THERMALLY CLEAVABLE MULTIARM and MIKTOARM STAR POLYMERS via DIELS-ALDER / RETRO DIELS-ALDER STRATEGY

by

Oyuntuya Munkhbat

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APPROVED BY:

Assoc. Prof. Amitav Sanyal ……...
(Thesis Supervisor)

Prof. İlknur Doğan ……

Assoc. Prof. Metin Tulu ……

DATE OF APPROVAL: …….

To my family

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LIST OF SYMBOLS/ABBREVIATIONS

J	Coupling constant
υ	Frequency

ATRP	Atom transfer radical polymerization
CCS	Core crosslinked
$CDCl_3$	Deuterated chloroform
CH_2Cl_2	Dichloromethane
D	Dendron
DA	Diels Alder reaction
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DMAP	Dimethylamino pyridine
DVB	Divinylbenzene
G	Generation
GPC	Gel Permeation Chromotography
In	Initiator
L-LA	L-lactide
MeOH	Methanol
MHz	Mega hertz
MMA	Methylmetacrylate
P	Polymer
PLA	Polylactide
PMMA	Polymethyl methacrylate
PS	Polystyrene
rDA	Retro Diels-Alder
ROP	Ring Opening Polymerization
TEA	Triethylamine
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
TU	Thiourea

ABSTRACT

THERMALLY CLEAVABLE MULTIARM and MIKTOARM STAR POLYMERS via DIELS-ALDER / RETRO DIELS-ALDER STRATEGY

Diels-Alder reaction is a well known [4+2] cycloaddition reaction between a diene and a dienophile. The fact that Diels-Alder reaction takes place even at room temperature without use of any other reagents and reverse reaction, retro Diels-Alder, occurs at elevated temperature makes this reaction a widely used method in synthesis of macromolecular chemistry. By using the thermoreversible feature of this reaction, thermally cleavable multiarm and miktoarm star polymers are synthesized.

Symmetrical and unsymmetrical multiarm star polymers containing thermoreversible furan-maleimide core have been synthesized by utilization of atom transfer radical polymerization (ATRP) of MMA using corresponding multiarm macroinitiators. Peripheries of dendritic macroinitiators contain multiple halogen groups which yield star shape upon polymerizaion. Thermal cleavge of the multiarm star polymers are achieved by the retro Diels-Alder reaction of furan-maleimide core at elavated temperature with the presence of maleimide group scavenger.

The second study involves the synthesis of thermally cleavable linear and star shaped miktoarm polymers based on unsymmetrically core functionalized initiators via Atom Transfer Radical Polymerization (ATRP) and Ring Opening Polymerization (ROP). Dendrons bearing maleimide groups in their core are furnished with initiators at end of their arms for polymerization of several methacrylates and lactides. Thermal cleavage of miktoarm polymers are achieved by the retro Diels-Alder reaction of furan-maleimide core at elavated temperature with the presence of maleimide group scavenger.

ÖZET

DİELS-ALDER / RETRO DİELS-ALDER STRATEJİ ile TERMAL OLARAK BÖLÜNEN ÇOK KOLLU VE FARKLI KOLLU POLİMERLER

Diels-Alder tepkimesi bir dien ve dienofil arasında gerçekleşen [4+2] halkasal katılım reaksiyonudur. Diels-Alder tepkimesinin, oda sıcaklığında, herhangi bir katalizör veya kimyasala ihtiyaç duymadan gerçekleşmesi ve ters tepkime olan retro Diels-Alder'in daha yüksek sıcaklıkta oluşması onu makromoleküler kimyada sıklıkla kullanılan bir metot haline getirmiştir. Bu reaksiyonun thermoreversible özelliğini kullanarak termal olarak bölünen çok kollu ve farklı kollu yıldız polimer sentezlenmiştir.

İlgili çok kollu başlatıcılar kullanılarak metil metakrilat (MMA) monomerlerin Atom Transfer Serbest Radikal Polimerleşme (ATRP) yöntemi ile thermoreversible furan-maleimid çekirdek içeren simetrik ve simetrik olmayan çok kollu star polimerler sentezlenmiştir. Dendritik makrobaşlatıcılar çevrelerindeki halojen gruplar sayesinde polimerler yıldız şekli alır. Çok kollu star polimerlerin termal bölünme maleimid grup koparıcı varlığı ile yüksek sıcaklığında furan-maleimid çekirdeğinin retro Diels-Alder reaksiyonu ile elde edilir.

İkinci çalışmada Atom Transfer Radikal Polimerizasyonu (ATRP) ve Halka Açılması Polimerizasyonu (ROP) kullanarak simetrik olmayan çekirdek fonksiyonlu başlatıcıya dayalı termal bölünebilir doğrusal ve yıldız şeklinde farklı kollu polimerlerin sentezlenmesi içerir. Çekirdeğinde maleimid grup taşıyan dendronlar birkaç metakrilatlar ve laktik asit polimerizasyonu için kollarının sonunda başlatanlarla döşenmiştir. Farklı kollu polimerlerin termal bölünme maleimid grup koparıcı varlığı ile yüksek sıcaklığında furan-maleimid çekirdeğin retro Diels-Alder reaksiyonu ile elde edilir.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1. INTRODUCTION

1.1. Diels-Alder Reaction

Diels-Alder reaction (DA) is a well known [4+2] cycloaddition reaction between electron rich diene and electron poor dienophile [1]. DA reaction results in a six membered ring formation with the generation of new bonds by inter- or intramolecular interactions. The product obtained is referred as an cycloadduct. Furan and anthracene derivatives have been widely explored as diene components in macromolecular construction. As the choice of dienophile, maleimides are mostly preferred due to their high reactivity and wide structural variability through the nature of the nitrogen substituents (Figure 1.1). Products of Diels-Adler reactions can be obtained in high yiels without formation of offensive by-products [2]. Diels-Alder reactions are effective modification reactions that are both tolerant towards other functional groups [3-4].

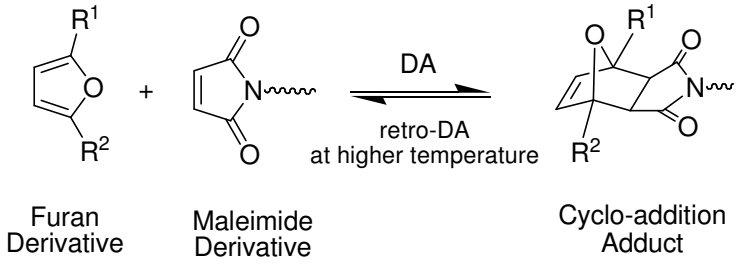

Figure 1.1. Representation of the DA and rDA reactions [2]

In addition to the advantages stated above, it is possible to shift reaction to the side of reactants simply by increasing the heat, a process known as “retro Diels-Alder reaction” (rDA) [5]. This property of Diels-Alder reaction can be used for the design of thermoreversible systems in polymer and material science. One of the pioneering work which shows the thermoreversible nature of DA was done by McGrath group. They have synthesized the thermally labile dendrimers based on the reversible furan-maleimide DA reaction. By studying the thermal degradation and reassembly of these dendrimers, they showed the thermoreversible capability of DA reaction [6].

1.1.1. Diels-Alder Reaction in Polymer and Macromolecular Chemistry

The reversibility of furan-maleimide DA reaction [7] has been shown to have utility in the production of thermally responsive systems including, segment block densrimers [8], simple linear polymers [9-10], cross-linking linear polymers [11], alternating copolymers [12], and multiarm star block copolymers [13]. As an example of segment block dendrimers, I propose a work published from our group in 2008 by Merve Kose and Gulen Yesilbag [8]. In this study, they synthesized segment block dendrimers by making use of Diels–Alder reaction (Figure 1.2). The proposed strategy not only allows synthesis of unsymmetrical dendrimers but also results in formation of thermo reversible structures. The methodology requires use of reaction conditions which is free of metal catalysts and hence provides products free of undesirable metal impurities.

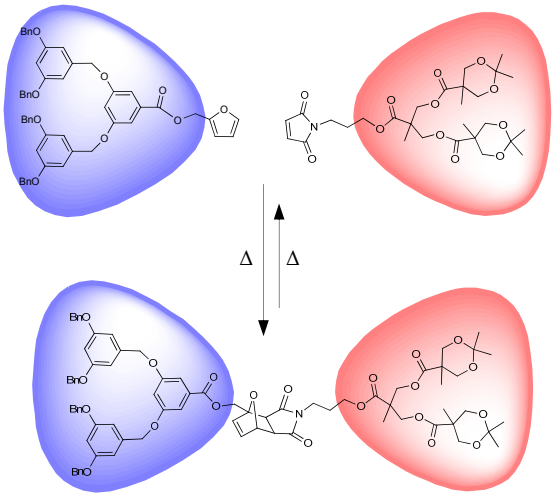

Figure 1.2. General representation of the strategy utilized [8]

In this research three generations of poly (aryl ether) dendrons functionalized with furan moieties at the core are reacted with maleimide functionalized acetal protected poly (ester) dendrons of the same generation via Diels-Alder cycloaddition to form desired unsymmetrical dendrimers in good yields. The thermoreversible nature of these macromolecules was investigated by subjecting them to elevated temperatures in the presence of anthracene as a scavenger diene.

1.1.2. The Use of Diels-Alder Reaction in Thermoreversible Polymers

DA is a reagent free thermoreversible reaction which can be readily utilized to make thermally responsive or thermoreversible scaffolds in polymer and macromolecular chemistry. After making thermoreversible symmetrical dendrimers based on DA reaction, McGrath group released new article which states the first example of linear covalent dendronized polymers with thermal reversibility [14].

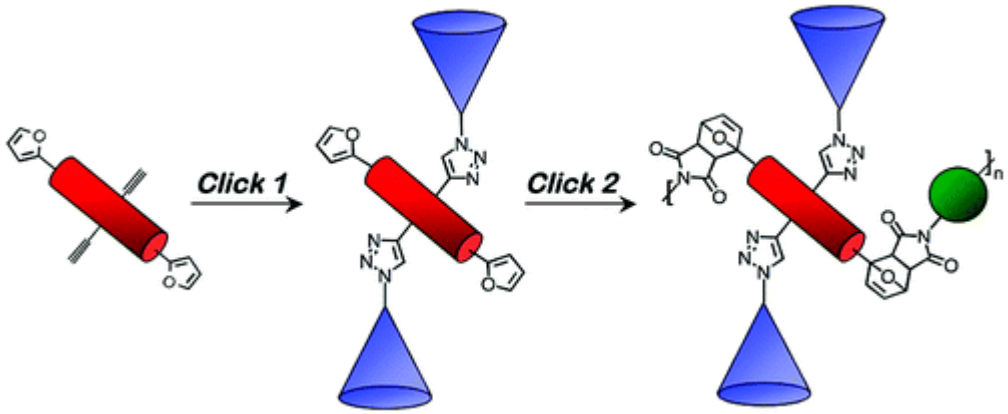

Figure 1.3. Synthesis of dendronized linear polymer [14]

In this work, they used 2 types of "click" reactions, Huisgen 1,3-dipolar cycloaddition reaction as "click 1" and DA cycloaddition as "click 2". Thermally labile dendronized AA-BB step polymers are described. First through third generation dendritic bisfuran monomers were prepared in part by the Cu(I)-catalyzed azide-alkyne Huisgen 1,3-dipolar cycloaddition reaction and in turn polymerized by the reversible furan-maleimide Diels-Alder reaction. Since the polymerization is achieved via DA reaction, these dendronized step polymers are able to disassemble and reassemble.

Haddleton and co-workers reported the synthesis of two bifunctional ATRP initiators bearing Diels–Alder adducts, one based on a furan–maleimide adduct and the other based on an anthracene–maleimide adduct, which were used for the synthesis of linear polymers of MMA. The presence of the Diels–Alder adduct in the middle of the polymer chains

allowed for their temperaturemodulated reversible cleavage. In particular, degradation was achieved by heating at high temperature, whereas bond healing was accomplished by heating at lower temperature [15].

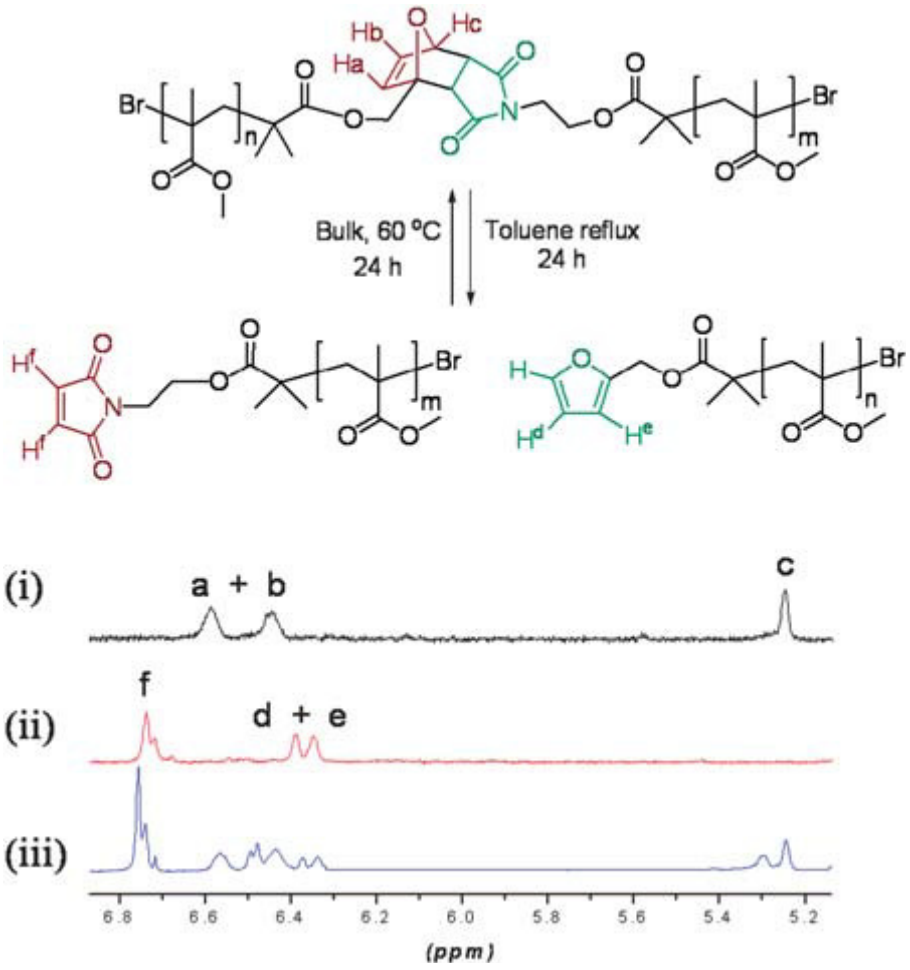

Figure 1.4. DA and rDA of self-healing linear polymer including ^{1}H NMR of original polymer (i) prior to heating, (ii) cleaved polymer following heating, and (iii) reformed polymer [15]

As an extention of this work, firstly they have preapared linear polymer bearing crosslinkable bromo units on it via Atom Transfer Radical Polymerization (ATRP). Then the polymer is crosslinked with divinyl crosslinker containing DA cycloadduct which can be thermally cleaved and reformed later.

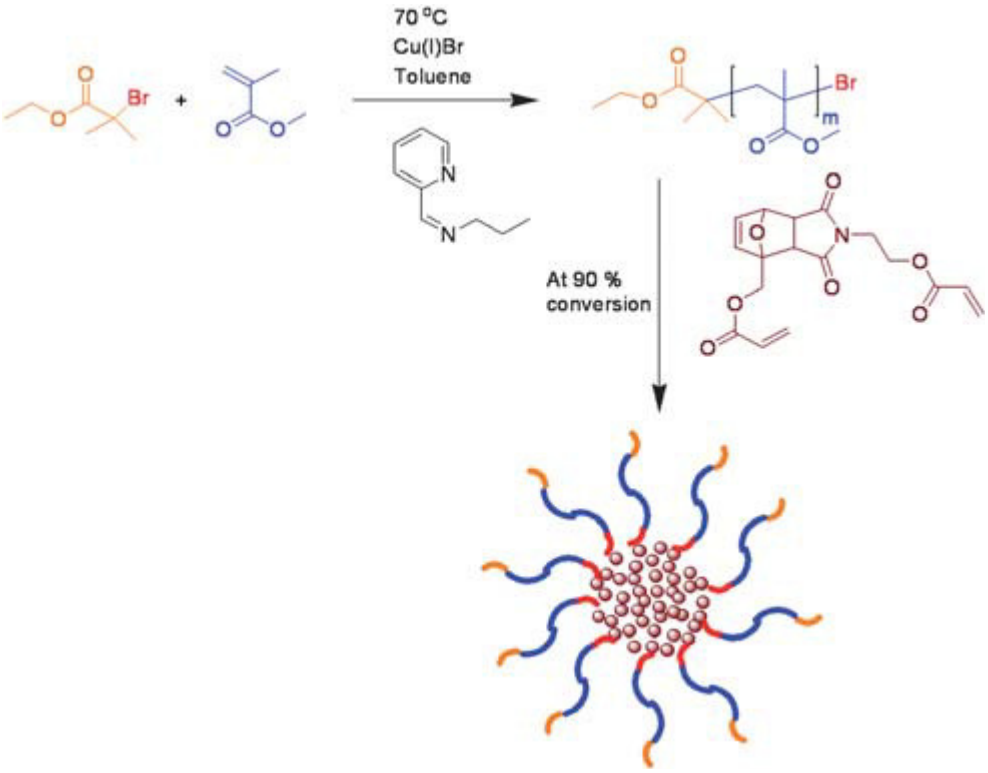

Figure 1.5. Synthesis of thermally reversible multiarm star polymer [15]

1.2. Dendrimers

Dendrimers, meaning treelike in Greec, are highly ordered, regularly branched globular macromolecules with well defined monodisperse architecture. It is synthesized with stepwise organic reactions resulting the structure mainly copmposed of three different units: a core, repeating units and surface groups (Figure 1.6) [16]. Symmetrically placed branching units around the core contribute to its uniform 3-D structure. The generation of dendrimer is defined as the number of branching units from the core to the periphery.

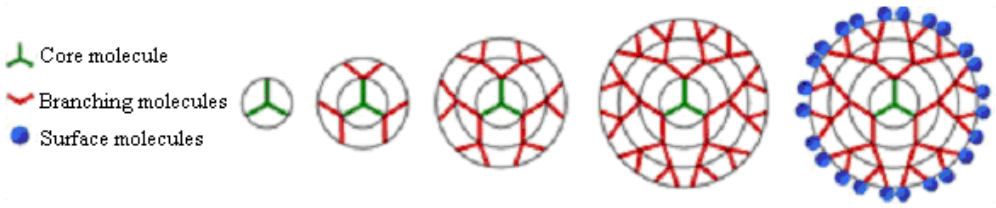

Figure 1.6. Schematic representation showing subunits of dendrimers

Due to its compact globular structure, inner layers and the core of dendrimer is sterically hindered, thus the functional groups at the surface usually interacts with surroundings and defines the physical and chemical properties of the dendrimers. A part of the dendrimer starting from the core and ending at the periphery is called dendron. It does not contain the 'core' part. The starting point of the dendron from where the repeating units built is known as the focal point, which may also bear chemically reactive groups on it (Figure 1.7).

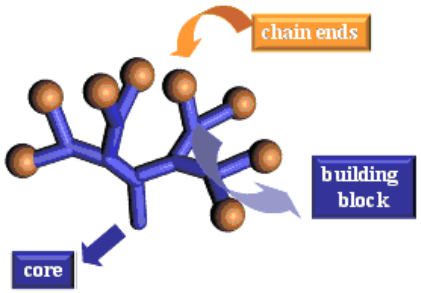

Figure 1.7. General structure of a dendron

Dendrimers can be synthesized with two different approaches, namely, "divergent" and "convergent" approaches. The divergent synthesis is the pioneering applied method where the branching units are attached to the core at the beginning and then the surface groups are placed on the periphery. On the other hand, convergent approach involves the attachment of surface groups onto the branching units first and then the combination of small dendrons with a multivalent core either via covalent bond through their reactive focal points or via non-covalent interactions (Figure 1.8).

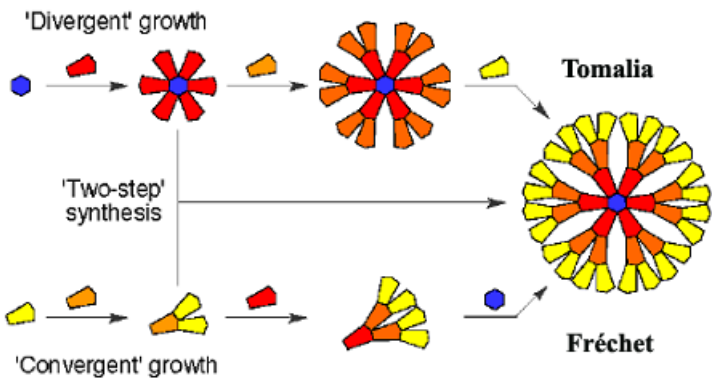

Figure 1.8. Synthesis of dendrimers via divergent and convergent method

Dendrimers are highly attractive building blocks for applications such as targeted drug delivery [17], formation of enzyme mimicking cavities [16], synthesis of multiarm star polymers [18] due to its totally monodisperse property given by the iterative stepwise organic reactions during its synthesis.

1.3. Atom Transfer Radical Polymerization

Atom transfer radical polymerization (ATRP) is an example of a living polymerization or a controlled / living radical polymerization (CRP). Like its counter part, ATRA or atom transfer radical addition, it is a means of forming carbon-carbon bond through transition metal catalyst. As the name implies, the atom transfer step is the key step in the reaction responsible for uniform polymer chain growth. ATRP (or transition metal-mediated living radical polymerization) was independently discovered by Mitsuo Sawamoto [19] and by Krzysztof Matyjaszewski in 1995 [20-21]. Atom Transfer Radical Polymerization is among the most effective and most widely used methods of controlled radical polymerization (CRP). ATRP allows scientists to easily form polymers by putting together component parts, called monomers, in a controlled, piece-by-piece fashion. Assembling polymers in such a manner has allowed scientists to create a wide range of polymers with highly specific, tailored functionalities. For example, polymers created using ATRP have been used for coatings and adhesives, and are currently under investigation for use in the medical and environmental fields.

Until the discovery of ATRP, polymer chemists were severely limited in their ability to control the composition and architecture of macromolecules, making it difficult to provide materials with highly specific, uniform characteristics. Nowadays, ATRP is widely utilized to make linear polymers [22], star shaped polymers, core crosslinked star polymers [23-24], etc.

