Chapter 4
End-Functionalized Polymers:
Synthesis Characterization
and
Chemical Modification
Chapter 4a
End-Functionalized Polymers
by ROP:
Synthesis, Characterization
and
Chemical Modification
4a.1. Introduction

Aliphatic polyesters based on \( \varepsilon \)-caprolactone, lactide, and glycolide are of interest for medical and pharmaceutical applications by virtue of their biocompatible and biodegradable properties\(^1,2\). Current targets for these materials include degradable sutures, resorbable implant materials, tissue engineering scaffolds, and drug delivery vehicles\(^3,5\). While suitable for many applications, such polyesters are hydrophobic, semi-crystalline solids that lack functionality for further modification and tailoring. The preparation of functionalized aliphatic polyesters is a synthetic challenge, irrespective of whether the functionality is introduced at the monomer stage or in post polymerization chemistry. In the former case, such functionality must be compatible with the polymerization conditions, while in the latter case the desired transformations must be achieved without degradation of the polyester backbone\(^6,9\).

4a.1.1. Poly \( \varepsilon \)-caprolactone containing different types of functional groups

Functionality at \( \alpha \)-, \( \omega \)-, as well as \( \gamma \)-position could be introduced on poly \( \varepsilon \)-caprolactone using different approaches. 1) \( \alpha \)-functionality can be introduced in a controlled way by the use of appropriate functional initiators 2) \( \omega \)-functionalized poly \( \varepsilon \)-caprolactone could be prepared by post modification reaction and 3) \( \gamma \)-functionalized poly \( \varepsilon \)-caprolactone might be accessible by use of \( \gamma \)-functionalized cyclic monomers.

4a.1.1.1. Poly \( \varepsilon \)-caprolactone containing functionality at \( \alpha \)-position

Functionality at \( \alpha \)-position could be introduced in a controlled way by the use of functional initiators e.g aluminium alkoxide initiators prepared by reaction of triethylaluminium (AlEt\(_3\)) with an alcohol\(^{10}\). Aluminium alkoxides [Al (OCH\(_2\)CH\(_2\)X\(_2\))] carrying a functional group (X- Br, CH\(_2\)NEt\(_2\), CH\(_2\)CH=CH\(_2\)) have been used as efficient initiators for ring opening polymerization (ROP) of lactones, lactides and glycolides. Hydrolysis of active aluminium alkoxide bond leads to the formation of an asymmetric telechelic aliphatic polyester, the end groups being X and OH, respectively. The reaction proceeds through the coordination of aluminium to the exocyclic carbonyl oxygen of \( \varepsilon \)-caprolactone, followed by the acyl-oxygen cleavage of the monomer and insertion into the Al-O bond of the initiator \{Scheme 4a.1\}.
Scheme 4a.1: α-Functionalization of poly ε-caprolactones using functional initiators

In addition, functional initiators have been synthesized through the exchange of the alkoxy group of (Al (OiPr)₃) with the desired functional alcohol or even macromonomers or end functional aliphatic esters could be synthesized by properly placing appropriate functional groups on alcoholic substrate {Scheme 4a.2}.

Scheme 4a.2: α-Functionalization of poly ε-caprolactones by initiator approach

Lipase catalyzed ROP was used to synthesize α-end functionalized poly ε-caprolactone with different functionalities such as vinyl, phenol, ether, ester using respective functionalized alcohols.

4a.1.1.2. Poly ε-caprolactone containing functionality at ω-position

ω-Functionalized poly ε-caprolactone could be prepared by post modification reaction. Representative example is depicted in Scheme 4a.3. Coupling reactions are mainly used to couple OH-functionaized poly ε-caprolactone but one need to consider the reaction conditions which must not affect polymer chain.

Scheme 4a.3: ω- Functionalized poly ε-caprolactones by end group modification
4a.1.1.3. Poly ε-caprolactone containing functionality at β- or γ-position

β- or γ-Functionalized poly ε-caprolactone could be accessible by the use of β- or γ-functionalized cyclic monomers. Various functionalities could be introduced at β- or γ-position by appropriately placed functionality on cyclic monomers. Representative examples of functional ε-caprolactone monomers are depicted in Figure 4a.1.

Figure 4a.1: Representative examples of functional caprolactone monomers

Unfortunately, this strategy presents severe drawbacks. Firstly, several of these lactones are not commercially available and several steps are often necessary for their synthesis. Moreover, it is mandatory to rigorously purify these lactones before polymerization, especially if sensitive alkoxides are used as initiators, which is sometimes a difficult task. Accordingly, the total yield of the synthesis is sometimes low and the functionalized lactone is thus quite expensive. Several functional groups such as epoxides, alcohols, and carboxylic acids are not tolerated by propagating species such as aluminum and tin (IV) alkoxides. To introduce such functionalities which are not compatible to ROP reaction conditions by this route, one has to use protected functional monomer and after polymerization protected group could be selectively deprotected into desired functionality. But it is not always easy to have deprotection conditions where no degradation takes place. After deprotection step, particular functionality could be converted into different functional groups. Jerome et al.\textsuperscript{10} reported synthesis of ketone functionalized polyester by deacetalization of ethylene ketal pendant group (Scheme 4a.4), which was further converted into alcohol functionality by carrying out reduction.

Scheme 4a.4: γ-Functionalized poly ε-caprolactones by chemical modification\textsuperscript{10}
4a.1.2. Functionalization of poly ε-caprolactone by chemical modification

4a.1.2.1. Chemical modification using anionic route

The most direct route towards functionalized aliphatic polyesters is based on the functionalization of polyester chains\textsuperscript{10}. This approach is very appealing because a wide range of functionalized aliphatic polyesters could then be made available from a single precursor. This approach was implemented by Vert and coworkers\textsuperscript{15} using a two-step process. First, poly ε-caprolactone was metallated by lithium diisopropylamide with formation of a poly (enolate). Next, the poly (enolate) was reacted with an electrophile (Scheme 4a.5) such as naphthoyl chloride\textsuperscript{16}, benzylchloroformate, acetophenone\textsuperscript{16}, or carbon dioxide\textsuperscript{17}. The implementation of this strategy is, however, difficult because of a severe competition between chain metallation and chain degradation. Moreover, the content of functionalization is quite low (<30%), even under optimized conditions.

Scheme 4a.5: Chemical modification of poly ε-caprolactones chain using anionic route\textsuperscript{15}

Substitution reactions via the α hydrogen of an ester have not been extended to aliphatic polyesters so far, probably because of the sensitivity of these macromolecules to lysis and intramolecular autocondensation (Scheme 4a.6) reaction of poly ε-caprolactone.

Scheme 4a.6: Intramolecular autocondesation reaction of poly ε-caprolactones\textsuperscript{15}

4a.1.2.2. Copolymerization and end functional modification

Reactivity of γ-bromo substituent allows for the new functional polyesters to be prepared\textsuperscript{10}. A polycationic poly ε-caprolactone has been made available by reaction of pyridine and poly (ε-CL-co-γBrCL). The quaterenization is close to completeness. This functionalization
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opens the way to the synthesis of hydrosoluble polyester (Scheme 4a.7). The reaction of 1, 8-diazabicyclo [5.4.0] undec-7-ene (DBU) with poly (ε-CL-co-γBrCL) in toluene at 80 °C leads to unsaturated polyester. The elimination reaction is not selective as a mixture of non-conjugated and conjugated olefin units is formed.

Scheme 4a.7: Chemical modification of poly ε-caprolactones by quaternization and elimination

The quantitative epoxidation of the non-conjugated double bonds has been carried out with 3-chloroperbenzoic acid. It must be noted that the epoxidation reaction doesn’t lead to degradation and provides versatile intermediates for further functionalization of the polyester backbone.

4a.1.2.3. Chemical substitution using atom transfer radical addition (ATRA)

Aluminum and tin alkoxides mediated ROP is not tolerant of hydroxyl, carboxylic acid and epoxy groups. In these specific cases, hydroxyl and carboxylic acid groups must be protected before ROP and deprotected afterwards\textsuperscript{18,19,20}, whereas post-polymerization epoxidation has to be considered for grafting epoxides along the chains\textsuperscript{21-23}. For all these reasons, straightforward strategies are highly desirable to prepare aliphatic polyesters with pendant hydroxyl, carboxylic acid and epoxide groups\textsuperscript{24}. Substitution of radical species for the anionic ones used in the ‘poly (enolate)’ strategy is an alternative worth being tested (Scheme 4a.8), because of the much higher tolerance of the aliphatic polyesters to radicals compared to nucleophiles\textsuperscript{16}. 

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4a.1.2.4. Chemical modification using click chemistry

“Click” chemistry has emerged as an attractive and promising tool to synthesis of novel polymers with well-defined architectures. The great success of this process relies on its simplicity, efficiency and selectivity, wide applicability regardless of the reagents, molecular complexity and ability to take place under aerobic conditions.

4a.1.2.4.1. Azide-alkyne click chemistry

Since the pioneering work of Sharpless, highly regioselective copper-mediated 1,3-dipolar cycloaddition of alkynes and azides, known as a “click” reaction, is extensively used in macromolecular engineering (Scheme 4a.9). Substitution of the pendent chlorides of poly(\(\alpha\)Cl-\(\varepsilon\)CL-co-\(\varepsilon\)CL) random copolymers by sodium azide, followed by the Huisgen’s 1, 3-dipolar cycloaddition of alkynes (functional and/or polymeric), is a valuable technique for grafting a variety of substituents onto poly \(\varepsilon\)-caprolactone.

4a.1.2.4.2. Thiol-ene click chemistry

Another reaction that is recently emerging as an attractive “click” process is the addition of thiols to alkenes (Scheme 4a.10), which is called thiol-ene click reaction. Thiol-ene
chemistry has many of the attributes of alkyne-azide click chemistry, such as tolerance to many different reaction conditions, facile synthetic strategies and clearly defined reaction pathways. Therefore, the thiol-ene click reaction has been utilized for a range of applications, including cross-linked polymeric matrices, such as hydrogels, polymer and nanoparticle functionalization, dendrimer synthesis, and nanoprinting and patterning.

Scheme 4a.10: Chemical modification of poly ε-caprolactones by thiol-ene click chemistry

4a.1.2.5. Chemical modification using Michael addition reaction

The Michael-type addition of thiol compounds onto γ-acryloyloxy ε-caprolactone unit is a very straightforward technique of functionalization and grafting of poly ε-caprolactone with the advantage of high reactivity and chemoselectivity of the reactants. This reaction is tolerant to a variety of functional groups and does not require intermediate protection/deprotection steps.

The characteristic features of this reaction are:
(i) occurrence under very mild conditions (preventing the polyester degradation),
(ii) tolerance to a wide range of functional groups (avoiding protection/deprotection steps),
(iii) no need for metallic catalyst, and thus no contamination that could be a problem for biomedical applications.

Scheme 4a.11: Chemical modification by Michael addition reaction

The easy synthesis and living (co) polymerization of γ-acryloyloxy-ε-caprolactone (ACL) makes it easy to have double bonds distributed along polyester backbones of different architectures and enable Michael-type addition.

To date, numerous successful modification examples have been reported, including chain end functionalized aliphatic polyesters with allyl, amino, thiol, hydroxyl,
carboxyl, epoxy\textsuperscript{24}, propargyl\textsuperscript{51-53}, and azide\textsuperscript{54} by ROP initiated by the functional group containing initiators or through post modification of polyesters.

A survey of literature revealed that major attention has been paid to the synthesis of $\alpha$-, $\omega$-, or $\alpha, \omega$-functionalized aliphatic polyesters by modification route or by use of functional initiator approach with little efforts on the preparation of $\alpha, \alpha'$-bifunctionalized polymers. Keeping these points in mind, synthesis of different $\alpha, \alpha'$-homobifunctionalized poly $\varepsilon$-caprolactones, possessing allyloxy, propargyloxy, azide and aldehyde functionality and $\alpha, \alpha'$-hetero bifunctionalized poly $\varepsilon$-caprolactones, featuring allyloxy- aldehyde, allyloxy-azido, and azido-aldehyde functionality was undertaken. End-functionalized polymers were characterized by FTIR and NMR spectroscopy and size exclusion chromatography. End functionality on the polymer was demonstrated by carrying out specific reactions of that particular functional group present on polymer.

\textbf{4a.2. Experimental}

\textbf{4a.2.1. Materials}

4,4'-Bis(4-(allyloxy)phenyl)pentan-1-ol, 4,4'-(((5-hydroxypentane-2,2-diyl)bis(4,1-phenylene))bis(oxy))dibenzaldehyde, 4,4'-bis(4-(prop-2-yn-1-yloxy)phenyl)pentan-1-ol, 4, 4'-bis (4-(2-azidoethoxy) phenyl) pentan-1-ol, 4-(4-(2-(4-(allyloxy)phenyl)-5-hydroxypentan-2-yl)phenoxy) benzaldehyde, 4-(4-(allyloxy)phenyl)-4-(4-(2-azidoethoxy) phenyl) pentan-1-ol and 4-(4-(2-(4-(2-azidoethoxy)phenyl)-5-hydroxypentan-2-yl)phenoxy) benzaldehyde were synthesized as per the procedures described in \textit{chapter 3a}. $\varepsilon$-Caprolactone (Aldrich), was stirred over calcium hydride for 4 h and distilled under reduced pressure. Toluene was dried over sodium wire. 3-Chloroperoxybenzoic acid, phenyl acetylene, stannous (II) octoate, 3-mercaptopyrrolic acid and azobisisobutyronitrile were received from Lancaster and were used as received. Sodium sulphate, potassium hydroxide, sodium hydrogen carbonate, methanol, chlorobenzene and chloroform, all received from S.D. Fine-Chem. Ltd., India, were used as received.

\textbf{4a.2.2. Characterization and measurements}

FTIR spectra were recorded on a Perkin-Elmer Spectrum \textit{GX} spectrophotometer. NMR spectra were recorded on a Bruker 200 MHz spectrometer for $^1$H-NMR and 125 MHz for $^{13}$C-NMR measurements using CDCl$_3$, CDCl$_4$ without TMS or DMSO-d$_6$ as a solvent. 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 $^\circ$C (Thermoseparation product) equipped with spectra
series UV 100 and spectra system RI 150 detectors. Two 60 cm PSS SDV-gel columns (102 – 105 ÅO and 100 ÅO) were used at 30 °C. The sample concentration was 2 to 3 mg mL−1 and the injection volume was 50 mL. HPLC grade chloroform was used as eluent at room temperature with a flow rate of 1 mL min⁻¹. Polystyrene was used as the calibration standard.

4a.2.3. Synthesis of functional poly ε-caprolactones

α, α'-Homo- as well as hetero-bifunctional poly ε-caprolactones having different functional groups were synthesized by ROP of ε-caprolactone using respective functional initiators in toluene in the presence of stannous (II) octoate as catalyst.

4a.2.3.1. Synthesis of α, α’-bisallyloxy functionalized poly ε-caprolactones

Schlenk tube equipped with a magnetic stir bar was charged with, ε-caprolactone (4.0 g, 35 mmol), stannous (II) octoate (0.8 mg, 0.0019 mmol), 4, 4’–bis (4-(allyloxy) phenyl) pentan-1-ol (134 mg, 0.38 mmol) and toluene (15 mL) under nitrogen atmosphere. The reaction mixture was degassed three times by freeze-pump-thaw cycles. ε-CL 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 (15 mL) and poured into cold methanol (150 mL). The polymer was collected by filtration and dried at room temperature in a vacuum for 24 h.

1H NMR (CDCl₃, δ/ppm): 7.06 (d, Ar-H meta to ether linkage), 6.79 (d, Ar-H ortho to ether linkage), 6.11-5.97(m, =CH), 5.43-5.23 (q, =CH₂), 4.49 (d, -OCH₂), 4.04 (t, -CH₂OOC from poly ε-caprolactone), 2.29 (t, -CH₂CH₂CO from poly ε-caprolactone), 1.64-1.57 (m, -CH₂CH₂ from poly ε-caprolactone + protons from initiator fragment), 1.39- 1.34 (m, -CH₂CH₂ from poly ε-caprolactone + protons from initiator fragment)

4a.2.3.1.1. Chemical transformation of α, α’-bisallyloxy functionalized poly ε-caprolactone into bis-epoxide functionalized poly ε-caprolactone

Into a 50 mL two necked round-bottom flask equipped with a dropping funnel were charged, bis-allyloxy functionalized poly ε-caprolactone (810 mg, 0.1 mmol) and dichloromethane (15 mL) and the solution was cooled to 0 °C with ice water. The solution of 3-chloroperoxybenzoic acid (86 mg, 0.5 mmol) in dichloromethane (10 mL) was added over a period of 30 minutes. After completion of addition, the reaction mixture was stirred at 0 °C for 2 h and then at room temperature for 24 h. The reaction mixture was washed with aqueous 5%
NaHCO₃ solution (3 x 15 mL) and de-ionized water (3 x 15 mL). The polymer was precipitated into methanol (50 mL), filtered and was dried under vacuum at 50 °C for 8 h.

¹H NMR (CDCl₃, δ/ppm): 7.06 (d, Ar-H meta to ether linkage), 6.80 (d, Ar-H ortho to ether linkage), 4.04 (t, -CH₂OOC from poly ε-caprolactone), 2.91 (bs, -CH₃O), 2.73 (bs, -CH₂O), 2.61-2.55 (m, -CH₂O), 2.33 (t, -CH₂CH₂CO from poly ε-caprolactone), 1.64-1.58 (m, -CH₂CH₂ from poly ε-caprolactone + protons from initiator fragment), 1.41-1.37 (m, -CH₂CH₂ from poly ε-caprolactone + protons from initiator fragment)

4a.2.3.2. Synthesis of α, α’-bisaldehyde functionalized poly ε-caprolactones

In a typical experiment, Schlenk tube equipped with a magnetic stir bar was charged with ε-caprolactone (2.85 g, 25 mmol), stannous (II) octoate (2 mg, 0.005 mmol), 4,4’-(4,4’-(5-hydroxypentane-2,2-diyl) bis(4,1-phenylene)) bis(oxy) dibenzaldehyde (480 mg, 1.0 mmol) and toluene (30 mL) under nitrogen atmosphere. The reaction mixture was degassed three times by freeze-pump-thaw cycles. The polymerization was carried out at 110 °C. After a given time, the polymerization mixture was cooled to room temperature, diluted with dichloromethane (20 mL) and poured into cold methanol (200 mL). The polymer was collected by filtration and dried at room temperature in a vacuum for 24 h.

