy click reaction, respectively. To the best of our knowledge, α,α'-heterobifunctional initiators containing "clickable" groups suitable for ROP and ATRP have not been reported in the literature.

Scheme 1 depicts route for synthesis of 4-(4-(2-(4-(allyloxy) phenyl)-5-hydroxy)pentan-2-yl)phenoxy)benzaldehyde and 4-(4-(allyloxy)phenyl)-4-(4-(4-formylphenoxy)phenyl)pentyl 2-bromo-2-methyl propanoate. The synthesis of new initiators was carried out starting from commercially available 4,4′-bis(4-hydroxyphenyl) pentanoic acid, which in turn is derived from levulinic acid—a platform chemical obtained from biomass. 4,4′-Bis(4-hydroxyphenyl) pentanoic acid was converted into 4,4′-(5-hydroxypentane-2,2-diyl)-diphenol by the reported procedure[28,35] and was subjected to allylation reaction using one equivalent of allyl bromide in the presence of K_2CO_3 in acetone. To minimize the formation of di-allyloxy substituted compound, addition of allyl bromide was performed slowly. However, the crude reaction product was found to be a mixture of desired mono-allyloxy product and minor amount of di-allyloxy compound. Column chromatography was found to be essential for isolation of mono allyloxy product 4-(2-(4-(allyloxy) phenyl) (5-(hydroxypentan-2-yl) phenol. The next step in the synthesis involved nucleophilic substitution reaction of 4-fluorobenzaldehyde with 4-(2-(4-(allyloxy) phenyl) (5-(hydroxypentan-2-yl) phenol in dry DMF using K_2CO_3 as a base to obtain 4-(4-(2-(4-(allyloxy) phenyl)-5-hydroxy) pentan-2-yl)phenoxy)benzaldehyde.

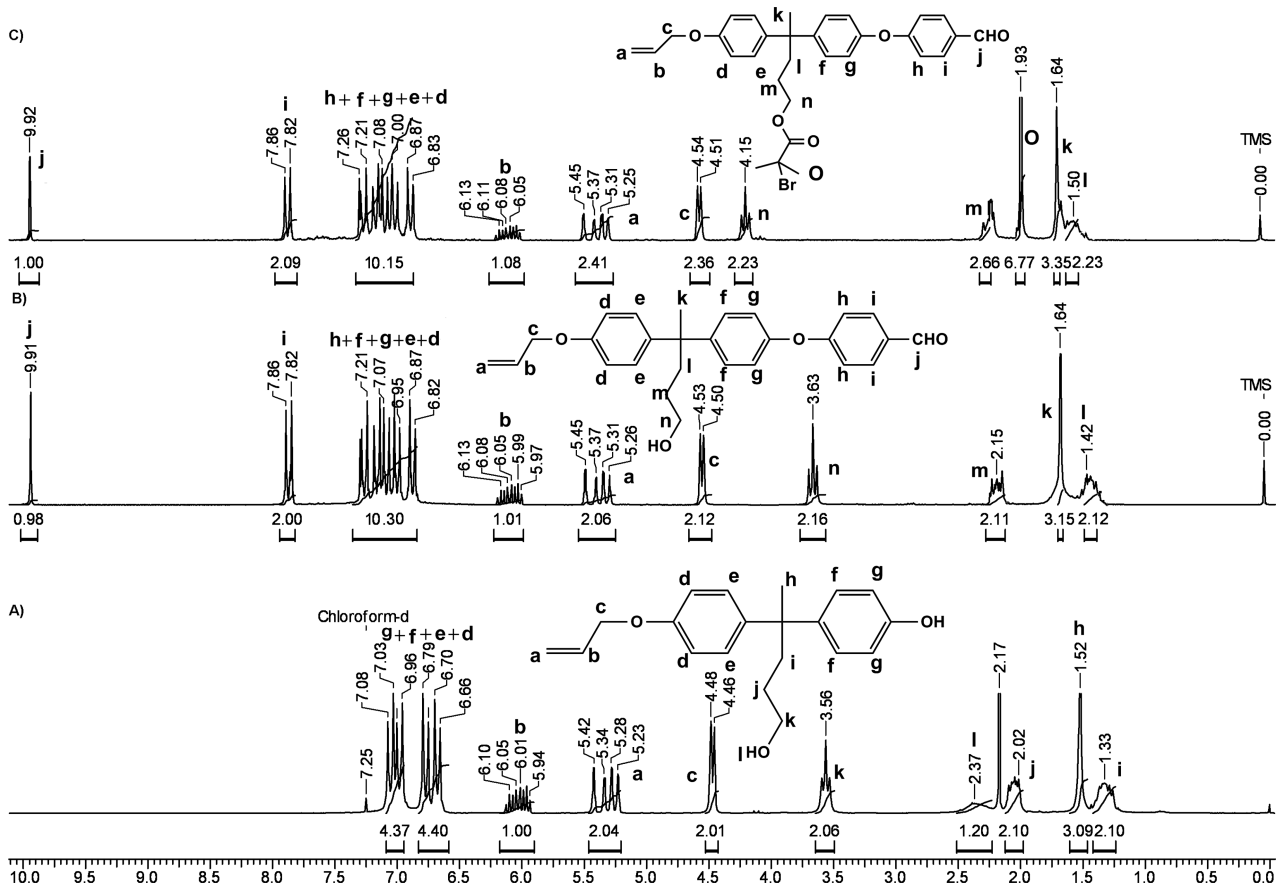
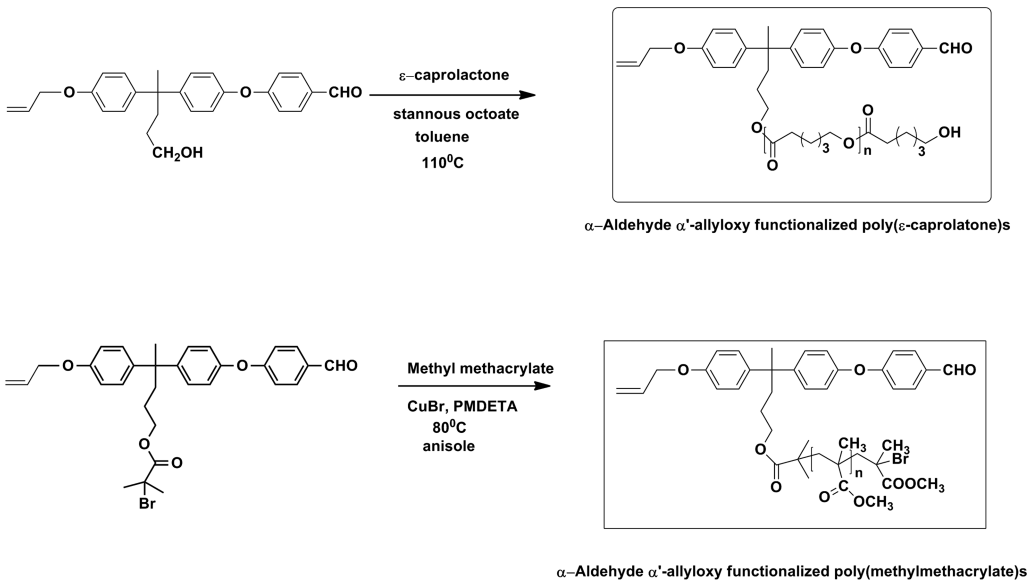


FIGURE 1 ^{1}H NMR spectra of (A) 4-(2-(4-(allyloxy)phenyl)-5-hydroxypentan-2-yl)phenol, (B) 4-(4-(2-(4-allyloxy)phenyl)-5-hydroxy)pentan-2-yl)phenoxy)benzaldehyde, and (C) 4-(4-(allyloxy) phenyl)-4-(4-(4-formylphenoxy) phenyl) pentyl 2-bromo-2-methyl propanoate.