Polymerization reaction initiates from halide unit of initiator and propagates with the halogen atom transfer between radical polymer and metal ion.

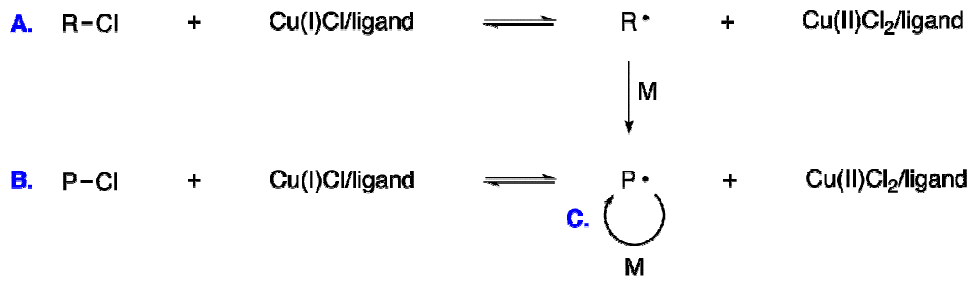

Figure 1.9. Mechanism of Atom Transfer Radical Polymerization

1.4. Ring Opening Polymerization

Ring opening polymerization (ROP) is an important class of polymerization technique to polymerize certain cyclic monomers [25]. A wide variety of polymers have been successfully synthesized via ring opening polymerization which enables predictable molecular weight (from the monomer to initiator ratio), narrow molecular weight distribution indices, end-group control and ability to access block copolymers by chain extention [26]. ROP is intensely utilized to synthesize biodegradable polymers from different cyclic ester monomers such as lactic acid, L-lactide, glycolic acid, etc.

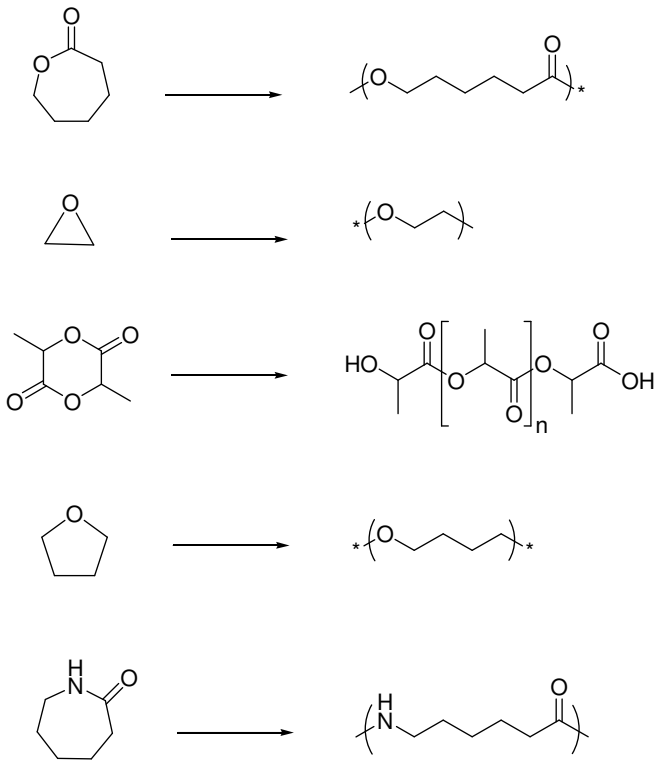

Figure 1.10. Some monomers that are polymerized via ROP

Thermodynamic and kinetic conditions are the most important factors for successful ring opening polymerization. Thermodynamically, the stability of cyclic monomer should allow the reaction. While the instability of small rings gets easier, the polymerization reaction is no longer favorable for less strained stable rings. So there should be reasonable kinetic factor over favourable thermodynamic factor for effectient polymerization [27].

Convenient catalyst system is crucial for ROP to proceed in rational conditions and reveal polymers with controlled properties. There are various catalytic systems have been explored and utilized to reach desired polymer via ROP technique.

In organometallic catalytic system, polymerization takes advantage of transition metals complexes. In order to find the appropriate catalyst system and to clarify the ROP mechanism, numerous scientists have carried out intensive research works. Nowadays tin (II) octanoate, [$Sn(Oct)_2$], is the most widely used catalyst in organometallic ROP, which is commercially available, easy to handle, and soluble in common organic solvents. Figure 1.11 illustrates the expected mechanism of polymerization with tin (II) octanoate, as an example of metal catalyzed process [28].

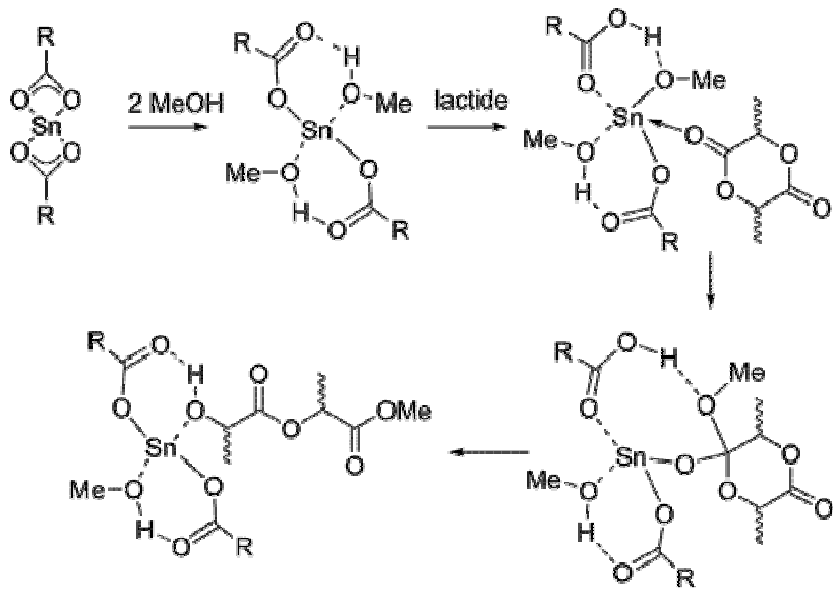

Figure 1.11. Predicted Mechanism for the $Sn(Oct)_2$-Catalyzed ROP [28]

Although organometallic catalysts have been used successfully to polymerize cyclic monomers, probable trace impurity of heavy metals may cause significant difficulties in some application area, especially in microelectronics and medical fields. Moreover, environment can be influenced by the residual heavy metals in resulting polymers. So, researchers have been interested in alternative catalyst for ROP.

Enzyme catalyst polymerization is another technique to polymerize various kinds of cyclic monomers. However, catalysis process of enzymes is quite long compared to other systems [29].

Finally as an alternative to above examples of catalysts, organic molecules are used as catalysts in ROP, especially thiourea-amine based catalysts.

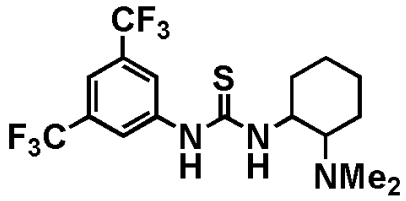

Figure 1.12. Structure of thiourea (TU) catalyst used in ROP [30]

Organocatalytic system is based on the activation of monomer or initiator, or both, with the help of H bonding. Figure 1.13 explains the catalytic process [31]. The carbonyl oxygen of heterocyclic monomer or lactide interacts with hydrogens of thiourea type catalyst. Thus, carbon atom of this carbonyl group becomes more electrophilic. On the other hand, because of the H bonding between H atom of alcohol initiator and N atom of catalyst, oxygen of initiator becomes more nucleophilic. As a result, initiator can easily react with monomer and proceed the polymerization.

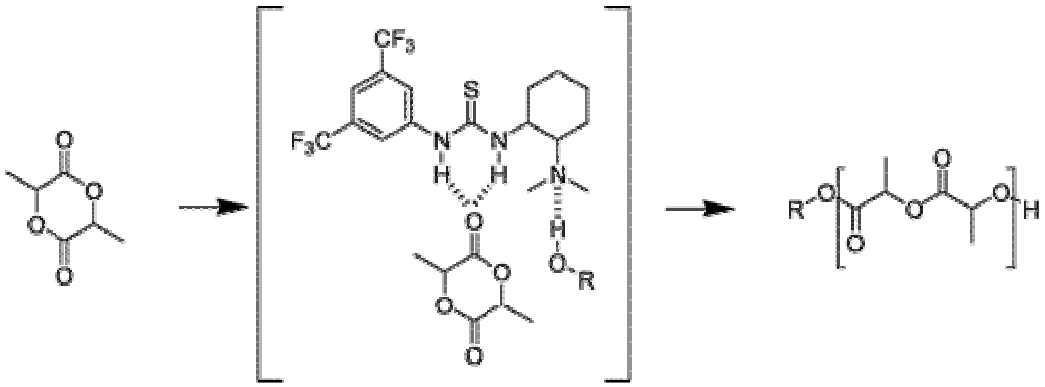

Figure 1.13. The catalytic effect of the organocatalyst in polymerization of lactide [31]

1.5. Multiarm Star Polymer

Multiarm star polymers are the branched macromolecules, in which multiple linear arms are extented from the core (Figure 1.14) [32]. During the last decade, star polymers have gained much interest because of interesting properties in bulk state and in solution because of their compactness and high functionality compared to those of linear analogues of the same molecular weight. By using a multifunctional initiator core, the number of arms in the final star like scaffold can be pre-determined as interested and further functionalization of these groups permit additional modifications or cross-linking which are useable in both biotechnology and material sciences.

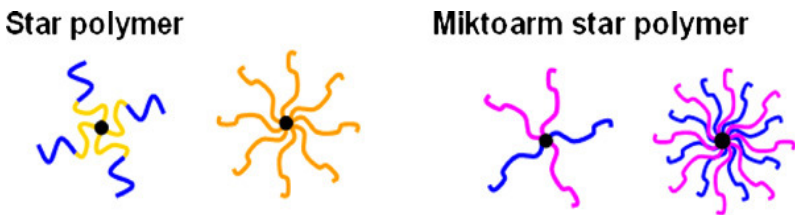

Figure 1.14. Categories of star polymers [32]

Till today, the most widely used methods to obtain well defined multiarm star polymers were living anionic [33] and cationic [34] polymerizations. Recently, new advances in various living free radical polymerization techniques such as nitroxide mediated polymerizations (NMP) [35] and atom transfer radical polymerizations (ATRP) [36] have enriched the toolbox to access multiarm star polymers due to the wider

functional group tolerance and less-stringent experimental conditions of these polymerizaion techniques.

The most commonly used approaches to synthesize multiarm star polymers are the "core-first", the "arm-first" and "couling-onto" methods. In the "core first" method, a multifunctional initiator (the core) is used to initiate the CRP of monomer to obtain multiarm star polymers [37-39]. For the "arms first" method, the terminally reactive linear arms are synthesized first and then the core is produced either by the reaction of the arms using multifunctional coupling agent (coupling-onto) [40-41] or by a cross-linking reaction of the arms with difunctional monomers through propagation [42-44].

There are several techniques to make core crosslinked multiarm star polymers with "arm-first" method.

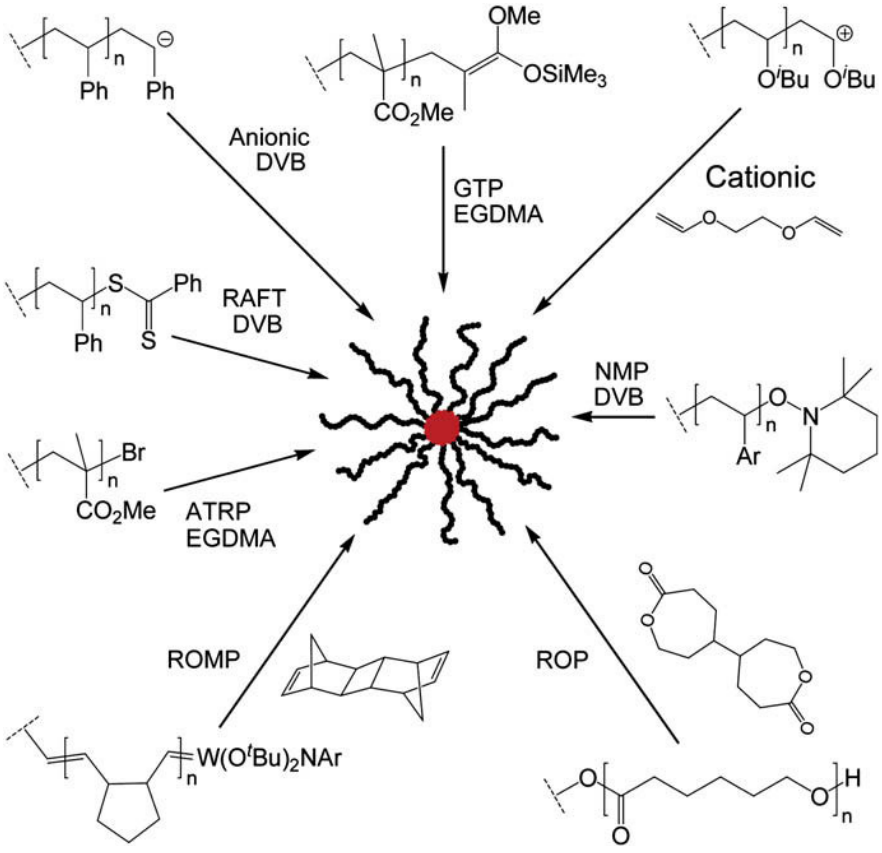

Figure 1.15. Synthesis of CCS polymers via the "arm-first" approach and controlled polymerisation techniques [45]

Gao and Matyjaszewski, in 2005, synthesized the degradable mikto arm core cross-linked star polymers (CCS) composed of PMMA and PBA chains via “arm-first” method by using the cleavable crosslinker, bis(2-methacryloyloxyethyl)disulfide. Degradable miktoarm star copolymers were cleaved by a redusing agent, tributylphosphine (Bu_3P) (Figure 1.16) [46].

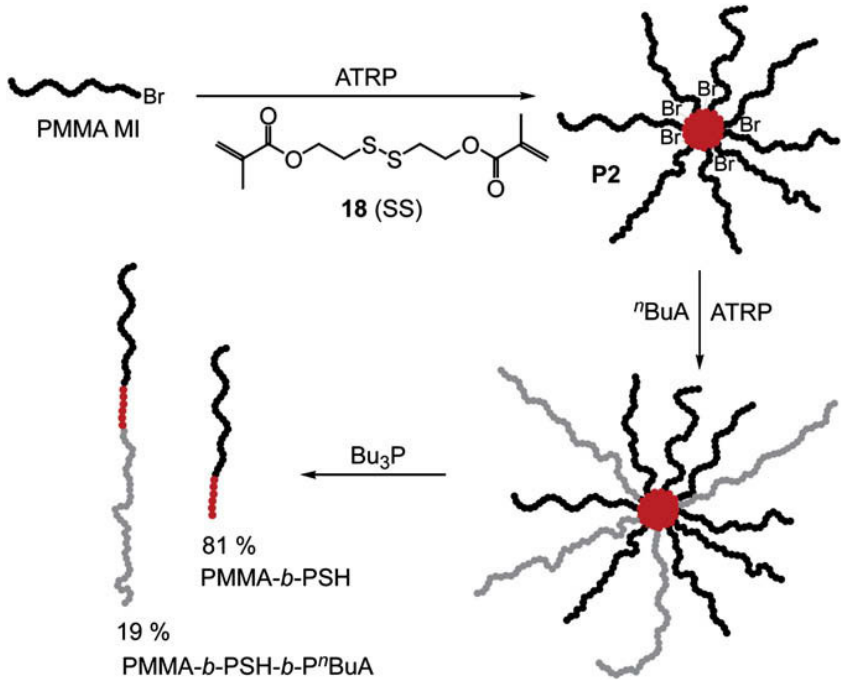

Figure 1.16. Synthesis and cleavage of miktoarm CCS polymers prepared via $ATRP_{(Cu)}$ and the ‘in–out’ approach [46]

Later on Hawker and Qiao has presented an exapmle of dendronized multiarm star polymer with “arm-first” method. They have used poly(ester) dendrons and PS linear polymer chain for this study. According to their result, as generation of dendron increases, number of arms in star polymer decreases (Figure 1.17) [47].

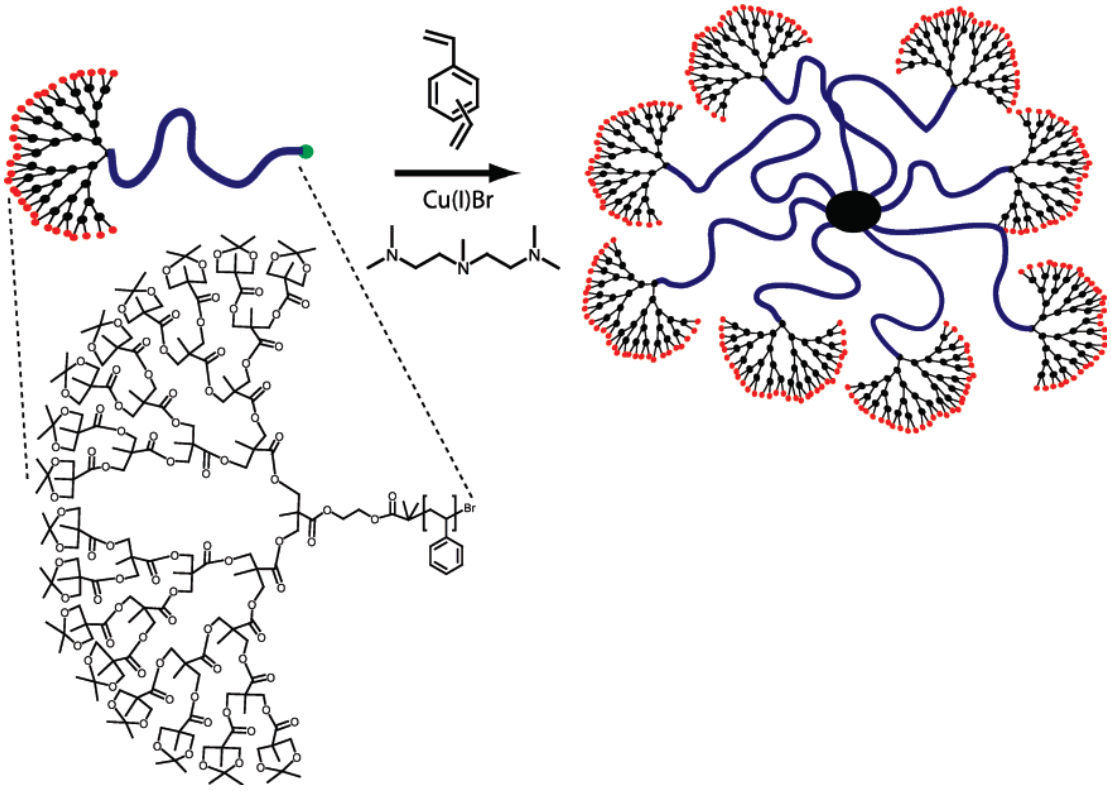

Figure 1.17. Synthesis of dendron functionalized CCS polymer [47]

Furthermore, water soluble multiarm macromolecular scaffolds are attractive candidates for polymer conjugated drug delivery. Attachment of water soluble polyethylene glycol chains to drug molecules has been studied extensively both as dendritic structures and as linear scaffolds to increase bioavailability. Interestingly, the polymer drug conjugates with multiarm structures possessed longer circulation time compared to the linear polymers of the same molecular weight. [48-49]

In 2010, from our group, Ozgul has synthesized thiol reactive multiarm star polymers via “core-first” method [50]. She prepared the macroinitiator from masked maleimide core and grew different types of monomers. Since it contains furan protected maleimide group, after unmasking, core of this multiarm polymer is functionalizable. Functionalization was successfully achieved by the reaction of glutathione molecule bearing a thiol group with the maleimide group at the core of the multiarm polymer via Michael addition reaction (Figure 1.18).

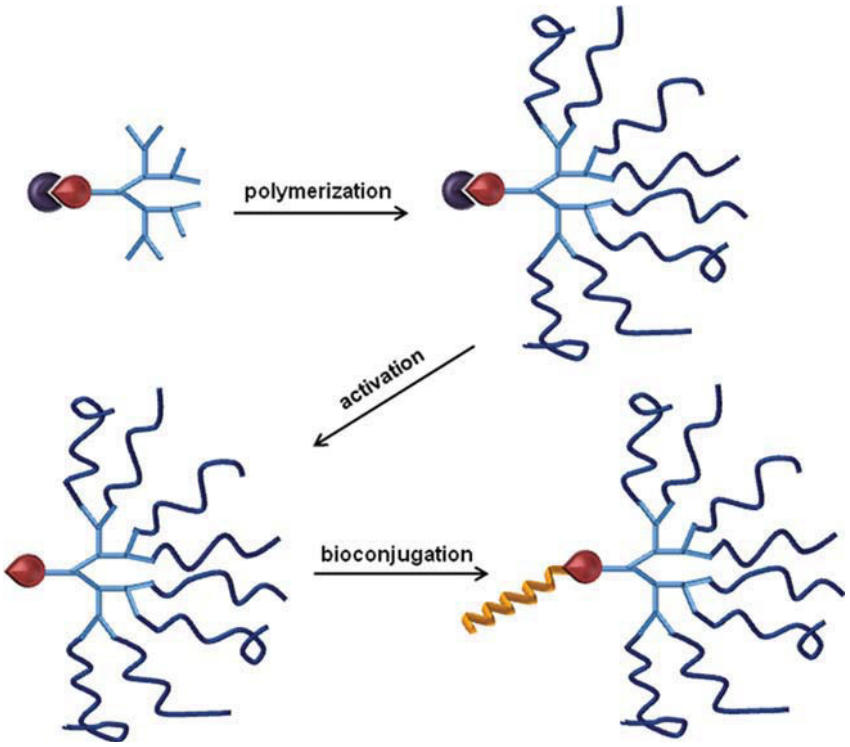

Figure 1.18. General strategy for the synthesis of multiarm polymers containing reactive maleimide core [50]

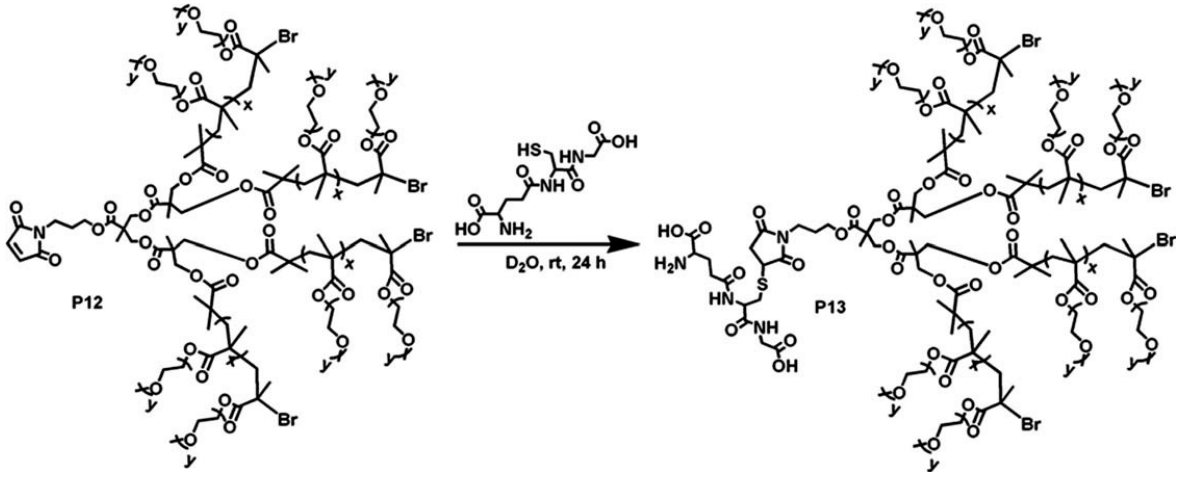

Figure 1.19. Glutathione conjugation to the reactive maleimide core [50]

It is known that the core-first approach has been applied to prepare the star polymers with well-defined arm number. Moreover, when a multifunctional initiator is used, the obtained star polymers will have a functional core inherited from the initiator. Fu and coworkwers have pulished a paper in 2010 about stepwise cleavable star polymers. In this study, they have used ester and disulfide linkages as cleavable units via hydrolysis and reduction respectively [51].