IR (CHCl₃, cm⁻¹): 1730, 1710

¹H NMR (CDCl₃, δ/ppm): 9.86 (s, aldehyde), 7.78 (d, Ar-H ortho to aldehyde), 7.20-7.15 (d, Ar-H meta to ether), 7.02-6.92 (m, Ar-H), 3.99 (t, -CH₂OOC from poly ε-caprolactone), 2.24 (t, -CH₂CH₂CO from poly ε-caprolactone), 1.58-1.53 (m, -CH₂CH₂ from poly ε-caprolactone + protons from initiator fragment), 1.34-1.31 (m, -CH₂CH₂ from poly ε-caprolactone + protons from initiator fragment)

4a.2.3.2.1. Chemical transformation by aldehyde-aminooxy click reaction

4a.2.3.2.1.1. Synthesis of O-(2-azidoethyl) hydroxylamine

4a.2.3.2.1.1.1. Synthesis of 2-azidoethanol

Synthesis of 2-azidoethanol was carried out as discussed in Chapter 3a Section 3a.2.1.1.1.
4a.2.3.2.1.1.2. Synthesis of 2-azidoethyl 4-methylbenzenesulfonylate

Synthesis of 2-azidoethyl 4-methylbenzenesulfonylate was carried out as discussed in Chapter 3a Section 3a.2.1.1.

4a.2.3.2.1.1.3. Synthesis of 2-(2-azidoethoxy) isoindoline-1, 3-dione

Into a 250 mL two necked round-bottom flask equipped with a dropping funnel were charged, 2-azidoethyl 4-methylbenzenesulfonate (8.9 g, 37 mmol), triethylamine (5.0 g, 56 mmol), and dry THF (70 mL). The reaction mixture was cooled to 0 °C. The solution of N-hydroxy phthalimide (9.15 g, 56 mmol) in dry THF (20 mL) was added drop-wise into the reaction mixture under constant stirring at 0 °C. The reaction mixture was stirred at 80 °C for 24 h. The reaction mixture was cooled, THF was evaporated under vacuum and chloroform (50 mL) was added. The chloroform solution was washed with 5% NaHCO₃ (3 x 100 mL) and de-ionized water (3 x 100 mL). The chloroform solution was dried over anhydrous sodium sulfate, filtered and solvent was evaporated under vacuum. The crude product was purified by silica gel column chromatography using a mixture of ethyl acetate:pet ether (10:90, v/v) as eluent. The removal of the solvent yielded 6.10 (71 %) of 2-(2-azidoethoxy) isoindoline-1, 3-dione a white solid

IR (CHCl₃, cm⁻¹): 2108, 1690.

¹H NMR (CDCl₃, δ/ppm): 7.87-7.83 (m, 2H), 7.78-7.74 (m, 2H), 4.34 (t, 2H), 3.65 (t, 2H).

4a.2.3.2.1.1.4. Synthesis of O-(2-azidoethyl) hydroxylamine

Into a 250 mL single necked round-bottom flask were charged, 2-(2-azidoethoxy) isoindoline-1, 3-dione (3.0 g, 12 mmol), and dichloromethane (50 mL). The solution of hydrazine hydrate (3.6 g, 72 mmol) in dichloromethane (20 mL) was added drop-wise into the reaction mixture under stirring. The reaction mixture was stirred at room temperature overnight. The reaction mixture was filtered and washed with 5% NaHCO₃ (3 x 100 mL) and de-ionized water (3 x 100 mL). The organic layer was dried over anhydrous sodium sulfate, filtered and dichloromethane was evaporated under reduced pressure to obtain O-(2-azidoethyl) hydroxylamine 750 mg (60 %) as a slight yellow liquid.

IR (CHCl₃, cm⁻¹): 3100, 2110

¹H NMR (CDCl₃, δ/ppm): 5.18 (bs, 2H), 3.77 (t, 2H), 3.39 (t, 2H).
4a.2.3.2.1.2. Reaction of α, α′-bisaldehyde functionalized poly ε-caprolactone with O-(2-azidoethyl) hydroxylamine

Into a 50 mL two necked round-bottom flask equipped with a dropping funnel were charged, bis-aldehyde functionalized poly ε-caprolactone (360 mg, 0.2 mmol), dichloromethane (10 mL) and a pinch of sodium sulfate. The 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 (50 mL). The polymer was filtered and dried under vacuum at 50 °C for 8 h.

IR (CHCl₃, cm⁻¹): 2110, 1730

¹H NMR (CDCl₃, δ/ppm): 8.11 (s, -CH=N), 7.56 (d, Ar-H ortho to oxime), 7.16 (d, Ar-H meta to ether linkage), 7.02-6.92 (m, Ar-H), 4.35 (t, -OCH₂) 4.06 (t, -CH₂CH₂OOC from poly ε-caprolactone), 3.57 (t, CH₂N₃), 2.31 (t, -CH₂CH₂CO, from poly ε-caprolactone), 1.65-1.61 (m, -CH₂CH₂ from poly ε-caprolactone+ protons from initiator fragment), 1.41- 1.35 (m, -CH₂CH₂ from poly ε-caprolactone+ protons from initiator fragment)

4a.2.3.3. Synthesis of α, α′-bispropargyloxoy functionalized poly ε-caprolactones

Schlenk tube equipped with a magnetic stir bar was charged, ε-caprolactone (3.76 g, 33 mmol) with, stannous (II) octoate (1 mg, 0.0025 mmol), PMDETA (17 mg, 0.1 mmol), 4, 4′-bis(4-(prop-2-yn-1-yloxy)phenyl)pentan-1-ol (174 mg, 0.5 mmol) and toluene (30 mL) under nitrogen atmosphere. ε-CL 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 (25 mL) and poured into cold methanol (250 mL). The polymer was collected by filtration and dried at room temperature in a vacuum for 24 h.

IR (CHCl₃, cm⁻¹): 1730

¹H NMR (CDCl₃, δ/ppm): 7.09 (d, Ar-H meta to ether linkage), 6.85 (d, Ar-H ortho to ether linkage), 4.64 (d, -OCH₂), 4.04 (t, -CH₂OOC, from poly ε-caprolactone), 2.51 (t, acetylene proton), 2.29 (t, -CH₂CH₂CO, from poly ε-caprolactone), 1.64-1.59 (m, -CH₂CH₂, from poly ε-caprolactone + protons from initiator fragment), 1.41- 1.37 (m, -CH₂CH₂, from poly ε-caprolactone + protons from initiator fragment)
4a.2.3.3.1. Chemical transformation of α, α’-bispropargyloxy functionalized poly ε-caprolactone

4a.2.3.3.1.1. Reaction of α, α’-bis-propargyloxy functionalized poly ε-caprolactone with 2-azidoethyl 4-methylbenzenesulfonate

Schlenk tube equipped with a magnetic stir bar was charged with, bis-propargyloxy functionalized poly ε-caprolactone (530 mg, 0.1 mmol), CuBr (15 mg, 0.1 mmol), 2-azidoethyl 4-methylbenzenesulfonate (450 mg, 2 mmol), DMF (20 mL) and N, N, N', N', N"-pentamethyldiethylenetriamine (20 µL, 0.85 mmol) under nitrogen atmosphere. The Schlenk tube was sealed and the reaction mixture was degassed three times by freeze-pump-thaw cycles and kept stirring for 24 h at room temperature. After the reaction time, DMF was removed under reduced pressure and reaction mixture was diluted with dichloromethane (50 mL) and the solution was passed through neutral alumina column to remove copper residue. The solution was concentrated and poured into excess methanol (500 mL) to precipitate the polymer. The polymer was filtered and dried at room temperature under vacuum for 24 h.

IR (CHCl₃, cm⁻¹): 1730

¹H NMR (CDCl₃, δ/ppm): 7.80 (d, ortho to sulfonate), 7.64 (d, meta to sulfonate), 7.37 (s, triazole ring proton), 7.04 (d, Ar-H meta to ether linkage), 6.80 (d, Ar-H ortho to ether linkage), 5.13 (d, OCH₂), 4.59 (d, OCH₂), 3.99 (t, CH₂OOC, poly ε-caprolactone), 2.24 (t, CH₂CH₂CO, from poly ε-caprolactone), 1.58-1.53 (m, CH₂CH₂, from poly ε-caprolactone + protons from initiator fragment), 1.34-1.31 (m, CH₂CH₂, from poly ε-caprolactone + protons from initiator fragment)

4a.2.3.4. Synthesis of α, α’-bisazido functionalized poly ε-caprolactones

Schlenk tube equipped with a magnetic stir bar was charged with, ε-caprolactone (2.36 g, 20.75 mmol), stannous octoate (1 mg, 0.002 mmol), 4, 4’-bis (4-(2-azidoethoxy) phenyl) pentan-1-ol, (170 mg, 0.415 mmol) and toluene (30 mL) under nitrogen atmosphere. The reaction mixture was degassed three times by freeze-pump-thaw cycles. ε-CL 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 (25 mL) and poured into cold methanol (250 mL). The polymer was collected by filtration and dried at room temperature in a vacuum for 24 h.

IR (CHCl₃, cm⁻¹): 2108, 1730
1H NMR (CDCl3, δ/ppm): 7.08 (d, Ar-H from initiator), 6.85 (d, Ar-H from initiator), 4.04 (t, -CH2OOC from poly ε-caprolactone + OCH2CH2N3 protons from initiator fragment), 2.29 (t, -CH2CH2CO from poly ε-caprolactone), 1.63-1.59 (m, -CH2CH2 from poly ε-caprolactone), 1.39-1.33 (m, -CH2CH2 from poly ε-caprolactone)

4a.2.3.4.1. Chemical transformation α, α'-bisazido functionalized poly ε-caprolactones

4a.2.3.4.1.1. Reaction of α, α'-bis-azido functionalized poly ε-caprolactone with phenyl acetylene

Schlenk tube equipped with a magnetic stir bar was charged with, α, α'-bisazido functionalized poly ε-caprolactone (490 mg, 0.1 mmol), CuBr (15 mg, 0.1 mmol), phenyl acetylene (204 mg, 2 mmol), DMF (20 mL) and N, N, N', N', N"-pentamethyldiethylenetriamine (20 µL, 0.1 mmol) under nitrogen atmosphere. The Schlenk tube was sealed and the reaction mixture was degassed three times by freeze-pump-thaw cycles and kept stirring for 24 h at room temperature. After the reaction time, DMF was removed under reduced pressure and reaction mixture was diluted with dichloromethane (50 mL) the solution was passed through neutral alumina column to remove copper residue. The solution was concentrated and poured into methanol (500 mL) to precipitate the polymer. The polymer was filtered and dried at room temperature under vacuum for 24 h.

IR (CHCl3, cm⁻¹): 1730

1H NMR (CDCl3, δ/ppm): 7.94 (s, Ar-H attached to triazole ring), 7.80 (d, Ar-H attached to triazole ring + triazole proton), 7.44-7.38 (m, Ar-H attached to triazole ring), 7.03 (d, Ar-H from initiator), 6.77 (d, Ar-H from initiator), 4.78 (t, -CH2), 4.35 (t, -CH2), 4.04 (t, -CH2OOC from poly ε-caprolactone), 2.29 (t, -CH2CH2CO from poly ε-caprolactone), 1.65-1.57 (m, -CH2CH2 from poly ε-caprolactone + protons from initiator fragment), 1.39-1.34 (m, -CH2CH2 from poly ε-caprolactone + protons from initiator fragment)

4a.2.3.5. Synthesis of α-aldehyde, α’-allyloxy heterobifunctionalized poly ε-caprolactones

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) benzoaldehyde (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-CL 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 (20 mL) and poured into cold methanol (200 mL). The polymer was collected by filtration and dried at room temperature in vacuum for 24 h.

IR (CHCl₃, cm⁻¹): 1730, 1710

\( ^1H \) NMR (CDCl₃, δ/ppm): 9.90 (s, -CHO), 7.84 (d, Ar-H ortho to aldehyde), 7.25-6.86 (m, Ar-H), 6.13-5.99 (m, -CH₂-CH =CH₂), 5.45-5.24 (q, -HC=CH₂), 4.50 (d, -OCH₂), 4.04 (t, -CH₂OOC from poly ε-caprolactone), 2.29 (t, -CH₂CH₂CO from poly ε-caprolactone), 1.58-1.53 (m, -CH₂CH₂ from poly ε-caprolactone + protons from initiator fragment), 1.34-1.31 (m, -CH₂CH₂ from poly ε-caprolactone)

**4a.2.3.5.1. Chemical modification of α-aldehyde, α’-allyloxy heterobifunctionalized poly ε-caprolactones**

**4a.2.3.5.1.1. 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-caprolactones (970 mg, 0.1 mmol), dichloromethane (10 mL) and a pinch of sodium sulfate. Then, solution of O-(2-azidoethyl) hydroxylamine (125 mg, 10 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 (50 mL). The obtained polymer was filtered and dried under vacuum at 50 °C for 8 h.

IR (CHCl₃, cm⁻¹): 2110, 1730

\( ^1H \) NMR (CDCl₃, 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=CH₂), 5.45-5.24 (q, -HC=CH₂), 4.50 (d, -OCH₂), 4.05 (t, -CH₂CH₂OOC from poly ε-caprolactone), 2.29 (t, -CH₂CH₂CO, from poly ε-caprolactone), 1.61-1.53 (m, -CH₂CH₂ from poly ε-caprolactone + protons from initiator fragment), 1.39-1.31 (m, -CH₂CH₂ from poly ε-caprolactone)

**4a.2.3.5.1.2. Thiol-ene thermal click reaction**

Into a clean and dry Schlenk tube were charged, allyloxy functionalized poly ε-caprolactone (490 mg, 0.05 mmol), 3- maracptopropionic acid (53 mg, 0.5 mmol), AIBN (82 mg,
0.5 mmol) and chlorobenzene (20 mL). The mixture was degassed via three freeze-pump-thaw cycles and subsequently vacuum sealed. The Schlenk tube was heated at 80 °C for 6 h. The reaction was quenched by cooling the reaction mixture 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 2 times into cold methanol. The polymer was dried under vacuum at 50 °C and was characterized by ^1H - NMR spectroscopy.

^1H NMR (CDCl3, 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, -CH2CH2OOC from poly ε-caprolactone), 2.89 (t, S-CH2), 2.75 (t, S-CH2), 2.63 (t, CH2-COOH), 2.31 (t, -CH2CH2CO, from poly ε-caprolactone), 1.69-1.63 (m, -CH2CH2 from poly ε-caprolactone + protons from initiator fragment), 1.41- 1.35 (m, -CH2CH2 from poly ε-caprolactone)

4a.2.3.6. Synthesis of α-allyloxy, α'- azido heterobifunctionalized poly ε-caprolactones

Schlenk tube equipped with a magnetic stir bar was charged with, ε-caprolactone (3.78 g, 33.2 mmol), stannous (II) octoate (1 mg, 0.002 mmol), 4-(4-(allyloxy)phenyl)-4-(4-(2-azidoethoxy)phenyl)pentan-1-ol (158 mg, 0.415 mmol) and toluene (30 mL) under nitrogen atmosphere. The reaction mixture was degassed three times by freeze-pump-thaw cycles. ε-CL 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 (20 mL) and poured into cold methanol (200 mL). The polymer was collected by filtration and dried at room temperature in a vacuum for 24 h.

IR (CHCl3, cm⁻¹): 2108, 1730

^1H NMR (CDCl3, δ/ppm): 7.06 (d, Ar-H meta to ether linkage), 6.80 (m, Ar-H ortho to ether linkage), 6.06-5.97 (m, -CH =CH2), 5.45-5.25 (q, HC=CH2), 4.50 (d, -OCH2), 4.04 (t, -CH2OOC from poly ε-caprolactone), 2.29 (t, -CH2CH2CO from poly ε-caprolactone), 1.65-1.55 (m, -CH2CH2 from poly ε-caprolactone + protons from initiator fragment), 1.39- 1.31 (m, -CH2CH2 from poly ε-caprolactone)
4a.2.3.6.1. Chemical modification of α-allyloxy, α’-azido heterobifunctionalized poly ε-caprolactones

4a.2.3.6.1.1. Azide-alkyne click reaction

Schlenk tube equipped with magnetic stir bar was charged with, α- allyloxy α’-azido heterobifunctionalized poly ε-caprolactone (730 mg, 0.1 mmol), CuBr (15 mg, 0.1 mmol), phenyl acetylene (106 mg, 1 mmol), DMF (20 mL) and N, N, N’, N’, N’”-pentamethyldiethylenetriamine (20µL, 0.1 mmol) under nitrogen atmosphere. The Schlenk tube was sealed and the reaction mixture was degassed three times by freeze-pump-thaw cycles and kept stirring for 24 h at room temperature. After the reaction time, DMF was removed under reduced pressure and reaction mixture was diluted with dichloromethane (50 mL) and the solution was passed through neutral alumina column to remove copper residue. The solution was concentrated and poured into excess methanol (500 mL) to precipitate the polymer. The polymer was isolated by filtration and dried at room temperature under vacuum for 24 h.

IR (CHCl₃, cm⁻¹): 1730

¹H NMR (CDCl₃, δ/ppm): 7.94 (s, Ar-H attached to triazole ring), 7.80 (d, Ar-H attached to triazole ring), 7.45-7.35 (m, Ar-H attached to triazole ring + triazole ring proton) 7.04 (d, Ar-H ortho to ether linkage from initiator), 6.75 (d, Ar-H meta to ether linkage from initiator), 6.12-5.95 (m, CH₂-CH =CH₂), 5.44-5.23 (q, -CH=CH₂), 4.78(t, OCH₂), 4.50 (d, -OCH₂), 4.04 (t, -CH₂OOC from poly ε-caprolactone), 2.29 (t, -CH₂CH₂CO from poly ε-caprolactone), 1.65-1.53 (m, -CH₂CH₂ from poly ε-caprolactone + protons from initiator fragment), 1.34-1.31 (m, -CH₂CH₂ from poly ε-caprolactone + protons from initiator fragment)

4a.2.3.6.1.2. Thiol-ene thermal click reaction

Into a clean and dry Schlenk tube, α- allyloxy α’-azido heterobifunctionalized poly ε-caprolactone (370 mg, 0.05 mmol), 3- maraçupropionic acid (53 mg, 0.5 mmol), AIBN (82 mg, 0.5 mmol) and chlorobenzene (20 mL) were mixed. The reaction mixture was degassed via three freeze-pump-thaw cycles and subsequently vacuum sealed. The schlenk tube was heated at 80 °C for 6 h. The reaction was quenched by cooling the reaction mixture 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 caring out precipitation for another 2 times into cold methanol. The polymer was dried under vacuum at 50 °C.
Chapter 4a: End-Functionalized Polymers by ROP: Synthesis

1H NMR (CDCl3, δ/ppm): 7.94 (s, Ar-H attached to triazole ring), 7.80 (d, Ar-H attached to triazole ring), 7.45-7.35 (m, Ar-H from phenyl acetylene + triazole ring proton) 7.04 (d, Ar-H ortho to ether linkage from initiator fragment), 6.77 (d, Ar-H meta to ether linkage from initiator fragment), 4.78 (t, OCH3), 4.04 (t, -CH2OOC from poly ε-caprolactone), 2.89 (t, S-CH2), 2.75 (t, S-CH2), 2.63 (t, CH2-COOH), 2.29 (t, -CH2CH2CO from poly ε-caprolactone), 1.65-1.53 (m, -CH2CH2 from poly ε-caprolactone + protons from initiator fragment), 1.34- 1.31 (m, -CH2CH2 from poly ε-caprolactone)

4a.2.3.7. Synthesis of α-aldehyde, α′-azido heterobifunctionalized poly ε-caprolactones

Schlenk tube equipped with a magnetic stir bar was charged with, ε-caprolactone (5.68 g, 50 mmol), stannous (II) octoate (50 mg, 0.002 mmol), 4-(4-(2-(4-(2-azidoethoxy) phenyl)-5-hydroxypentan-2-yl)phenoxy)benzaldehyde (184 mg, 0.415 mmol) and toluene (30 mL) under nitrogen atmosphere. The reaction mixture was degassed three times by freeze-pump-thaw cycles. ε-CL 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 (20 mL) and poured into cold methanol (200 mL). The polymers were collected by filtration and dried at room temperature in a vacuum for 24 h.