The product was purified by column chromatography and was characterized by FT-IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. FT-IR spectrum of 4-(4-(2-(4-(allyloxy)phenyl)-5-hydroxy)pentan-2-yl)phenoxy)benzaldehyde showed absorption band at 3200 cm^{-1} which corresponds to asymmetric stretching of alcohol functionality, and a characteristic peak at 1715 cm^{-1} that corresponds to asymmetric stretching to aldehyde functionality. Figure 1 represents ^{1}H NMR spectrum of 4-(4-(2-(4-(allyloxy) phenyl)-5-hydroxy) pentan-2-yl)phenoxy)benzaldehyde along with the assignments. The presence of aldehyde functionality was confirmed by the appearance of a singlet at 9.91 ppm. The aromatic protons *ortho* to aldehyde group were deshielded and appeared as a doublet at 7.84 ppm. The presence of allyloxy functionality was confirmed by the appearance of multiplets in the range 6.13–5.97 ppm, and 5.45–5.26 ppm corresponding to methine and vinyl protons, respectively. The spectral data corresponding to other protons was in good agreement with the proposed structure. In ^{13}C NMR spectrum, a peak due to aldehyde carbonyl carbon was observed at 191.4 ppm, the peaks corresponding to carbon atoms in allyloxy functionality appeared at 133.4 and at 118.3 ppm. The data corresponding to other carbon atoms was in good agreement with the proposed structure.

4-(4-(Allyloxy)phenyl)-4-(4-(4-formylphenoxy)phenyl)pentyl 2-bromo-2-methyl propanoate was synthesized by esterification of 4-(4-(2-(4-(allyloxy)phenyl)-5-hydroxy)pentan-2-yl) phenoxy)benzaldehyde with 2-bromoisobutyryl bromide in dry chloroform Scheme 1. The product was purified by silica gel column chromatography and was characterized using FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy. FT-IR spectrum of 4-(4-(allyloxy)phenyl)-4-(4-(4-formylphenoxy) phenyl)pentyl 2-bromo-2-methyl propanoate showed absorption bands at 1735, and 1710 cm^{-1} that correspond to ester carbonyl and aldehyde asymmetric stretching, respectively. ^{1}H NMR spectrum of 4-(4-(allyloxy) phenyl)-4-(4-(4-formylphenoxy) phenyl) pentyl 2-bromo-2-methyl propanoate along with assignments is shown in Figure 1. The presence of aldehyde functionality was confirmed by the appearance of a singlet at 9.92 ppm. The presence of allyloxy functionality was confirmed by the appearance of multiplets in the range 6.13–6.05 ppm, and 5.45–5.25 ppm corresponding to methine and vinyl protons, respectively. The singlet appeared at 1.93 ppm could be attributed to protons corresponding to methyl group of halo ester. The spectral data corresponding to other protons was in good agreement with the proposed structure. In ^{13}C NMR spectrum, a peak corresponding to carbonyl carbon of aldehyde group was observed at 191.3 ppm and



SCHEME 2 Synthesis of (A) α-aldehyde, α′-allyloxy heterobifunctionalized poly(ε-caprolactones) (B) α-aldehyde, α′-allyloxy heterobifunctionalized poly(methyl methacrylate)s.

peak due to ester carbonyl carbon was observed at 170.5 ppm. The carbon atoms corresponding to allyloxy group appeared at 134.0 and 118.5 ppm. The data corresponding to other carbon atoms was in good agreement with the proposed structure.

Synthesis of α-Aldehyde, α′-Allyloxy Hetero Bifunctionalized Poly(ε-caprolactones)

ROP of ε-caprolactone was carried out using 4-(4-(2-(4-(allyloxy) phenyl)-5-hydroxy)pentan-2-yl)phenoxy)benzaldehyde as initiator in the presence of stannous octoate as a catalyst in toluene [Scheme 2(a)]. The conditions and results of synthesis of α-aldehyde, α′-allyloxy heterobifunctionalized poly (ε-caprolactones) are summarized in Table 1. Poly(ε-caprolactones) with molecular weights ranging from $M_{n,GPC}$-5900 to 29,000 were synthesized by varying monomer to initiator ratio. ^{1}H NMR spectrum of α-aldehyde, α′-allyloxy heterobifunctionalized poly(ε-caprolactone) is represented in Figure 2. The appearance of a singlet at 9.90 ppm and multiplets in the range 6.12–5.99 ppm, and 5.45–5.23 ppm confirmed the presence of aldehyde and allyloxy functionality, respectively on poly(ε-caprolactone). Molecular weights for α-aldehyde, α′-allyloxy hetero functionalized poly(ε-caprolactones) were determined by ^{1}H NMR spectroscopy by comparing integral intensity of peak belonging to —OCH_2 in poly(ε-caprolactone) at 4.04 ppm to a singlet at 9.90 ppm corresponding to aldehyde group. The degree of polymerization (Dpn) was calculated from NMR analysis using the relation,

$$\text{Dpn} = [I_{4.04}/2/(I_{9.91}/1)_{\text{(aldehyde proton)}}]$$

Molecular weights were calculated using the equation,

$$M_{n,NMR} = [\text{Dpn} \times \text{mol. wt. of monomer } (114)] + \text{mol. wt. inititor } (416)$$

$M_{n,NMR}$ values were in reasonably good agreement with theoretical molecular weights ($M_{n,theo}$) calculated from the monomer to initiator ratio. In addition, GPC data revealed monomodal distribution with PDI values in the range 1.26–1.43, for poly(ε-caprolactone). Thus, 4-(4-(2-(4-(allyloxy) phenyl)-5-hydroxy) pentan-2-yl)phenoxy)benzaldehyde was found to be a useful ROP initiator for synthesis of α-aldehyde, α′-allyloxy heterobifunctionalized poly(ε-caprolactones).

TABLE 1 Reaction Conditions and Results for Synthesis of α-Aldehyde, α′-Allyloxy Heterobifunctionalized Poly(ε-caprolactones)

Sr. No.	$[M]_0/[I]_0$[a]	Time (h)	Conv. (%)[b]	$M_{n,theo}$[c]	$M_{n,NMR}$[d]	$M_{n,GPC}$[e]	M_w/M_n
1	60:1	8	61	4,600	5,100	5,900	1.43
2	120:1	16	71	10,100	9,700	11,800	1.34
3	240:1	24	69	19,300	23,000	29,000	1.26

Temperature = 110 °C, Solvent: Toluene), [CL]/ [Sn $(Oct)_2$] = 200.
[a] $[M]_O/[I]_O$ = [Monomer]$_O$/[Initiator]$_O$.
[b] Gravimetry.
[c] $M_{n,theo} = \left\{\frac{[M]_O}{[I]_O} \times \frac{(\%\text{ Conv.})}{100} \times \text{mol. wt. of monomer } (114)\right\} +$ mol. wt. initiator (416).
[d] $M_{n,NMR}$ = determined from NMR.
[e] $M_{n,GPC}$ = Polystyrene standard; $CHCl_3$ eluent.