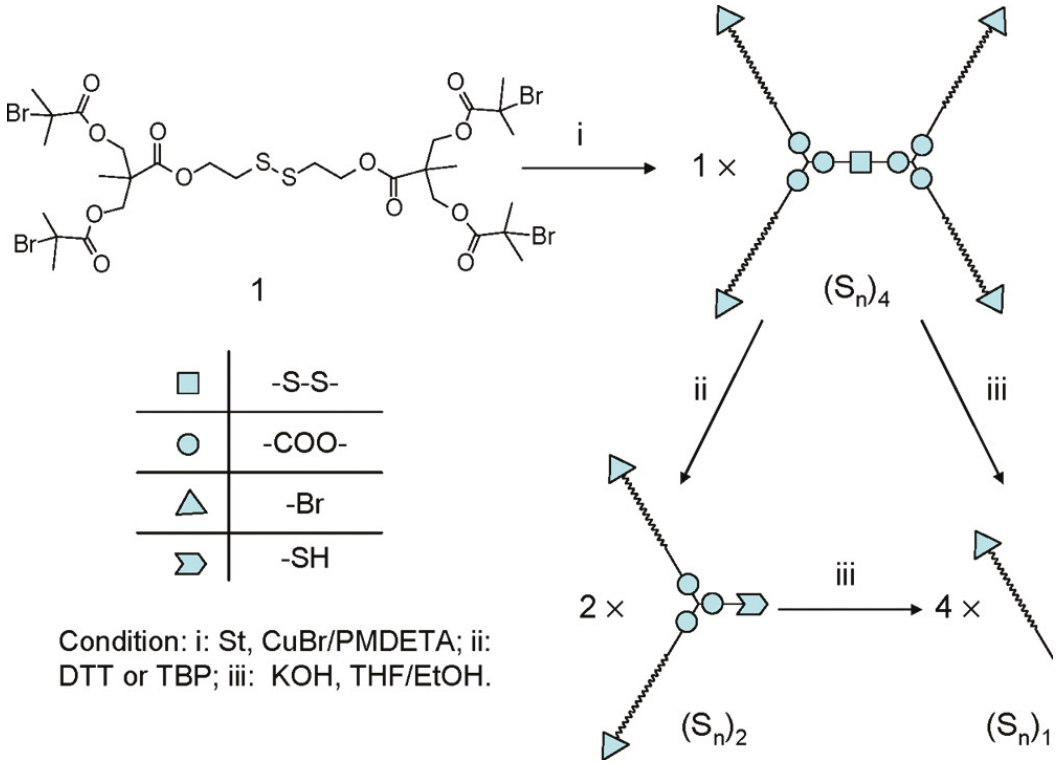

Figure 1.20. Stepwise degradation of star polymer [51]

2. AIM OF THE STUDY

2.1. Thermally Cleavable Multiarm Star Polymers

During the last decade, star polymers have gained much interest because of interesting properties in bulk state and in solution because of their compactness and high functionality compared to those of linear analogues of the same molecular weight. Aim of this study is to make thermally cleavable symmetrical multiarm star polymers via "core first" method by using cleavable dendritic core. In this work, a Diels-Alder/retro Diels-Alder (rDA) reaction based strategy is utilized to synthesize multiarm polymers containing thermally cleavable furan-maleimide cycloadduct unit at the core. Polymerizations of methylmethacrylate from the dendritic initiators are successfully carried out via atom transfer radical polymerization (ATRP). Afterwards, resulting polymers were thermally cleaved with the help of retro Diels-Alder reaction of furan-maleimide unit upon heating in the presence of anthracene as maleimide group scavenger (Figure 2.1).

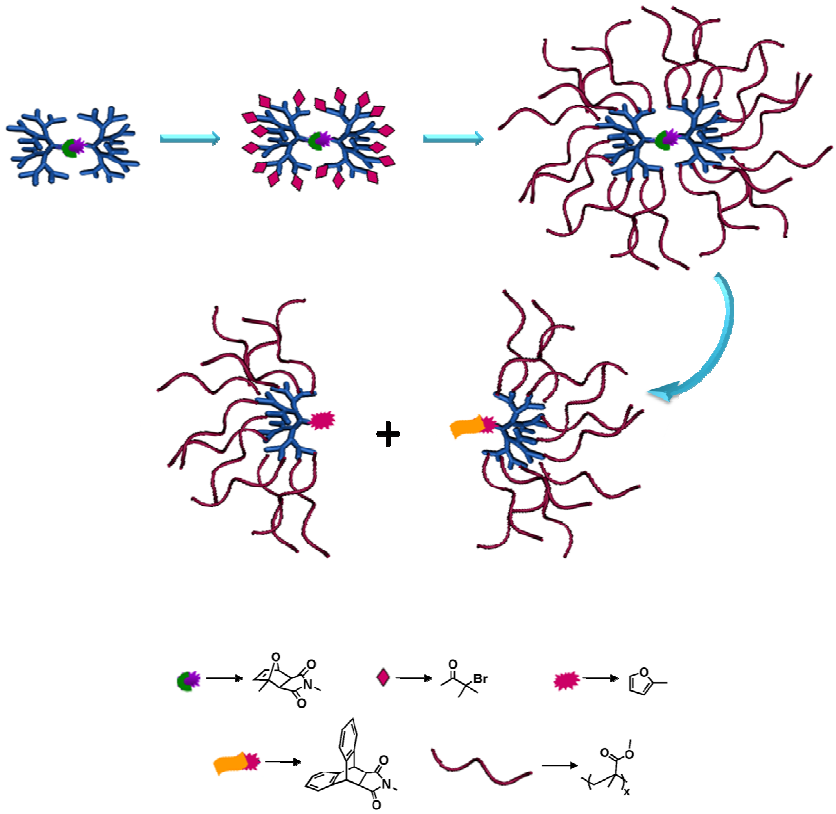

Figure 2.1. Synthetic approach for multiarm polymer and thermal cleavage

2.2. Thermally Cleavable Miktoarm Star Polymers

Multi-armed star polymers possess interesting solution properties that make them attractive candidates for polymer conjugated drug delivery. In this study, a Diels-Alder/retro Diels-Alder (rDA) reaction based strategy is utilized to synthesize miktoarm polymers containing a thermoreversible furan-maleimide functional group at the core. Thermoreversible property comes from furan-maleimide unit based dendritic initiators with which polymerization with methylmethacrylate and lactide monomers is successfully carried out. Afterwards, retro Diels-Alder reaction is examined to cleave the furan-maleimide unit at the core, whose reactivity is then verified by the molecular weight decrease from GPC and proton NMR spectroscopy (Figure 2.2).

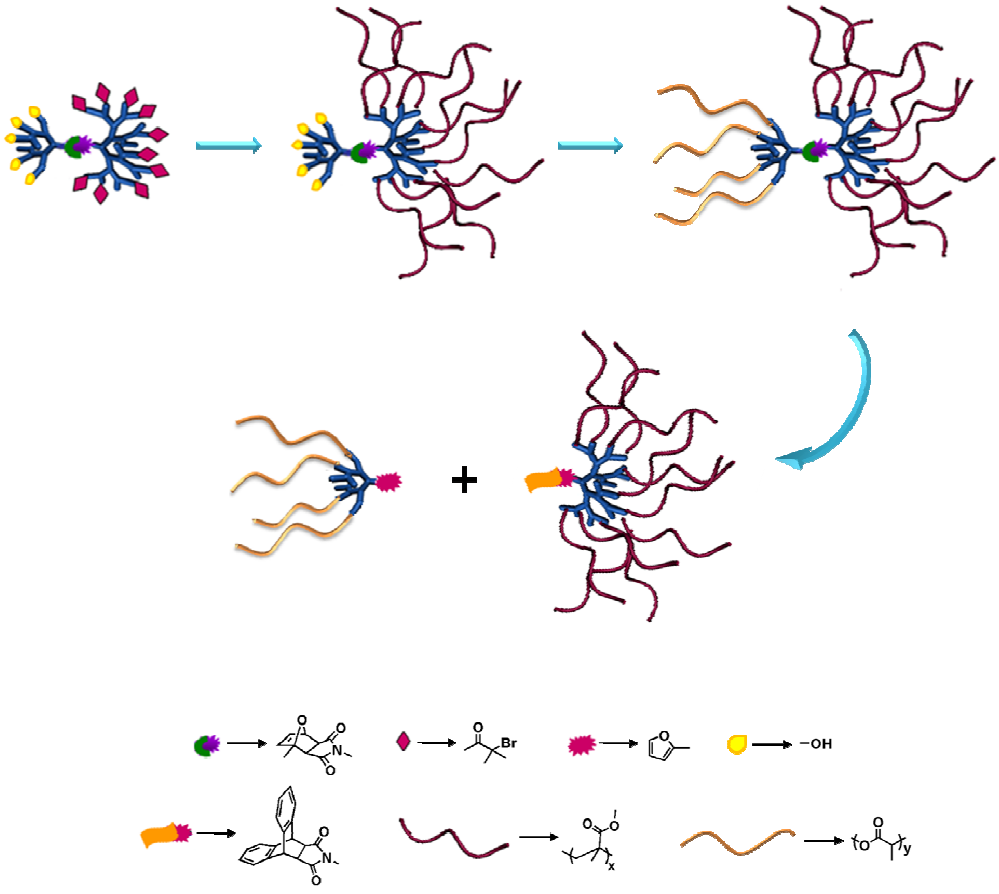

Figure 2.2. Synthetic approach for miktoarm polymer and thermal cleavage.

3. RESULTS AND DISCUSSION

3.1. Thermally Cleavable Multiarm Star Polymers

The synthesis of multiarm star polymers bearing thermally cleavable furan-maleimide core was synthesized using Diels-Alder / retro Diels-Alder strategy and the Atom Transfer Radical Polymerization (ATRP) method. Thermal cleavage of these dendritic polymers was achieved by retro Diels-Alder reaction upon heatind in the presence of anthracene as a maleimide group scavenger. Synthesis of multiarm star polymers via ATRP, and the thermal cleavage with retro Diels-Alder reaction is shown in Figure 3.1.

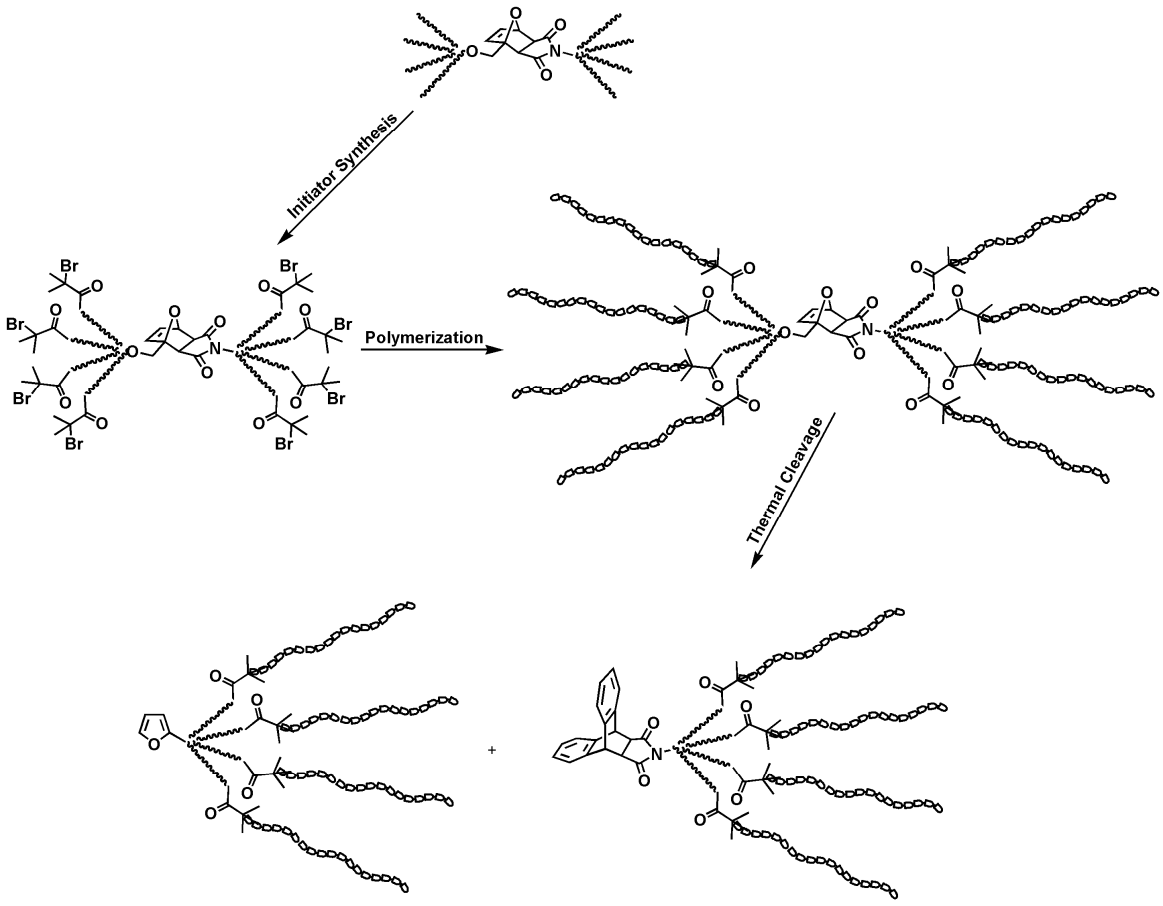

Figure 3.1. General scheme for the synthesis of multiarm star polymers

3.1.1. Synthetic Approach of Multiarm Star Polymers

Diels-Alder reaction is a temperature sensitive reversible reaction of diene and dienophile. Multiarm star polymers grown from dendritic initiators containing furan-maleimide cycloadduct unit at the core is thermoreversible since the Diels-Alder reaction between furan and maleimide unit occurs at 80 ^{o}C, and retro Diels-Alder reaction, reverse DA, occurs at 110 ^{o}C.

In order to make thermally cleavable core, both furan and maleimide units have functional group which could be utilized to grow dendrons for multiarm. We had furan protected maleimide containing alcohol, *N*-hydroxy propyl maleimide, which have previously synthesized in our laboratory [52]. Hydroxy functional group has been attached to the furan part of this compound by using retro Diels-Alder and Diels-Alder reaction shown in the Figure 3.2.

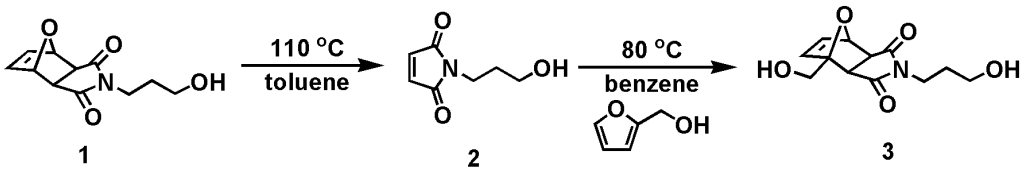

Figure 3.2. Synthesis of furan-maleiimide-diol **3**

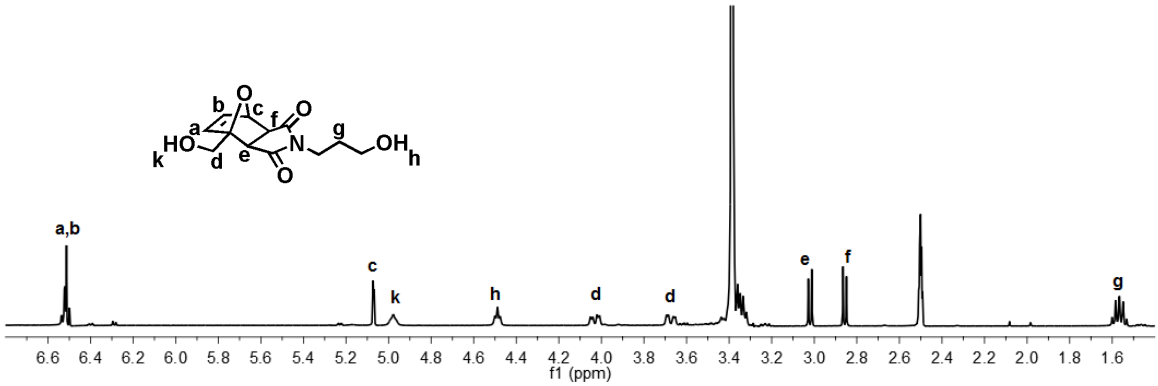

Figure 3.3. ^{1}H NMR spectrum of furan-maleimide-diol **3**

The synthesis of first through fourth generation dendrons **(8, 10, 12, and 14)** were obtained according to previously reported literature procedure [53] starting from furan-maleimide-diol **3**. The acetal protecting groups at the periphery of these dendrons were deprotected to polyols utilizing the acidic resin DOWEX 50W-X2. Consequently, the hydroxyl groups at the periphery of the dendrons were esterified by 2-bromoisobutyryl bromide in the presence of triethylamine and DMAP to give the thermally cleavable multiarm initiators (**In2-In5**) in sufficient yields shown in Figure 3.4.

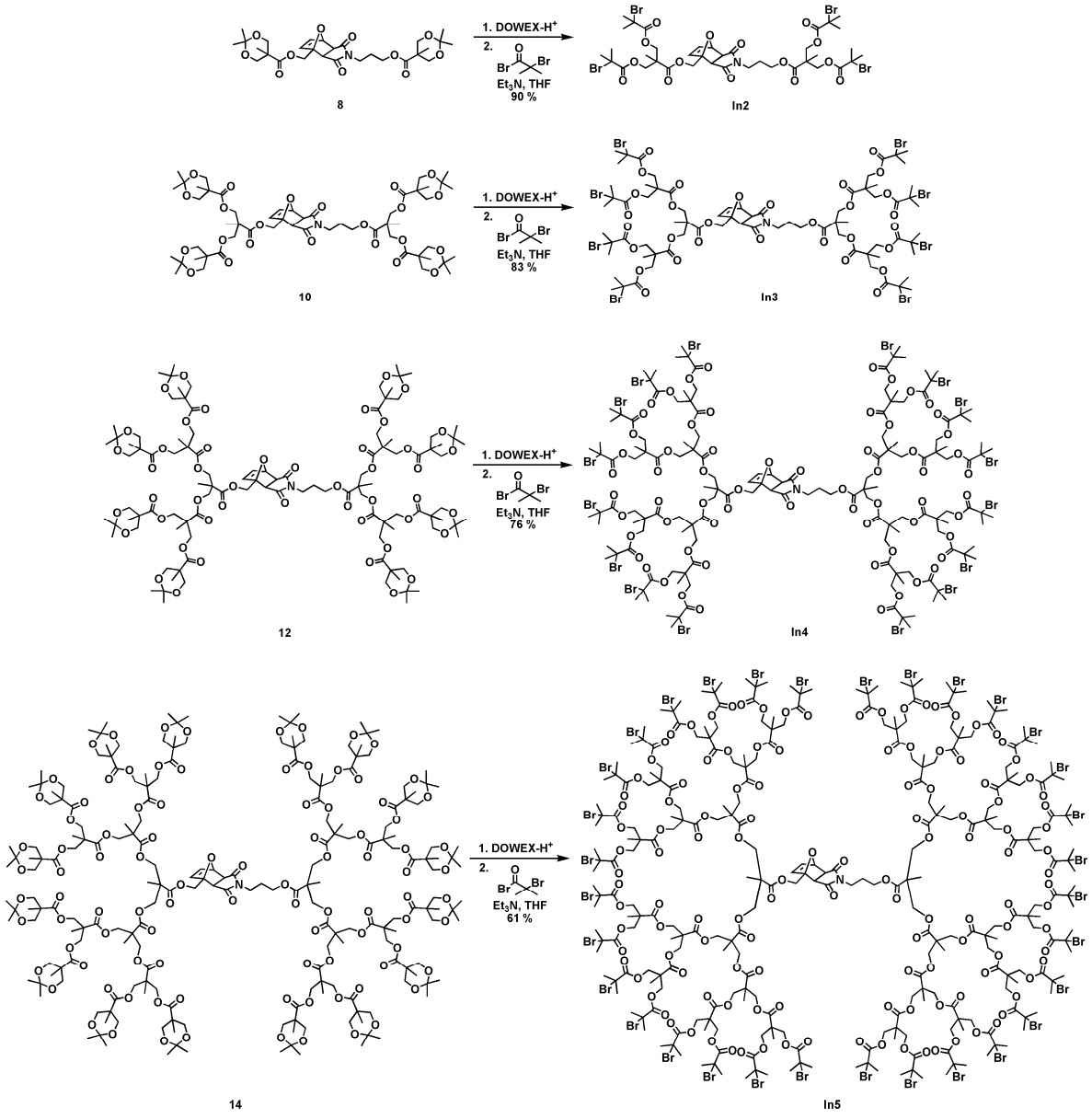

Figure 3.4. Synthesis of Maleimide based Initiators

All multiarm initiators were purified through column chromatography and characterized with ^{1}H NMR, and elemental analysis for their structural assignment and purity. For instance, the presence of bycyclic unit composed of furfuryl alcohol protected maleimide unit was evident from the proton resonances at 2.92, 2.98, 5.23, 6.43 and 6.56 ppm for the second generation dendritic initiator **In3** (Figure 3.5). Presence of eight initiator moieties on the molecule was evident from the ration of the number of protons on the bicyclic core (e.g., 1H at 6.56 ppm) to the protons corresponding to the dimethyl groups on the carbon bearing the bromide atom (48H for $(CH_3)_2$). It is very important to obtain the multiarm initiators in very high purity in order to synthesize polymers with monomodal molecular weight distribution.