IR (CHCl3, cm⁻¹): 1730, 1710

1H NMR (CDCl3, δ/ppm): 9.92 (s, -aldehyde), 7.85 (d, Ar-H ortho to aldehyde), 7.19-6.98 (m, Ar-H), 4.06 (t, -CH2OOC from poly ε-caprolactone), 2.31 (t, -CH2CH2CO from poly ε-caprolactone), 1.66-1.58 (m, -CH2CH2 from poly ε-caprolactone + protons from initiator fragment), 1.41- 1.38 (m, -CH2CH2 from poly ε-caprolactone)

4a.2.3.7.1. Chemical modification of α-aldehyde, α′-azido heterobifunctional poly ε-caprolactones

4a.2.3.7.1.1. Azido-alkyne click reaction

Schlenk tube equipped with a magnetic stir bar was charged with, α-aldehyde, α′-azido heterobifunctional poly ε-caprolactone (1.21 g, 0.1 mmol), phenyl acetylene (106 mg, 1 mmol), CuBr (15 mg, 0.1 mmol), PMDETA (20 µL, 0.1 mmol) and DMF (20 mL). The reaction mixture was degassed via three freeze-pump-thaw cycles and subsequently vacuum sealed. The Schlenk tube was heated at 80 °C for 6 h. DMF was removed under reduced pressure. The polymer was
dissolved in dichloromethane (15 mL) and purified by precipitation in cold methanol (150 mL). The polymer was collected by filtration and dried at 50 °C under vacuum for 18 h.

\[^{1}\text{H} \text{NMR (CDCl}_3, \delta/\text{ppm): 9.92 (s, aldehyde), 7.94 (s, triazole ring proton), 7.90 (d, Ar-H attached to triazole ring) 7.85 (d, Ar-H ortho to aldehyde), 7.45-7.35 (m, Ar-H attached to triazole ring), 7.19-6.96 (m, Ar-H), 4.06 (t, -CH\text{OOC from poly }\varepsilon\text{-caprolactone), 2.31 (t, -CH}_2\text{CH}_2\text{CO from poly }\varepsilon\text{-caprolactone), 1.65-1.58 (m, -CH}_2\text{CH}_2 \text{ from poly }\varepsilon\text{-caprolactone + protons from initiator fragment), 1.41- 1.38 (m, -CH}_2\text{CH}_2 \text{ from poly }\varepsilon\text{-caprolactone}}\]

**4a.2.3.7.1.2. Aldehyde-aminooxy click reaction**

Into a 50 mL two necked round-bottom flask equipped with a dropping funnel were charged, \(\alpha\)-aldehyde, \(\alpha\)'-azido heterobifunctional poly \(\varepsilon\)-caprolactone (605 mg, 0.05 mmol), dichloromethane (10 mL) and a pinch of sodium sulfate. Solution of O-(2-azidoethyl) hydroxylamine (102 mg, 1 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 (50 mL). The obtained polymer was filtered and dried under vacuum at 50 °C for 8 h.

IR (CHCl\text{3, cm}^{-1}): 2110, 1730

\[^{1}\text{H} \text{NMR (CDCl}_3, \delta/\text{ppm}: 8.07 (s, -CH=N), 7.94 (s, Ar-H attached to triazole ring) 7.90 (d, Ar-H attached to triazole ring) 7.85 (d, Ar-H attached to triazole ring), 7.48-7.40 (m, Ar-H attached to triazole ring and proton from triazole ring) 7.19-6.96 (m, Ar-H), 4.06 (t, -CH\text{OOC from poly }\varepsilon\text{-caprolactone), 2.31 (t, -CH}_2\text{CH}_2\text{CO from poly }\varepsilon\text{-caprolactone), 1.65-1.61 (m, -CH}_2\text{CH}_2 \text{ from poly }\varepsilon\text{-caprolactone + protons from initiator fragment), 1.41- 1.35 (m, -CH}_2\text{CH}_2 \text{ from poly }\varepsilon\text{-caprolactone}}\]

**4a.3. Results and Discussion**

**4a.3.1. Synthesis of \(\alpha\), \(\alpha\)'-bisallyloxy functionalized poly \(\varepsilon\)-caprolactones**

Scheme 4a.12 depicts the ROP of \(\varepsilon\)-caprolactone using 4, 4'-bis(4-(allyloxy)phenyl)pentan-1-ol as the initiator.


Scheme 4a.12: Synthesis of α, α’-bisallyloxy functionalized poly ε-caprolactones

The conditions and results of synthesis of bis-allyloxy functionalized poly ε-caprolactones are summarized in Table 4a.1

Table 4a.1: Reaction conditions and results for synthesis of α, α’-bisallyloxy functionalized poly ε-caprolactones

<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>[M]₀/[I]₀</th>
<th>Time (h)</th>
<th>Conv. (%)</th>
<th>Mₙ, theo</th>
<th>Mₙ,NMR</th>
<th>Mₙ, GPC</th>
<th>M_w/M_n</th>
</tr>
</thead>
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<td>8</td>
<td>71</td>
<td>4000</td>
<td>4500</td>
<td>6000</td>
<td>1.38</td>
</tr>
<tr>
<td>2</td>
<td>90:1</td>
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<td>76</td>
<td>8100</td>
<td>7900</td>
<td>10300</td>
<td>1.46</td>
</tr>
<tr>
<td>3</td>
<td>135:1</td>
<td>24</td>
<td>81</td>
<td>12800</td>
<td>13500</td>
<td>19400</td>
<td>1.33</td>
</tr>
</tbody>
</table>

(Temperature-110 °C Solvent: toluene) [CL]/ [Sn(Oct)₂]=200

a- [M]₀/[I]₀: [Monomer]:[Initiator],
b- Gravimetry
c- Mₙ, theo = \([\frac{[M]₀ \times (% \text{ Conv.}) \times \text{ Mol. Wt. of monomer (114)}}{[I]₀}] + \text{mol. wt. initiator (352)}\)
d- Mₙ,NMR= Determined from NMR
e- Mₙ,GPC= Determined from GPC; Polystyrene standard; CHCl₃ eluent

Three different monomer/initiator ratios were utilized to obtain α, α’-bisallyloxy functionalized poly ε-caprolactones with different molecular weights. ¹H-NMR spectrum of α, α’-bisallyloxy functionalized poly ε-caprolactone featuring allyloxy functional groups is reproduced in Figure 4a.2. The appearance of multiplet in the range 6.11-5.97 ppm and 5.43-5.39 ppm confirmed the presence of allyloxy functionality. Molecular weights could be calculated for α, α’-bisallyloxy functionalized poly ε-caprolactones by ¹H-NMR spectroscopy.
Figure. 4a.2: $^1$H-NMR spectra of A) 4, 4'-bis (4-(allyloxy) phenyl) pentan-1-ol

B) $\alpha, \alpha'$-bisallyloxy functionalized poly $\varepsilon$-caprolactones in CDCl$_3$

$M_{n, \text{NMR}}$ of $\alpha, \alpha'$-bisallyloxy functionalized poly $\varepsilon$-caprolactones was calculated by comparing the intensity of multiplet in the range 6.11-5.97 ppm for allyloxy group to a peak belonging to $\text{–OCH}_2$ in PCL at 4.04 ppm.

$D_{pn} = \left[ \frac{I_{4.04}}{2} / \left( \frac{I_{6.11-5.97}}{2} \right) \right]$

Molecular weights were calculated using the equation,

$M_{n, \text{NMR}} = [Dpn \times 114 \text{ (mol. wt. of monomer)}] + 352 \text{ (mol. wt. of initiator)}$

Molecular weights of $\alpha, \alpha'$-bisallyloxy functionalized poly $\varepsilon$-caprolactones calculated by $^1$H-NMR spectroscopy ($M_{n,\text{NMR}}$: 4500-13500) were in close agreement to the molecular weights calculated from the monomer-to-initiator ratio ($M_{n,\text{theo}}$). In addition, GPC trace was found to be monomodal with PDI values in the range 1.33-1.46 for $\alpha, \alpha'$-bisallyloxy functionalized poly $\varepsilon$-caprolactones.

Thus, 4, 4'-bis (4-(allyloxy) phenyl) pentan-1-ol was demonstrated to be a useful ROP initiator for synthesis of $\alpha, \alpha'$-bisallyloxy functionalized poly $\varepsilon$-caprolactones.
4a.3.1.1. Chemical modification of α, α’-bis-allyloxy functionalized poly ε-caprolactone

4a.3.1.1.1. Chemical modification of α, α’-bis-allyloxy functionalized poly ε-caprolactone by epoxidation reaction

In order to illustrate the reactivity of allyloxy functionality, the organic reaction of allyloxy group such as epoxidation of bis-allyloxy functionalized poly ε-caprolactone with 3-chloroperoxybenzoic acid as an oxidant was carried out (Scheme 4a.13).

Scheme 4a. 13: Chemical modification of α, α’-bisallyloxy functionalized poly ε-caprolactones

The epoxidised product was characterized by 1H-NMR spectroscopy (Figure 4a. 3B).

Figure 4a. 3: 1H-NMR spectra of A) α, α’-bis-allyloxy functionalized poly ε-caprolactone  
B) α, α’-bis-epoxide functionalized poly ε-caprolactone in CDCl3

The complete disappearance of the resonances corresponding to allyloxy group protons and the appearance of new signals corresponding to oxirane ring protons at 2.91, 2.73 and 2.61-2.55 ppm indicated complete conversion of bis-allyloxy into bis-epoxy functionalized poly ε-caprolactone macromonomer. These epoxy functionalized poly ε-caprolactone could find application as an
impact modifier in conventional epoxy resins\textsuperscript{55}. The photoinduced cationic polymerization of epoxy type of macromonomers could lead to different types of block and graft copolymers\textsuperscript{56}.

4a.3.2. Synthesis of $\alpha$, $\alpha'$-bisaldehyde functionalized poly $\varepsilon$-caprolactones

ROP of $\varepsilon$-caprolactone was carried out using, 4, 4'-(5-hydroxypentane 2,2-diyl bis(4,1-phenylene))bis(oxy) dibenzaldehyde as the initiator (Scheme 4a.14).

Scheme 4a.14: Synthesis of $\alpha$, $\alpha'$-bisaldehyde functionalized poly $\varepsilon$-caprolactones

The conditions and results of synthesis of bis-aldehyde functionalized polycaprolactones are summarized in Table 4a.2.

Table 4a.2: Reaction conditions and results for synthesis of $\alpha$, $\alpha'$-bisaldehyde functionalized poly $\varepsilon$-caprolactones

<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>$[^{\text{a}}][\text{M}]<em>{0}/[^{\text{a}}][\text{I}]</em>{0}$</th>
<th>Time (h)</th>
<th>$^b$Conv. (%)</th>
<th>$^{c}\text{M}_{n,\text{theo}}$</th>
<th>$^{d}\text{M}_{n,\text{NMR}}$</th>
<th>$^{e}\text{M}_{n,\text{GPC}}$</th>
<th>$\text{M}<em>{w}/\text{M}</em>{n}$</th>
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</tr>
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<td>14500</td>
<td>19400</td>
<td>1.47</td>
</tr>
</tbody>
</table>

(Temperature-110 °C, Solvent: toluene) [CL]/ [Sn(Oct)$_2$]=200

a-$[^{\text{a}}][\text{M}]_{0}/[^{\text{a}}][\text{I}]_{0}$: [Monomer]:[Initiator]
b- Gravimetry
c- $\text{M}_{n,\text{theo}}= \left\{[^{\text{a}}][\text{M}]_{0} \times (\% \text{ Conv.}) \times \text{mol. wt. of monomer (114)} \right\} + \text{mol. wt. initiator(480)}$
d- $\text{M}_{n,\text{NMR}}$: Determined from NMR
e- $\text{M}_{n,\text{GPC}}$: Determined from GPC; Polystyrene standard; CHCl$_3$ eluent
Polycaprolactones possessing molecular weights ($M_{n,NMR}$) from 1800 to 14500 were synthesized by varying monomer to initiator ratio. $^1$H-NMR spectrum of $\alpha$, $\alpha'$-bisaldehyde functionalized poly $\varepsilon$-caprolactone is reproduced in Fig. 4a.4. The appearance of a singlet at 9.86 ppm confirmed the presence of aldehyde functionality.

![1H-NMR spectra of A) 4, 4’-(4, 4’-(5-hydroxypentane 2,2-diyl bis(4,1-phenylene))bis(oxy) dibenzaldehyde B) $\alpha$, $\alpha'$-bisaldehyde functionalized poly $\varepsilon$-caprolactone in CDCl$_3$](image)

Figure 4a. 4: $^1$H-NMR spectra of A) 4, 4’-(4, 4’-(5-hydroxypentane 2,2-diyl bis(4,1-phenylene))bis(oxy) dibenzaldehyde B) $\alpha$, $\alpha'$-bisaldehyde functionalized poly $\varepsilon$-caprolactone in CDCl$_3$

Molecular weights for bis-aldehyde functionalized poly $\varepsilon$-caprolactone were determined by $^1$H-NMR spectroscopy by comparing integral intensity of peak belonging to $-$OCH$_2$ in poly $\varepsilon$-caprolactone at 3.99 ppm to a singlet at 9.86 ppm corresponding to aldehyde groups. The degree of polymerization was calculated from NMR analysis using the relation,

$$Dp_{n} = \frac{I_{3.99}}{I_{9.86}}$$

Molecular weights were calculated using the equation,

$$M_{n,NMR} = [Dp_{n} \times 114 \text{ (mol. wt. of monomer)}] + 480 \text{ (mol. wt. of initiator)}$$
Mₙ,NMR values were in reasonably good agreement with theoretical molecular weights (Mₙ,th) calculated from the monomer to initiator ratio. In addition, GPC data revealed monomodal distribution with PDI values 1.33-1.47 for poly ε-caprolactones.

Thus, 4, 4’-(4, 4’-(5-hydroxypentane 2, 2-diyl bis(4,1- phenylene)bis(oxy) dibenzaldehyde was found to be a useful ROP initiator for synthesis of α, α’-bisaldehyde functionalized poly ε-caprolactone

4a.3.2.1. Chemical modification of α, α’-bisaldehyde functionalized poly ε-caprolactone

4a.3.2.1.1. Reaction of α, α’-bisaldehyde functionalized poly ε-caprolactone with O-(2-azidoethyl) hydroxylamine

The aldehyde functionality is known to undergo aldehyde-aminooxy click reaction. The reactivity of aldehyde functionality was illustrated by carrying out click reaction with O-(2-azidoethyl) hydroxylamine on α, α’-bisaldehyde functionalized poly ε-caprolactone at room temperature. (Scheme 4a.15). The conversion was assessed by FT-IR and ¹H-NMR spectroscopy. In FT-IR spectrum, in addition to the peak corresponding to poly ε-caprolactone at 1730 cm⁻¹, characteristic peak corresponding to azido functionality appeared at 2110 cm⁻¹ confirming the coupling reaction.

Scheme 4a.15: a) Synthesis of O-(2-azidoethyl) hydroxylamine

b) reaction of α, α’- bisaldehyde functionalized poly ε-caprolactone with O-(2-azidoethyl) hydroxylamine

Figure 4a.5 represents ¹H-NMR spectra of α, α’-bisaldehyde functionalized poly ε-caprolactone (Mₙ,NMR: 1800) 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 at 8.11 ppm (-CH=Ｎ-O) which indicated oxime formation without disturbing peaks related to poly ε-caprolactone attesting completion of the reaction without any side reaction such as degradation of poly ε-caprolactone backbone. The model aldehyde-aminoxy click reaction study with O-(2-azidooethyl) hydroxylamine introduces azido moiety on poly ε-caprolactone chain which further opens up plethora of opportunities to introduce different types of functional groups on poly ε-caprolactone by well known azide-alkyne click reaction\textsuperscript{58}.

Figure 4a.5: \textsuperscript{1}H-NMR spectra of A) O-(2-azidooethyl) hydroxylamine B) \(\alpha, \alpha'\)-bisaldehyde functionalized poly ε-caprolactone and C) the product formed by reaction of \(\alpha, \alpha'\)-bisaldehyde functionalized poly ε-caprolactone with O-(2-azidooethyl) hydroxylamine in CDCl\textsubscript{3}

4a.3.3. Synthesis of \(\alpha, \alpha'\)-bis propargyloxy functionalized poly ε-caprolactones

ROP of ε-caprolactone was carried out using, 4, 4'-bis (4-(prop-2-yn-1-yloxy)phenyl) pentan-1-ol as the initiator in the presence of PMDETA (Scheme 4a.16). As propargyl groups are reactive, the synthesis of propargyl terminated poly ε-caprolactone at high temperature still proves to be challenging. The reactivity issue of propargyl group could be suppressed by the use
of PMDETA in polymerization system whose huge steric hindrance provides the protective effect\textsuperscript{61}. Therefore, PMDETA was deliberately added in the polymerization system.

Scheme 4a.16: Synthesis of $\alpha, \alpha'$-bispropargyloxy functionalized poly $\varepsilon$-caprolactones

The conditions and results of synthesis of bis-propargyloxy functionalized poly $\varepsilon$-caprolactones are summarized in Table 4a.3. Poly $\varepsilon$-caprolactones with molecular weights of 5300 and 11800 ($M_{n,\text{NMR}}$) were synthesized by varying monomer to initiator ratio.