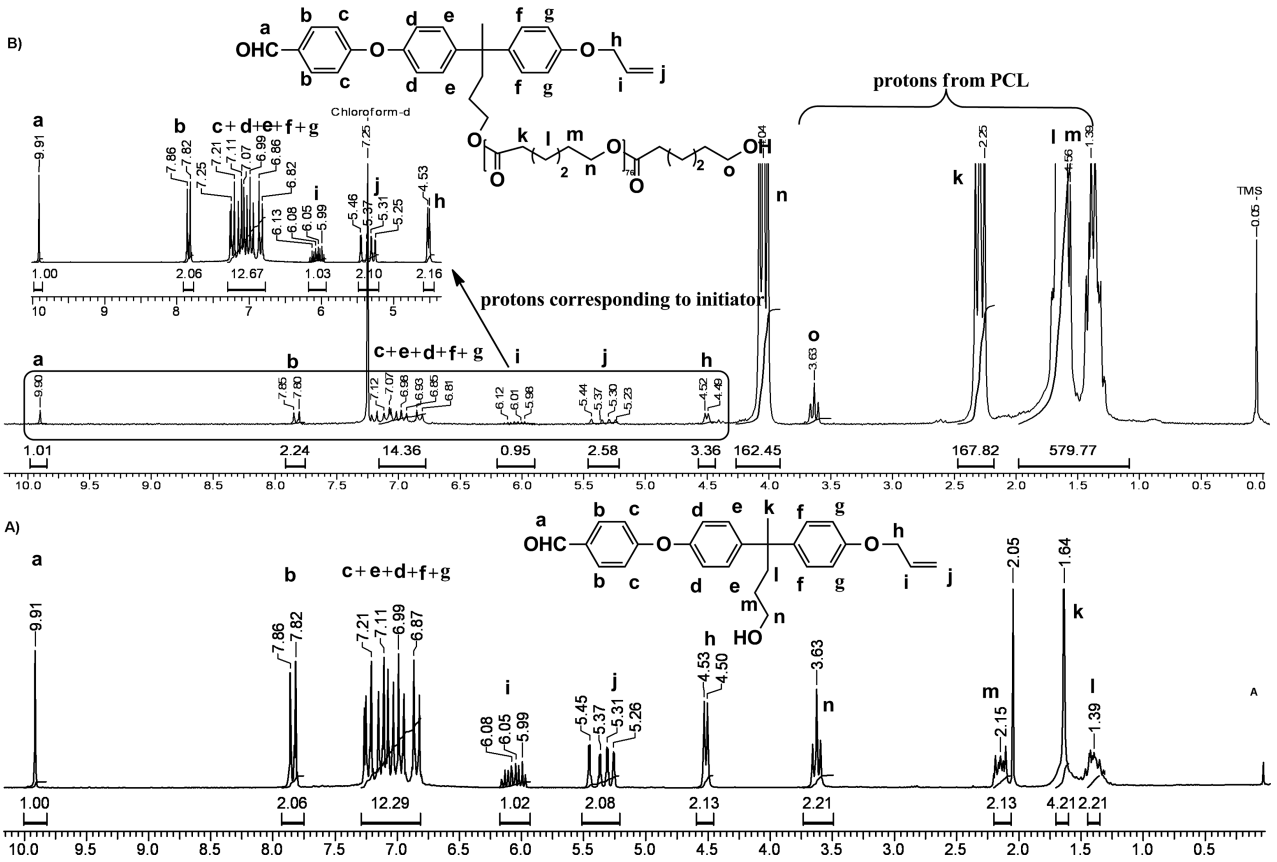


FIGURE 2 ^{1}H NMR spectra of (A) 4-(4-(2-(4-(allyloxy)phenyl)-5-hydroxy)pentan-2-yl)phenoxy)benzaldehyde and (B) α-aldehyde, α′-allyloxy heterobifunctionalized poly(ε-caprolactone) in $CDCl_3$.

Synthesis of α-Aldehyde, α′-Allyloxy Hetero Bifunctionalized Poly(methyl methacrylate)s

ATRP of methyl methacrylate was carried out using 4-4-(allyloxy) phenyl)-4-(4-(4-formylphenoxy) phenyl) pentyl 2-bromo-2-methylpropanoate as the initiator Scheme 2(b). The conditions and results of synthesis of α-aldehyde α′-allyloxy hetero bifunctionalized poly(methyl methacrylate)s are summarized in Table 2. Different ratios of $[M_0]/[I_0]$ with different reaction intervals were chosen so as to obtain polymers with a range of molecular weights ($M_{n,GPC,}$: 5300–28,800). The conversions were determined by gravimetric analysis. The reaction conversions were kept in the range 55–67% to ensure avoidance of potential side reactions related to allyloxy functional group, if any.[36] ^{1}H NMR spectrum of α-aldehyde, α′-allyloxy functionalized poly(methyl methacrylate) is reproduced in Figure 3. The appearance of a singlet at 9.93 ppm confirmed the presence of aldehyde functionality. The appearance of multiplets in the range 6.14–6.0 ppm and 5.46–5.26 ppm confirmed the presence of allyloxy functionality. Integration of signals for aldehyde functionality and comparison with the integration values for methoxy protons in poly(methyl methacrylate) allows the molecular weight to be determined. The Dpn was calculated from NMR analysis using the relation,

$$\text{Dpn} = \{(I_{3.58}/3)/I_{9.93}/1(\text{aldehyde proton})\}$$

where $I_{3.58}$ and $I_{9.93}$ are integrals of the signals positioned at 3.58 corresponding to methoxy protons of poly(methyl methacrylate) and at 9.93 ppm corresponding to aldehyde proton, respectively.

Molecular weights were calculated by ^{1}H NMR spectroscopy using equation,

$$M_{n,NMR} = [\text{Dpn} \times 100\ (\text{mol. wt. of monomer})] + \text{mol. wt. initiator}\ (565)$$

Molecular weights determined by ^{1}H NMR spectroscopy ($M_{n,NMR}$) were in reasonably good agreement with theoretical molecular weights ($M_{n,theo}$) indicating good initiator efficiency (I^{eff} = 0.71–0.89). In addition, GPC trace revealed monomodal distribution (Fig. 4) with PDI values in the range 1.19–1.25 for poly(methyl methacrylate)s. The PDIs were relatively narrow, which is a characteristic behavior of a controlled radical polymerization method. A kinetic study was performed to verify the control over the polymerization of methyl methacrylate. The linearity of plot of ln (M_0/M_t) versus polymerization time (Fig. 5) where M_0 and M_t are initial and the actual monomer concentration indicated the pseudo first order kinetics. The concentration of radicals remained constant during the polymerization reaction and therefore it can be concluded that no detectable side reactions occurred during polymerization. The linear increase of molecular weight with increasing conversion and PDI below 1.25 (Fig. 6) represents an additional indication for a controlled

TABLE 2 Reaction Conditions and Results of Synthesis of α-Aldehyde α′-Allyloxy Hetero Bifunctionalized Poly(methyl methacrylate)s

Sr. No.	$[M]_0/[I]_0$[a]	Time (h)	Conv. (%)[b]	$M_{n,theo}$[c]	$M_{n,NMR}$[d]	$M_{n,GPC}$[e]	M_w/M_n	I^{eff}
1	50:1	3	55	3,300	3,700	5,300	1.21	0.89
2	100:1	5	60	6,600	7,800	12,100	1.25	0.84
3	200:1	8	67	14,000	19,700	28,800	1.19	0.71

Temperature = 80 °C, Solvent: Anisole (50%, w/v w.r.t monomer).
[a] $[M]_O/[I]_O$: $[Monomer]_O/[Initiator]_O$
[b] Gravimetry.
[c] $M_{n,theo} = \left\{\frac{[M]_O}{[I]_O} \times \frac{(\%\ Conv.)}{100} \times \text{mol. wt. of monomer (100)}\right\} +$ mol. wt. initiator (565).
[d] $M_{n,NMR}$ = determined from NMR.
[e] $M_{n,GPC}$ = determined from GPC; Polystyrene standard; $CHCl_3$ eluent
$I^{eff} - M_{n,theo}/M_{n,NMR}$.

polymerization mechanism. Thus, 4-(4-(allyloxy) phenyl)-4-(4-(4-formylphenoxy) phenyl)pentyl 2-bromo-2-methyl propanoate was found to be an useful ATRP initiator for controlled polymerization of methyl methacrylate.