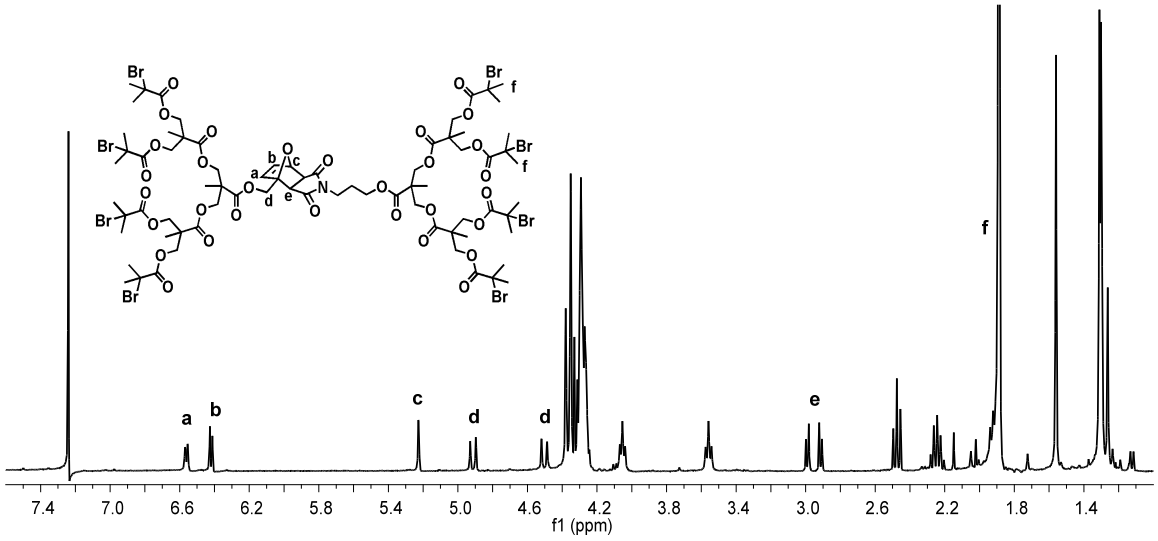

Figure 3.5. ^{1}H NMR spectrum of G2-Initiator **(In3)**

Before starting the synthesis of dendritic polymers, in order to check the thermal cleavage via retro Diels-Alder reaction, model experiment on 3-arm initiator (**In1**) is prepared upon heating. ^{1}H NMR results revealed after retro Diels-Alder reaction of this initiator in the presence of anthracene proves the cleavage by resonance disappearance of furan-maleimide bicyclic unit and appearance of anthracene-maleimide cycloadduct and naked (uncycled) furan compartment (Figure 3.6-3.7).

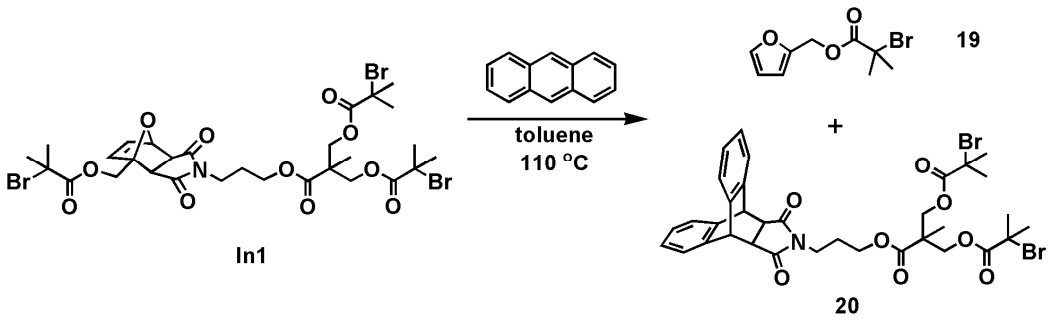

Figure 3.6. retro Diels-Alder reaction of 3-arm initiator **(In1)**

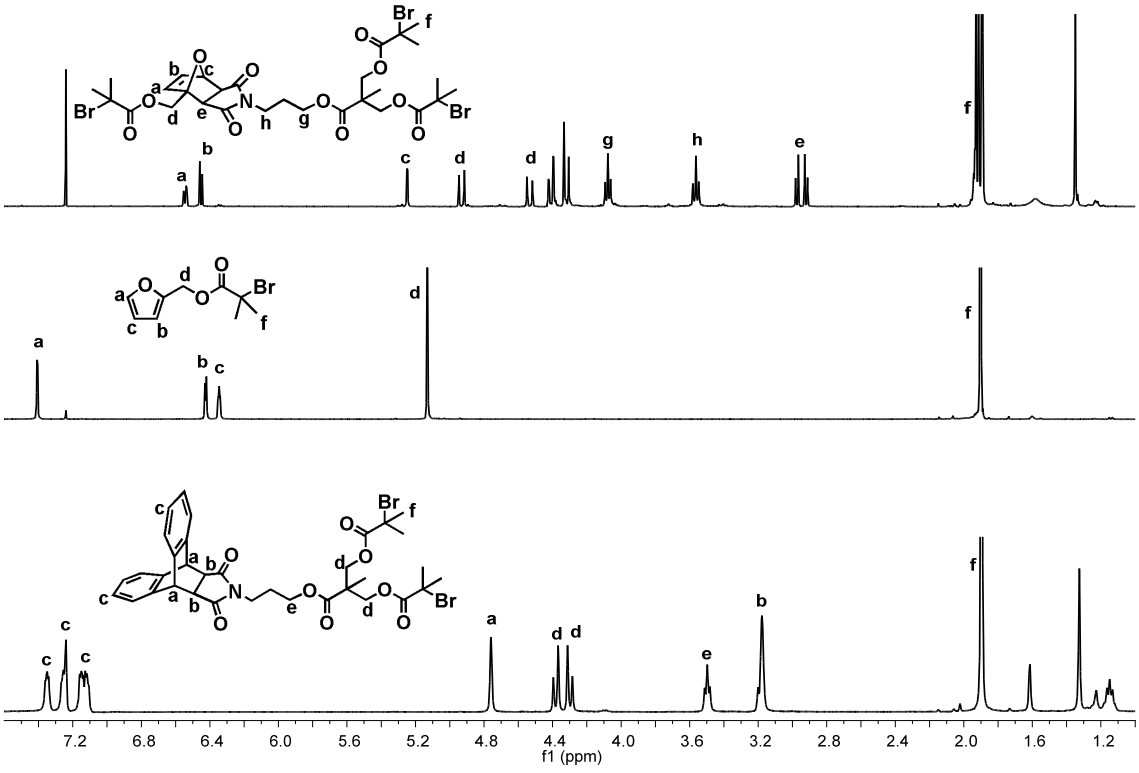

Figure 3.7. ^{1}H NMR spectra of 3-arm initiator **(In3)** and rDA products in the presence of anthracene

Cleavage of star polymer was evident from disappearance of proton resonances at 2.93, 2.97, 5.25, 6.46 and 6.54 ppm due to the cycloadduct core, and appearance of new proton resonances at 3.17, 4.75, 7.12 and 7.33 ppm belong to new anthracene-maleimide

cycloadduct and resonances at 5.13, 6.35, 6.42 and 7.40 ppm belong to remaining furan moiety.

To have control over molecular weight distribution, a living free radical polymerization (ATRP) is chosen for obtaining desired polymers. As a controlled living polymerization method, ATRP is initiated by an alkyl halide (R-X) and catalyzed by a transition metal complex. In this study, dendritic initiators were used along with CuBr/PMDETA complex as the catalyst system. Reaction time and solvent ratio were adjusted for obtaining polymers with narrow polydispersities.

Polymerizations of MMA monomer were carried out using different dendritic initiators (**In1-In5**). Polymerization temperatures were kept at or below 70 ^{o}C to prevent retro Diels-Alder reaction of initiators. *M*n values from TD-GPC for all multiarm PMMA fit well with those obtained from ^{1}H NMR and relatively comparable as expected in terms of number of arms. Polymers with low polydispersity and good conversions were obtained at 70 ^{o}C. Moreover, *M*n values from conventional GPC gave lower values than those of TD-GPC due to different hydrodynamic volume of star polymers to the corresponding linear polymers (Table 1, entries 1-6). Polymerization reaction of 8-arm initiator is shown in Figure 3.8.

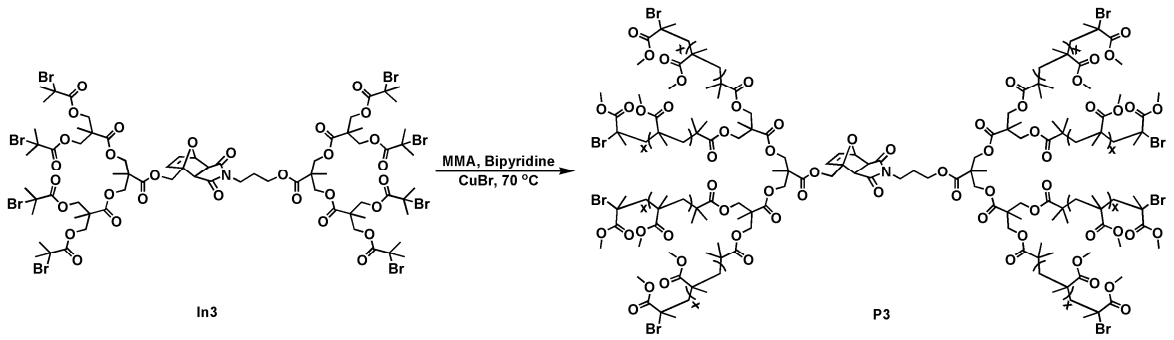

Figure 3.8. Synthesis of 8-arm PMMA (G2) polymer

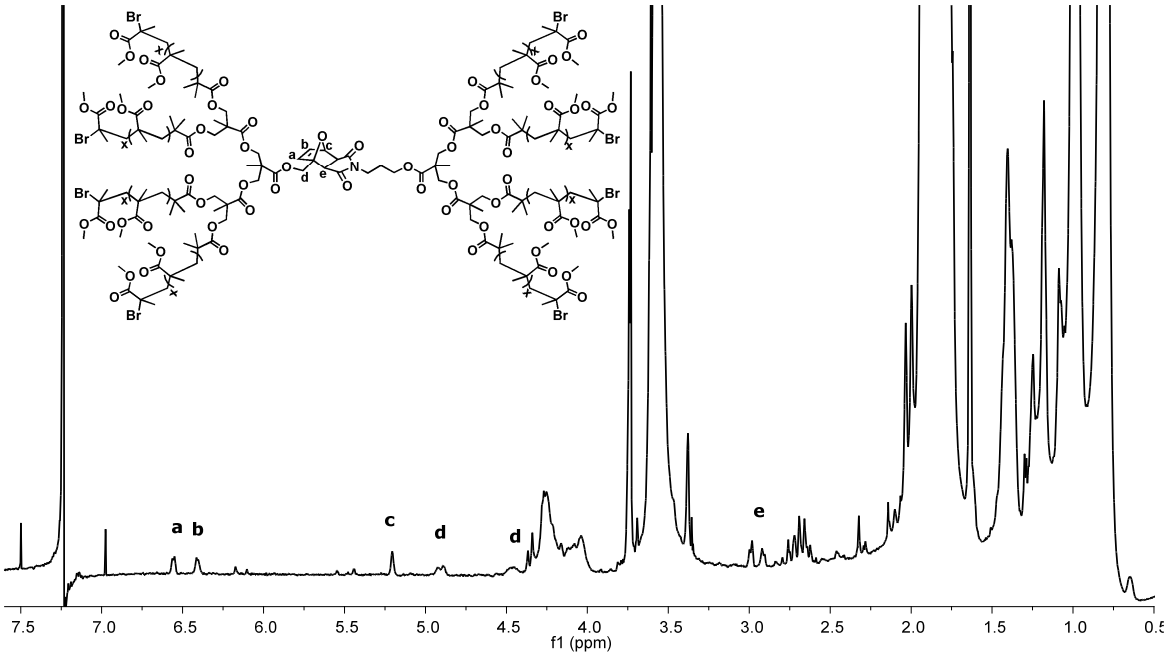

Figure 3.9. ^{1}H NMR spectrum of 8-arm PMMA (G2) Polymer **(P3)**

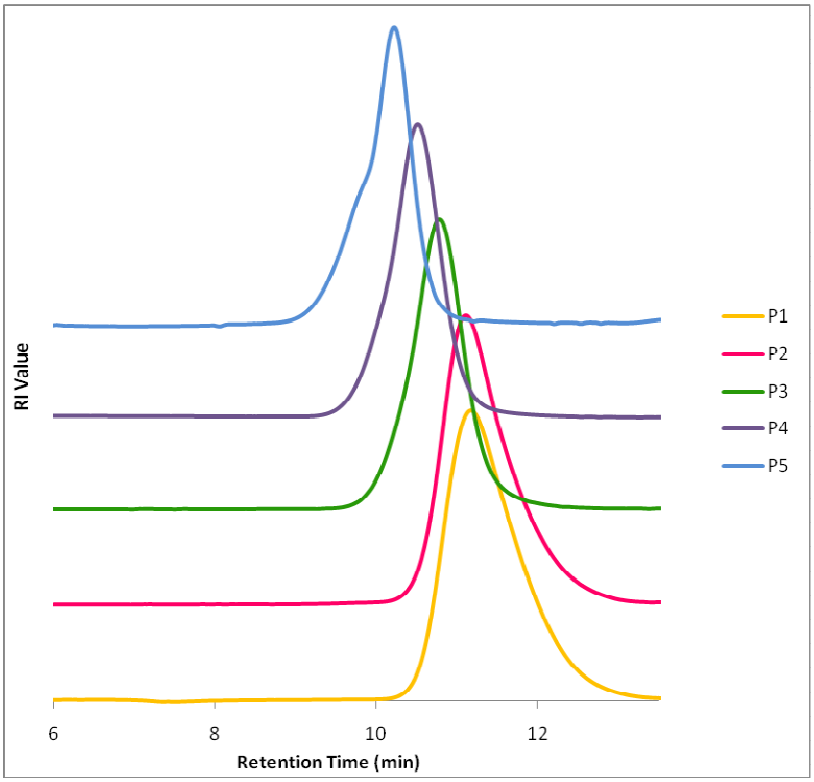

Figure 3.10. GPC traces of **P1-P5**

Table 3.1. Synthesis and Characterization of Thermally Cleavable Multiarm Star Polymers

Entry	**Polymer**[a]	**$[M]_0/[I]_0$**	**[I]**	**Time (min)**	**Temp. (^oC)**	**Conv. (%)**	**GPC**[b]		**TD-GPC**		**$M_{n,\,theo}$**	**$M_{n,\,NMR}$**
							M_n (g/mol)	**M_w/M_n**	**M_n (g/mol)**	**M_w (g/mol)**		
1	G1-PMMA (**P2**)	400	**In2**	120	70	24	12580	1.35	18000	20000	9870	15930
2	G2-PMMA (**P3**)	800	**In3**	120	70	30	26990	1.24	36000	40000	24690	31840
3	G3-PMMA (**P4**)	1600	**In4**	120	70	28	39830	1.23	57000	64000	46040	73580
4	G4-PMMA (**P5**)	3200	**In5**	120	70	31	65570	1.25	100500	112300	101950	148800
5	3armPMMA (**P1**)	300	**In1**	120	70	26	10450	1.30	13000	16000	8020	11190
6	3armPMMA (**P6**)	1500	**In1**	120	70	71	85790	1.38	113000	133000	107205	134040

[a] $[I]_0$:[CuCl]:[Bipyridine] = 1:2:4 (entries 1-6). [b]Calibration with linear PS

3.1.2. Thermal Cleavage of Multiarm Star Polymers

Retro Diels-Alser reactions of star polymers (**P1-P6**) were carried out by heating at 110 ^{o}C in the presence of anthracene as a maleimide group scavenger to prevent the reassembly of products at lower temperature shown in Figure 3.11.

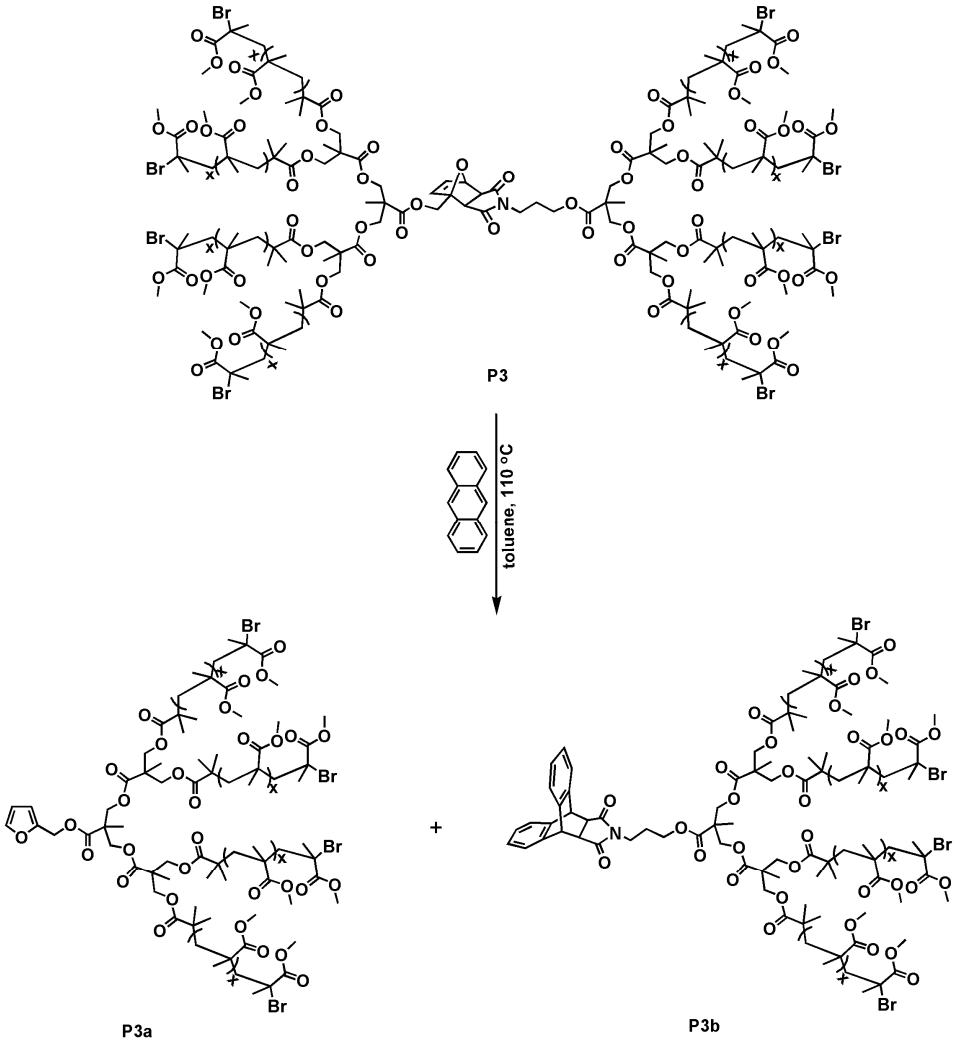

Figure 3.11. Retro Diels-Alder of 8-arm polymer **(P3)** into **P3a** and **P3b**

Cleavage of star polymer was evident from disappearance of proton resonances at 2.92, 2.98, 5.21, 6.42 and 6.55 ppm due to the cycloadduct core, and appearance of new proton resonances at 3.18, 4.76, 7.15 and 7.35 ppm belong to new anthracene-maleimide

cycloadduct and resonances at 5.09, 6.34, 6.42 and 7.40 ppm belong to remaining furan moiety (Figure 3.12).