**Table 4a.3: Reaction conditions and results for synthesis of $\alpha, \alpha'$-bis propargyloxy functionalized poly $\varepsilon$-caprolactones**

<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>$[M]_0/[I]_0$</th>
<th>Time (h)</th>
<th>Conv. (%)</th>
<th>$M_{n,\text{theo}}$</th>
<th>$M_{n,\text{NMR}}$</th>
<th>$M_{n,\text{GPC}}$</th>
<th>$M_w/M_n$</th>
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</thead>
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<td>65:1</td>
<td>12</td>
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<td>4800</td>
<td>5300</td>
<td>5900</td>
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</tr>
<tr>
<td>2</td>
<td>130:1</td>
<td>24</td>
<td>68</td>
<td>10500</td>
<td>11800</td>
<td>13500</td>
<td>1.33</td>
</tr>
</tbody>
</table>

(Temperature-110 °C Solvent: toluene) [CL]/ [Sn(Oct)$_2$]=200

a- $[M]_0 / [I]_0$: [Monomer]:[Initiator]

b- Gravimetry
c- $M_{n,\text{theo}}= \frac{([M]_0 \times (\% \text{ Conv.}) \times \text{mol. wt. of monomer} (114))}{[I]_0} + \text{mol. wt. initiator} (348)$
d- $M_{n,\text{NMR}}$= Determined from NMR
c- $M_{n,\text{GPC}}$= Determined from GPC; Polystyrene standard; CHCl$_3$ eluent

$^1$H-NMR spectrum of $\alpha, \alpha'$-bis propargyloxy functionalized poly $\varepsilon$-caprolactones is reproduced in Figure 4a.6.
Chapter 4a: End-Functionalized Polymers by ROP: Synthesis

Figure 4a.6: $^1$H-NMR spectra of a) 4,4'-bis(4-(prop-2-yn-1-yroxy) phenyl)pentan-1-ol  
b) $\alpha$, $\alpha'$-bis-propargyloxy functionalized poly $\varepsilon$-caprolactone in CDCl$_3$

The appearance of a triplet at 2.51 ppm confirmed the presence of propargyloxy functionality. Molecular weights for $\alpha$, $\alpha'$-bis propargyloxy functionalized poly $\varepsilon$-caprolactones were determined using $^1$H-NMR spectroscopy by comparing integral intensity of peak belonging to $-\text{OCH}_2$ in poly $\varepsilon$-caprolactone at 4.04 ppm to a triplet at 2.51 ppm corresponding to propargyloxy groups. The degree of polymerization was calculated from NMR analysis using the relation,

$$Dpn = \frac{[I_{4.04}/2]}{[I_{2.51}/2]} \quad (\text{propargyloxy proton})$$

Where $I_{4.04}$ and $I_{2.51}$ are integrals of the signals positioned at 4.04 and 2.51 ppm for CH$_2$ of poly $\varepsilon$-caprolactone chain and propargyloxy functionality, respectively.

Molecular weights were calculated using the equation,

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

$M_{n,NMR}$ values were in reasonably good agreement with theoretical molecular weights ($M_{n,\text{theo}}$) calculated from the monomer to initiator ratio. In addition, GPC data revealed monomodal distribution with PDI values of 1.24-1.33 for poly $\varepsilon$-caprolactone.
Thus, 4, 4’-bis (4-(prop-2-yn-1-yl)oxy) phenyl) pentan-1-ol was found to be a useful ROP initiator in the presence of PMDETA for synthesis of α, α’ bis-propargyloxy functionalized poly ε-caprolactones.

4a.3.3.1. Chemical modification of α, α’-bis propargyloxy functionalized poly ε-caprolactones

4a.3.3.1.1. Reaction of α, α’-bis propargyloxy functionalized poly ε-caprolactones with 2-azidoethyl 4-methylbenzenesulfonate

It is well known that propargyloxy functionality undergoes azide-alkyne click reaction. The reactivity of propargyloxy functionality was illustrated by carrying out click reaction with 2-azidoethyl 4-methylbenzenesulfonate on α, α’ bis-propargyloxy functionalized poly ε-caprolactone in the presence of CuBr/PMDETA (Scheme 4a.17).

Scheme 4a.17: Reaction of bis-propargyloxy functionalized poly ε-caprolactone with 2-azidoethyl 4-methylbenzenesulfonate

The transformation was assessed by FT-IR and 1H-NMR spectroscopy. In FT-IR spectrum, the characteristic peak corresponding to ester group of poly ε-caprolactone at 1730 cm⁻¹ retained while the peak belonging to propargyloxy functionality at 2310 cm⁻¹ completely disappeared confirming the coupling reaction without any backbone degradation.

Figure 4a.7 represents 1H-NMR spectra of α, α’-bis propargyloxy functionalized poly ε-caprolactones (Mn,NMR: 5300) and its click reaction product with 2-azidoethyl 4-methylbenzenesulfonate. 1H-NMR spectra revealed complete disappearance of the peak corresponding to propargyloxy functionality and appearance of a new peak at 8.11 ppm (proton corresponding to triazole ring) which indicated triazole ring formation without disturbing peaks related to poly ε-caprolactone attesting completion of the reaction without any side reaction such as degradation of poly ε-caprolactone backbone.
Figure 4a.7: $^1$H-NMR spectra of A) $\alpha$, $\alpha'$-bis propargyloxy functionalized poly $\varepsilon$-caprolactones B) product formed by reaction of $\alpha$, $\alpha'$-bis propargyloxy functionalized poly $\varepsilon$-caprolactone with 2-azidoethyl 4-methylbenzene sulfonate in CDCl$_3$

Model click reaction with azido compound opens up the possibilities of click reaction for functionalization of poly $\varepsilon$-caprolactone with different useful functional groups just by making use of appropriately substituted azido compounds.

4a.3.4. Synthesis of $\alpha$, $\alpha'$-bisazido functionalized poly $\varepsilon$-caprolactones

ROP of $\varepsilon$-caprolactone was carried out using, 4, 4'$\text{-}$bis (4-(2-azidoethoxy) phenyl) pentan-1-ol as the initiator (Scheme 4a.18) under the conditions reported for $\varepsilon$-caprolactone polymerization in the presence of azido group containing initiator$^{59}$

Scheme 4a.18: Synthesis of $\alpha$, $\alpha'$-bisazido functionalized poly $\varepsilon$-caprolactones
The conditions and results for synthesis of α, α’-bis-azido functionalized poly ε-caprolactones are summarized in **Table 4a.4**. Poly ε-caprolactones with molecular weights (Mₙ,NMR) ranging from 4900 to 14600 were synthesized by varying monomer to initiator ratio.

**Table 4a.4: Reaction conditions and results for synthesis of α, α’-bisazidofunctionalized poly ε-caprolactones**

<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>a[M]₀/[I]₀</th>
<th>Time (h)</th>
<th>bConv. (%)</th>
<th>cMₙ, theano</th>
<th>dMₙ,NMR</th>
<th>eMₙ,GPC</th>
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<td>61</td>
<td>7400</td>
<td>8400</td>
<td>13500</td>
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<tr>
<td>3</td>
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<td>70</td>
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<td>14600</td>
<td>18600</td>
<td>1.28</td>
</tr>
</tbody>
</table>

(Temperature-110 °C Solvent: toluene)  [CL]/ [Sn(Oct)₂]=200

a- [M]₀/ [I]₀: [Monomer]:[Initiator]

b- Gravimetry

c- \( Mₙ, theo = \left( \frac{[M]₀ \times (\% \text{ Conv.}) \times \text{mol. wt. of monomer (114)}}{[I]₀} \right) + \text{mol. wt. initiator (410)} \)

d- \( Mₙ, \text{NMR} = \text{Determined from NMR} \)

e- \( Mₙ, \text{GPC} = \text{Determined from GPC; Polystyrene standard; CHCl₃ eluent} \)

\(^1\text{H}-\text{NMR spectrum of α, α’-bisazidofunctionalized poly ε-caprolactone is reproduced in Figure 4a.8.}\) Molecular weights for α, α’-bisazidofunctionalized poly ε-caprolactones were determined by \(^1\text{H}-\text{NMR spectroscopy by comparing integral intensity of peak belonging to –OCH}_{2} \) in ε-caprolactone at 4.04 ppm to a doublet at 7.08 ppm corresponding to aromatic protons from initiator fragment. The degree of polymerization was calculated from NMR analysis using the relation,

\[
Dpn = \left( \frac{I_{4.04}}{I_{7.08}} \right)_{(\text{aromatic proton})}
\]

Molecular weights were calculated using the equation,

\[
Mₙ,NMR = [Dpn \times 114 \times \text{(mol. wt. of monomer)}] + \text{mol. wt. initiator}
\]
Figure 4a.8: $^1$H-NMR spectra of a) 4, 4'-bis (4-(2-azidoethoxy) phenyl) pentan-1-ol

b) bis-azido functionalized poly $\varepsilon$-caprolactone in CDCl$_3$

$M_{n,NMR}$ values were in reasonably good agreement with theoretical molecular weights ($M_{n,th}$) calculated from the monomer to initiator ratio. In addition, GPC data revealed monomodal distribution for poly $\varepsilon$-caprolactone. The PDIs were in the range 1.24-1.33.

Thus, 4, 4'-bis (4-(2-azidoethoxy) phenyl) pentan-1-ol was found to be a useful ROP initiator for synthesis of $\alpha$, $\alpha'$-bisazido functionalized poly $\varepsilon$-caprolactones under our experimental conditions.

4a.3.4.1. Chemical modification of $\alpha$, $\alpha'$-bisazido functionalized poly $\varepsilon$-caprolactones

4a.3.4.1.1. Reaction of $\alpha$, $\alpha'$-bisazido functionalized poly $\varepsilon$-caprolactones with phenyl acetylene

The azido functionality is well known for azide-alkyne click reaction\textsuperscript{58}. The reactivity of azido functionality was illustrated by carrying out click reaction with phenyl acetylene on $\alpha$, $\alpha'$-bisazidofunctionalized poly $\varepsilon$-caprolactones at room temperature (Scheme 4a.19).
Scheme 4a.19: Reaction of α, α'-bis-azido functionalized poly ε-caprolactone with phenyl acetylene

The transformation was characterized by FT-IR and $^1$H-NMR spectroscopy. In FT-IR spectrum, the peak corresponding to poly ε-caprolactone at 1730 cm$^{-1}$ was retained while the characteristic peak corresponding to azido functionality at 2108 cm$^{-1}$ completely disappeared confirming coupling reaction without backbone degradation. Figure 4a.9 represents $^1$H-NMR spectra of azido-terminated poly ε-caprolactone ($M_{n,NMR}$: 4900) and its click reaction product with phenyl acetylene.

Figure 4a.9: $^1$H-NMR spectra of A) α, α'-bis-azido functionalized poly ε-caprolactone

B) product formed by reaction of α, α'-bis-azido functionalized poly ε-caprolactone with phenyl acetylene in CDCl$_3$

$^1$H-NMR spectra indicated appearance of new peaks at 7.94, 7.80, 7.40 ppm (proton corresponding to phenyl ring + triazole ring) which elucidated triazole formation without
disturbing peaks related to poly ε-caprolactone attesting completion of the reaction without any side reaction such as degradation of poly ε-caprolactone backbone.

Model click reaction with phenyl acetylene opens up a simple methodology to functionalize poly ε-caprolactone with those functional groups which are otherwise difficult to introduce on poly ε-caprolactone just by making use of appropriately substituted acetylene compounds.

4a.3.5. Synthesis of α-aldehyde, α’-allyloxy heterobifunctionalized 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 the initiator (Scheme 4a.20).

Scheme 4a.20: Synthesis of α-aldehyde, α’-allyloxy heterobifunctionalized poly ε-caprolactones

The conditions and results of synthesis of α-aldehyde, α’-allyloxy heterobifunctionalized poly ε-caprolactones are summarized in Table 4a.5. Poly ε-caprolactones with molecular weights (M_n,NMR) ranging from 5100 to 23000 were synthesized by varying monomer to initiator ratio.
Table 4a.5: Reaction conditions and results for synthesis of α-aldehyde, α’-allyloxy heterobifunctionalized poly ε-caprolactones

<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>a[M]/[I]₀</th>
<th>Time (h)</th>
<th>bConv. (%)</th>
<th>cM&lt;sub&gt;n&lt;/sub&gt; theo</th>
<th>dM&lt;sub&gt;n&lt;/sub&gt;NMR</th>
<th>eM&lt;sub&gt;n&lt;/sub&gt;GPC</th>
<th>M&lt;sub&gt;w&lt;/sub&gt;/M&lt;sub&gt;n&lt;/sub&gt;</th>
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<td>16</td>
<td>71</td>
<td>10100</td>
<td>9700</td>
<td>11800</td>
<td>1.34</td>
</tr>
<tr>
<td>3</td>
<td>240:1</td>
<td>24</td>
<td>69</td>
<td>19300</td>
<td>23000</td>
<td>29000</td>
<td>1.26</td>
</tr>
</tbody>
</table>

(Temperature-110 °C Solvent: Toluene) [CL]/[Sn(Oct)₂]=200

a-[M]₀/[I]₀: [Monomer]:[Initiator],

b- Gravimetry

c- M<sub>n</sub> theo= \{[M]₀ x (% Conv.) x mol. wt. of monomer(114)\} + mol. wt. initiator (416)

d- M<sub>n</sub>NMR= Determined from NMR,

e- M<sub>n</sub>GPC=; Polystyrene standard; CHCl₃ eluent

1H-NMR spectrum of α-aldehyde, α’-allyloxy heterobifunctionalized poly ε-caprolactone is represented in Figure 4a.10. The appearance of a singlet at 9.91 ppm and multiplets in the range 6.11-5.97 ppm, and 5.43-5.39 ppm confirmed the presence of aldehyde functionality and allyloxy functionality, respectively on poly ε-caprolactone.
Molecular weights for aldehyde-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 9.91 ppm corresponding to aldehyde group. The degree of polymerization was calculated from NMR analysis using the relation,

$$Dpn = \frac{I_{4.04}}{I_{9.91}} (\text{aldehyde proton})$$

Molecular weights were calculated using the equation,

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

$M_{n,NMR}$ values were in reasonably good agreement with theoretical molecular weights ($M_{n,\text{theo}}$) 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.
4a.3.5.1. Chemical modification of α-aldehyde, α’-allyloxy heterobifunctionalized poly ε-caprolactone

The aldehyde and allyloxy functionalities are known to undergo different types of click reactions without use of any metal catalyst. Aldehyde group is known to undergo aldehyde-aminooxy click reaction\(^\text{57}\) while allyloxy group can undergo thiol-ene addition click reaction. We first performed aldehyde-aminooxy click reaction by considering the fact that aldehyde would undergo addition reaction with thiols and then thiol–ene click reaction was performed.

4a.3.5.1.1. Reaction of α-aldehyde, α’-allyloxy heterobifunctionalized poly ε-caprolactone with O-(2-azidoethyl) hydroxylamine

The reactivity of aldehyde functionality was illustrated by carrying out click reaction with O-(2-azidoethyl) hydroxylamine on poly ε-caprolactone at room temperature (Scheme 4a (21a)).

![Scheme 4a.21: a) Reaction of α-aldehyde, α’-allyloxy heterobifunctionalized poly ε-caprolactone with O-(2-azidoethyl) hydroxylamine b) reaction of α-azido, α’-allyloxy functionalized poly ε-caprolactone with 3-mercaptopropionic acid](image)

In FT-IR spectrum, in addition to the peak corresponding to poly ε-caprolactone at 1730 cm\(^{-1}\), characteristic peak corresponding to azido functionality at 2110 cm\(^{-1}\) appeared confirming introduction of azido group via formation of oxime. Fig. 4a.11 represents \(^1\)H-NMR spectra of α-aldehyde, α’-allyloxy heterobifunctionalized poly ε-caprolactone (\(M_\text{n,NMR}=9700\)) and its click reaction product with O-(2-azidoethyl) hydroxylamine. \(^1\)H-NMR spectra showed complete disappearance of the peak corresponding to aldehyde functionality and appearance of a new peak at 8.07 ppm (-CH=N-O) which elucidated oxime formation without disturbing peaks related to
poly ε-caprolactone attesting completion of the reaction without any side reaction such as degradation of poly ε-caprolactone backbone. The model aldehyde-aminooxy click reaction study with O-(2-azidoethyl) hydroxylamine introduces azido moiety on poly ε-caprolactone chain which further opens up plethora of opportunities to introduce different types of functional groups on poly ε-caprolactone by well known azide-alkyne click reaction 60.

![Figure 4a.11: 1H-NMR spectra of A) α-aldehyde, α’-allyloxy heterobifunctionalized poly ε-caprolactone B) product formed by reaction of α-aldehyde, α’-allyloxy heterobifunctionalized poly ε-caprolactone with O-(2-azidoethyl) hydroxylamine in CDCl₃](image)

4a.3.5.1.2. Reaction of α-azido, α’-allyloxy functionalized poly ε-caprolactone with 3-mercaptopropionic acid

The presence of allyloxy functionality was illustrated by carrying out click reaction with 3-mercaptopropionic acid in the presence of AIBN at 110 °C in chlorobenzene (Scheme 4a.21b). The transformation was characterized by ¹H-NMR spectroscopy. Figure 4a.12 depicts ¹H-NMR spectra of α-azido, α’-allyloxy functionalized poly ε-caprolactone (Mₙ,NMR: 9700) and its thiol-ene click reaction product. Complete disappearance of the peak corresponding to allyloxy functionality was observed in the spectra.
functionality and appearance of new peaks at 2.79, 2.75, 2.69 ppm indicated addition of thiol without any side reaction such as degradation of poly ε-caprolactone backbone.

Figure 4a.12: \(^1\text{H}-\text{NMR spectra of A) }\alpha\text{-azido, }\alpha’\text{-allyloxy functionalized poly }\varepsilon\text{-caprolactone B) product of reaction of }\alpha\text{-azido, }\alpha’\text{-allyloxy functionalized poly }\varepsilon\text{-caprolactone with 3-mercaptopropionic acid in CDCl}_3\)

The presence of aldehyde and allyloxy functionalities engenders opportunities to introduce various types of useful functionalities by carrying out different types of click reactions.

4a.3.6. Synthesis of \(\alpha\)-allyloxy, \(\alpha’\)-azido heterobifunctionalized poly \(\varepsilon\)-caprolactones

ROP of \(\varepsilon\)-caprolactone was carried out using, 4-(4-(allyloxy) phenyl)-4-(4-(2-azidoethoxy) phenyl) pentan-1-ol as the initiator (Scheme 4a.22).

Scheme 4a.22: Synthesis of \(\alpha\)-allyloxy, \(\alpha’\)-azido heterobifunctionalized poly \(\varepsilon\)-caprolactones
The conditions and results of synthesis of α-allyloxy, α’-azido heterobifunctional poly ε-caprolactones are summarized in Table 4a.6.