Chemical Modification of α-Aldehyde, α′-allyloxy Hetero Bifunctionalized Poly(ε-caprolactone) /Poly(methyl methacrylate)

The allyloxy and aldehyde functionalities introduced deliberately on poly(ε-caprolactone)/poly(methyl methacrylate) are known to undergo different types of metal-free click reactions. Aldehyde and allyloxy functional groups undergo aldehyde-aminooxy[37,38] and thiol-ene click reactions,[39–41] respectively. Aldehyde-aminooxy click reaction was first performed by considering the fact that aldehyde group would undergo addition reaction with thiol compounds and in the second step, thiol-ene click reaction was performed.

Aldehyde-Aminooxy Click Reaction of α-Aldehyde, α′-Allyloxy Hetero bifunctionalized Poly(ε-caprolactone)/ Poly(methyl methacrylate) with O-(2-Azidoethyl) hydroxylamine

The reactivity of aldehyde functionality on poly(ε-caprolactone)/poly(methyl methacrylate) was illustrated by carrying out click reaction on poly(ε-caprolactone)/poly(methyl methacrylate) with O-(2-azidoethyl) hydroxylamine at room temperature (Scheme 3). The conversion was assessed by FT-IR and ^{1}H NMR spectroscopy. In FT-IR spectrum, in addition to

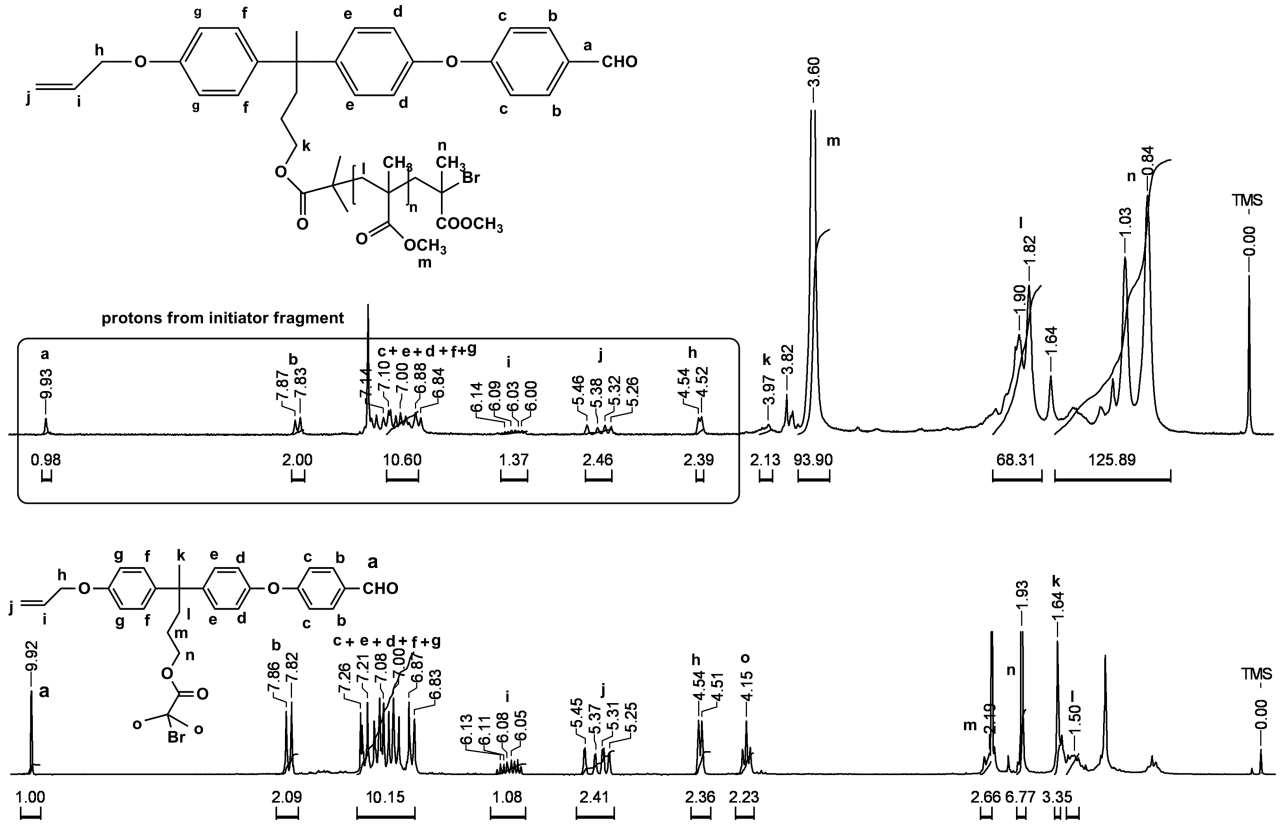


FIGURE 3 ^{1}H NMR spectra of (A) 4-(4-(allyloxy)phenyl)-4-(4-(4-formylphenoxy)phenyl)pentyl 2-bromo-2-methyl propanoate and (B) α-aldehyde, α′-allyloxy heterobifunctionalized poly(methyl methacrylate) in $CDCl_3$.

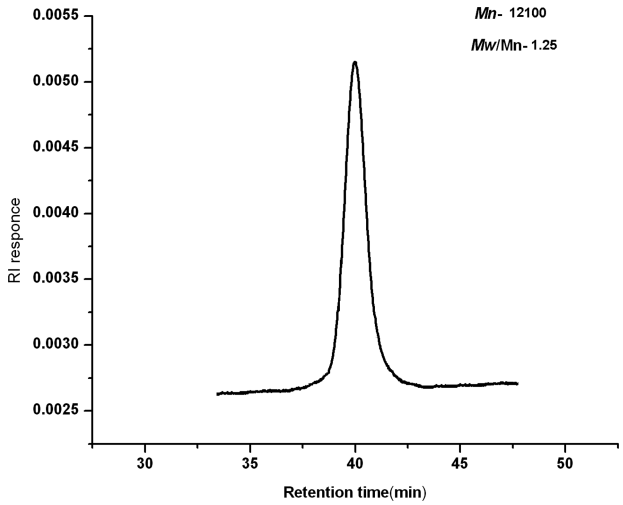


FIGURE 4 GPC trace of α-aldehyde, α′-allyloxy heterobifunctionalized poly(methyl methacrylate) (Table 2, Run 2).