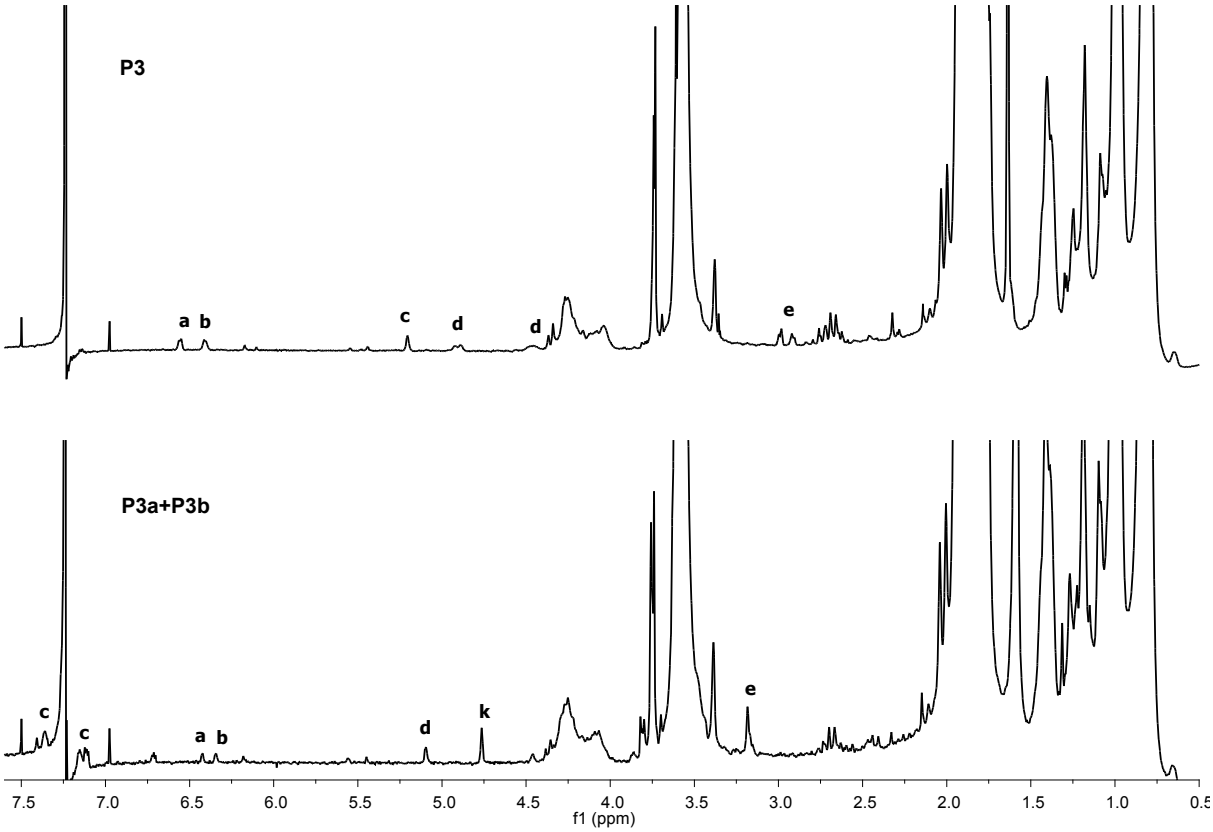

Figure 3.12. ^{1}H NMR spectrum of retro Diels-Alder products of 8-arm polymer, **3a** and **3b**

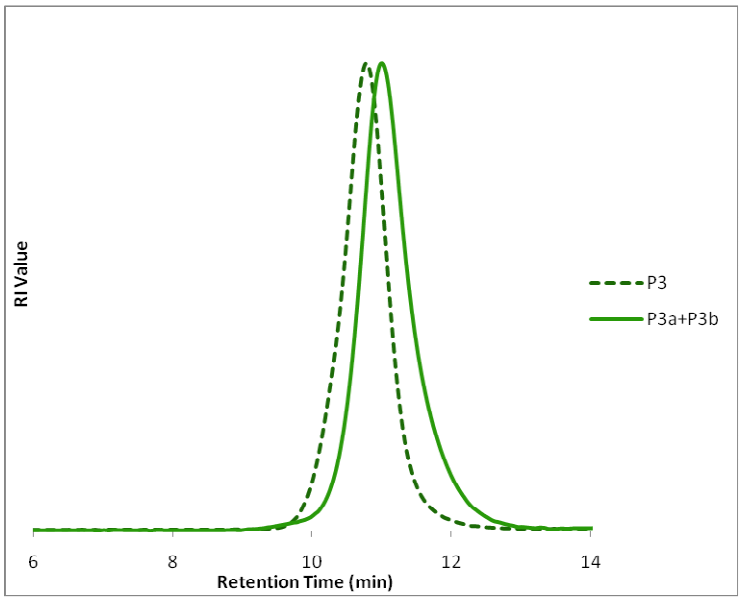

Figure 3.13. GPC traces of **P3a** and **P3b** with **P3**

Although, it was evident from proton resonances that cleavage has occurred, observation of separate peaks on GPC was impossible due to the symmetric structure of star polymers. Molecular weight of resultant products from retro Diels-Alder reaction of unsymmerical 3-arm polymer was not high enough to reveal different peaks on conventional GPC. Consequently, conversion of 3-arm star polymer has increased to 71% reaching a value of 85,790 g/mol. After retro DA reaction, resulting polymer mixture has shown nice separation on gel permeation chromatography (Figure 3.14).

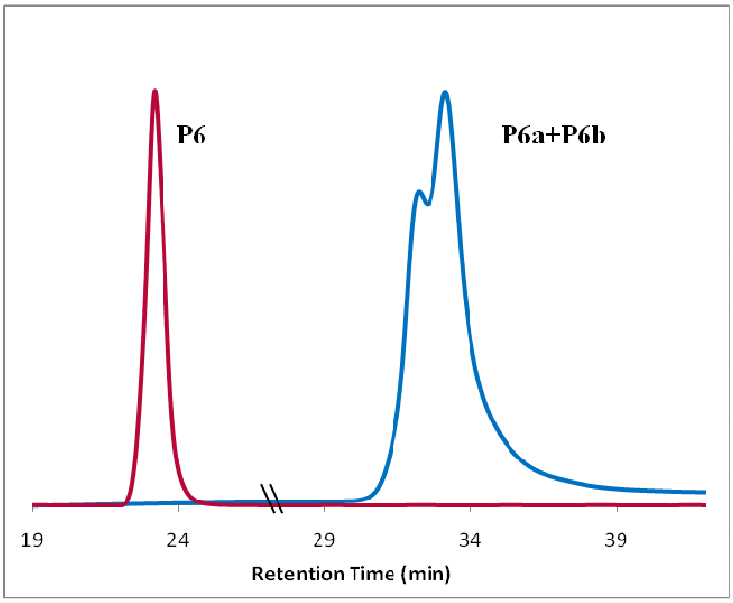

Figure 3.14. GPC traces of **P6a** and **P6b** with **P6**

Table 3.1. Characterization of **(P1-P6)** polymers after retro Diels-Alder reaction

Entry	**Polymer**	**Time (h)**	**Temp. (°C)**	**GPC**		**TD-GPC**	
				M_n (g/mol)	M_w/M_n	M_n (g/mol)	M_w (g/mol)
1	G1-PMMA (**P2**)	16	110	8910	1.40	14000	15800
2	G2-PMMA (**P3**)	16	110	16680	1.34	25000	27000
3	G3-PMMA (**P4**)	16	110	26000	1.23	34000	38000
4	G4-PMMA (**P5**)	16	110	42060	1.20	62000	69400
5	3armPMMA (**P1**)	16	110	8330	1.36	10000	13000
6	3armPMMA (**P6**)	16	110	54400	1.32	73000	80000

3.1.3. Reassembly Test of Multiarm Star Polymers

Since the furan-maleimide Diels-Alder reaction is reversible reaction, reassembly test is performed for all the cleaved reaction mixtures. For this purpose, retro Diels-Alder reaction of multiarm star polymers were tried without anthracene (Scheme 4). Proton NMR characterization of resultant polymer mixture demonstrated the possibility of retro Diels-Alder reaction for these star polymers without anthracene revealing no remaining original polymer. Completeness of reaction was evident from disappearance of furan-maleimide cycloadduct peaks at 2.89, 2.97, 5.24, 6.46 and 6.54 ppm and appearance of free maleimide protons at 6.69 ppm (Figure 3.16).

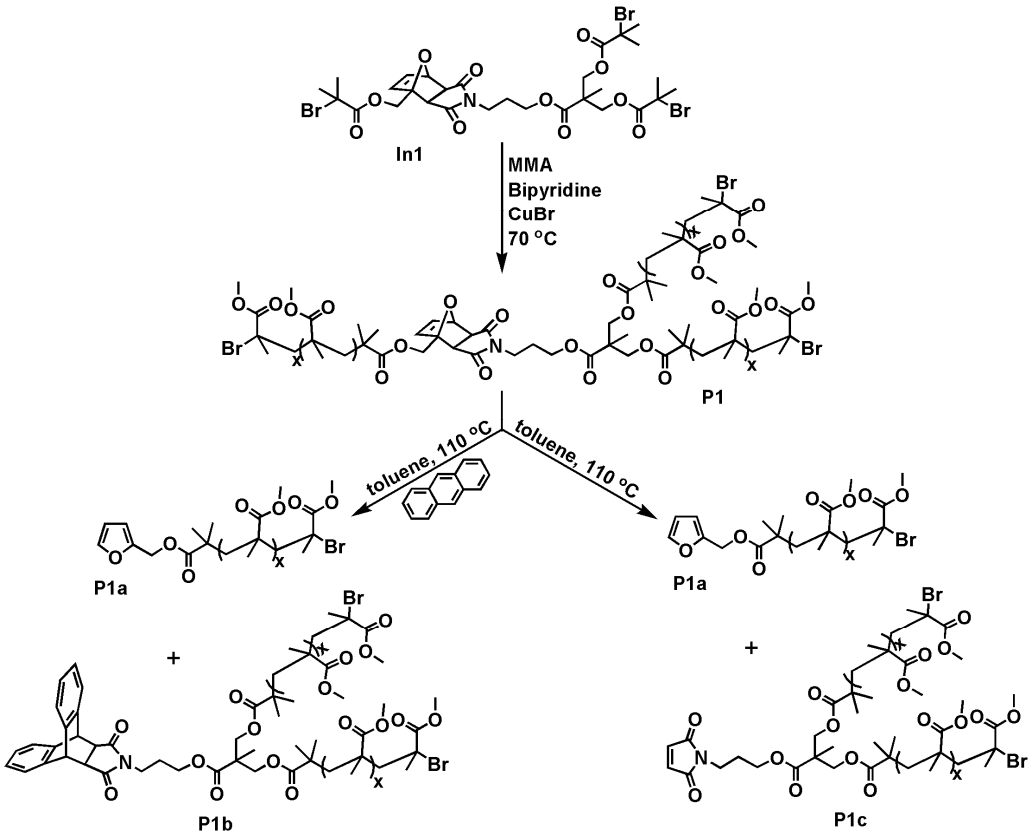

Figure 3.15. ATRP of **In1** to 3-arm PMMA polymer (**P1**), rDA reaction of **P1** both in the presence of anthracene and without anthracene yielding linear 1-arm PMMA polymer (**P1a**) and 2-arm PMMA polymers (**P1b** and **P1c**).

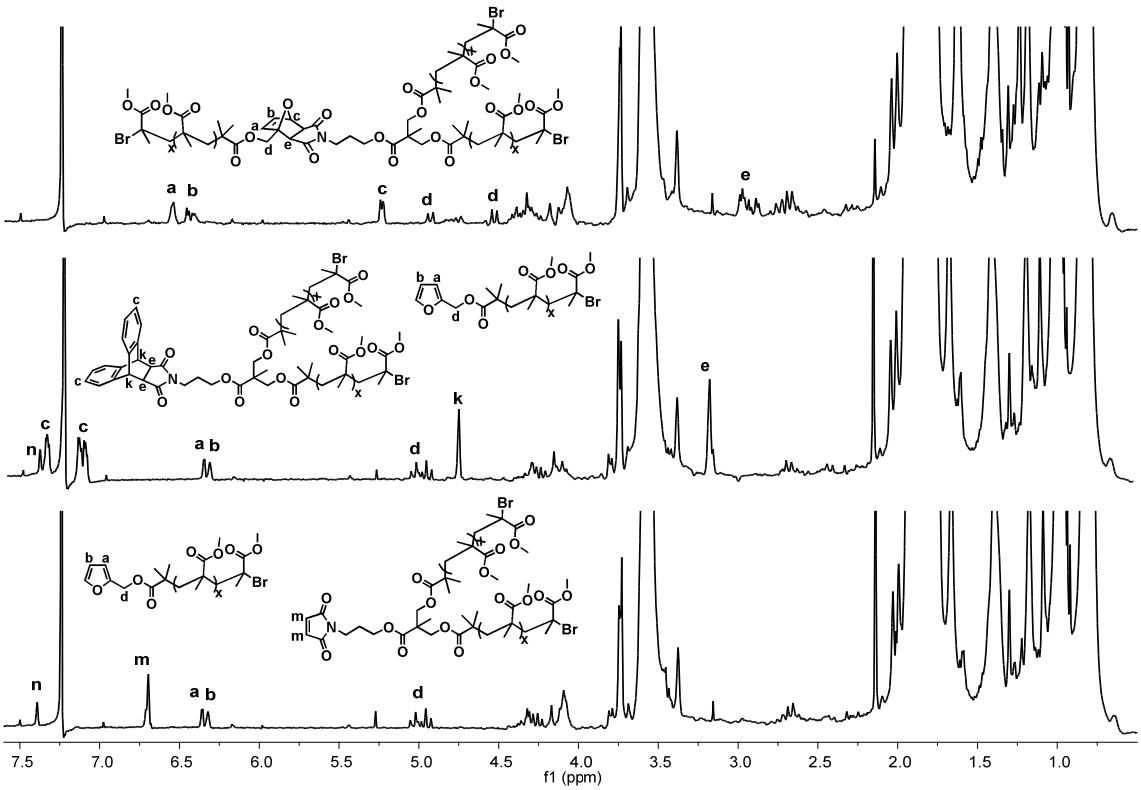

Figure 3.16. ^{1}H NMR spectra of thermally cleavable 3-arm PMMA polymer **(P1)**, rDA products **(P1a, P1b and P1c)** in the presence of anthracene and without anthracene in $CDCl_3$.

Finally, a solution of retro DA rection mixture of 3-arm star polymer was heated to 80 ^{o}C and monitored by ^{1}H NMR at regular time intervals. After 24 h, 48 h and 72 h, no change is observed from proton NMR. Moreover, it was evidenced by no appearance of bridgehead proton of furan-maleimide cycloadduct. Consequently, from this study, we have drawn a result stating reassembly of bigger molecules is not favourable rather than small molecules via DA reaction. In order to demonstrate this trend, DA rection of deprotected maleimide containing 2-arm polymer with small molecule (furan) and furan functionalized linear polymer was performed (Figure 3.17) at the same condition. Proton NMR results were pretty understandable that the reassembly of cleaved polymers is not favourable because of the steric hinderance of supramolecular structure of these star shaped polymers (Figure 3.18).

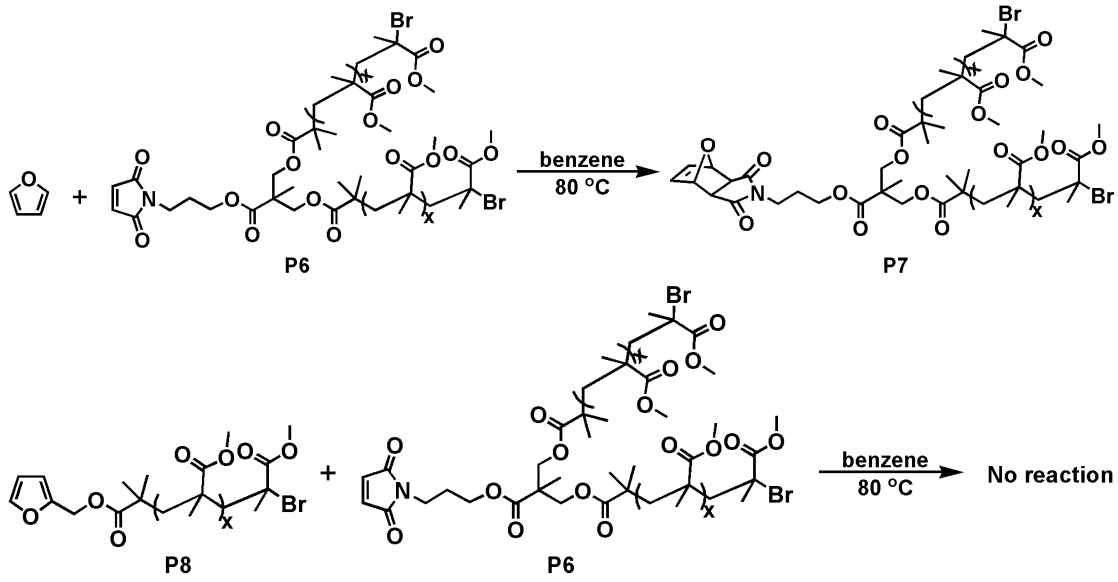

Figure 3.17. Reactivity of maleimide polymer towards small molecule **(furan)** and large molecule **(P8)**

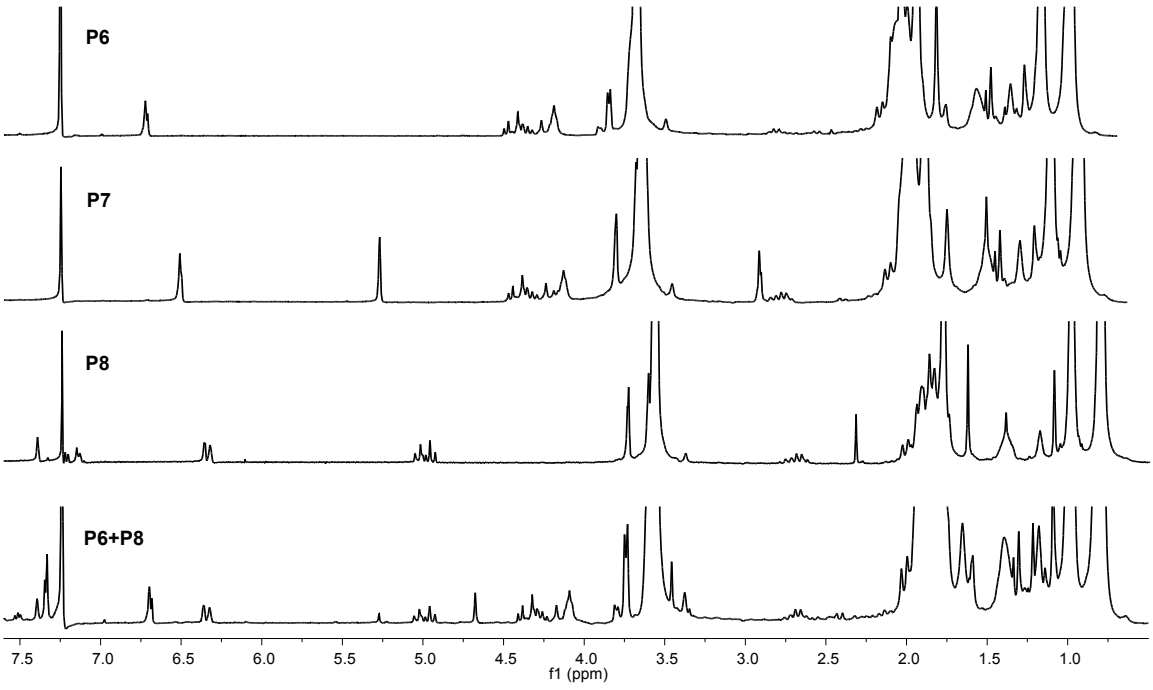

Figure 3.18. ^{1}H NMR spectra of **P6**, **P7**, **P8** and mixture of **P6** and **P8**

3.2. Thermally Cleavable Miktoarm Star Polymers

The synthesis of miktoarm stra polymers bearing thermally cleavable furan-maleimide core was synthesized using Diels-Alder / retro Diels-Alder strategy, the Atom Transfer Radical Polymerization (ATRP) and Ring Opening Polymerization (ROP) method. Thermal cleavage of these dendritic polymers was achieved by retro Diels-Alder reaction upon heatind in the presence of anthracene as a maleimide group scavenger. Synthesis of miktoarm star polymers via ATRP and ROP, and the thermal cleavage with retro Diels-Alder reaction is shown in Figure 3.19.

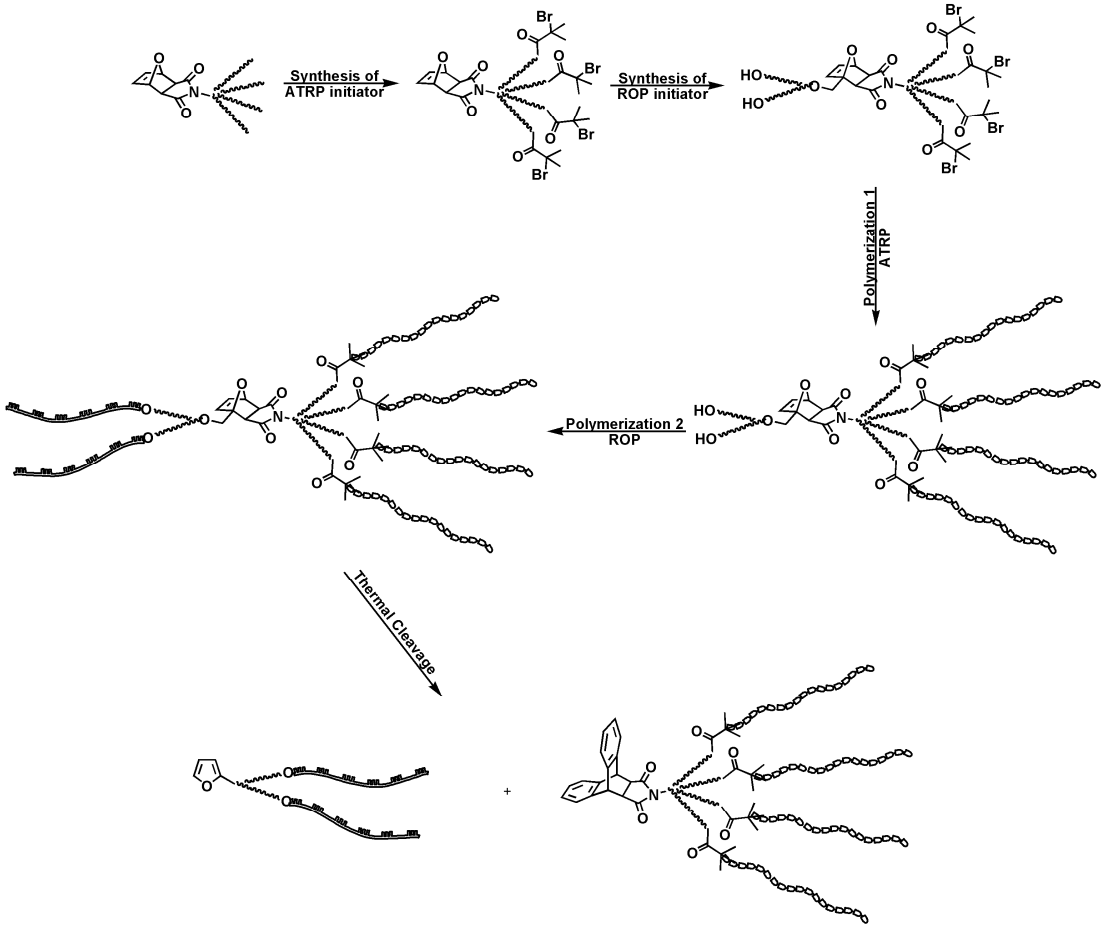

Figure 3.19. General synthesis of thermally cleavable miktoarm star polymer

3.2.1. Synthetic Approach of Miktoarm Star Polymers

As I mentioned in the previous study, multiarm star polymers grown from dendritic initiators containing furan-maleimide cycloadduct unit at the core is thermoreversible. In this study, aim is to make thermally cleavable miktoarm star polymers. For this purpose, two different kind of initiating percursors was needed. ATRP initiator was used in the previous work. In addition to this, we have chosen ROP initiator which is hydroxyl group. Again PMMA was grown from ATRP initiator side and polylactide was grown from hydroxy ROP initiator side. We had furan protected maleimide containing alcohol, *N*-hydroxy propyl maleimide, which have previously synthesized in our laboratory [52]. Generation 1 and 2 poly(ester) dendron have been grown from this alcohol first with following literature procedure [50]. After this, in order to attach hydroxyl functional group to the furan side of compound, retro Diels-Alder and Diels-Alder reactions have been used (Figure 3.19). Finally, it is possible to grow the same type of dendron from newly attached hydroxyl functional group.