Table 4a.6: Reaction conditions and results for synthesis of α-allyloxy, α’-azido heterobifunctionalized poly ε-caprolactones

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>$a[M]_0/[I]_0$</th>
<th>Time (h)</th>
<th>$^b$Conv. (%)</th>
<th>$^cM_n$theo</th>
<th>$^dM_n$NMR</th>
<th>$^eM_n$GPC</th>
<th>$^{M_w}/M_n$</th>
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</table>

(Temperature-110 °C Solvent: toluene) [CL]/[Sn(Oct)$_2$]=200

a- $[M]_0/[I]_0$: [Monomer]:[Initiator]
b- Gravimetry
c- $M_n$theo=$\frac{[M]_0}{[I]_0} \times (\% \text{ Conv.}) \times \text{ mol. wt. of monomer} + \text{ mol. wt. initiator (381)}$
d- $M_n$NMR= Determined from NMR
e- $M_n$GPC= Determined from GPC; Polystyrene standard; CHCl$_3$ eluent

Poly ε-caprolactones with molecular weights of 4800 and 7300 ($M_n$NMR) were synthesized by varying monomer to initiator ratio. $^1$H-NMR spectrum of α-allyloxy, α’-azido heterobifunctional poly ε-caprolactone is represented in Figure 4a.13. The appearance of multiplets in the range 6.06-5.97 ppm and 5.43-5.23 ppm, confirmed the presence of allyloxy functionality.
Figure 4a.13: $^1$H-NMR spectra of A) 4-(4-(allyloxy)phenyl)-4-(4-(2-azidoethoxy)phenyl)pentan-1-ol B) α-allyloxy, α’-azido heterobifunctionalized poly ε-caprolactone in CDCl$_3$

Molecular weights for α-allyloxy, α’-azido heterobifunctional 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 6.06-5.97 ppm corresponding to allyloxy groups. The degree of polymerization was calculated from NMR analysis using the relation,

$$Dpn = \left[ \frac{I_{4.04}}{2} \right] \left[ \frac{I_{6.06-6.9}}{1} \right]$$ (allyloxy proton)

Molecular weights were calculated using the equation,

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

$M_{n,NMR}$ values were in reasonably good agreement with theoretical molecular weights ($M_{n,\text{theo}}$) calculated from the monomer to initiator ratio. In addition, GPC data revealed monomodal distribution with PDI values of 1.34 and 1.43 for poly ε-caprolactone. Thus, 4-(4-(allyloxy)phenyl)-4-(4-(2-azidoethoxy)phenyl) pentan-1-ol was found to be a useful ROP initiator for synthesis of α-allyloxy, α’-azido heterobifunctional poly ε-caprolactones.
4a.3.6.1. Chemical modification of α-allyloxy, α’-azido heterobifunctionalized poly ε-caprolactones

4a.3.6.1.1. Reaction of α-allyloxy, α’-azido functionalized poly ε-caprolactone with phenyl acetylene

The azido functionality is known to undergo azide-alkyne click reaction\(^5\). The reactivity of azido functionality was illustrated by carrying out click reaction with phenyl acetylene on poly ε-caprolactone containing allyloxy and azido functional groups at room temperature. (Scheme 4a.23). In FT-IR spectrum, the peak corresponding to poly ε-caprolactone at 1730 cm\(^{-1}\) was retained while the characteristic peak corresponding to azido functionality at 2108 cm\(^{-1}\) completely disappeared confirming the coupling reaction without backbone degradation.

Scheme 4a.23: Reaction of α-allyloxy, α’-azido heterobifunctionalized poly ε-caprolactones with phenyl acetylene

Figure 4a. 14 depicts \(^1\)H-NMR spectra of α-allyloxy, α’-azido heterobifunctional poly ε-caprolactones (M\(_n\), NMR: 7300) and its click reaction product with phenyl acetylene. \(^1\)H-NMR spectra indicated appearance of new peaks at 7.94, 7.80, 7.40 ppm (proton corresponding to phenyl ring + triazole ring) which elucidated triazole formation without disturbing peaks related to poly ε-caprolactone attesting completion of the reaction without any side reaction such as degradation of poly ε-caprolactone backbone.
Figure 4a.14: $^1$H-NMR spectra of A) $\alpha$-allyloxy, $\alpha'$-azido heterobifunctionalized poly $\varepsilon$-caprolactones B) product formed by the reaction of $\alpha$-allyloxy, $\alpha'$-azido functionalized poly $\varepsilon$-caprolactone with phenyl acetylene in CDCl$_3$

4a.3.6.1.2. Reaction of $\alpha$-allyloxy functionalized poly $\varepsilon$-caprolactones with 3-mercaptopropionic acid

The reactivity of allyloxy functionality was illustrated by carrying out click reaction with 3-mercaptopropionic acid on poly $\varepsilon$-caprolactone in the presence of AIBN at 110 °C in chlorobenzene as a solvent (Scheme 23 (b)). The conversion was assessed by $^1$H-NMR spectroscopy. Figure 4a.15 represents $^1$H-NMR spectra of $\alpha$-allyloxy terminated poly $\varepsilon$-caprolactone ($M_{n, \text{NMR}}$: 7300) and its thiol-ene click reaction product with 3-mercaptopropionic acid. $^1$H-NMR spectra showed complete disappearance of the peak corresponding to allyloxy functionality and appearance of new peaks at 2.79, 2.75, 2.69 ppm which illustrated addition of thiol without disturbing peaks related to poly $\varepsilon$-caprolactone attesting completion of the reaction without any side reaction such as degradation of poly $\varepsilon$-caprolactone backbone.
Thus, poly ε-caprolactone with azido and allyloxy functionalities provide an opportunity to introduce functional groups by azido-propargyloxy and thiol-ene click reactions.

4a.3.7. Synthesis of α-aldehyde, α'-azido heterobifunctionalized poly ε-caprolactones

ROP of ε-caprolactone was carried out using 4-(4-(2-(4-(2-azidoethoxy)phenyl)-5-hydroxypentan-2-yl)phenoxy)benzaldehyde as the initiator (Scheme 4a.24).

Scheme 4a.24: Synthesis of α-aldehyde, α'-azido heterobifunctionalized poly ε-caprolactones
The reaction conditions and results of synthesis of α-aldehyde, α’-azido heterobifunctionalized poly ε-caprolactones are summarized in **Table 4a.7**.

**Table 4a.7: Reaction conditions and results for synthesis of α-aldehyde, α’-azido heterobifunctionalized poly ε-caprolactones**

<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>[^{a}{[M]}_0/[^{b}{I]}_0]</th>
<th>Time (h)</th>
<th>[^{c}{\text{Conv.}}] (%)</th>
<th>[^{d}{M}_n,NMR]</th>
<th>[^{e}{M}_n,GPC]</th>
<th>[^{f}{M}_w/M_n]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60:1</td>
<td>12</td>
<td>67</td>
<td>5000</td>
<td>5600</td>
<td>5900</td>
</tr>
<tr>
<td>2</td>
<td>120:1</td>
<td>24</td>
<td>71</td>
<td>10200</td>
<td>11800</td>
<td>13500</td>
</tr>
</tbody>
</table>

(Temperature-110 °C Solvent: toluene) \([\text{CL}]/[\text{Sn(Oct)}_2] = 200\)

- a- \[^{a}{[M]}_0/[^{b}{I]}_0\]: [Monomer]:[Initiator]
- b- Gravimetry
- c- \[^{c}{M}_n,\text{theo}\] = \(\frac{[^{a}{[M]}_0 \times (\% \text{ Conv.}) \times \text{mol. wt. of monomer}}{[^{b}{I]}_0} + \text{mol. wt. Initiator (445)}\)
- d- \[^{d}{M}_n,NMR\] = Determined from NMR
- e- \[^{e}{M}_n,GPC\] = Determined from GPC; Polystyrene standard; CHCl₃ eluent

Poly ε-caprolactones with molecular weights of 5600 and 11800 \((M_n,NMR)\) were synthesized by varying monomer to initiator ratio. \(^1\)H-NMR spectrum of α-aldehyde, α’-azido heterobifunctionalized poly ε-caprolactone is represented in **Figure 4a.16**. The appearance of a singlet at 9.92 ppm confirmed aldehyde functionality. Molecular weights were determined by \(^1\)H-NMR spectroscopy by comparing integral intensity of peak belonging to –OCH₂ in poly ε-caprolactone at 4.06 ppm to a singlet at 9.92 ppm corresponding to aldehyde groups.
Figure 4a. 16: $^1$H-NMR spectra of A) 4-(4-(2-(4-(2-azidoethoxy) phenyl)-5-hydroxypentan-2-yl)phenoxy) benzaldehyde B) $\alpha$-aldehyde, $\alpha'$- azido heterobifunctionalized poly $\varepsilon$-caprolactones in CDCl$_3$

Degree of polymerization was calculated from NMR analysis using the relation,

$$Dpn = \left[ \frac{I_{4.06/2}}{I_{1.9/2.0}} \right]_{\text{(aldehyde proton)}}$$

Molecular weights were calculated using the equation,

$$M_{n,NMR} = [Dpn \times \text{mol. wt. of monomer (114)] + mol.wt.inititor (445)}$$

$M_{n,NMR}$ values were in reasonably good agreement with theoretical molecular weights ($M_{n, \text{theo}}$) calculated from the monomer to initiator ratio. In addition, GPC data revealed monomodal with PDI values of 1.21 and 1.36, for poly $\varepsilon$-caprolactones.

Thus, 4-(4-(2-(4-azidoethoxy) phenyl)-5-hydroxypentan-2-yl) phenoxy) benzaldehyde was found to be a useful ROP initiator for synthesis of $\alpha$-aldehyde, $\alpha'$- azido heterobifunctionalized poly $\varepsilon$-caprolactones.
4a.3.7.1 Chemical modification of α-aldehyde, α’-azido heterobifunctionalized poly ε-caprolactone

4a.3.7.1.1. Reaction of α-aldehyde, α’-azido heterobifunctionalized poly ε-caprolactone with phenyl acetylene

The azido functionality is well known for azide-alkyne click reaction\textsuperscript{58}. The reactivity of azido functionality was illustrated by carrying out click reaction with phenyl acetylene on poly ε-caprolactone containing aldehyde and azido functional groups at room temperature. (Scheme 4a.25).

Scheme 4a.25: Reaction of α-aldehyde, α’-azido heterobifunctionalized poly ε-caprolactones a) with phenyl acetylene b) with O-(2-azidoethyl) hydroxylamine

In FT-IR spectrum, the peak corresponding to poly ε-caprolactone at 1730 cm\textsuperscript{-1} was retained while the characteristic peak corresponding to azido functionality at 2108 cm\textsuperscript{-1} completely disappeared confirming the coupling reaction. Figure 4a.17 represents \textsuperscript{1}H-NMR spectra of poly ε-caprolactone containing aldehyde-azido functional groups (M\textsubscript{n,NMR}: 11800) and its click reaction product with phenyl acetylene.
Chapter 4a: End-Functionalized Polymers by ROP: Synthesis

Figure 4a.17: $^1$H-NMR spectra of A) $\alpha$- aldehyde, $\alpha'$- azido heterobifunctionalized poly $\varepsilon$-caprolactone B) product formed by reaction of $\alpha$- aldehyde, $\alpha'$- azido heterobifunctionalized poly $\varepsilon$-caprolactone with phenyl acetylene in CDCl$_3$

$^1$H-NMR spectra showed appearance of new peaks at 7.94, 7.80, 7.40 ppm (proton corresponding to phenyl ring + triazole ring) in addition to the peaks corresponding to poly $\varepsilon$-caprolactone which indicated triazole formation without disturbing peaks related to poly $\varepsilon$-caprolactone attesting completion of the reaction without any side reaction such as degradation of poly $\varepsilon$-caprolactone backbone.

4a.3.7.1.2. Reaction of $\alpha$- aldehyde functionalized poly $\varepsilon$-caprolactone with O-(2-azidoethyl) hydroxylamine

The aldehyde functionality is known to undergo aldehyde-aminooxy click reaction. The reactivity of aldehyde functionality was illustrated by carrying out click reaction with O-(2-azidoethyl) hydroxylamine on poly $\varepsilon$-caprolactone at room temperature (Scheme 4a.25(b)). The transformation was characterized by FT-IR and $^1$H-NMR spectroscopy. In FT-IR spectrum, the peak corresponding to poly $\varepsilon$-caprolactone at 1730 cm$^{-1}$ was retained while the characteristic peaks corresponding to aldehyde functionality at 1710 cm$^{-1}$ completely disappeared confirming the coupling reaction. Figure 4a.18 represents $^1$H-NMR spectra of poly $\varepsilon$-caprolactone containing
aldehyde-azido functional groups ($M_{n,\text{NMR}}$: 11800) and its click reaction product with O-(2-azidoethyl) hydroxylamine.

Figure 4a.18: $^1$H-NMR spectra of A) α- aldehyde functionalized poly ε-caprolactone B) product formed by reaction of α- aldehyde functionalized poly ε-caprolactone with O-(2-azidoethyl) hydroxylamine in CDCl$_3$.

Thus, advantage of availability of azido and aldehyde heterofunctionality on polycaprolactone could be taken for functionalization of polycaprolactone by azido-propargyloxy and aldehyde-aminoxy click reaction is demonstrated.
4a.4. Conclusions

✓ Functionalized ROP initiators were demonstrated to be useful initiators for the synthesis of α, α’- homo and α, α’- hetero bifunctionalized poly ε-caprolactones

1) α, α’- Homo bifunctionalized polycaprolactones containing allyloxy, aldehyde, azido, and propargyloxy functional groups possessing different molecular weights were prepared.

2) α, α’- Hetero bifunctionalized poly ε-caprolactones featuring allyloxy-aldehyde, allyloxy- azido and azido-aldehyde with different molecular weights were prepared.

✓ Reactivity of end functional groups on the poly ε-caprolactones was demonstrated by carrying out specific reactions of that particular functional group present on polymer without backbone degradation.

✓ Poly ε-caprolactones possessing clickable end functional groups represent valuable precursors for synthesis of Y-shaped miktoarm star copolymers
Chapter 4a: End-Functionalized Polymers by ROP: Synthesis

References:

29. Summerlin, B.; Tsarevsky, N.; Louche, G.; Lee, R.; Matyjaszewski, K.,
Chapter 4b
End-Functionalized Polymers
by ATRP:
Synthesis, Characterization
and
Chemical Modification
4b.1. Introduction

A major concern of polymer and material scientists is to design functional materials with properties tuned to match the needs of expanding technology. In particular, end-functional polymers have an important position because of their potential applications as components in the synthesis of block copolymers, thermoplastic elastomers, polymer networks, surfactants, macromonomers, etc. According to the IUPAC, end-functional polymers are defined as polymeric molecules with reactive end groups that have the capacity to enter into further polymerization or other reactions. Pioneering work on the synthesis of functional polymers, their conversion to the final products with specific properties by reacting with functional groups may be dated to 1947. However, the concept was not fully recognized until 1960. Significant contributions to the development of this class of polymeric materials prolong in the current literature. In the last two decades there has been a rapid growth in the development and understanding of controlled/living radical polymerizations (C/LRP). Precise control of functionality, molecular weight, and uniformity (molecular weight distribution) can now be made not only by living ionic polymerization routes but also by newly developed controlled/living radical polymerization techniques.

4b.1.1 Synthesis of telechelic/end-functionalized polymers by CRP

Accurate control of polymerization process is an important aspect for the preparation of well-defined telechelics and end-functionalized macromolecules. Such control of chain ends was traditionally accomplished using living ionic polymerization techniques. But it is well known that the ionic processes suffer from rigorous synthetic requirements and in some cases they are sensitive to the functional groups to be incorporated. On the other hand, free radical polymerization is flexible and less sensitive to the polymerization conditions and functional groups. However, conventional free radical processes yield polymers without control of molecular weight and chain end. Competing coupling and disproportionation steps and the inefficiency of the initiation step lead to functionalities less than or greater than those theoretically expected. Recent developments in controlled/living radical polymerization provided the possibility to synthesize well-defined telechelic polymers with controlled functionality. As described below, all the controlled/living radical polymerization methods, namely atom transfer radical polymerization (ATRP), nitroxide mediated radical polymerization (NMP) also called as stable free radical mediated polymerization (SFRP), reversible addition-fragmentation chain transfer polymerization (RAFT), iniferters, iodine transfer polymerization (ITP) can be used for preparation of telechelic/end-functional polymers. There are two strategies for synthesizing telechelic polymers using the widely used C/LRP methods including ATRP, RAFT, or NMP processes. Functionality can be incorporated onto the initiating segment of ATRP, RAFT, or
NMP initiators which afford $\alpha$-functional polymers. Equally, functionality can be affixed to the terminating portion of initiators which provides $\omega$-functional polymer (Scheme 4b.1).

![Scheme 4b.1: General synthetic strategies for telechelic polymers by ATRP, NMP and RAFT methods](image)

Polymers can be functionalized at one end (semi-telechelic), both ends (telechelic), or possess differing functionality at the ends (heterotelechelic). As an alternative, functionalization of polymer can be achieved by post-polymerization reactions.

4b.1.1.1. End-functionalized polymers by NMP

NMP was reported as a successful method to obtain end-functional polymers\textsuperscript{17}. The utilization of functional alkoxyamine during polymerization generally gives functional polymers. Several examples are reported where functionalities such as acid\textsuperscript{18-21}, azide\textsuperscript{22, 23}, alcohol\textsuperscript{24, 25}, protected amine\textsuperscript{26, 27}, halide\textsuperscript{28, 29} were introduced in polymers. The use of TEMPO with a hydroxyl-functional initiator gives hydroxyl-terminated polymers\textsuperscript{30} (Scheme 4b.2).

![Scheme 4b.2: Synthesis of hydroxyl-terminated polystyrene using NMP](image)

4b.1.1.2. End-functionalized polymers by RAFT polymerization

RAFT polymerization is an extremely versatile process and has been utilized in the preparation of narrow MWD polymers or copolymers from most monomers amenable to radical polymerization. There is compatibility with a wide range of functionality in monomers, solvents and initiators. Due to its compatibility with functional groups, it is also known for the synthesis of end-functionalized polymers via functional RAFT agent. In RAFT polymerization, an easy way to synthesize end-functionalized polymers is the polymerization in the presence of functionalized RAFT agents. A variety of functionalities such as alcohol\textsuperscript{31, 32}, acid\textsuperscript{33, 34}, amine\textsuperscript{35}, azide\textsuperscript{36, 37}, alkyne\textsuperscript{38, 39}, allyl\textsuperscript{40, 41}, epoxy\textsuperscript{42} could be introduced in polymers via functional RAFT agents. Figure 4b.1 shows selected functionalized RAFT agents utilized in preparation of end-functional
polymers through RAFT polymerization\textsuperscript{40, 43-45}. There are certain reported difficulties with RAFT polymerization such as retardation and poor control which is frequently attributable to inappropriate choice of RAFT agent for the monomers and reaction conditions. RAFT agents that perform well under a given set of circumstances are not necessarily optimal for all circumstances.

\begin{center}
\begin{align*}
 & \text{R} - \text{S} - \text{S} - \text{COOH} & \quad & \text{Z} - \text{S} - \text{S} - \text{COOCH}_2\text{CH}_2\text{OH} & \quad & \text{S} - \text{S} - \text{OH} \\
 & \text{CH}_3 & & \text{CH}_3 & & \text{CH}_3 \\
 & \text{R} = \text{R}_2\text{N}, \text{RO} \\
 & \text{R}1 & & \text{R}2 & & \text{R}3 \\
 & \text{R}_1 & & \text{R}2 & & \text{R}3 \\
 & \text{R}_4 & & \text{R}5 & & \text{R}6 \\
\end{align*}
\end{center}

\textbf{Figure 4b.1: Selected functionalized RAFT agents}

4b.1.1.3. End-functionalized polymers by ATRP

Matyjazewski et al\textsuperscript{46} and Sawamoto et al\textsuperscript{47} introduced ATRP in 1995 simultaneously. The principle is based on the Kharasch\textsuperscript{48} reaction, the Atom Transfer Radical Addition (ATRA)\textsuperscript{49}, which is widely used by organic chemists for carbon-carbon bond formation. The control in an ATRP system is induced by the presence of an organic halide initiator and a transition metal complex. The reversible exchange of the halogen atom between the growing polymer chain and the transition metal complex (in its higher oxidation state) ensures the control over the polymerization (\textbf{Scheme 4b.3}). As in other living polymerizations, ATRP process can be effectively employed for the synthesis of end-functionalized polymers. Compared to NMP and RAFT polymerization, ATRP is known to be the most promising polymerization technique for synthesis of end-functionalized polymers on the basis of the present vast amount of literature\textsuperscript{17,50}

\begin{center}
\begin{align*}
 & \text{R}_-\text{X} + \text{Mt}^{n/L} \xrightleftharpoons[\text{K}^{-}\text{act}]{\text{K}^{+}\text{deact}} \text{R}^- + \text{X-Mt}^{n+1/L} \\
 & \text{K}^{+}\text{deact} \xrightarrow[\text{K}_p]{\text{K}^{-}\text{act}} \text{Monomer} \\
\end{align*}
\end{center}

\textbf{Scheme 4b.3: Mechanism of ATRP}

Four major routes for functional polymers via ATRP have been reported (\textbf{Figure 4b.2}):  

1) Use of functional initiators
2) Substitution of the terminal halogen atom

3) Direct polymerization of functional monomers

4) Polymerization of "protected" monomers, followed by post-polymerization

![Diagram of polymerization strategies via ATRP](image)

**Figure 4b.2: Major strategies for functional polymers via ATRP**

The first two approaches yield end-functionalized polymers whereas the last two yield polymers with multiple functionalities along the backbone. To this end, using functional initiators, two general methods are employed to synthesize functional polymers a) using functional initiator having functional group on α chain end b) halide displacement method. In the former, polymerization is initiated with a functionalized organic halide initiator coupled with a metal catalyst to form polymers with an α-end (head) functionality\(^{51}\). In the latter, end-functionalization is achieved through transformation of a stable carbon-halogen terminal bond\(^{52}\).