the peaks corresponding to ester carbonyl of poly(ε-caprolactone)/poly(methyl methacrylate) around 1730 cm^{-1}, characteristic peak corresponding to azido functionality appeared at 2110 cm^{-1} confirming introduction of azido groups via oxime formation. Figure 7 represents ^1H NMR spectrum of α-aldehyde, α′-allyloxy heterobifunctionalized poly(ε-caprolactone) (M_n: 9700) and its click reaction product with O-(2-azidoethyl) hydroxylamine while Figure 8 represents ^1H NMR spectra of α-aldehyde, α′-allyloxy heterobifunctionalized poly(methyl methacrylate) (M_n: 3700) and its click reaction product with O-(2-azidoethyl) hydroxylamine. ^1H NMR spectra showed complete disappearance of the peak corresponding to aldehyde functionality and appearance of a new peak around 8.11 ppm (—CH=N—O) which elucidates oxime formation without affecting peaks related to poly(ε-caprolactone)/poly(methyl methacrylate) attesting completion of the reaction without any side reaction such as degradation of poly(ε-caprolactone)/poly(methyl methacrylate) backbone. The model aldehyde-aminooxy click reaction study with O-

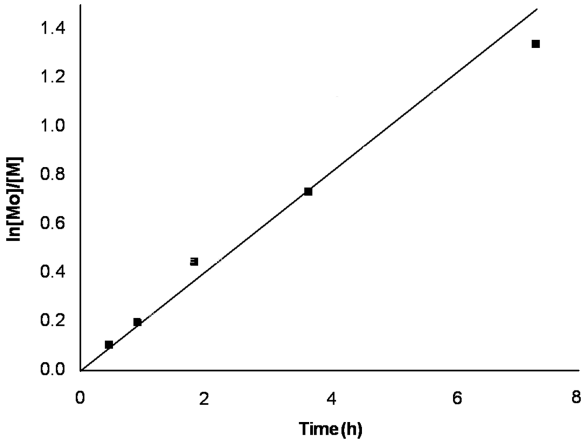


FIGURE 5 Relationship between ln ($[M_0]/[M_t]$) and the polymerization time for ATRP of methyl methacrylate at 80 °C in anisole.

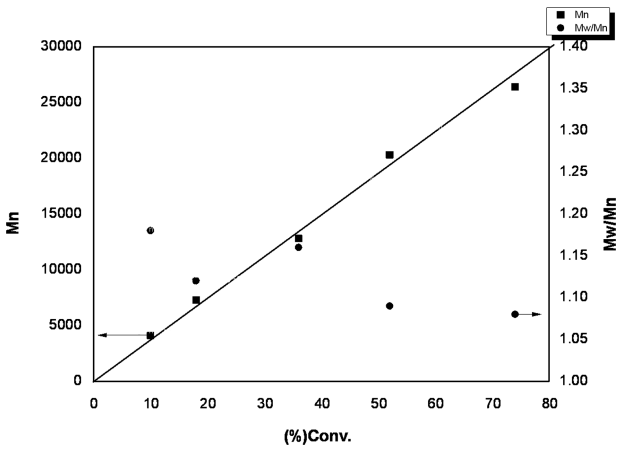
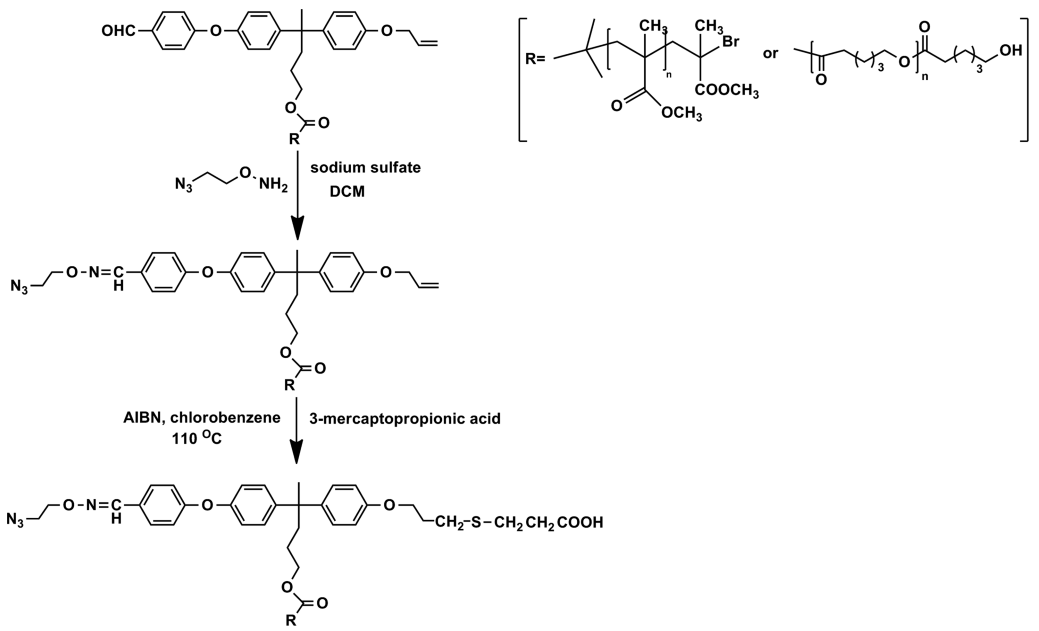


FIGURE 6 Dependence of number-average molecular weight and PDI on monomer conversion for ATRP of methyl methacrylate at 80 °C in anisole.

(2-azidoethyl) hydroxylamine introduces azido moiety on palycaprolactone/poly(methylmethacrylate) chain which further opens up plethora of opportunities to introduce different types of functional groups on poly(ε-caprolactone)/poly(-methylmethacrylate) by well-known azide-alkyne click reaction.[42] Furthermore, polymers possessing clickable end functional groups represent valuable precursors for synthesis of Y-shaped miktoarm star copolymers.

Thiol-Ene Click Reaction on α-Allyloxy α′-Azido Hetero Bifunctionalized Poly(ε-caprolactone) and Poly(methyl methacrylate)

The reactivity of allyloxy functionality on poly(ε-caprolactone) and poly(methyl methacrylate) was illustrated by carrying out click reaction with 3-mercaptopropionic acid in the presence of AIBN at 80 °C in chlorobenzene as a solvent [Schemes 3(b) and 4(b)]. The conversion was assessed by ^1H NMR spectroscopy. ^1H NMR spectra of α-allyloxy α′-azido functionalized poly(ε-caprolactone) (M_n: 9700) and its click reaction product with 3-mercaptopropionic acid is depicted in Figure 9. Although Figure 10 represents ^1H NMR spectra of α-allyloxy α′-azido functionalized poly(methyl methacrylate) (M_n: 3700) and its click reaction product with 3-mercaptopropionic acid. ^1H NMR spectra showed complete disappearance of the peak corresponding to allyloxy functionality and appearance of new signals at 2.89, 2.75, and 2.63 ppm (CH—S) which evidenced the successful thiol addition reaction. The peaks corresponding to polycaprolactone/poly(methylmethacrylate) backbones remained intact in the product polymer attesting completion of the reaction without any side reaction. The model thiol-ene click reaction study with 3-mercaptopropionic acid opens up additional opportunities to introduce different functionalities on poly(ε-caprolactone)/poly(methyl methacrylate) via utilization of functionalized thiols.[43] For instanace, thiols containing functional groups such as furan, pyrene, trimethoxysilyl, perfluoroalkyl, and so forth, could be utilized to introduce the corresponding functional groups on poly(ε-caprolactone)/poly(methyl methacrylate).