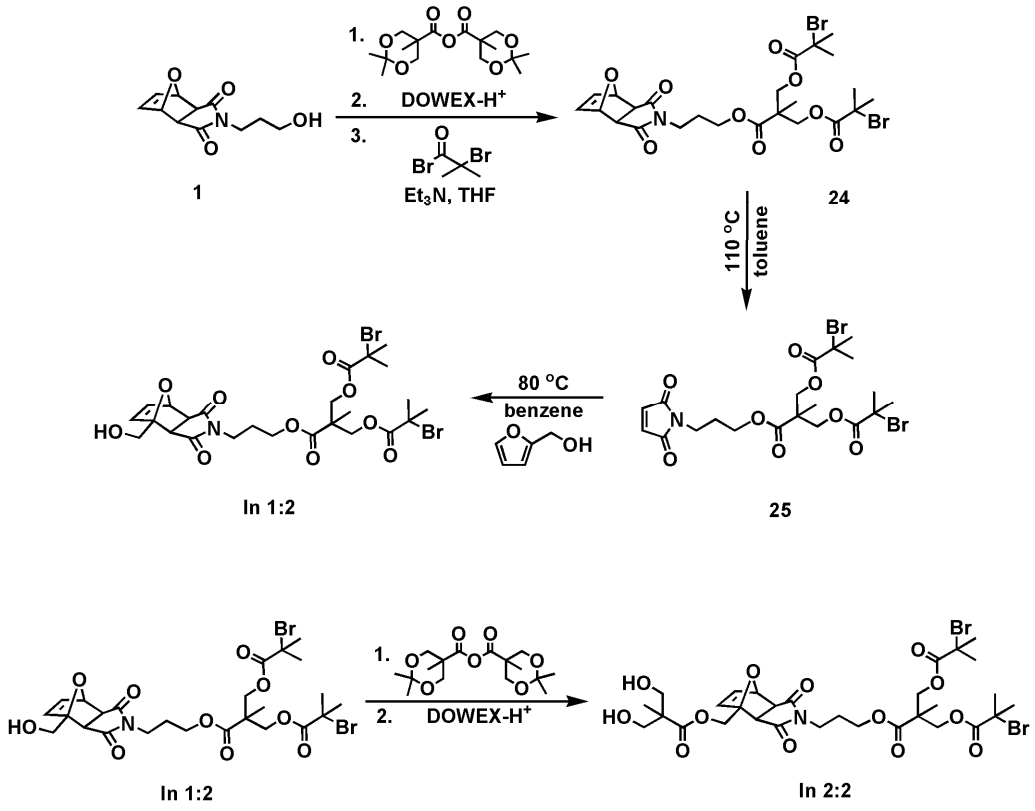

Figure 3.20. Synthesis of 1OH:2Br **(In 1:2)** and 2OH:2Br **(In 2:2)** ATRP and ROP initiators

As a result, we have ended up with unsymmetrical ATRP and ROP dendritic initiators which is thermally cleavable, 1OH:1Br **(In 1:1)**, 1OH:2Br **(In 1:2)**, 2OH:2Br **(In 2:2)**, 1OH:4Br **(In 1:4)**, 2OH:4Br **(In 2:4)**, and 4OH:4Br **(In 4:4)**.

All dendritic initiators were purified through column chromatography and characterized with ^{1}H NMR, and elemental analysis for their structural assignment and purity. For instance, the presence of bycyclic unit composed of furan-maleimide unit was evident from the proton resonances at 2.94, 2.98, 5.26, 6.48 and 6.55 ppm for the initiator 1OH:1Br, **(In 1:1)**, shown in Figure 3.21. It was also evident prom proton resonances at 2.89 and 2.94 ppm that there are two hydroxyl groups. Moreover, presence of two bromo ATRP initiator moieties on the molecule was evident from the ratio of the number of protons on the bicyclic core (e.g., 1H at 6.55 ppm) to the protons corresponding to the dimethyl groups on the carbon bearing the bromide atom (24H for $(CH_3)_2$). It is very important to obtain the initiators in very high purity in order to synthesize polymers with narrow molecular weight distribution.

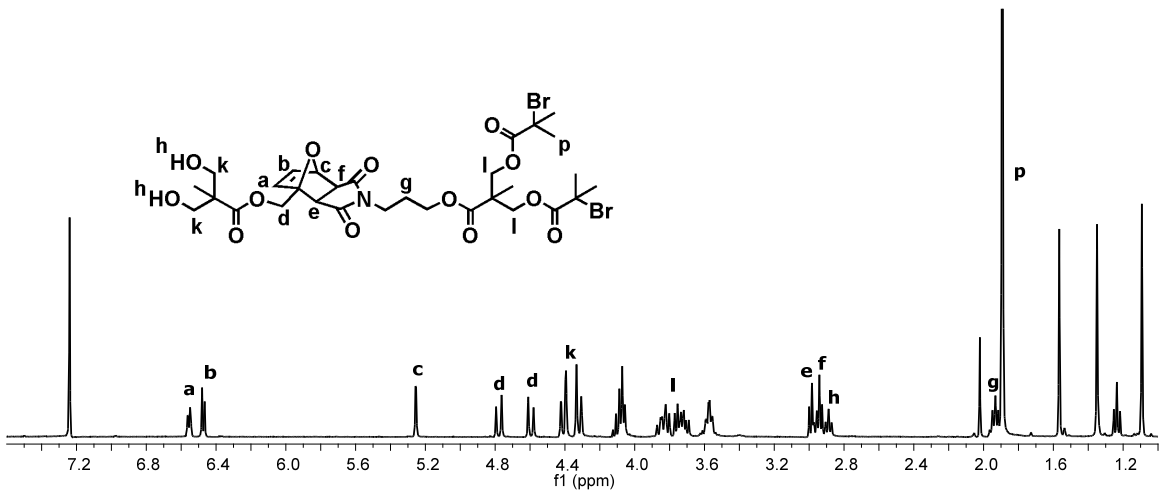

Figure 3.21. ^{1}H NMR spectrum of 2OH:2Br initiator **(In 2:2)**

Two types of polymerization methods are utilized to make miktoarm star polymers, namely ATRP and ROP as I mentioned above. ATRP have been chosen as first polymerization over ROP considering the reaction conditions and solubility of resultant polymers. Anisole and toluene was the choice of solvents usually in ATRP while it is

dichloromethane in case of ROP. Since the polylactide solubility is very low in toluene and anisole, ATRP was carried out first regarding good PMMA solubility in dichloromethane. ATRP polymerization reaction of 2OH:2Br iniatior is shown in Figure 3.22.

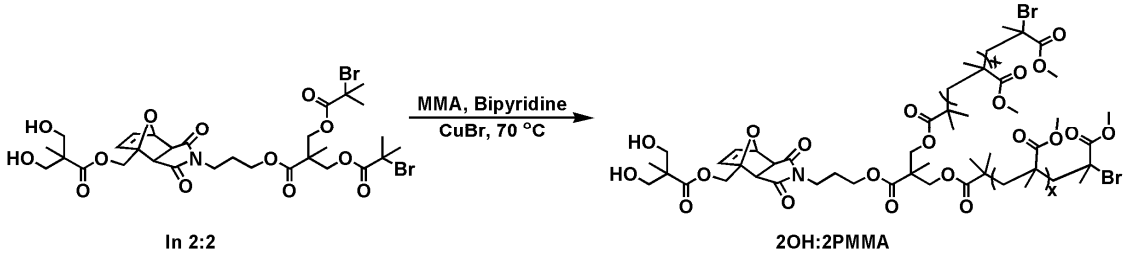

Figure 3.22. Synthesis of 2OH:2PMMA homopolymer

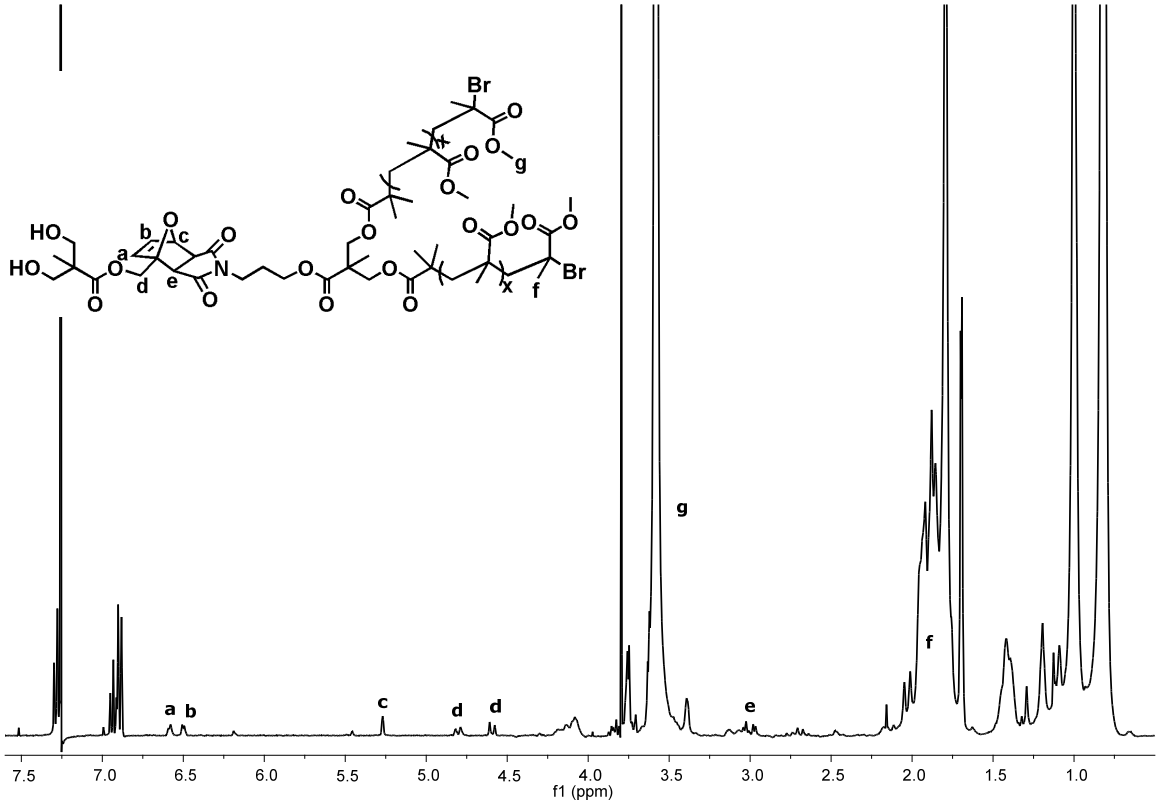

Figure 3.23. ^{1}H NMR spectrum of 2OH:2PMMA homopolymer

Polymerizations of MMA monomer were carried out using all dendritic initiators. Polymerization temperatures were kept at or below 70 ^{o}C to prevent retro Diels-Alder reaction of initiators. *M*n values from GPC for all multiarm PMMA fit well with those obtained from ^{1}H NMR and relatively comparable as expected in terms of number of arms. Polymers with low polydispersity and good conversions were obtained at 70 ^{o}C. (Table 3.3, entries 1-6).

After the synthesis of PMMA homopolymers via ATRP method, polymerization of lactide have been performed via ROP method with the help of hydroxyl initiators in the PMMA homopolymers. According to the GPC and NMR results after ROP, all the macroinitiators have been polymerizaed successfully. Ring opening polymerization reaction of all macroinitiators are carried out at room temperature in presence of organocatalysts DBU and TU. ROP reaction of 2OH:2PMMA homopolymer is shown in the Figure 3.24.

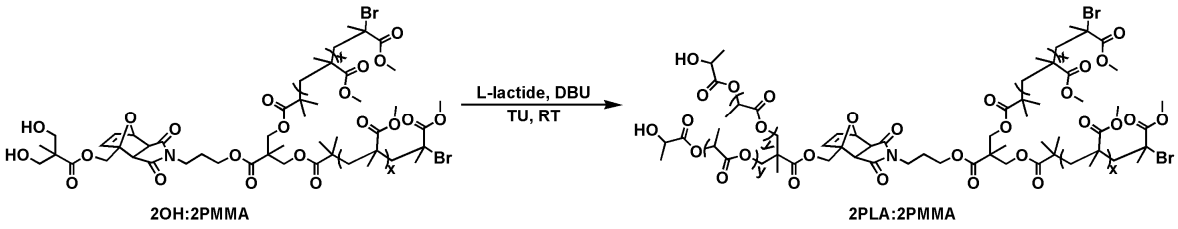

Figure 3.24. Synthesis of 2PLA:2PMMA diblock copolymer

It is evident from the proton NMR specra of resultant diblock copolymer that the ROP has successfully performed.

Table 3.3. Synthesis and Characterization of PMMA homopolymers containing ROP initiator

Entry	Polymer[a]	$[M]_0/[I]_0$	[I]	Time (min)	Temp. (^oC)	Conv. (%)	GPC[b]		$M_{n,\,theo}$	$M_{n,\,NMR}$
							M_n (g/mol)	M_w/M_n		
1	1OH:1PMMA	100	**In 1:1**	60	70	65	7730	1.26	6770	15930
2	1OH:2PMMA	200	**In 1:2**	60	70	62	14070	1.39	12828	31840
3	2OH:2PMMA	200	**In 2:2**	60	70	66	15340	1.24	13733	73580
4	1OH:4PMMA	400	**In 1:4**	60	70	57	27360	1.30	22750	148800
5	2OH:4PMMA	400	**In 2:4**	60	70	57	24880	1.22	25770	11190
6	4OH:4PMMA	400	**In 4:4**	60	70	63	29850	1.21	26204	134040

[a] $[I]_0$:[CuBr]:[Bipyridine] = 1:1:2 (entries 1-6). [b] Calibration with linear PS

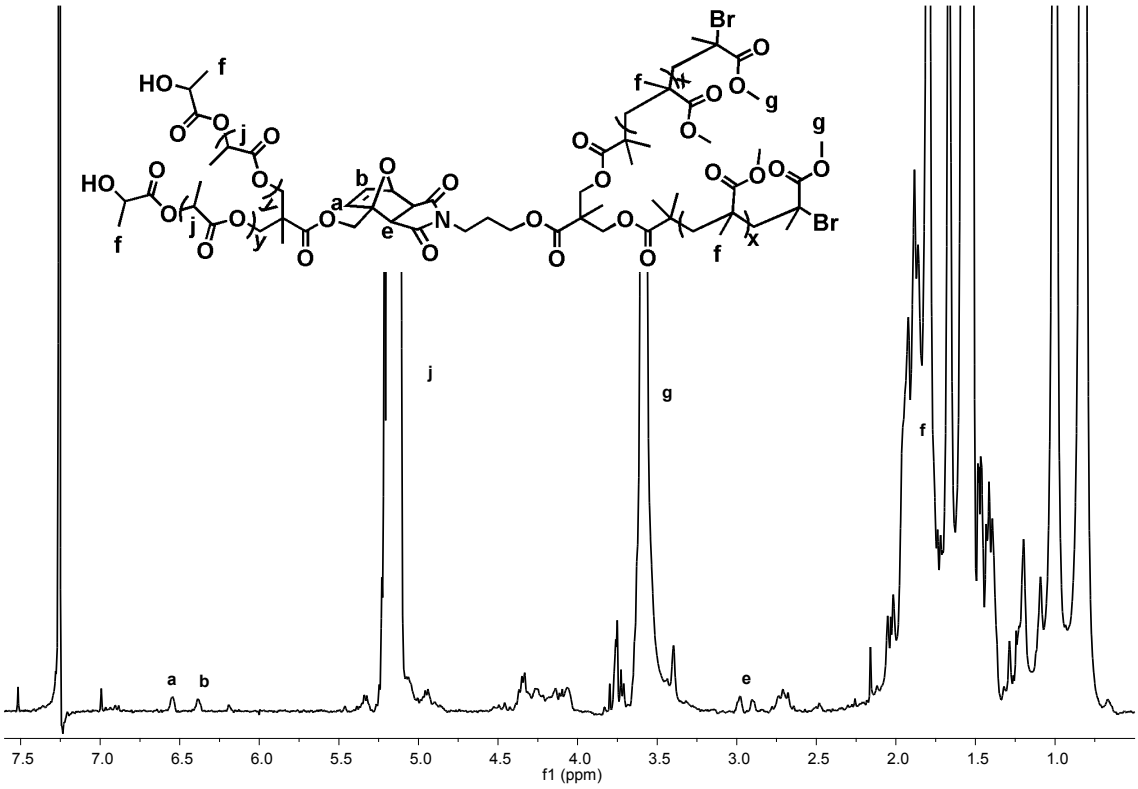

Figure 3.25. ^{1}H NMR spectrum of 2PLA:2PMMA miktoarm polymer

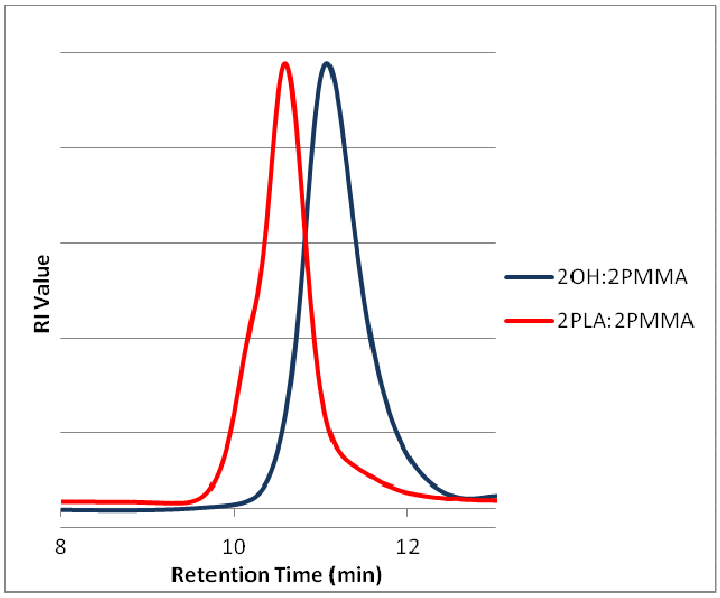

Figure 3.26. GPC traces of 2OH:2PMMA homopolymer and 2PLA:2PMMA miktoarm polymer

Table 3.4. Synthesis and Characterization of PMMA homopolymers containing ROP initiator

Entry	Polymer[a]	$[M]_0/[I]_0$	[I]	Time (min)	Temp. (^oC)	Conv. (%)	GPC[b]		$M_{n,\,theo}$	$M_{n,\,NM}$
							M_n (g/mol)	M_w/M_n		
1	1PLA:1PMMA	120	1OH:1PMMA	90	RT	85	14060	1.31	24403	2629
2	1PLA:2PMMA	120	1OH:2PMMA	90	RT	84	22520	1.27	29144	3635
3	2PLA:2PMMA	240	2OH:2PMMA	90	RT	80	32770	1.26	40672	4637
4	1PLA:4PMMA	120	1OH:4PMMA	90	RT	75	27880	1.31	37580	4803
5	2PLA:4PMMA	240	2OH:4PMMA	90	RT	81	33850	1.28	51420	5640
6	4PLA:4PMMA	480	4OH:4PMMA	90	RT	77	43520	1.44	80774	8085

[a] $[I]_0$:[DBU]:[TU] = 1:1:2 (entries 1-6). [b] Calibration with linear PS

3.2.2. Thermal Cleavage of Miktoarm Star Copolymers

Retro Diels-Alser reactions of miktoarm star polymers were carried out by heating at 110 ^{o}C in the presence of anthracene as a maleimide group scavenger to prevent the reassembly of products at lower temperature shown in Figure 3.27.

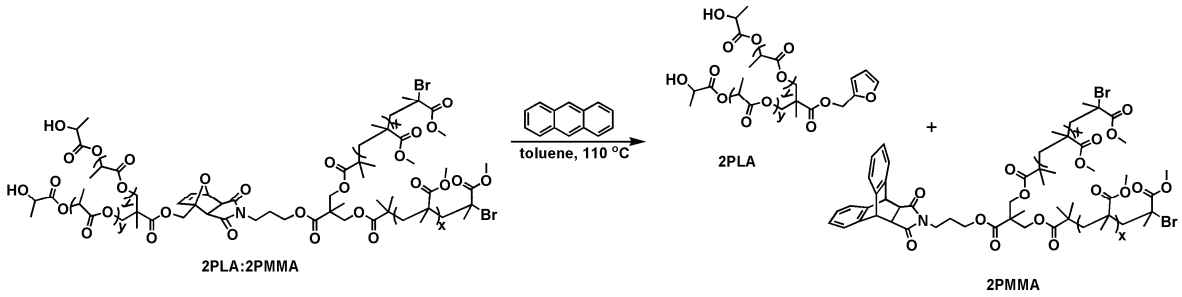

Figure 3.27. Thermal cleavage of 2PLA:2PMMA miktoarm polymer

After retro Diels-Alder reaction, GPC and NMR results proved the cleavage has completed. Molecular weight of the original polymer was decreased from 32700 g/mol to 18200 g/mol. Cleavage of the polymer was evident from disappearance of proton resonances at 2.89, 2.96, 6.37 and 6.53 ppm due to the cycloadduct core, and appearance of new proton resonances at 3.19, 4.76, 7.15 and 7.37 ppm belong to new anthracene-maleimide cycloadduct composed of PMMA and resonances at 6.32, 6.38 and 7.43 ppm belong to remaining furan moiety composed of PLA (Figure 3.28).