**4b.1.1.3.1. Polymerization of functional monomers**

The simplest approach to a functional polymer is the direct polymerization of a monomer containing the desired functionality\(^{53}\). ATRP is generally tolerant to many polar functional groups and this route has often been successfully used. Water-soluble monomers (both neutral and ionic) can be polymerized in a controlled fashion by ATRP directly in protic (aqueous) media, provided that some basic rules for catalyst selection are obeyed\(^{54}\). In some cases, polar monomers especially those that are strongly coordinating (basic, nucleophilic or acidic)-can react with the ATRP catalyst, the alkyl halide-type initiator or the polymeric dormant species. In these cases, monomers with ‘protected’ groups should be used. They can be transformed into the desired polar functionalities after the polymerization\(^{55, 56}\).

**4b.1.1.3.2. Use of functional ATRP initiators**

In ATRP, the incorporation of α-functional groups is achieved by making use of appropriately functionalized initiators. It should be pointed out that besides the desired functionality, the initiators need to be equipped with a radical stabilizing group on the α-carbon atom such as aryl, carbonyl, nitrile to ensue successful ATRP. Taking advantage of the tolerance of ATRP for functional groups, a variety of functionalized initiators have been synthesized and
used for preparation of end functionalized polymers. Functional ATRP initiators have been documented by Yagci et al.\textsuperscript{17} and Matyjaszewski et al.\textsuperscript{10}

**4b.1.1.3.3. End-functionalized polymers via halide displacement**

This is another important method for the synthesis of end-functionalized polymers by ATRP\textsuperscript{10}. Polymers obtained by ATRP contain a halogen atom as end group, if termination and transfer reactions are essentially absent. The halogen atom can be replaced through a variety of reactions leading to end functional polymers. A common method of dehalogenation is, reaction of polymer synthesized by ATRP with trialkyltin hydride\textsuperscript{49, 52}.

Such substitutions are often desirable for high-temperature applications where some evidence for halogen loss has been described\textsuperscript{57}. By replacing tributyltin hydride with allyl tri-\textit{n}-butylstannane, polymers with allyl end groups were produced\textsuperscript{58}. The terminal halogen can also be displaced by other methods such as nucleophilic substitution, cyclo-addition, free-radical chemistry, or electrophilic addition catalyzed by Lewis acids. (Scheme 4b.4)

Scheme 4b.4: End-functionalized polymers synthesized by displacement of terminal halogen atom using electrophilic substitution, nucleophilic substitution, cyclo addition and radical addition reactions\textsuperscript{59}

A survey of literature revealed that \(\alpha\)- or \(\omega\)-functional polymers have been frequently reported in the literature employing the appropriate strategies which have been summarized in previous sections. Scant attention has been paid to synthesize \(\alpha\), \(\alpha\)' homo bifunctional and \(\alpha\), \(\alpha\)'-heterobifunctional polymers by ATRP technique. The present study encompasses synthesis of different end-functionalized polymers viz. polystyrene and poly (methyl methacrylate). \(\alpha\), \(\alpha\)'-Homobifunctional polystyrene and poly (methyl methacrylate) having different functionalities such as allyloxy, aldehyde, propargyloxy, azido and \(\alpha\)-aldehyde, \(\alpha\)'-allyloxy heterobifunctional poly (methyl methacrylate) with different molecular weights were prepared using appropriate initiators. FT-IR, NMR spectroscopy and GPC techniques were used to characterize end-
functionalized polymers. End functionality on the polymer was demonstrated by carrying out specific reactions of that particular functional group present on polymer.

4b.2. Experimental

4b.2.1. Materials

4,4’-Bis(4-(allyloxy)phenyl)pentyl 2-bromo-2-methylpropanoate, 4,4’-bis(4-(4-formylphenoxy)phenyl)pentyl 2-bromopropanoate, 4,4’-bis(4-(prop-2-yn-1-ylloxy)phenyl)pentyl-2-bromo2-methylpropanoate, 4-4-(allyloxy)phenyl)-4-(4-(4-formylphenoxy)phenyl)pentyl 2-bromo-2-methylpropanoate, and 4,4’-bis(4-(2-azidoethoxy)phenyl)pentyl 2-bromopropanoate, were synthesized starting from 4, 4’-bis (4-hydroxyphenyl) pentanoic acid as described in chapter 3b. Synthesis of O-(2-azidoethyl) hydroxylamine has been detailed in chapter 4a. N, N, N’, N’, N”-Pentamethyldiethylenetriamine (PMDETA), 2-bromoisobutyryl bromide (98%), phenyl acetylene (Aldrich), chlorobenzene, AIBN (Spectochem), bromine (Loba), chloroplatinic acid monohydrate, 3-chloroperoxybenzoic acid, lithium aluminium hydride (LAH), and triethylsilane were used as received. Copper (I) bromide (Aldrich, 99.9%) was washed with glacial acetic acid in order to remove any soluble oxidized species, filtered, washed with ethanol, and dried. Methyl methacrylate (MMA) and styrene were stirred over calcium hydride for 4 h and distilled under reduced pressure just before use.

4b.2.2. Characterization and measurements

FTIR spectra were recorded on a Perkin-Elmer Spectrum GX spectrophotometer. NMR spectra were recorded on a Bruker 200 MHz spectrometer for ‘H-NMR and 125 MHz for ‘C-NMR measurements using CDCl3, CDCl3 without TMS as a solvent. 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 (Thermoseparation product) equipped with spectra series UV 100 and spectra system RI 150 detectors. The sample concentration was 2 to 3 mg mL⁻¹ and the injection volume was 50 mL. HPLC grade chloroform was used as eluent at room temperature with a flow rate of 1 mL min⁻¹. Polystyrene and PMMA were used as the calibration standards.

4b.2.3. Synthesis of functional polystyrenes and poly (methyl methacrylate)s

4b.2.3.1. Synthesis of α, α’- bis-allyloxy functionalized polystyrenes and poly (methyl methacrylate)s

ATRP of styrene in bulk at 110 °C and that of methyl methacrylate in anisole at 80 °C was carried out. In a typical experiment, Schlenk tube equipped with a magnetic stir bar was charged with, CuBr (120 mg, 0.85 mmol). The Schlenk tube was thoroughly flushed with argon.
4,4'-Bis(4-(allyloxy) phenyl) penty1 2-bromo-2-methylpropanoate (425 mg, 0.85 mmol) was dissolved in styrene (11.0 g, 106 mmol) in a separate sample vial, 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 an argon atmosphere, the reaction mixture was opened and PMDETA (173 µL, 0.85 mmol) was rapidly added. The Schlenk tube was sealed with a stopper and was kept in an oil bath at 110 °C. Kinetic study was performed by taking aliquots at regular intervals. After the reaction time, polymerization was quenched by cooling the reaction mixture in a liquid nitrogen bath. The reaction mixture was diluted with THF (50 mL) and the solution was passed through neutral alumina column to remove copper residue. The solution was concentrated and poured into excess methanol (500 mL) to precipitate the polymer. The polymer was dried under reduced pressure for 24 h. The monomer conversion was determined gravimetrically.

$^1$H NMR (CDCl$_3$, δ/ppm): 7.07 (d, Ar-H from initiator), 6.80 (d, Ar-H from initiator), 6.09-5.98 (m, =CH), 5.45-5.23 (q, =CH$_2$), 4.49 (d, -OCH$_2$), 3.58 (s, -OCH$_3$ from poly (methyl methacrylate), 1.87-0.81 (m, CH$_2$, -CH from poly (methyl methacrylate) + protons from initiator)

$^1$H NMR (CDCl$_3$, δ/ppm): 7.05-6.39 (m, Ar-H from polystyrene + Ar-H from initiator), 6.09-5.95 (m, 2H, =CH), 5.45-5.23 (q, =CH$_2$), 4.49 (d, -OCH$_2$), 1.86-1.43 (m, -CH$_2$-CH- from polystyrene + protons from initiator)

4b.2.3.1.1. Chemical modification of α, α'- bis-allyloxy functionalized polystyrene

4b.2.3.1.1.1. Reaction of α, α'- bis-allyloxy functionalized polystyrene with bromine

Into a 50 mL two necked round-bottom flask equipped with a dropping funnel were charged, α, α'- bis-allyloxy functionalized polystyrene (730 mg, 0.066 mmol, M$_{\text{NMR}}$=11100) and carbon tetrachloride (10 mL). The solution of bromine (2.5 mL) in carbon tetrachloride (5 mL) was added until solution turned to red and the reaction mixture was stirred at room temperature for 2 h. The reaction mixture was precipitated into methanol (100 mL). The obtained polymer was dried under vacuum at 50 °C for 8 h and was characterized by $^1$H NMR spectroscopy.

$^1$H NMR (CDCl$_3$, δ/ppm): 7.12-6.39 (m, Ar-H from polystyrene + Ar-H from initiator), 4.59-4.52 (m, CH$_2$Br and CHBr), 1.86-1.43 (br, -CH$_2$-CH- from polystyrene)

4b.2.3.1.1.2. Hydrosilylation reaction of α, α'- bis-allyloxy functionalized polystyrene with triethylsilane using chloroplatinic acid monohydrate as a catalyst

Into a 100 mL two necked round-bottom flask equipped with a dropping funnel were charged, solution of chloroplatinic acid monohydrate (560 mg, 1.36 mmol,) in acetonitrile (5
ml), triethyl silane (2.30 g, 1.36 mmol) in acetonitrile (5 mL) and α, α’-bis-allyloxy functionalized polystyrene (730 mg, 0.066 mmol, \(M_n,\text{NMR}=11100\)) in dry toluene (15 mL) under the stream of argon. The reaction mixture was stirred at room temperature for 30 minutes. The dark green colored solution was precipitated in cold methanol and the polymer was separated by filtration. The polymer was dried under vacuum at 50 °C for 8 h and was characterized by \(^1\)H – NMR spectroscopy.

\[^1\]H NMR (CDCl\(_3\) without TMS, δ/ppm): 7.12-6.39 (m, Ar-H from polystyrene + Ar-H from initiator), 4.31 (t, -CH\(_2\)O), 1.86-1.43 (m, -CH\(_2\)-CH from polystyrene), 0.84-0.79 (m, -CH\(_3\)), 0.49-0.44 (m, Si-CH\(_2\))

### 4b.2.3.1.1.3. Transformation of α, α’-bis-allyloxy functionalized polystyrene into α, α’-bis-epoxide functionalized polystyrene

Into a 100 mL two necked round-bottom flask equipped with a dropping funnel was charged, α, α’-bis-allyloxy functionalized polystyrene (730 mg, 0.066 mmol, \(M_n,\text{NMR}=11100\)) dissolved in dichloromethane (10 mL) and the solution was cooled to 0 °C with ice water. The solution of 3-chloroperoxybenzoic acid (1.0 g, 6.8 mmol) in dichloromethane (25 mL) was slowly added over a period of 30 minutes. After completion of addition, the reaction mixture was stirred at 0 °C for 2 h and then at room temperature for 24 h. The solution was washed with aqueous 5% NaHCO\(_3\) solution (3 x 100 mL) and de-ionized water (3 x 100 mL). The polymer was precipitated into methanol (25 mL). The polymer was dried under vacuum at 50 °C for 8 h and was characterized by \(^1\)H-NMR spectroscopy.

\[^1\]H NMR (CDCl\(_3\), δ/ppm): 7.12-6.39 (m, Ar-H in polystyrene + Ar-H in initiator), 3.15-3.13 (m, -CH\(_2\)O), 2.74-2.70 (m, -CH\(_2\)O), 2.59-2.55 (m, 2H, CH\(_2\)O), 1.86-1.43 (br, -CH\(_2\), -CHPh- from polystyrene)

### 4b.2.3.2. Synthesis of α, α’-bisaldehyde functionalized polystyrene

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. 4, 4’-Bis (4-(4-((formylphenoxy) phenyl) pentyl 2-bromopropanoate (0.52 g, 0.85 mmol) was dissolved in styrene (3.1 g, 29.75 mmol) in a separate sample vial, degassed and the solution 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 an argon atmosphere, the reaction mixture was opened and N, N, N’, N’, N”-pentamethyldiethylenetriamine (173 µL, 0.85 mmol) was added rapidly. The Schlenk tube was sealed with a stopper and was kept in an oil bath at 110 °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 excess methanol (500 mL) to precipitate the polymer. The polymer was dried under reduced pressure for 24 h and weighed. The monomer conversion was determined gravimetrically.

$^{1}$H NMR (CDCl$_3$ δ/ppm): 9.85 (s, 2H, aldehyde), 7.77 (d, Ar-H ortho to aldehyde), 7.02-6.50 (m, Ar-H from polystyrene + Ar-H from initiator), 2.12-1.99 (m, -CH$_2$ from polystyrene + protons from initiator fragment), 1.75-1.50 (m, -CH from polystyrene + protons from initiator fragment)

### 4b.2.3.3. Synthesis of α, α'-bis propargyloxy functionalized 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. 4,4'-Bis (4-(prop-2-ynyloxy) phenyl) pentyl 2-bromo-2-methylpropanoate (420 mg, 0.85 mmol) was dissolved in methyl methacrylate (2.65 g, 25.5 mmol) in a separate sample vial, degassed and the solution 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 an argon atmosphere, the reaction mixture was opened and N, N, N', N', N"-pentamethyldiethylenetriamine (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. 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 excess methanol (500 mL) to precipitate the polymer. The polymer was dried under vacuum for 24 h and weighed. The monomer conversion was determined gravimetrically.

$^{1}$H NMR (CDCl$_3$ δ/ppm): 7.08 (d, Ar-H from initiator fragment), 6.86 (d, Ar-H from initiator fragment) 4.65 (t, -OCH$_2$ from initiator fragment), 3.58 (s, -OCH$_3$ from poly (methyl methacrylate) and -OCH$_2$ from initiator fragment), 2.52 (t, acetylene proton), 1.85- 0.82 (m, CH$_2$, -CH$_3$ from poly (methyl methacrylate + protons from initiator fragment))

### 4b.2.3.4. Synthesis of α, α'-bisazido functionalized 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. 4,4'-Bis(4-(2-azidoethoxy) phenyl) pentyl 2-bromopropanoate (470 mg, 0.85 mmol) was dissolved in methyl methacrylate (6.8 g, 68 mmol) in a separate sample vial, degassed and the solution 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 an argon atmosphere, the reaction mixture was opened and N, N, N’, N’, N”-pentamethyldiethylenetriamine (173 µL, 0.85 mmol) was added rapidly. 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 excess 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.

$^1$H NMR (CDCl$_3$, δ/ppm): 7.09 (d, Ar-H from initiator fragment), 6.81 (d, Ar-H from initiator fragment) 4.12 (t, -OCH$_2$ from initiator fragment), 3.58 (s, -OCH$_3$ from poly (methyl methacrylate) and -OCH$_2$ from initiator fragment), 1.85-0.83 (m, CH$_2$, -CH$_3$ from poly (methyl methacrylate + protons from initiator fragment))

4b.2.3.4.1. Chemical modification of α, α’- bis-azido functionalized poly (methyl methacrylate)s

4b.2.3.4.1.1. Reaction of α, α’- bis-azido functionalized poly (methyl methacrylate)s with phenyl acetylene

In a typical experiment, Schlenk tube equipped with a magnetic stir bar were charged with, α, α’- bis-azido functionalized poly (methyl methacrylate) (750 mg, 0.1 mmol), CuBr (30 mg, 0.2 mmol), phenyl acetylene (204 mg, 2 mmol), N, N, N’, N’, N”-pentamethyldiethylenetriamine (20 µL, 0.1 mmol) and DMF (20 mL) under nitrogen atmosphere. The Schlenk tube was sealed and the reaction mixture was degassed three times by freeze-pump-thaw cycles and kept stirring for 24 h at room temperature. After reaction time, DMF was removed under vacuum and reaction mixture was diluted with dichloromethane (50 mL). 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 and dried under vacuum for 24 h.

$^1$H NMR (CDCl$_3$, δ/ppm): 7.94 (s, Ar-H attached to triazole ring), 7.80 (d, Ar-H attached to triazole ring), 7.44-7.38 (m, Ar-H attached to triazole ring + triazole ring proton), 7.08 (d, Ar-H from initiator), 6.80 (d, Ar-H from initiator), 4.78 (t, -CH$_2$), 4.35 (t, -CH$_3$), 3.58 (s, -OCH$_3$ from poly (methyl methacrylate) and -OCH$_2$ from initiator fragment), 1.85-0.83 (m, CH$_2$, -CH$_3$ from poly (methyl methacrylate + protons from initiator fragment))
4b.2.3.5. Synthesis of α-aldehyde, α’-allyloxy heterobifunctionalized poly (methyl methacrylate)

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. 4-4-(Allyloxy)phenyl)-4-(4-(4-formylphenoxy) phenyl) penty l 2-bromo-2-methylpropanoate (480 mg, 0.85 mmol) was dissolved in methyl methacrylate (4.25 g, 42.5 mmol) in a separate sample vial, degassed and the solution was transferred via argon-purged syringe to 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 N, N, N’, N’, N”-pentamethyldiethylenetriamine (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 (CDCl3 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, -OCH2), 3.60 (s, -OCH3 from poly (methyl methacrylate), 1.90-0.84 (m, CH2, -CH from poly (methyl methacrylate + protons from initiator fragment))

4b.2.3.5.1. Chemical modification of α-aldehyde, α’-allyloxy heterobifunctionalized poly (methyl methacrylate)

4b.2.3.5.1.1. 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 (methyl methacrylate) (740 mg, 0.2 mmol), dichloromethane (10 mL) and a pinch of sodium sulfate. The solution of O-(2-azidoethyl)hydroxylamine (1.02 g, 10 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 (50 mL). The obtained polymer was filtered and dried under vacuum at 50 °C for 8 h.