SCHEME 3 Post-functionalization of α-aldehyde, α′-allyloxy heterobifunctionalized poly(ε-caprolactone)/poly(methyl methacrylate) by (A) aldehyde-aminooxy and (B) thiol-ene click rection.

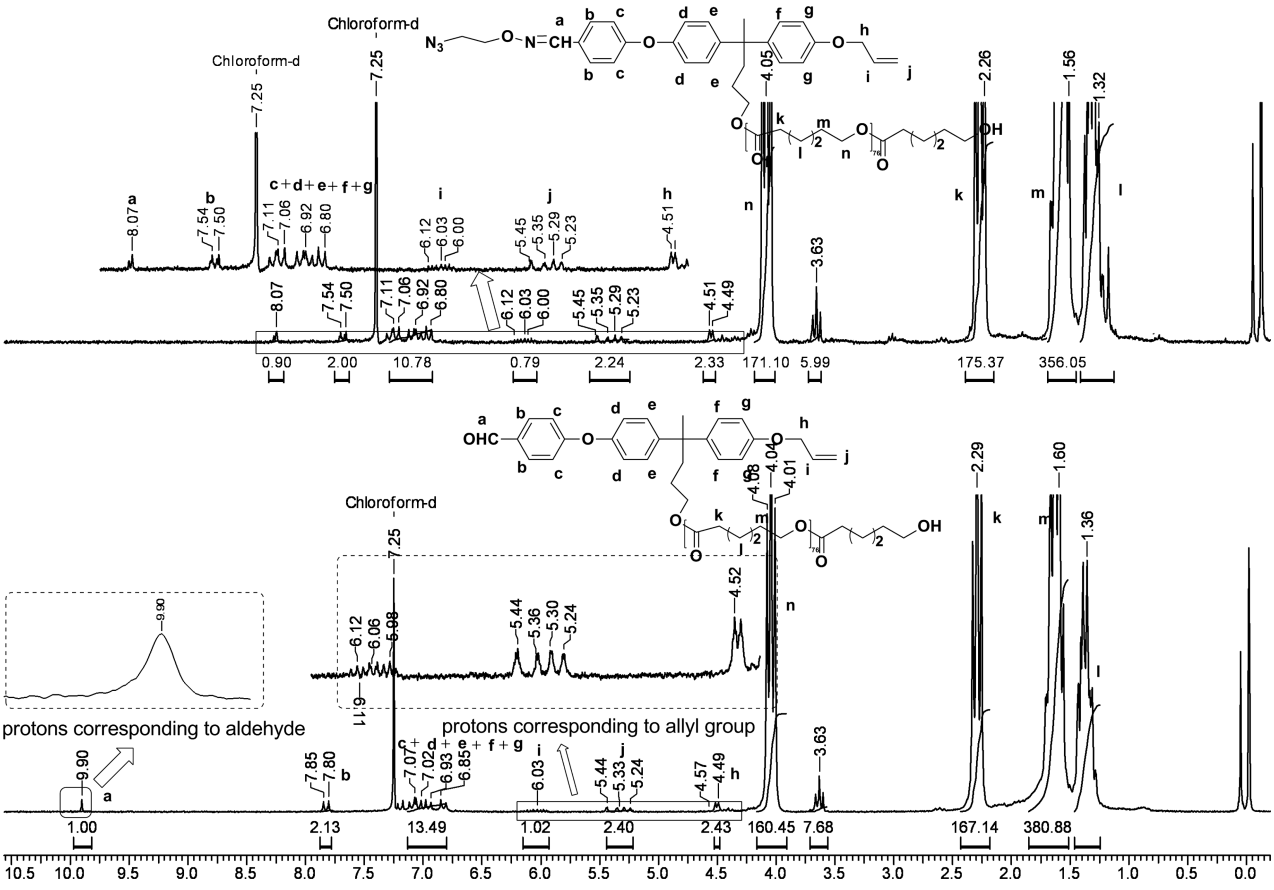


FIGURE 7 ^{1}H NMR spectra of (A) α-aldehyde, α′-allyloxy heterobifunctionalized poly(ε-caprolactone) and (B) the product of aldehyde-aminooxy click reaction in $CDCl_3$.

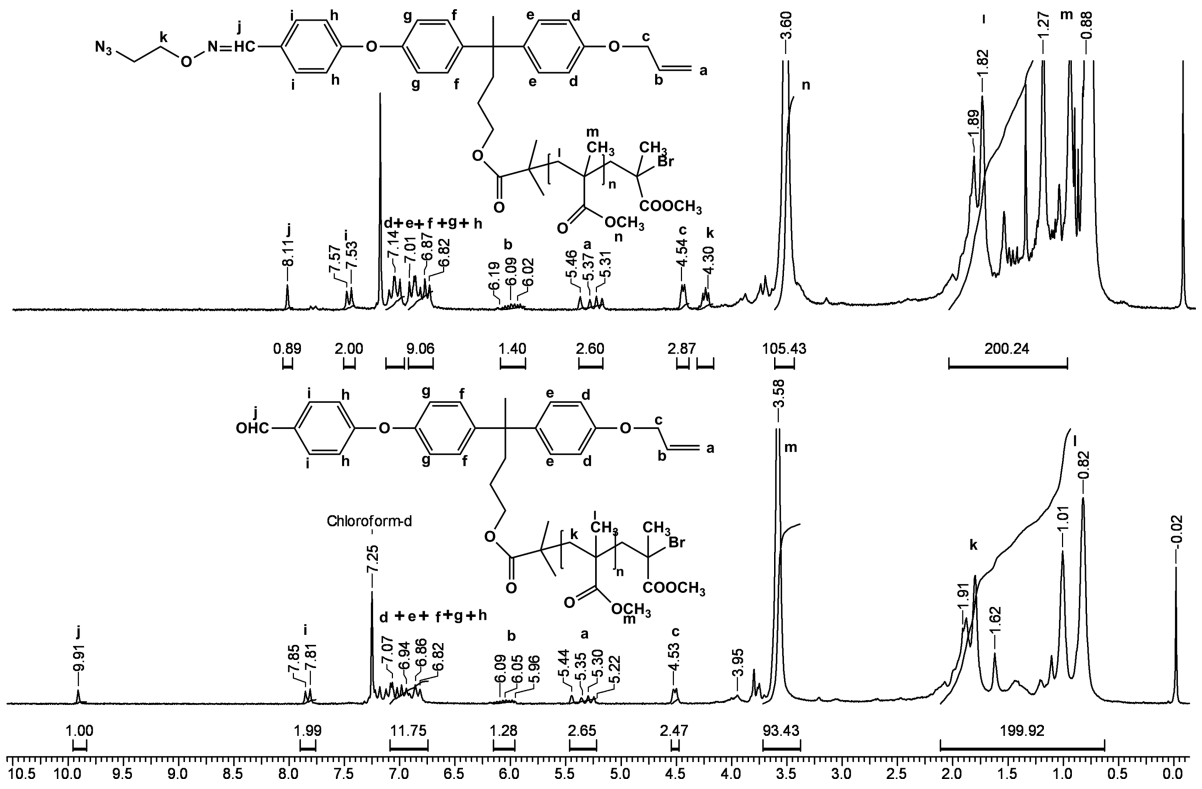


FIGURE 8 ^{1}H NMR spectra of (A) α-aldehyde, α'-allyloxy heterobifunctionalized poly(methyl methacrylate) and (B) the product of aldehyde-aminooxy click reaction in $CDCl_3$.