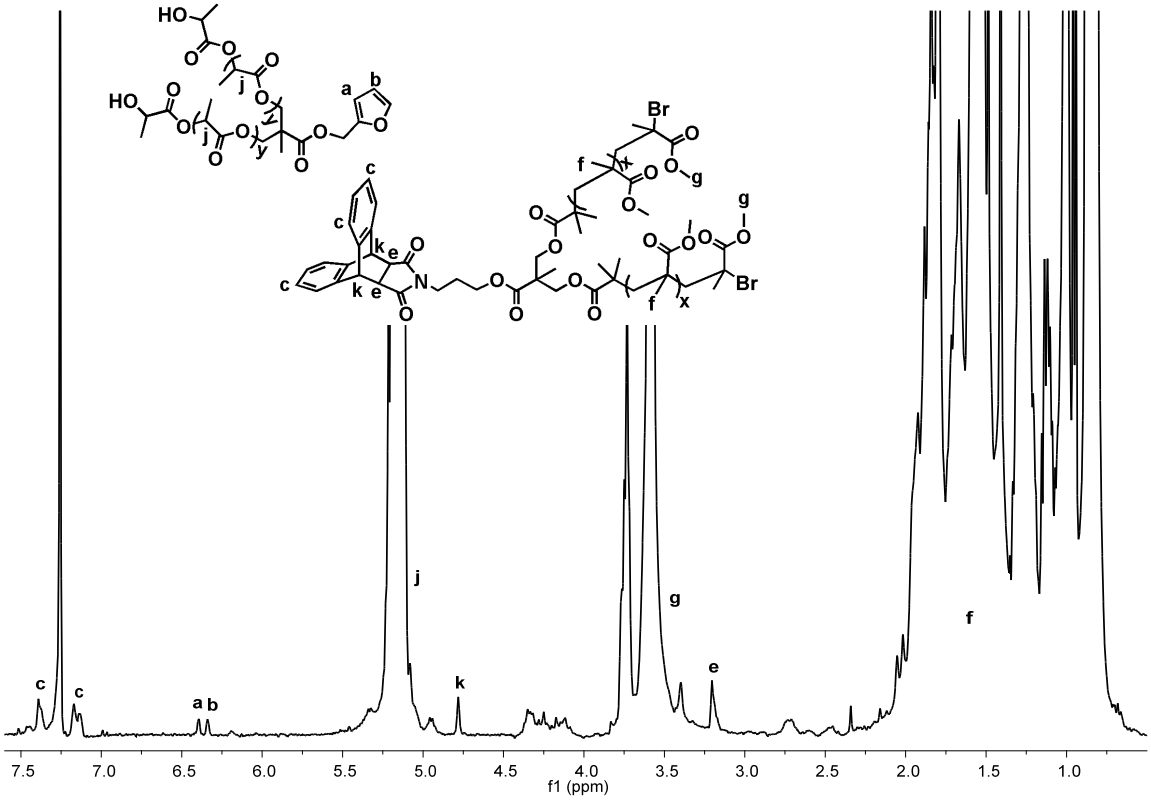

Figure 3.28. ^{1}H NMR spectrum of retro of 2PLA:2PMMA miktoarm polymer which containing the mixture of PLA and PMMA blocks

Table 3.5. Characterization of retro Diels-Alder products of miktoarm polymers

Entry	Polymer	Time (h)	Temp. (^{o}C)	GPC[a]	
				M_n (g/mol)	M_w/M_n
1	1PLA+1PMMA	9	110	9880	1.62
2	1PLA+2PMMA	9	110	11860	1.68
3	2PLA+2PMMA	9	110	18250	1.30
4	1PLA+4PMMA	9	110	22000	1.44
5	2PLA+4PMMA	9	110	24570	1.23
6	4PLA+4PMMA	9	110	30120	1.26

[a] Calibration with linear PS

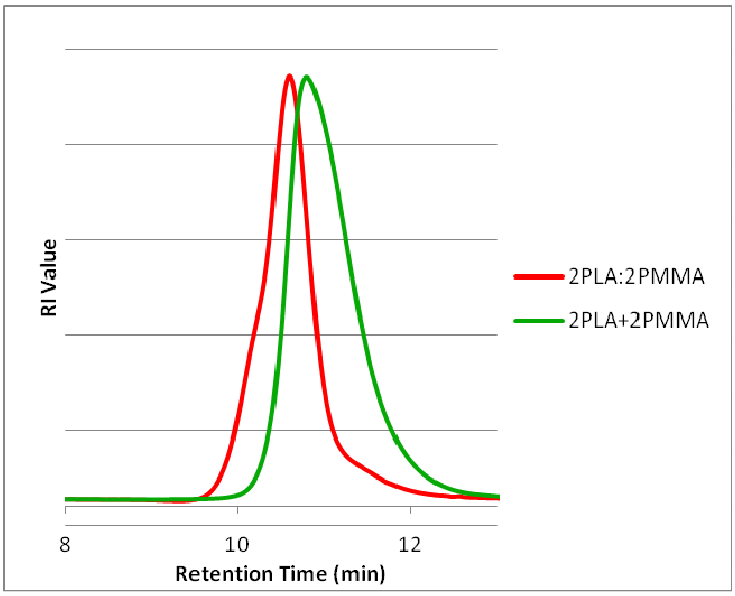

Figure 3.29. GPC trace of retro of 2PLA:2PMMA miktoarm polymer

3.3. Dendritic Functionalizable Multiarm Polymer Brushes

For both multiarm and miktoarm star polymer project, dendrimers were the main buiding block for making multiarm initiators. Furan-maleimide unit of these dendritic initiators make these polymers thermally cleavable. At the same time, this furan protected maleimide core enables these multiarm polymers to be reactive. After unmasking of furan protected maleimide unit or thermal cleavage of star polymers, resulting maleimide group is reactive towards thiols via Micheal addition reaction in a reagent free condition.

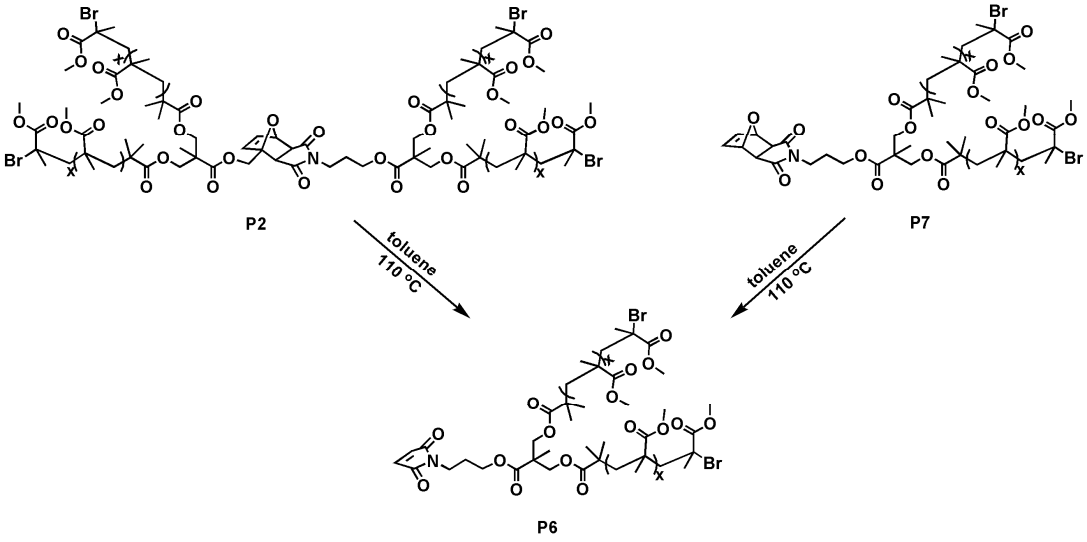

Figure 3.30. Synthesis of reactive polymer

These reacrtive polymers can be used for many purposes such as drug delivery agent, molecular immobilization and polymer brushes. We have prepared thiol containing silicon surface in order to make polymer brushes from our reactive polymers. Then the thiolated silicon surface was coated with reactive maleimide polymer.

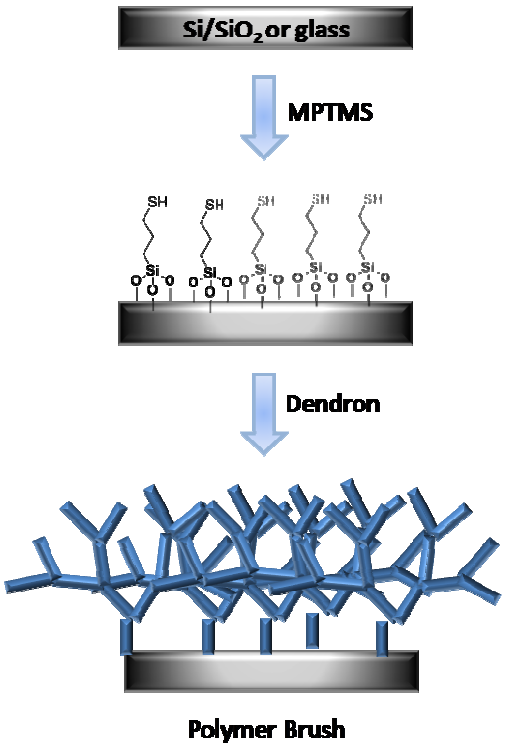

Figure 3.31. Fabrication of multiarm polymer brush

As an extension to this work, functionalizable reactive multiarm polymer have been synthesized in order to make functionalizable dendritic polymer brushes. These polymers contain N-hydroxysuccinimide (NHS) functional groups in side chains and deprotected maleimide reactive unit at the core. By means of NHS groups on the side chains, funtionalization via amine group is possible.

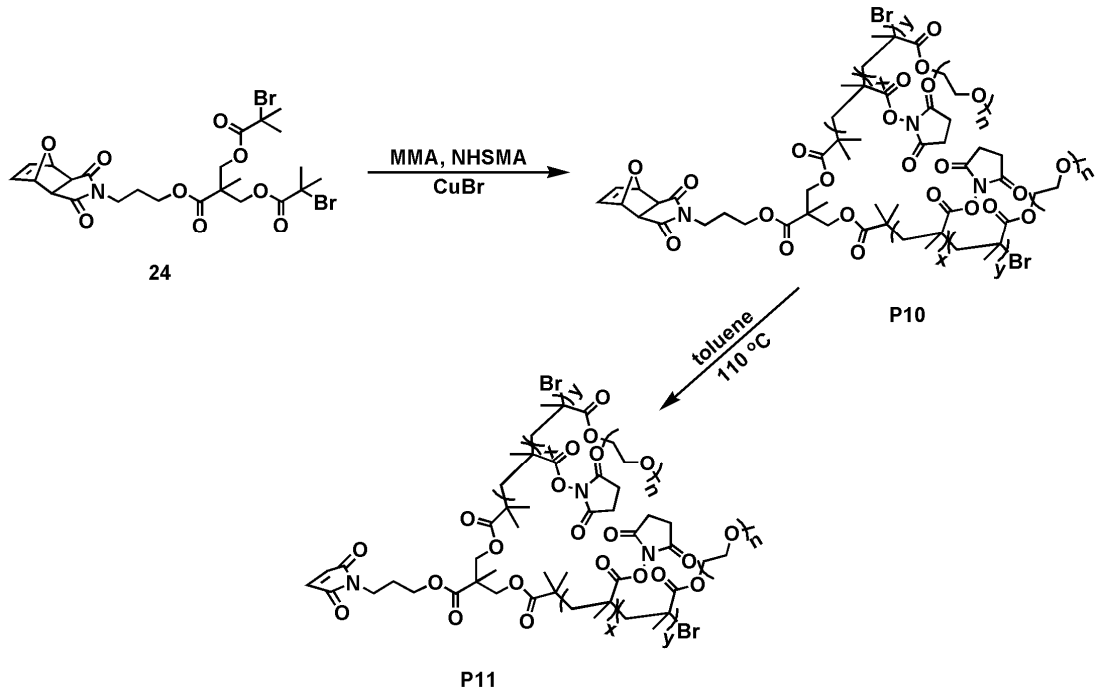

Figure 3.32. Synthesis of functionalizable reactive polymer

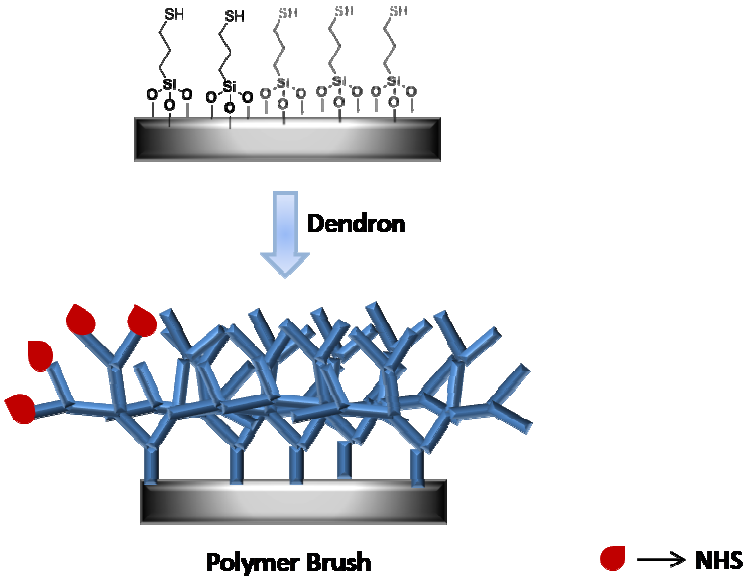

Figure 3.33. Fabrication of functionalizable multiarm polymer brush

4. EXPERIMENTAL

4.1. Materials and Methods

. **1** is produced according to literature procedure [52]. Methyl methacrylate (MMA, 99% Aldrich) was passed through basic alumina column to remove inhibitor and then distilled over CaH_2 in vacuum before use. 2,2'-dipyridyl (Bipyridine), *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA), 99%, Aldrich) was distilled over NaOH before use. 4-Dimethylaminopyridine (DMAP, 99%, Aldrich), CuBr (99.9%, Aldrich), furfuryl alcohol (98%, Aldrich) and 2-bromo-2-methylpropionyl bromide (98%, Aldrich) were used as received. The dendron and polymer characterizations involved ^1H solution NMR spectroscopy (Varian 400 MHz), FlashEA^R 1112 Series Elemental Analyzer (CHNS Separation Column, PTFE; 2m; 6x5mm). The molecular weights were estimated by gel permeation chromatography (GPC) analysis using a Viscotek GPCmax VE-2001 analysis system. PLgel (length/ID 300 mm 3 7.5 mm, 5 lm particle size) Mixed-C column was caliberated with polystyrene standards, using refractive index detector. THF was used as elutent at a flow rate of 1 mL/min at 30 ^oC.

4.2. Thermally Cleavable Multiarm Star Polymers

4.2.1. Synthesis of 4-arm ATRP Initiator (In2)

Furan-protected *N*-hydroxypropylmaleimide (3.00 g, 13.44 mmol) was dissolved in toluene (30 mL) and then refluxed for 24 h. The product **2** (2.06 g, 99% yield) was obtained as pure colorless liquid after concentrated in vacuo. **2** (3.00 g, 19.33 mmol) was then dissolved in benzene (45 mL) and to this solution furfuryl alcohol (2.52 mL, 29.00 mmol) was added with syringe. The resulting mixture was refluxed for 24 h. The crude product was purified by column chromatography to obtain white solid **3** (4.36 g, 89% yield). To a solution of **7** (3.92 g, 11.85 mmol) in dry CH_2Cl_2 (50 mL), **3** (1.00 g, 3.95 mmol), DMAP (0.39 g, 3.16 mmol) and pyridine (1.44 mL, 17.78mmol) was added. The mixture was stirred at ambient temperature for 16 h followed by quenching of excess anhydride with water (1.44 mL) for 5 h. Crude product was purified according to the

literature procedures [53] to give 1.97 g of **8** as a white solid (88% yield). Compound **8** (1.00 g, 1.77 mmol) was dissolved in MeOH (25 mL) and to this solution Dowex H^+ resin was added with a tip of spatula. The resulting mixture was stirred at ambient temperature until the consumption of **8** was observed via TLC. The resin was filtered of and washed with MeOH. The crude product was then purified by recrystallization with CH_2Cl_2. The product obtained by filtration to give a white solid **9** (0.83 g, 97% yield). The solid product **9** (0.5 g, 1.03 mmol) was then added to a solution of triethylamine (0.78 mL, 7.21 mmol) and DMAP (0.075 g, 0.62 mmol) in THF (30 mL) under nitrogen. The mixture was cooled to 0 ^oC in ice bath. On the other side, 2-bromo-isobutyryl bromide (0.76 mL, 6.18 mmol) was diluted in THF (6 mL) and added into the former mixture drop wise (15 min). The obtained white suspension was stirred for 3 hours at 0 ^oC, warmed to room temperature and stirred for 21 h. The ammonia salt formed was filtered off and the residue was concentrated in *vacuo*. The product was obtained as a viscous yellow liquid **In2** (1.01 g, 90% yield) after purification via column chromatography.

^1H NMR ($CDCl_3$, δ, ppm) 6.53 (d, 1H, J = 5.7 Hz, C*H* = CH), 6.43 (d, 1H, J = 5.7 Hz, CH = C*H*), 5.22 (s, 1H, C*H* bridgehead proton), 4.90 (d, 1H, J = 12.8 Hz, CH_2), 4.51 (d, 1H, J = 12.8 Hz, CH_2), 4.42-4.28 (m, 8H, J = 53.1 Hz, CH_2 ester protons), 4.06 (t, 2H, J = 6.2 Hz, OCH_2), 3.55 (t, 2H, J = 6.8 Hz, NCH_2), 2.96 (d, 1H, J = 6.4 Hz, C*H*-CH bridge proton), 2.90 (d, 1H, J = 6.4 Hz, CH-C*H* bridge proton), 1.91-1.89 (m, 26H, $NCH_2CH_2CH_2O$, $CBr(CH_3)$), 1.34 (s, 3H, $C(CH_3)$), 1.32 (s, 3H, $C(CH_3)$). Anal. Calcd. for **In2** [$C_{38}H_{51}Br_4NO_{15}$]: C, 42.20; H, 4.75; N, 1.29. Found: C, 42.51; H, 5.13; N, 1.32.

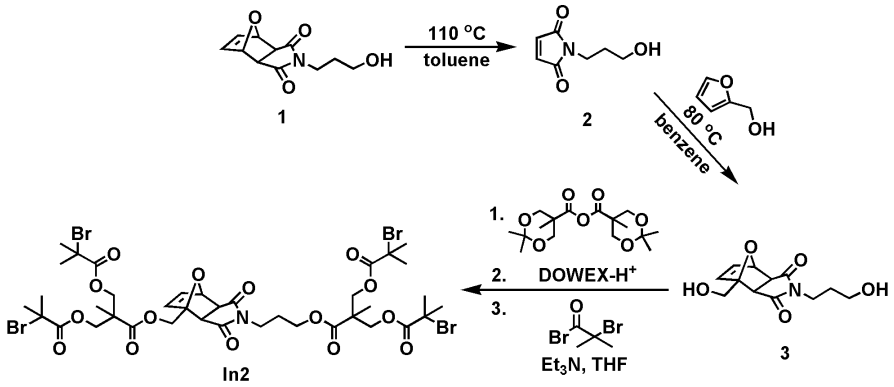

Figure 4.1. Synthesis of 4-arm **In2**

4.2.2. Synthesis of 8-arm ATRP Initiator (In3)

To a solution of **7** (2.04 g, 6.18 mmol) in dry CH_2Cl_2 (25 mL), **9** (0.5 g, 1.03 mmol), DMAP (0.20 g, 1.65mmol) and pyridine (0.75 mL, 9.27 mmol) was added. The mixture was stirred at ambient temperature for 16 h followed by quenching of excess anhydride with water (0.75 mL) for 5 h. Crude product was purified according to the literature procedures [53] to give 1.08 g of **10** as a white solid (89% yield). Compound **10** (0.5 g, 0.42 mmol) was dissolved in MeOH (25 mL) and to this solution Dowex H^+ resin was added with a tip of spatula. The resulting mixture was stirred at ambient temperature until the consumption of **10** was observed via TLC. The resin was filtered of and washed with MeOH. The crude product was then purified by recrystallization with CH_2Cl_2. The product obtained by filtration to give a white solid **11** (0.33 g, 78% yield). Compound **11** (0.2 g, 0.20 mmol) was then added to a solution of triethylamine (0.39 mL, 2.8 mmol) and DMAP (0.029 g, 0.24 mmol) in THF (20 mL) under nitrogen. The mixture was cooled to 0 ^oC in ice bath. On the other side, 2-bromo-isobutyryl bromide (0.30 mL, 2.4 mmol) was diluted in THF (4 mL) and added into the former mixture drop wise (15 min). The obtained white suspension was stirred for 3 hours at 0 ^oC, warmed to room temperature and stirred for 21 h. The ammonia salt formed was filtered off and the residue was concentrated in *vacuo*. The product was obtained as a viscous yellow liquid **In3** (0.36 g, 83% yield) after purification via column chromatography.

^1H NMR ($CDCl_3$, δ, ppm) 6.56 (d, 1H, J = 5.7 Hz, C*H* = CH), 6.43 (d, 1H, J = 5.7 Hz, CH = C*H*), 5.23 (s, 1H, C*H* bridgehead proton), 4.90 (d, 1H, J = 12.8 Hz, CH_2), 4.52 (d, 1H, J = 12.7 Hz, CH_2), 4.38-4.26 (m, 24H, J = 46.1 Hz, CH_2 ester protons), 4.05 (t, 2H, J = 6.1 Hz, OCH_2), 3.56 (t, 2H, J = 6.8 Hz, NCH_2), 2.98 (d, 1H, J = 6.4 Hz, C*H*-CH bridge proton), 2.92 (d, 1H, J = 6.4 Hz, CH-C*H* bridge proton), 2.24 (q, 2H, J = 7.3 Hz, J = 7.5 Hz, $NCH_2CH_2CH_2O$), 1.91-1.89 (m, 48H, CBr(CH_3)), 1.56 (s, 3H, C(CH_3)), 1.31 (m, 12H, C(CH_3)), 1.26 (s, 3H, C(CH_3)). Anal. Calcd. for **In3** [$C_{74}H_{103}Br_8NO_{31}$]: C, 41.50; H, 4.85; N, 0.65. Found: C, 41.67; H, 5.17; N, 0.70.