IR (CHCl3, cm⁻¹): 2110, 1730
4b NMR (CDCl$_3$, $\delta$/ppm): 8.11 (s, -CH=N), 7.56 (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)).

4b.2.3.5.1.2 Thiol-ene thermal click reaction

Into a clean and dry Schlenk tube $\alpha$-allyloxy $\alpha'$-azido functionalized poly (methyl methacrylate) (185 mg, 0.05 mmol), 3-mercaptopropanoic acid (53 mg, 0.5 mmol) and AIBN (82 mg, 0.5 mmol) were dissolved in chlorobenzene (20 mL). The mixture was degassed via three freeze-pump-thaw cycles and subsequently vacuum sealed. The Schlenk tube was heated at 80 °C for 6 h. The polymer was purified by precipitation in cold methanol. The polymer was dried at 50 °C under vacuum for 18 h.

1H NMR (CDCl$_3$, $\delta$/ppm): 8.11 (s, -CH=N), 7.56 (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), 1.87-0.81 (m, CH$_2$, -CH from poly (methyl methacrylate)).

4b.3. Results and Discussion

ATRP technique has been routinely employed for the synthesis of polymers with $\alpha$-, $\omega$- and $\alpha$, $\omega$-functional end groups and a wide variety of functional groups have been introduced. However, there are limited examples of synthesis of $\alpha$, $\alpha'$-homobifunctional polymers such as dihydroxyl, dicarboxylic acid, di(4-fluorobenzoyl), and di(aromatic bromo) using initiator approach. To the best of our knowledge, there are no reports on synthesis of $\alpha$, $\alpha'$-hetero bifunctionalized polymers using ATRP initiators.

In the present work, we report synthesis of $\alpha$, $\alpha'$-homo- and $\alpha$, $\alpha'$-hetero bifunctionalized polymers using initiator approach. The functionalities introduced on polymers such as allyloxy, propargyloxy, azido and aldehyde were chosen by considering the fact that all these functionalities are capable of undergoing click reactions.

4b.3.1. Synthesis of $\alpha$, $\alpha'$-bisallyloxy functionalized polystyrenes and poly (methyl methacrylate)

ATRP of styrene in bulk and that of methyl methacrylate in anisole was carried out using bis-allyloxy functionalized ATRP initiator viz, 4,4'-bis(4-(allyloxy) phenyl)pentyl 2-bromo-2-methylpropanoate (Scheme 4b.5).
Scheme 4b.5: Synthesis of α, α’-bisallyloxy functionalized polystyrenes and poly (methyl methacrylate)

The reaction conditions and results of synthesis of α, α’-bis-allyloxy functionalized poly (methyl methacrylate)s and polystyrenes are summarized in Tables 4b.1 and Table 4b.2, respectively.

Table 4b.1: Reaction conditions and results for synthesis of α, α’-bis allyloxy functionalized poly (methyl methacrylate)s

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>([M_0]:[I]:[Cu]:[L])</th>
<th>(\text{Conv.} , (%))</th>
<th>(M_n,\text{theo})</th>
<th>(M_n,\text{NMR})</th>
<th>(M_w/M_n)</th>
<th>(I_{\text{eff}})</th>
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<td>200:1:1:1</td>
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<td>9100</td>
<td>11900</td>
<td>10500</td>
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<td>3</td>
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<td>11900</td>
<td>12000</td>
<td>11700</td>
<td>1.23</td>
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<tr>
<td>4</td>
<td>500:1:1:1</td>
<td>32</td>
<td>16500</td>
<td>21500</td>
<td>18500</td>
<td>1.23</td>
</tr>
</tbody>
</table>

(Time-8 h, Temperature- 80 °C solvent: Anisole 50 % w/v w.r.t. monomer)

a- \([M]:[I]:[Cu]:[L] = [\text{Monomer}]:[\text{Initiator}]:[\text{CuBr}]:[\text{PMDETA}]\)
b- Gravimetry
c- Mol. wt. monomer x \([\text{M}] / [I_0]\) x % conv. + mol. wt. initiator (500)
d- PMMA standard
e- \(I_{\text{eff}} = M_{n,\text{theo}}/M_{n,NMR}\)

Different ratios of \([M_0] / [I_0]\) with same reaction interval were chosen so as to obtain polymers with different molecular weights. The conversions were determined by gravimetric analysis. The reaction conversions were kept low (32 – 74%) so as to avoid potential side reactions involving allyloxy groups. Molecular weights of poly (methyl methacrylate)s (\(M_{n,NMR}\): 9000-21500) were in close agreement to the molecular weights calculated from the monomer-to-
initiator ratio. In addition, GPC data revealed PDI values in the range 1.23-1.34 for poly (methyl methacrylate).

Table 4b. 2: Reaction conditions and results for synthesis of α, α'- bis-allyloxy functionalized polystyrenes

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th><em>a</em>[M]₀: [I] : [Cu]: [L]</th>
<th><em>b</em>Conv. (%</th>
<th><em>c</em>Mₙ,theo</th>
<th><em>d</em>Mₙ,NMR</th>
<th><em>e</em>Mₙ,GPC</th>
<th><em>f</em>Mₙ/Mₙ</th>
<th><em>g</em>Eff</th>
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<td>13600</td>
<td>1.09</td>
<td>0.83</td>
</tr>
<tr>
<td>2</td>
<td>300:1:1:1</td>
<td>61</td>
<td>18800</td>
<td>19800</td>
<td>16990</td>
<td>1.06</td>
<td>0.94</td>
</tr>
<tr>
<td>3</td>
<td>500:1:1:1</td>
<td>51</td>
<td>26000</td>
<td>29600</td>
<td>28300</td>
<td>1.07</td>
<td>0.87</td>
</tr>
</tbody>
</table>

(Time – 8 h, Temperature-110 °C in bulk)

a- [M]:[I]:[Cu]:[L] = [Monomer]:[Initiator]:[CuBr]:[PMDETA]
b- Gravimetry
c- Mol. wt. monomer x [Mo] / [I₀] x % conv. + mol. wt. initiator (500)
d- PS standard
e- $I_{eff} = \frac{M_{n,theo}}{M_{n,NMR}}$

Different ratios of [M₀] / [I₀] with same reaction interval were chosen so as to obtain polymers with different range of molecular weights. The conversions were determined by gravimetric analysis. The reaction conversions were kept low (51–68%) so as to avoid potential side reactions involving allyloxy groups. Molecular weights of polystyrenes ($M_{n,NMR}: 11100-29600$) were in close agreement to the molecular weights calculated from the monomer-to-initiator ratio. In addition, GPC trace (Figure 4b.3) revealed monomodal distribution with PDI values in the range 1.07-1.09 for polystyrene. The PDIs were relatively narrow, which is in good agreement with a controlled polymerization method.
Figure 4b.3 GPC trace of α, α’-bis-allyloxy functionalized polystyrene

A kinetic study was performed to verify the control over the polymerization of styrene. The linearity of plot of ln (M₀/Mₜ) vs polymerization time, (Figure 4b.4) where M₀ and Mₜ are initial and the actual monomer concentration indicated the pseudo first order kinetics.

Figure 4b.4: Relationships between ln ([M₀]/[Mₜ]) and the polymerization time for ATRP of styrene at 110 °C in bulk

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 1.4 (Figure 4b.5) represents an additional indication for a controlled polymerization mechanism.

Figure 4b.5: Dependence of number-average molecular weight and PDI on monomer conversion for ATRP of styrene at 110 °C in bulk
These results are consistent with the results previously reported using allyl group containing ATRP initiators\textsuperscript{64,65}. \textsuperscript{1}H-NMR spectra of $\alpha, \alpha'$-bis-allyloxy functionalized poly (methyl methacrylate) and polystyrene are reproduced in Figure \ref{fig:nmr-a} and Figure \ref{fig:nmr-b}, respectively.

Figure \ref{fig:nmr-a}: \textsuperscript{1}H-NMR spectrum of $\alpha, \alpha'$-bisallyloxy functionalized poly(methyl methacrylate) in CDCl$_3$

Figure \ref{fig:nmr-b}: \textsuperscript{1}H-NMR spectrum of $\alpha, \alpha'$-bisallyloxy functionalized polystyrene in CDCl$_3$
The appearance of multiplets in the range 6.09-5.95 ppm and 5.43-5.23 ppm confirmed the presence of allyloxy functionality. Molecular weights can be calculated for bis-allyloxy functionalized polystyrene and poly (methyl methacrylate) by $^1$H-NMR spectroscopy. $M_{n,NMR}$ of poly (methyl methacrylate) was calculated by comparing integrated intensity of peak belonging to -OCH$_3$ in PMMA at 3.58 ppm to a multiplet in the range 6.09-5.95 ppm corresponding to allyloxy functionality.

$$Dpn = \left[ \frac{I_{3.58}}{3} \right] \left( \frac{I_{5.95} (allyloxy proton)}{2} \right)$$

Molecular weights were calculated using the equation,

$$M_{n,NMR} = [Dpn x 100 \text{ (mol. wt. of monomer)}] + 500 \text{ (mol. wt. of initiator)}$$

$M_{n,NMR}$ of allyloxy-functionalized PS was calculated by comparing integrals of phenyl ring protons with methylene protons attached to ether linkage.

$$Dpn = \left[ \frac{I_{7.05-6.39}}{5} \right] \left( \frac{I_{5.97} (allyloxy proton)}{2} \right)$$

Molecular weights were calculated using the equation,

$$M_{n,NMR} = [Dpn x 104 \text{ (mol. wt. of monomer)}] + 500 \text{ (mol. wt. of initiator)}$$

Molecular weights calculated by $^1$H-NMR spectroscopy ($M_{n,NMR}$) were in reasonably good agreement with theoretical molecular weights ($M_{n, \text{theo}}$) indicating good initiator efficiency ($I_{\text{eff}} = 0.83-0.94$).

Thus, 4, 4’-bis (4-(allyloxy) phenyl) pentyl 2-bromo-2-methylpropanoate was found to be useful ATRP initiator for controlled polymerization of methyl methacrylate and styrene under specified conditions.

4b.3.1.1. Chemical modification

4b.3.1.1.1. Reaction of α, α’- bisallyloxy functionalized polystyrene with bromine and triethylsilane

In order to illustrate the reactivity of allyloxy functionality, the organic reactions of allyloxy group such as addition of bromine and hydrosilylation were studied on polystyrene (Scheme 4b.6). α, α’- Bis-allyloxy functionalized polystyrene was treated with bromine in order to study general and simple diagnostic reaction for unsaturation.
Scheme 4b.6: Reactions of \( \alpha, \alpha' \)-bisallyloxy functionalized polystyrene

The brominated product was characterized by \(^1\)H-NMR spectroscopy (Figure 4b.8 B). \(^1\)H-NMR spectrum revealed complete disappearance of the signal corresponding to allyloxy functionality (6.09-5.95 and 5.43-5.23 ppm) confirming the completion of reaction. Furthermore, hydrosilylation reaction using triethylsilane was carried out on bis-allyloxy functionalized polystyrene in the presence of chloroplatinic acid monohydrate as a catalyst. The reaction product was characterized by \(^1\)H-NMR spectrum (Figure 4b.8D) in which total disappearance of the peaks corresponding to allyloxy protons in the range 6.09-5.95 and 5.43-5.23 ppm indicated completion of reaction.

Figure 4b.8: \(^1\)H-NMR spectra of A) bis-allyloxy functionalized polystyrene B) polystyrene after bromination C) bis-epoxide functionalized polystyrene in CDCl\(_3\) D) hydrosilylation product of bis-allyloxy functionalized polystyrene in CDCl\(_3\) without TMS
Chapter 4b: End-Functionalized Polymers by ATRP: Synthesis

The model hydrosilylation study with triethylsilane opens up further detailed investigation of hydrosilylation reaction with mono- and di-hydride-terminated polydimethylsiloxane to yield Y-shaped miktoarm copolymer PS-b-(PDMS)$_2$ and PDMS -g- PS, respectively.

4b.3.1.1.2. Transformation of $\alpha, \alpha'$-bisallyloxy functionalized polystyrene into $\alpha, \alpha'$-bis-epoxy functionalized polystyrene

Epoxidation of bis-allyloxy functionalized polystyrene with 3-chloroperoxybenzoic acid as an oxidant was carried out (Scheme 4b.7). The epoxidised product was characterized by $^1$H-NMR spectroscopy (Figure 4b.8 C). The complete disappearance of the resonances corresponding to allyloxy group protons and the appearance of new signals corresponding to oxirane ring protons at 3.15-3.13, 2.74-2.70 and 2.59-2.50 ppm indicated complete conversion of bis-allyloxy into bis-epoxy functionalized polystyrene.

![Scheme 4b.7 Chemical transformation of $\alpha, \alpha'$-bis-allyloxy functionalized polystyrene into $\alpha, \alpha'$-bis-epoxy functionalized polystyrene](image)

4b.3.2. Synthesis of $\alpha, \alpha'$-bis-aldehyde functionalized polystyrenes

ATRP of styrene in bulk was carried out using 4, 4'-bis (4-(4- (formylphenoxy) phenyl)pentyl 2-bromopropanoate as an initiator Scheme 4b.8

![Scheme 4b.8: Synthesis of $\alpha, \alpha'$-bis-aldehyde functionalized polystyrenes](image)

The conditions and results of synthesis of $\alpha, \alpha'$-bisaldehyde functionalized polystyrene are summarized in Table 4b.3.
Table 4b.3: Reaction conditions and results for synthesis of \( \alpha, \alpha' \)-bis-aldehyde functionalized polystyrenes

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>([M]:[I]:[Cu]:[L])</th>
<th>Time (h)</th>
<th>Conv (%)</th>
<th>(M_{n,\text{theo}})</th>
<th>(M_{n,\text{NMR}})</th>
<th>(M_{w}/M_n)</th>
<th>(I_{\text{eff}})</th>
</tr>
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<td>3100</td>
<td>1.16</td>
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</tr>
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<td>9700</td>
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<td>3</td>
<td>225:1:1:1</td>
<td>8</td>
<td>76</td>
<td>18400</td>
<td>21500</td>
<td>1.11</td>
<td>0.85</td>
</tr>
</tbody>
</table>

(Temperature-110 °C in bulk)

a- \([M]:[I]:[Cu]:[L] = \text{[Monomer]}:[\text{Initiator]}:[\text{CuBr}]:[\text{PMDETA}]\)

b- Gravimetry

c- \[\text{Mol. wt. of monomer} \times \text{[M]}_0 \times (\% \text{ conv.}) + \text{mol. wt. initiator} (614) \times \text{[I]}_0\]

d- Polystyrene standard,

e- \(I_{\text{eff}} = \frac{M_{n,\text{theo}}}{M_{n,\text{NMR}}}\)

Different ratios of \([M_0]/[I_0] \) with same reaction interval were chosen so as to obtain polymers with a range of molecular weights combined with convenient polydispersity. The conversions were determined by gravimetric analysis. \(^1\text{H}-\text{NMR} \) spectrum of bis-aldehyde functionalized polystyrene is reproduced in Figure 4b.9. The appearance of a singlet at 9.85 ppm confirmed the presence of aldehyde functionality.
Integration of signals for aldehyde functionality and comparison with the integration values for phenyl ring protons in polystyrene allows molecular weight to be determined. The degree of polymerization was calculated from NMR analysis using the relation,

$$Dpn = \frac{(I_{7.01-6.50}/5)}{I_{9.85}/2 \text{ (aldehyde proton)}}$$

Where $I_{7.01-6.50}$ corresponds to integration of phenyl ring protons of polystyrene chain. The contribution of aromatic ring protons from initiator fragment was subtracted from the total integration of the peaks appearing in the range 7.01-6.50 ppm. $I_{9.85}$ represents integration of the signal positioned at 9.85 ppm corresponding to aldehyde protons.

Molecular weights were calculated by using equation,

$$M_{n,\text{NMR}} = [Dpn \times 104 \text{ (Mol. Wt. of monomer)}] + 614 \text{ (Mol. Wt. of initiator)}$$

Molecular weights determined by $^1$H-NMR spectroscopy ($M_{n,\text{NMR}}$) were in reasonably good agreement with theoretical molecular weights ($M_{n,\text{theo}}$) (Table 4b.3) indicating good initiator efficiency ($I_{\text{eff}} = 0.85-0.93$). In addition, GPC trace revealed monomodal distribution with PDI values in the range 1.11-1.16 for polystyrene. The PDI values 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 styrene. The linearity of plot of \( \ln \left( \frac{M_0}{M_t} \right) \) vs polymerization time, (Figure 4b.10) where \( M_0 \) and \( M_t \) are initial and the actual monomer concentration indicated the pseudo first order kinetics.

![Figure 4b.10: Relationship between \( \ln \left( \frac{[M_0]}{[M_t]} \right) \) and the polymerization time for ATRP of styrene at 110 °C in bulk](image)

The concentration of radicals remained constant during the polymerization reaction and therefore it can be concluded that no side reactions occurred during polymerization. The linear increase of molecular weight with conversion and PDI below 1.3 (Figure 4b.11) represents an additional indication for a controlled polymerization mechanism.

![Figure 4b.11: Dependence of number-average molecular weight and PDI on monomer conversion for ATRP of styrene at 110 °C in bulk](image)

Thus, 4, 4'-bis (4-(4- (formyl phenoxy) phenyl) pentyl 2-bromopropanoate was found to be useful ATRP initiator for controlled polymerization of styrene under specified conditions.