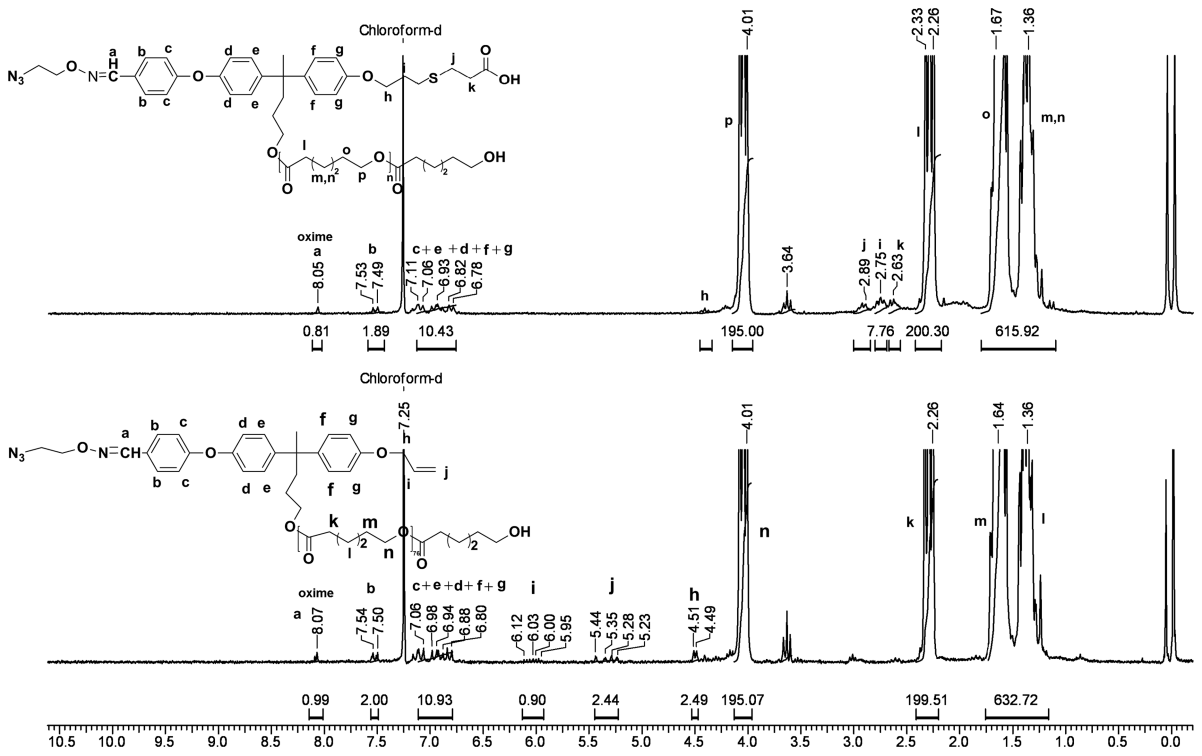


FIGURE 9 ^{1}H NMR spectra of (A) α-allyloxy, α'-azido heterobifunctionalized poly(ε-caprolactone) and (B) the product of thiol-ene click reaction in $CDCl_3$.

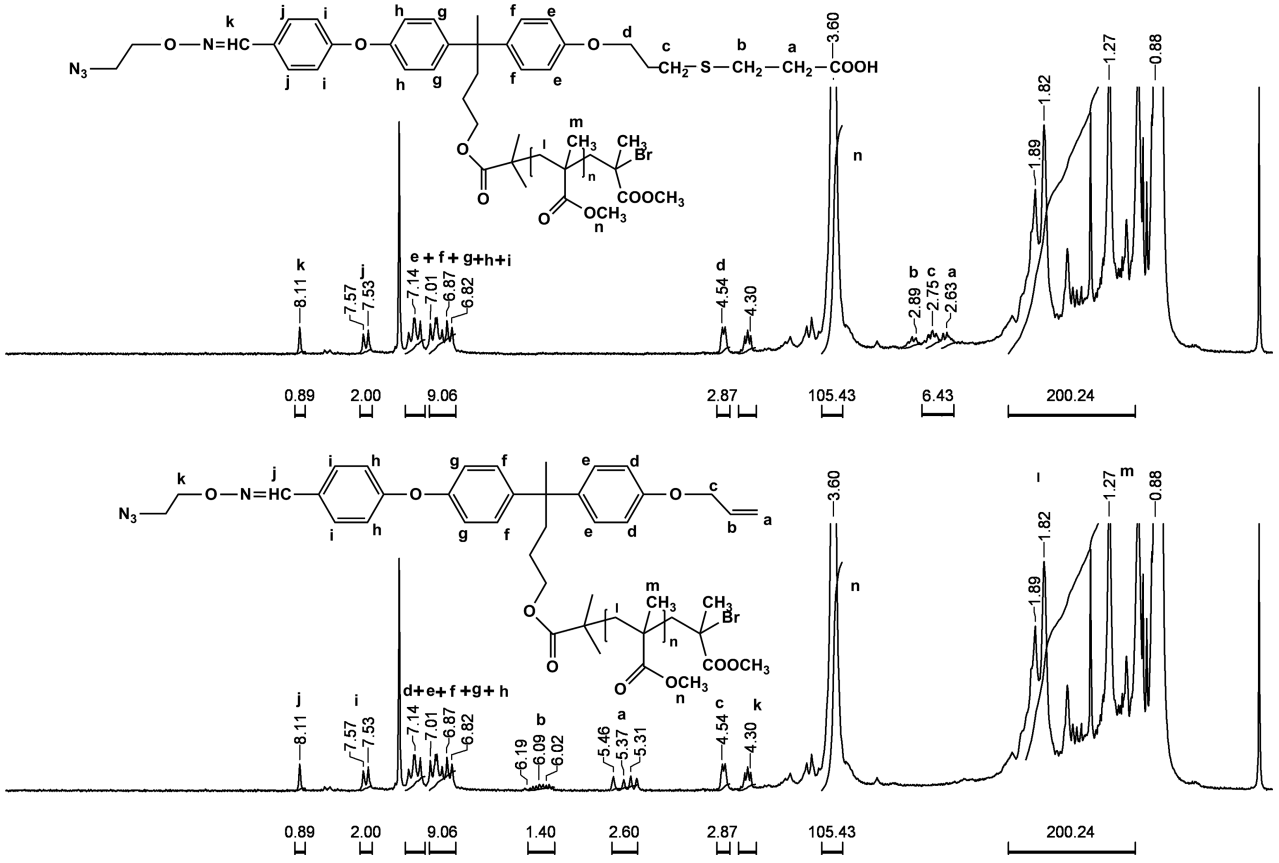


FIGURE 10 ^{1}H NMR spectra of (A) α-allyloxy, α′-azido heterobifunctionalized poly(methylmethacrylate) and (B) the product of thiol-ene click reaction in $CDCl_3$.

CONCLUSIONS

In summary, starting from common precursor namely 4,4′-bis(4-hydroxyphenyl) pentanoic acid, which in turn is derived from levulinic acid—a platform chemical obtained from biomass-, two new initiators namely, 4-(4-(2-(4-(allyloxy)phenyl)-5-hydroxypentane 2-yl) phenoxy) benzaldehyde and 4-(4-(allyloxy)phenyl)-4-(4-(4-formylphenoxy)phenyl) pentyl 2-bromo-2-methyl propanoate with hetero-functionalities such as allyloxy and aldehyde were synthesized. These initiators were used for ROP of ε-caprolatone and ATRP of methyl methacrylate. Well-defined poly(ε-caprolactone) and poly(methyl methacrylate) containing α-aldehyde, α′-allyloxy functional groups were obtained. Hetero-functional groups present on polymers were further modified into different heterofunctionalities by carrying out aldehyde-aminooxy and thiol-ene metal free click reactions. Given the utility of ATRP and ROP polymerization to produce a wide range of different polymers and chain architectures, this approach will widen the range of possible end functional polymers.

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REFERENCES AND NOTES

1 P. Rempp, E. Franta, In Advance in Polymer Science; Springer: Berlin/Heidelberg, **1984**; p 1–53.

2 C. Cheng, E. Khoshdel, K. L. Wooley, *Macromolecules* **2005,** *38*, 9455–9465.

3 K. V. Bernaerts, Du F. E. Prez, *Prog. Polym. Sci.* **2006,** *31*, 671–722.

4 D. Taton, X. Feng, Y. Gnanou, *New J Chem* **2007,** *31*, 1097–1110.

5 N. Hadjichristidis, H. Iatrou, M. Pitsikalis, S. Pispas, A. Avgeropoulos, *Prog. Polym. Sci.* **2005,** *30*, 725–782.

6 V. Sciannamea, R. Jerome, C. Detrembleur, *Chem. Rev.* **2008,** *108*, 1104–1126.

7 V. Coessens, T. Pintauer, K. Matyjaszewski, *Prog. Polym. Sci.* **2001,** *26*, 337–377.

8 M. Ouchi, T. Terashima, M. Sawamoto, *Chem. Rev.* **2009,** *109*, 4963–5050.

9 C. Boyer, M. H. Stenzel, T. P. Davis, *J. Polym. Sci. Part A: Polym. Chem.* **2011,** *49*, 551–595.

10 J. Chiefari, Y. K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo, S. H. Thang, *Macromolecules* **1998,** *31*, 5559–5562.

11 C. Detrembleur, M. Mazza, O. Halleux, P. Lecomte, D. Mecerreyes, J. L. Hedrick, *Macromolecules* **1999,** *33*, 14–18.

12 M. Degirmenci, A. Acikses, N. Genli, *J. Appl. Polym. Sci.* **2012,** *123*, 2567–2573.

13 M. Kamigaito, T. Ando, M. Sawamoto, *Chem. Rev.* **2001,** *101*, 3689–3745.

14 Y. L. Cai, S. P. Armes, *Macromolecules* **2005,** *38*, 271–279.

15 G. Deng, L. Zhang, C. Liu, L. He, Y. Chen, *Eur. Polym. J.* **2005,** *41*, 1177–1186.

16 V. Deimede, J. K. Kallitsis, *Chem. Eur. J.* **2002,** *8*, 467–473.

17 Y. Yamazaki, N. Ajioka, A. Yokoyama, T. Yokozawa, *Macromolecules* **2009,** *42*, 606–611.

18 S. Yurteri, I. Cianga, A. L. Demirel, Y. Yagci, *J. Polym. Sci. Part A: Polym. Chem.* **2005,** *43*, 879–896.

19 G. J. Summers, M. P. Ndawuni, C. A. Summers, *Polym. Int.* **2012,** *61*, 1353–1361.

20 R. Francis, B. Lepoittevin, D. Taton, Y. Gnanou, *Macromolecules* **2002,** *35*, 9001–9008.

21 R. Matmour, B. Lepoittevin, T. J. Joncheray, El-Khouri, R. J.; D. Taton, R. S. Duran, Y. Gnanou, *Macromolecules* **2005,** *38*, 5459–5467.

22 J. Babin, C. Leroy, S. Lecommandoux, R. Borsali, Y. Gnanou, D. Taton, *Chem. Commun.* **2005**, 1993–1995.

23 C. N. Urbani, C. A. Bell, D. Lonsdale, M. R. Whittaker, M. J. Monteiro, *Macromolecules* **2008,** *41*, 76–86.

24 Y. Zhang, H. Liu, H. Dong, C. Li, S. Liu, *J. Polym. Sci. Part A: Polym. Chem.* **2009,** *47*, 1636–1650.

25 S. Yurteri, I. Cianga, Y. Yagci, *Macromol. Chem. Phys.* **2003,** *204*, 1771–1783.

26 G. W. Wang, C. Liu, M. G. Pan, J. L. Huang, *J. Polym. Sci. Part A: Polym. Chem.* **2009,** *47*, 1308–1316.

27 Y. Wang, L. Lu, H. Wang, D. R. Lu, K. Tao, R. K. Bai, *Macromol. Rapid Commun.* **2009,** *30*, 1922–1927.

28 P. S. Sane, D. V. Palaskar, P. P. Wadgaonkar, *Eur. Polym. J.* **2011,** *47*, 1621–1629.

29 P. S. Sane, B. V. Tawade, D. V. Palaskar, S. K. Menon, P. P. Wadgaonkar, *React. Funct. Polym.* **2012,** *72*, 713–721.

30 M. Karesoja, H. Jokinen, E. Karjalainen, P. Pulkkinen, M. Torkkeli, A. Soininen, J. Ruokolainen, H. Tenhu, *J. Polym. Sci. Part A: Polym. Chem.* **2009,** *47*, 3086–3097.

31 Y. Nakagawa, K. Matyjaszewski, *Polym. J.* **1998,** *30*, 138–141.

32 F. Zeng, Y. Shen, S. Zhu, R. Pelton, *Macromolecules* **2000,** *33*, 1628–1635.

33 D. Mecerreyes, R. D. Miller, J. L. Hedrick, C. Detrembleur, R. Jérôme, *J. Polym. Sci. Part A: Polym. Chem.* **2000,** *38*, 870–875.

34 A. Cordova, T. Iversen, K. Hult, *Polymer* **1999,** *40*, 6709–6721.

35 K.-Y. Chen, C. B. Gorman, *J. Org. Chem.* **1996,** *61*, 9229–9235.

36 R. París, de la J. L. Fuente, *J. Polym. Sci. Part A: Polym. Chem.* **2005,** *43*, 2395–2406.

37 B. S. Murray, A. W. Jackson, C. S. Mahon, D. A. Fulton, *Chem. Commun.* **2010,** *46*, 8651–8653.

38 A. W. Jackson, D. A. Fulton, *Macromolecules* **2009,** *43*, 1069–1075.

39 C. R. Becer, R. Hoogenboom, U. S. Schubert, *Angew. Chem. Int. Ed. Engl.* **2009,** *48*, 4900–4908.

40 B. Yu, J. W. Chan, C. E. Hoyle, A. B. Lowe, *J. Polym. Sci. Part A: Polym. Chem.* **2009,** *47*, 3544–3557.

41 C. E. Hoyle, T. Y. Lee, T. Roper, *J. Polym. Sci. Part A: Polym. Chem.* **2004,** *42*, 5301–5338.

42 J. E. Moses, A. D. Moorhouse, *Chem. Soc. Rev.* **2007,** *36*, 1249–1262.

43 J. A. Hensbergen, R. P. Burford, A. B. Lowe, *J. Polym. Sci. Part A: Polym. Chem.* **2013,** *51*, 487–492.