4b.3.3. Synthesis of \( \alpha, \alpha' \)-bis-propargyloxy functionalized poly (methyl methacrylate)

ATRP of methyl methacrylate in anisole was carried out using 4, 4'-bis (4-(prop-2-yn-1-yloxy)phenyl)pentyl 2-bromo-2-methylpropanoate as an initiator (Scheme 4b.9).
Scheme 4b.9: Synthesis of $\alpha$, $\alpha'$-bis-propargyloxy functionalized poly (methyl methacrylate)s

The conditions and results of synthesis of $\alpha$, $\alpha'$-bis-propargyloxy functionalized poly (methyl methacrylate)s are summarized in Table 4b.4

Table 4b.4: Reaction conditions and results for synthesis of $\alpha$, $\alpha'$-bis-propargyloxy functionalized poly (methyl methacrylate)

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>$^a[M]$:[I]:[Cu]:[L]</th>
<th>Time (h)</th>
<th>$^b$Conv (%)</th>
<th>$^c$M_n,tho</th>
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<td>7600</td>
<td>1.59</td>
</tr>
<tr>
<td>2</td>
<td>[140]:[1]:[1]:[1]</td>
<td>6</td>
<td>73</td>
<td>10700</td>
<td>15700</td>
<td>25800</td>
<td>1.50</td>
</tr>
<tr>
<td>3</td>
<td>[210]:[1]:[1]:[1]</td>
<td>9</td>
<td>66</td>
<td>14400</td>
<td>22300</td>
<td>32900</td>
<td>1.46</td>
</tr>
</tbody>
</table>

(Temperature-80 °C solvent: Anisole (50%, w/v w.r.t monomer))

- $^a[M]$:[I]:[Cu]:[L] = [Monomer]:[Initiator]:[CuBr]:[PMDETA]
- $^b$Gravimetry
- $^c[M]_0$ x [% conv.] + mol. wt. initiator (496)
- $^d$Polystyrene standard
- $^e$I_eff = M_n,tho/M_n,NMR

Different ratios of $[M_0]$ / $[I_0]$ with different reaction interval were chosen so as to obtain polymers with different molecular weights. The conversions were determined by gravimetric analysis. $^1$H-NMR spectrum of $\alpha$, $\alpha'$-bis-propargyloxy functionalized poly (methyl methacrylate) is reproduced in Figure 4b.12.
Figure 4b.12: \( ^1H\)-NMR spectra of A) 4,4-bis(4-(prop-2-yn-1-yloxy)phenyl)pentyl 2-bromo2-methylpropanoate B) \( \alpha, \alpha' \)-bis-propargyloxy functionalized poly(methyl methacrylate) in CDCl\(_3\)

The appearance of a triplet at 2.52 ppm confirmed the presence of propargyloxy functionality. It was presumed that two propargyloxy groups are present per polymer chain. Integration of signals for propargyloxy functionality and comparison with the integration values for methoxy protons in poly (methyl methacrylate) allows the molecular weight to be determined. The degree of polymerization was calculated from NMR analysis using the relation,

\[
D_p = \frac{(I_{3.58}/3)}{(I_{2.52}(\text{acetylene proton})/2)}
\]

Where \( I_{3.58} \) corresponds to integration of methoxy protons of poly (methyl methacrylate). \( I_{2.52} \) represents integration of the signal positioned at 2.52 ppm corresponding to acetylene protons.

Molecular weights were calculated using equation,

\[
M_{n,NMR} = [D_p \times 100 \text{ (mol. wt. of monomer)}] + 496 \text{ (mol. wt. of initiator)}
\]

It was observed that molecular weights determined by \(^1\)H-NMR spectroscopy (\( M_{n,NMR} \)) were higher than theoretical molecular weights (\( M_{n,\text{theo}} \)) indicating lower initiator efficiency (\( I_{\text{eff}} = 0.64-0.68 \)). In addition, GPC trace revealed broad distribution with PDI values in the range 1.46-1.59 for poly (methyl methacrylate). The PDIs were relatively on higher side, which indicated some deviation from characteristic behavior of a controlled radical polymerization method. A kinetic study was performed to verify the control over the polymerization of methyl methacrylate. The
plot of \( \ln \left( \frac{M_0}{M_t} \right) \) vs polymerization time, (Figure 4b.13) where \( M_0 \) and \( M_t \) are initial and the actual monomer concentration indicated deviation from linearity and hence, the deviation from pseudo first order kinetics.

**Figure 4b.13: Relationship between \( \ln \left( \frac{[M_0]}{[M_t]} \right) \) and the polymerization time for ATRP of methyl methacrylate at 80 °C in anisole**

The concentration of radicals may vary during the polymerization reaction and therefore it can be concluded that some sort of side reactions involving propargyloxy functionality occurred during polymerization. However, no efforts were made to probe the nature of such side reactions. The linear increase of molecular weight with increasing conversion and PDI above 1.4 (Figure 4b.14) represents an additional point to substantiate the occurrence of side reaction during polymerization. This could be attributed to the complexation of copper catalyst with alkyne functionality.

**Figure 4b.14: Dependence of number-average molecular weight and PDI on monomer conversion for ATRP of methyl methacrylate at 80 °C in anisole**

4b.3.4. **Synthesis of \( a, a'-\)bis-azido functionalized poly (methyl methacrylate)**

ATRP initiators containing azido functional group(s) have been successfully employed for synthesis of corresponding azido-terminated polymers under carefully designed conditions.
Care needs to be taken in selecting the reaction conditions as azido groups are known to be thermally labile and shock sensitive. Furthermore, depending on the initiator structure there is a possibility of participation of azido group in intramolecular cyclisation reaction.

ATRP of methyl methacrylate was carried out in anisole using 4, 4’-bis (4-(2-azidoethoxy) phenyl) penty 2-bromopropanoate as the initiator (Scheme 4b.10).

Scheme 4b.10: Synthesis of $\alpha$, $\alpha'$- bis-azido functionalized poly (methyl methacrylate)

The conditions and results of synthesis of $\alpha$, $\alpha'$-bis-azido functionalized poly (methyl methacrylate)s are summarized in Table 4b.5

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>$^[M]_0$: [I]: [Cu]: [L]</th>
<th>Time (h)</th>
<th>$^b$ Conv (%)</th>
<th>$^c M_{n,\text{theo}}$</th>
<th>$^d M_{n,\text{GPC}}$</th>
<th>$^e M_w/M_n$</th>
<th>$^e I_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>80:1:1:1</td>
<td>3</td>
<td>66</td>
<td>5800</td>
<td>7500</td>
<td>8200</td>
<td>1.24</td>
</tr>
<tr>
<td>2</td>
<td>160:1:1:1</td>
<td>7</td>
<td>62</td>
<td>10500</td>
<td>12600</td>
<td>17600</td>
<td>1.28</td>
</tr>
<tr>
<td>3</td>
<td>240:1:1:1</td>
<td>9</td>
<td>59</td>
<td>14700</td>
<td>18700</td>
<td>26000</td>
<td>1.17</td>
</tr>
</tbody>
</table>

(Temperature-80 °C Solvent: Anisole (50%, w/v w.r.t monomer))

a- $^[M]:[I]:[Cu]:[L] = [\text{Monomer}]:[\text{Initiator}]:[\text{CuBr}]:[\text{PMDETA}]$

b- Gravimetry

c- $[\text{Mol. wt. of monomer } [M]_0 \times (\% \text{ conv.})] + \text{mol. wt. initiator (558)}$

d- Polystyrene standard,

e- $I_{\text{eff}} = M_{n,\text{theo}}/M_{n,\text{NMR}}$
Different ratios of \([M_0] / [I_0]\) with different reaction intervals were chosen so as to obtain polymers with different molecular weights. The conversions were determined by gravimetric analysis. \(^1\)H-NMR spectrum of \(\alpha, \alpha'-\)bis-azido functionalized poly (methyl methacrylate) is reproduced in Figure. 4b.15. Integration of signals for aromatic functionality and comparison with the integration values for methoxy protons in poly (methyl methacrylate) allows the molecular weight to be determined. The degree of polymerization was calculated from NMR analysis using the relation,

\[
D_{pn} = \left\{ \frac{I_{3.58}}{I_{7.09}} \right\}^{4/4}_{3/3} \text{ (aromatic proton)}
\]

Where \(I_{3.58}\) and \(I_{7.09}\) are integrals of the signals positioned at 3.58 corresponds to methoxy protons of poly (methyl methacrylate) and 7.09 ppm for aromatic protons, respectively.

Molecular weights were calculated by \(^1\)H-NMR spectroscopy using equation,

\[
M_{n,NMR} = [D_{pn} \times 100 \text{ (mol. wt. of monomer)}] + \text{mol. wt. initiator} (558)
\]

Figure 4b. 15: \(^1\)H-NMR spectra of A) 4,4'-bis(4-(2-azidoethoxy)phenyl)penty1 2- bromopropanoate and B) \(\alpha, \alpha'-\)bis-azido functionalized poly (methyl methacrylate) in CDCl\(_3\)

Molecular weights determined by \(^1\)H-NMR spectroscopy \((M_{n,NMR})\) were in reasonably good agreement with theoretical molecular weights \((M_{n,\text{theo}})\) indicating good initiator efficiency \((I_{\text{eff}} = 0.77-0.83)\). In addition, GPC study revealed monomodal distribution with PDI values in the range
1.17-1.28 for poly (methyl methacrylate). 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 \( \ln (M_0/M) \) vs polymerization time, (Figure 4b.16)

![Figure 4b. 16: Relationship between \( \ln ([M_0] / [M]) \) and the polymerization time for ATRP of methyl methacrylate at 80 °C in anisole](image)

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 1.3 (Figure 4b. 17) represents an additional indication for a controlled polymerization mechanism.

![Figure 4b. 17: Dependence of number-average molecular weight and PDI on monomer conversion for ATRP of methyl methacrylate at 80 °C in anisole](image)

Thus, 4, 4’-bis (4-(2-azidoethoxy) phenyl) pentyl 2-bromopropanoate was found to be a useful ATRP initiator for controlled polymerization of methyl methacrylate under the specified reaction conditions.
4b.3.4.1. Chemical modification of α, α’-bis-azido functionalized poly (methyl methacrylate)

4b.3.4.1.1. Azide-alkyne click reaction of α, α’-bis-azido functionalized poly (methyl methacrylate) with phenyl acetylene

The reactivity of α, α’-azido functionality on poly (methyl methacrylate) was illustrated by carrying out click reaction with phenyl acetylene (Scheme 4b.11).

Scheme 4b.11: Post-functionalization of α, α’-bis-azido functionalized poly (methyl methacrylate) by azide-alkyne click reaction

In FT-IR spectrum, characteristic peak corresponding to azido functionality disappeared while the peak corresponding to carbonyl group of poly (methyl methacrylate) was retained at 1730 cm⁻¹ confirming completion of the coupling reaction. The coupling reaction was characterized by ¹H-NMR spectroscopy (Figure 4b.18). In addition to the peaks corresponding to aromatic protons, a characteristic peak corresponding to triazole ring was observed at 7.94 ppm.

Figure 4b.18: ¹H-NMR spectra of A) α, α’-bis-azido functionalized poly (methyl methacrylate) and B) product of the reaction of α, α’-bis-azido functionalized poly (methyl methacrylate) with phenyl acetylene in CDCl₃
4b.3.5. 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 4b.12).

![Scheme 4b. 12: Synthesis of α-aldehyde α′-allyloxy hetero bifunctionalized poly (methyl methacrylate)s](image)

The conditions and results of synthesis of α-aldehyde α′-allyloxy hetero bifunctionalized poly (methyl methacrylate)s are summarized in Table 4b.6

**Table 4b.6: Reaction conditions and results of synthesis of α-aldehyde α′-allyloxy hetero bifunctionalized poly (methyl methacrylate)s**

<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>a[M]₀/[I]₀</th>
<th>Time (h)</th>
<th>bConv. (%)</th>
<th>cMₙ theo</th>
<th>dMₙ,NMR</th>
<th>eMₙ,GPC</th>
<th>M_w/M_n</th>
<th>I eff</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50:1</td>
<td>3</td>
<td>55</td>
<td>3300</td>
<td>3700</td>
<td>5300</td>
<td>1.21</td>
<td>0.89</td>
</tr>
<tr>
<td>2</td>
<td>100:1</td>
<td>5</td>
<td>60</td>
<td>6600</td>
<td>7800</td>
<td>12100</td>
<td>1.25</td>
<td>0.84</td>
</tr>
<tr>
<td>3</td>
<td>200:1</td>
<td>8</td>
<td>67</td>
<td>14000</td>
<td>19700</td>
<td>28800</td>
<td>1.19</td>
<td>0.71</td>
</tr>
</tbody>
</table>

(Temperature-80 °C, Solvent: Anisole (50%, w/v w.r.t monomer))

- a- [M]₀ / [I]₀: [Monomer]:[Initiator]
- b- Gravimetry
- c- \( M_{n,\text{th}} = \frac{[M]₀ x (\%) \text{Conv.} \times \text{mol. wt. of monomer}}{[I]₀} + \text{mol. wt. initiator (565)} \)
- d- \( M_{n,NMR} \) Determined from NMR
- e- \( M_{n,GPC} \) Determined from GPC; Polystyrene standard; CHCl₃ eluent

Different ratios of \([M]₀ / [I]₀\) with different reaction interval were chosen so as to obtain polymers with range of molecular weights. The conversions were determined by gravimetric analysis. The reaction conversions were kept in the range 55 – 67% in order to ensure avoidance...
of potential side reactions related to allyloxy functional group. $^1$H-NMR spectrum of α-aldehyde, α'-allyloxy functionalized poly (methyl methacrylate) is reproduced in Figure 4b.19. The appearance of a singlet at 9.93 ppm confirmed the presence of aldehyde functionality. The appearance of multiplets in the range 6.14-6.00 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.

Figure 4b. 19: $^1$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 hetero bifunctionalized poly (methyl methacrylate) in CDCl₃

The degree of polymerization was calculated from NMR analysis using the relation,

$$D_{pn} = \frac{I_{3.58}}{I_{9.93}} \frac{3}{1} \text{ (aldehyde proton)}$$

Where $I_{3.58}$ and $I_{9.93}$ are integrals of the signals positioned at 3.58 corresponds to methoxy protons of poly (methyl methacrylate) and 9.93 ppm for aldehyde functionality, respectively.

Molecular weights were calculated by $^1$H-NMR spectroscopy using equation,

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

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 ($I_{eff} = \ldots$)
0.71-0.89). In addition, GPC trace revealed monomodal distribution with PDI values in the range 1.19-1.25 for poly (methyl methacrylate). 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 styrene. The linearity of plot of ln (M₀/Mₜ) vs polymerization time (Figure 4b.20)

![Figure 4b.20: Relationship between ln ([M₀] / [Mₜ]) and the polymerization time for ATRP of methyl methacrylate at 80 °C in anisole](image)

where M₀ and Mₜ 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 (Figure 4b. 21) represents an additional indication for a controlled polymerization mechanism.

![Figure 4b. 21: Dependence of number-average molecular weight and PDI on monomer conversion for ATRP of methyl methacrylate at 80 °C in anisole](image)

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 under specified conditions.
4b.3.5.1. Chemical modification of α-aldehyde α’-allyloxy hetero bifunctionalized poly (methyl methacrylate)s

4b.3.5.1.1. Aldehyde-aminooxy click reaction of α-aldehyde α’-allyloxy hetero bifunctionalized poly (methyl methacrylate) with O-(2-azidoethyl) hydroxylamine

The reactivity of aldehyde functionality was illustrated by carrying out click reaction with O-(2-azidoethyl) hydroxylamine at room temperature (Scheme 4b.13).

Scheme 4b. 13: Post-functionalization of α-aldehyde α’-allyloxy hetero bifunctionalized poly (methyl methacrylate) by A) aldehyde-aminooxy click reaction

B) thiol-ene click reaction

In FT-IR spectrum, in addition to the peak corresponding to poly (methyl methacrylate) at 1730 cm⁻¹, characteristic peak corresponding to azido functionality appeared at 2110 cm⁻¹ confirming formation of oxime by the coupling reaction. Figure 4b.22 represents ¹H-NMR spectra of aldehyde terminated poly (methyl methacrylate) (Mₙ,NMR: 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 at 8.11 ppm (-CH=N-O) which elucidates oxime formation without affecting peaks related to poly (methyl methacrylate) attesting completion of the reaction without any side reaction such as degradation of poly (methyl methacrylate) backbone.
The model aldehyde-amine click reaction study with O-(2-azidoethyl) hydroxylamine introduces azido moiety on poly (methyl methacrylate) chain which further opens up plethora of opportunities to introduce different types of functional groups on poly (methyl methacrylate) by well known azide-alkyne click reaction.

4b.3.5.1.2 Thiol-ene click reaction of α-allyloxy, α’-azido heterobifunctionalized poly (methyl methacrylate)

The reactivity of allyloxy functionality was illustrated by carrying out click reaction with 3-mercaptopropionic acid on poly (methyl methacrylate) in presence of AIBN at 110 °C in chlorobenzene as a solvent (Scheme 4b.13). The conversion was assessed by 1H-NMR spectroscopy. 1H-NMR spectra of allyloxy functionalized poly (methyl methacrylate) (Mn,NMR: 3700) and its click reaction product with 3-mercaptopropionic acid is shown in Figure 4b.23.
Figure 4b. 23: $^1$H-NMR spectra of A) $\alpha$-allyloxy, $\alpha'$-azido hetero bifunctionalized poly(methyl methacrylate) and B) the product of thiol-ene click reaction in CDCl$_3$

From $^1$H-NMR spectrum, it is observed that the peak corresponding to allyloxy functionality disappeared completely and appearance of new peaks at 2.79, 2.75, 2.69 ppm indicated addition of thiol without any side reaction such as degradation of poly (methyl methacrylate) backbone.
4b.4. Conclusions

- Homogeneous and \( \alpha, \alpha' \)-hetero bifunctionalized polystyrenes and poly (methyl methacrylate)s having different molecular weights were synthesized using appropriate ATRP initiators.
  1) \( \alpha, \alpha' \)-Bis allyloxy-terminated polystyrenes and poly (methyl methacrylate)s were synthesized by ATRP using 4,4'-bis(4-(allyloxy) phenyl)pentyl 2-bromo-2-methylpropanoate as the initiator and reactivity of allyloxy functionality was demonstrated by carrying out bromination, epoxidation and hydrosilylation reaction.
  2) \( \alpha, \alpha' \)-Bis-aldehyde terminated polystyrenes were synthesized by ATRP using 4,4'-bis(4-(4-formylphenoxy)phenyl)pentyl 2-bromopropanoate as the initiator.
  3) 4, 4'-Bis (4-(prop-2-yn-1-ylxy) phenyl)pentyl 2-bromo-2-methylpropanoate was studied as the ATRP initiator for polymerization of methyl methacrylate which resulted into poor control over molecular weight and broader molecular weight distribution of PMMA.
  4) \( \alpha, \alpha' \)-Bisazido terminated poly (methyl methacrylate)s were synthesized by ATRP using 4,4'-bis(4-(2-azidoethoxy) phenyl) pentyl 2-bromopropanoate as the initiator and the reactivity azido functionality was demonstrated by carrying out azido-propargyl click reaction with phenyl acetylene.
  5) \( \alpha \)-Aldehyde,\( \alpha' \)-allyloxy hetero bifunctionalized poly (methyl methacrylate)s were synthesized using 4-(4-(allyloxy) phenyl)-4-(4-(4-formylphenoxy) phenyl) pentyl 2-bromo-2-methyl propanoate as the ATRP initiator and the reactivity aldehyde and allyloxy functionality was demonstrated by carrying out aldehyde-aminooxy and thiol-ene click reactions, respectively.

- Polystyrenes and poly (methyl methacrylate)s possessing clickable end functional groups represent valuable precursors for synthesis of Y-shaped miktoarm star copolymers.
References