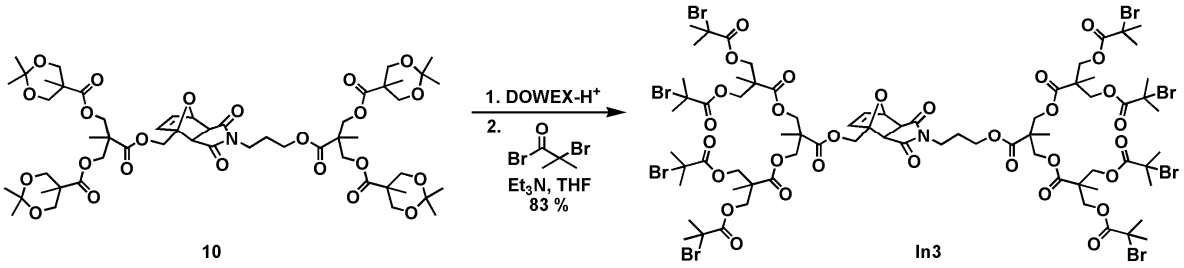

Figure 4.2. Synthesis of 8-arm **In3**

4.2.3. Synthesis of 16-arm ATRP Initiator (In4)

To a solution of **7** (1.27 g, 3.84 mmol) in dry CH_2Cl_2 (13 mL), **11** (0.3 g, 0.32 mmol), DMAP (0.12 g, 1.02 mmol) and pyridine (0.46 mL, 5.76 mmol) was added. The mixture was stirred at ambient temperature for 24 h followed by quenching of excess anhydride with water (0.46 mL) for 5 h. Crude product was purified according to the literature procedures [53] to give 0.58 g of **12** as a white solid (84% yield). Compound **12** (0.3 g, 0.13 mmol) was dissolved in MeOH (20 mL) and to this solution Dowex H^+ resin was added with a tip of spatula. The resulting mixture was stirred at ambient temperature until the consumption of **12** was observed via TLC. The resin was filtered of and washed with MeOH. The crude product was then purified by recrystallization with CH_2Cl_2. The product obtained by filtration to give a white solid **13** (0.20 g, 80% yield). Compound **13** (0.2 g, 0.11 mmol) was then added to a solution of triethylamine (0.43 mL, 3.08 mmol) and DMAP (0.032 g, 0.26 mmol) in THF (15 mL) under nitrogen. The mixture was cooled to 0 ^oC in ice bath. On the other side, 2-bromo-isobutyryl bromide (0.43 mL, 3.52 mmol) was diluted in THF (4 mL) and added into the former mixture drop wise (15 min). The obtained white suspension was stirred for 3 hours at 0 ^oC, warmed to room temperature and stirred for 48 h. The ammonia salt formed was filtered off and the residue was concentrated in *vacuo*. The product was obtained as a viscous yellow liquid **In4** (0.34 g, 76% yield) after purification via column chromatography.

^1H NMR ($CDCl_3$, δ, ppm) 6.58 (d, 1H, J = 5.7 Hz, C*H* = CH), 6.44 (d, 1H, J = 5.7 Hz, CH = C*H*), 5.22 (s, 1H, C*H* bridgehead proton), 4.92 (d, 1H, J = 12.8 Hz, CH_2), 4.49 (d, 1H, J = 12.7 Hz, CH_2), 4.38-4.26 (m, 56H, J = 46.1 Hz, CH_2 ester protons), 4.05 (t, 2H, J = 6.2 Hz, OCH_2), 3.55 (t, 2H, J = 6.8 Hz, NCH_2), 3.00 (d, 1H, J = 6.4 Hz, C*H*-CH bridge

proton), 2.97 (d, 1H, J = 6.4 Hz, CH-C*H* bridge proton), 1.95-1.89 (m, 98H, CBr(CH_3)) and (q, 2H, $NCH_2CH_2CH_2O$), 1.31 (m, 24H, C(CH_3)), 1.26 (m, 18H, C(CH_3)). Anal. Calcd. for **In4** [$C_{146}H_{207}Br_{16}NO_{63}$]: C, 41.14; H, 4.89; N, 0.33. Found: C, 40.95; H, 4.96; N, 0.36.

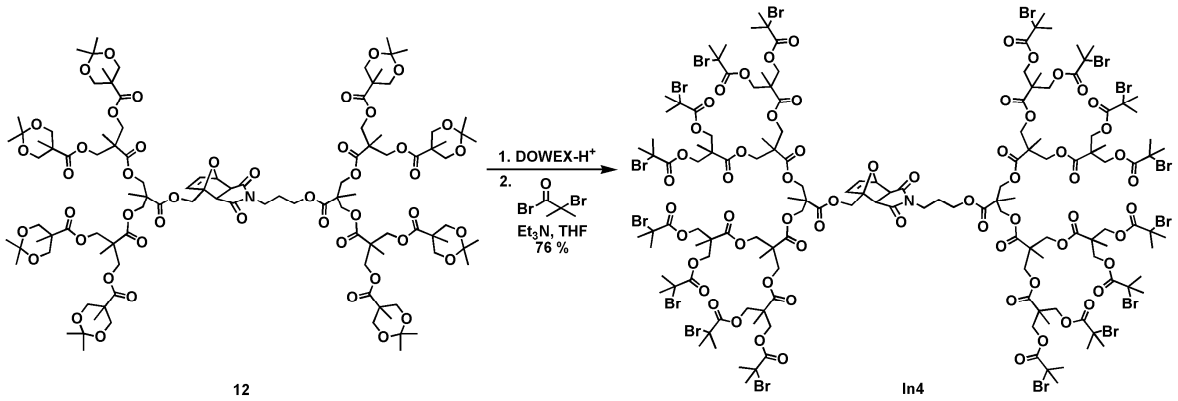

Figure 4.3. Synthesis of 16-arm **In4**

4.2.4. Synthesis of 32-arm ATRP Initiator (In5)

To a solution of **7** (1.27 g, 3.84 mmol) in dry CH_2Cl_2 (15 mL), **13** (0.3 g, 0.16 mmol), DMAP (0.13 g, 1.02 mmol) and pyridine (0.46 mL, 5.76 mmol) was added. The mixture was stirred at ambient temperature for 52 h followed by quenching of excess anhydride with water (0.46 mL) for 5 h. Crude product was purified according to the literature procedures [53] to give 0.60 g of **14** as a white solid (87% yield). Compound **14** (0.5 g, 0.114 mmol) was dissolved in MeOH (20 mL) and to this solution Dowex H^+ resin was added with a tip of spatula. The resulting mixture was stirred at ambient temperature until the consumption of **12** was observed via TLC. The resin was filtered of and washed with MeOH. The crude product was then purified by recrystallization with CH_2Cl_2. The product obtained by filtration to give a white solid **13** (0.38 g, 90% yield). Compound **13** (0.3 g, 0.08 mmol) was then added to a solution of triethylamine (2.08 mL, 14.9 mmol) and DMAP (0.094 g, 0.77 mmol) in THF (15 mL) under nitrogen. The mixture was cooled to 0 ^oC in ice bath. On the other side, 2-bromo-isobutyryl bromide (1.58 mL, 12.8 mmol) was diluted in THF (6 mL) and added into the former mixture drop wise (15 min). The obtained white suspension was stirred for 3 hours at 0 ^oC, warmed to room temperature and stirred

for 5 days. The ammonia salt formed was filtered off and the residue was concentrated in *vacuo*. The product was obtained as a viscous yellow liquid **In5** (0.52 g, 76% yield) after purification via column chromatography.

^{1}H NMR ($CDCl_3$, δ, ppm) 6.58 (d, 1H, J = 5.3 Hz, C*H* = CH), 6.44 (d, 1H, J = 5.5 Hz, CH = C*H*), 5.21 (s, 1H, C*H* bridgehead proton), 4.97 (d, 1H, J = 12.8 Hz, CH_2), 4.47 (d, 1H, J = 12.8 Hz, CH_2), 4.39-4.26 (m, 120H, J = 51.9 Hz, CH_2 ester protons), 4.06 (bs, 2H, OCH_2), 3.54 (bs, 2H, NCH_2), 3.01 (d, 1H, J = 6.3 Hz, C*H*-CH bridge proton), 2.98 (d, 1H, J = 6.3 Hz, CH-C*H* bridge proton), 1.89 (bs, 194H, CBr(CH_3)) and (q, 2H, $NCH_2CH_2CH_2O$), 1.56 (bs, 12H, C(CH_3)), 1.31 (bs, 48H, C(CH_3)), 1.26 (bs, 30H, C(CH_3)). Anal. Calcd. for **In5** [$C_{290}H_{415}Br_{32}NO_{127}$]: C, 40.96; H, 4.92; N, 0.16. Found: C, 41.28; H, 5.29; N, 0.18.

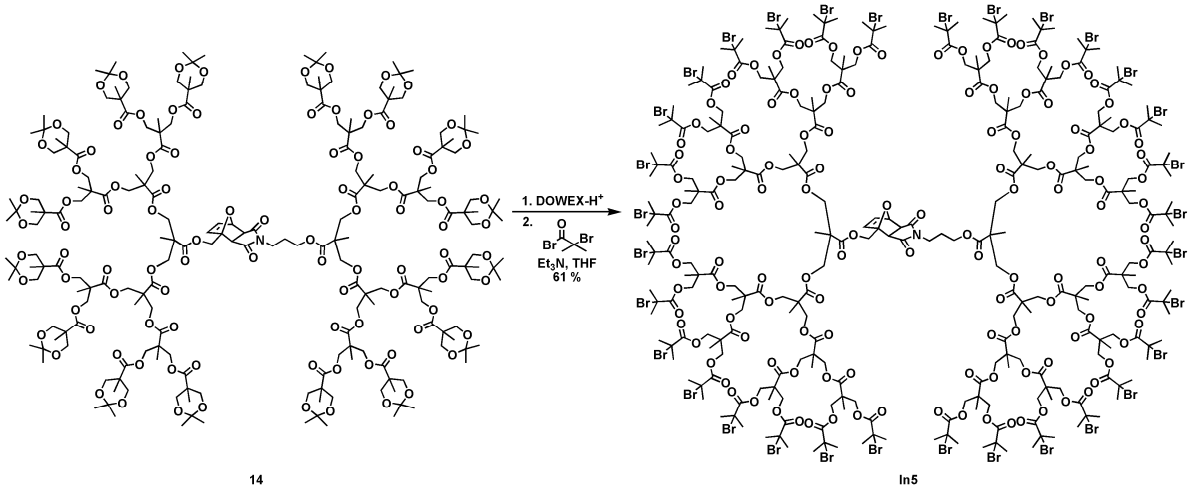

Figure 4.4. Synthesis of 32-arm **In5**

4.2.5. Synthesis of 3-arm ATRP Initiator (In1)

16 (1.0 g, 3.2 mmol) was dissolved in benzene (12 mL) and to this solution furfuryl alcohol (0.31 mL, 3.5 mmol) was added with a syringe. The resulting mixture was refluxed 24 h. The crude product was purified by column chromatography to obtain white solid **3** (1.3 g, 99% yield). The solid product **3** (1.00 g, 2.45 mmol) was dissolved in MeOH (50 mL) and to this solution Dowex H^+ resin was added with a tip of spatula. The mixture obtained was stirred at ambient temperature until the consumption of starting material was

observed via TLC. The resin was filtered of and washed with MeOH. The crude product was then purified by recrystallization with CH_2Cl_2. The product obtained by filtration to give a white solid **4** (0.89 g, 99% yield). The solid compound **4** (1.00 g, 2.71 mmol) was the added to a solution of triethylamine (1.98 mL, 14.23 mmol) and DMAP (0.15 g, 1.22 mmol) in THF (60 mL) under nitrogen. The mixture was cooled to 0 ^{o}C in ice bath. On the other side, 2-bromo-isobutyryl bromide (1.51 mL, 12.20 mmol) was diluted in THF (15 mL) and added into the former mixture drop wise (30 min). The obtained white suspension was stirred for 3 hours at 0 ^{o}C, warmed to room temperature and stirred for 21 h. The ammonia salt formed was filtered off and the residue was concentrated in *vacuo*. The product was obtained as a viscous yellow liquid **In1** (2.01 g, 91% yield) after purification via column chromatography.

^{1}H NMR ($CDCl_3$, δ, ppm) 6.54 (d, 1H, J = 5.7 Hz, C*H* = CH), 6.46 (d, 1H, J = 5.7 Hz, CH = C*H*), 5.25 (s, 1H, C*H* bridgehead proton), 4.91 (d, 1H, J = 12.6 Hz, CH_2), 4.55 (d, 1H, J = 12.6 Hz, CH_2), 4.40 (d, 2H, J = 11.1 Hz, CH_2 ester protons), 4.33 (d, 2H, J = 11.1 Hz, CH_2 ester protons), 4.08 (t, 2H, J = 6.3 Hz, OCH_2), 3.56 (t, 2H, J = 6.3 Hz, NCH_2), 2.97 (d, 1H, J = 6.9 Hz, C*H*-CH bridge proton), 2.93 (d, 1H, J = 6.9 Hz, CH-C*H* bridge proton), 1.93-1.89 (m, 20H, $NCH_2CH_2CH_2O$, $CBr(CH_3)$), 1.35 (s, 3H, $C(CH_3)$). Anal. Calcd. for **In1** [$C_{29}H_{38}Br_3NO_{11}$]: C, 42.67; H, 4.69; N, 1.72. Found: C, 42.71; H, 4.93; N, 1.65.

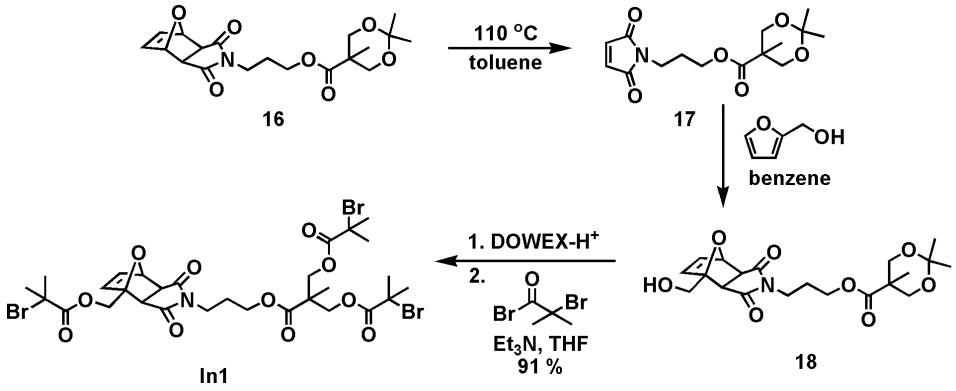

Figure 4.5. Synthesis of 3-arm **In1**

4.2.6. Synthesis of 4-arm PMMA Polymer (P2)

4-arm PMMA was prepared by ATRP of MMA. In 10 mL Shlenk tube, MMA (0.789 mL, 7.40 mmol), Bipyridine (0.023 mg, 0.148 mmol), CuBr (0.0106 g, 0.074 mmol), toluene (3.94 mL), and 4-arm initiator **(In2)** (0.020 g, 0.0185 mmol) were added, and the reaction mixture was degassed, and left in niterogen. The tube was then placed in thermostated oil bath at 70 ^{o}C for 2 h. Polymerization mixture was diluted with THF, passed through a neutral alumina column to remove the catalyst, and precipitated in hexane. The polymer was dried for 24 h in vacuum line at ambient temperature. The 4-arm PMMA (**P2**) was obtained as white solid ($[M]_o/[I]_o = 400$, $[I]_o$:[CuBr]:[Bipyridine] = 1:4:8, conversion = 24%, $M_{n,theo}$ = 9,870, $M_{n,NMR}$ =15,930, $M_{n,GPC}$ = 12,580, M_w/M_n = 1.35, relative to linear PS).

^{1}H NMR ($CDCl_3$, δ, ppm) 6.54 (br s, 1H, C*H* = CH), 6.41 (br s, 1H, CH = C*H*), 5.21 (br s, 1H, C*H* bridgehead proton), 4.92 (d, 1H, CH_2), 4.47 (d, 1H, CH_2), 4.32-4.06 (m, 10H, OCH_2 and CH_2 ester protons), 3.56 (br s, 5H, OCH_3 of PMMA and NCH_2), 2.97 (br s, 1H, C*H*-CH bridge proton), 2.90 (br s, 1H, CH-C*H* bridge proton), 2.69 (q, 2H, $NCH_2CH_2CH_2O$), 1.88-0.80 (m, 35H, CBr(CH_3), C(CH_3), CH_2 and CH_3 along polymer backbone).

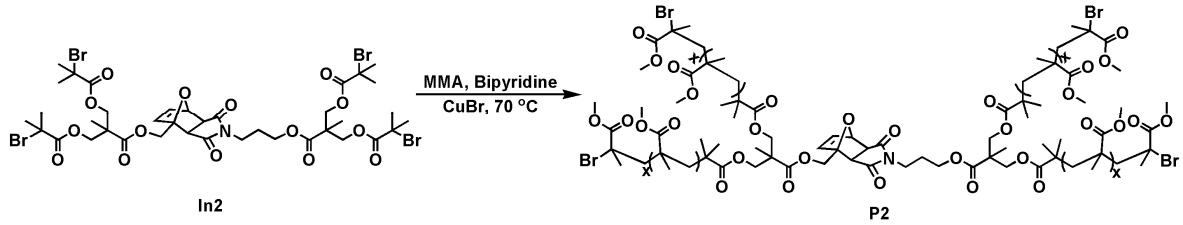

Figure 4.6. Synthesis of 4-arm PMMA polymer

4.2.7. Synthesis of P2a and P2b by Retro-Diels-Alder Reaction

The mixture of **P2** (4-arm PMMA) (50.0 mg, 4.16 µmol) and anthracene (2.22 mg, 12.5 µmol) were dissolved in toluene (0.7 ml) and refluxed at 110 ^{o}C for 16 h. ^{1}H NMR analysis and GPC result of resulting mixture indicated a cleavage of **P2** into **P2a** and **P2b**. ($M_{n,GPC}$ = 8,910, M_w/M_n = 1.40, relative to linear PS).

^{1}H NMR ($CDCl_3$, δ, ppm) 7.38 (br s, 1H, CH=CH), 7.35 (m, 4H, aromatic protons), 7.15 (m, 4H, aromatic protons), 6.40 (br s, 1H, C*H* = CH), 6.33 (br s, 1H, CH = C*H*), 5.11 (d, 2H, CH_2), 4.75 (br s, 2H, C*H*-C*H* bridge head protons), 4.29-4.08 (m, 10H, OCH_2 and CH_2 ester protons), 3.56 (br s, 5H, OCH_3 of PMMA and NCH_2), 3.17 (br s, 2H, C*H*-C*H* bridge protons), 2.69 (q, 2H, $NCH_2CH_2CH_2O$), 1.86-0.81 (m, 35H, CBr(CH_3), C(CH_3), CH_2 and CH_3 along polymer backbone).

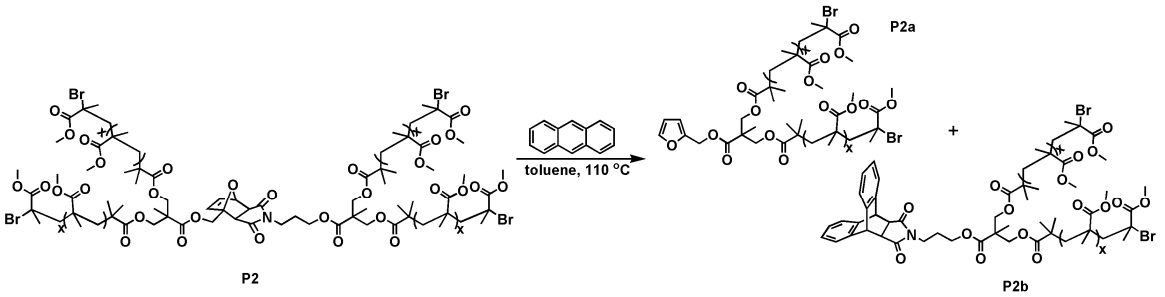

Figure 4.7. Retro of 4-arm PMMA polymer

4.2.8. Synthesis of 8-arm PMMA Polymer (P3)

8-arm PMMA was prepared by ATRP of MMA. In 10 mL Shlenk tube, MMA (0.774 mL, 7.26 mmol), Bipyridine (0.023 mg, 0.145 mmol), CuBr (0.0104 g, 0.073 mmol), toluene (3.87 mL), and 8-arm initiator **(In3)** (0.020 g, 9.08 µmol) were added, and the reaction mixture was degassed, and left in niterogen. The tube was then placed in thermostated oil bath at 70 ^{o}C for 2 h. Polymerization mixture was diluted with THF, passed through a neutral alumina column to remove the catalyst, and precipitated in hexane. The polymer was dried for 24 h in vacuum line at ambient temperature. The 8-arm PMMA (**P3**) was obtained as white solid ($[M]_o/[I]_o$ = 800, $[I]_o$:[CuBr]:[Bipyridine] = 1:8:16, conversion = 30%, $M_{n,theo}$ = 24,690, $M_{n,NMR}$ =31,840, $M_{n,GPC}$ = 26,990, M_w/M_n = 1.24, relative to linear PS).

^{1}H NMR ($CDCl_3$, δ, ppm) 6.55 (br s, 1H, C*H* = CH), 6.42 (br s, 1H, CH = C*H*), 5.21 (br s, 1H, C*H* bridgehead proton), 4.89 (d, 1H, CH_2), 4.48 (br s, 1H, CH_2), 4.34-4.05 (m, 26H, OCH_2 and CH_2 ester protons), 3.57 (br s, 5H, OCH_3 of PMMA and NCH_2), 2.98 (br s, 1H, C*H*-CH bridge proton), 2.92 (br s, 1H, CH-C*H* bridge proton), 2.69 (q, 2H,

$NCH_2CH_2CH_2O$), 1.88-0.81 (m, 71H, $CBr(CH_3)$, $C(CH_3)$, CH_2 and CH_3 along polymer backbone).

4.2.9. Synthesis of P3a and P3b by Retro-Diels-Alder Reaction

The mixture of **P3** (8-arm PMMA) (40.0 mg, 1.53 µmol) and anthracene (1.10 mg, 6.12 µmol) were dissolved in toluene (0.5 ml) and refluxed at 110 °C for 16 h. ^{1}H NMR analysis and GPC result of resulting mixture indicated a cleavage of **P3** into **P3a** and **P3b**. ($M_{n,GPC}$ = 16,680, M_w/M_n = 1.34, relative to linear PS).

^{1}H NMR ($CDCl_3$, δ, ppm) 7.40 (br s, 1H, C*H*=CH), 7.35 (m, 4H, aromatic protons), 7.15 (m, 4H, aromatic protons), 6.42 (br s, 1H, C*H* = CH), 6.34 (br s, 1H, CH = C*H*), 5.09 (d, 2H, CH_2), 4.76 (br s, 2H, C*H*-C*H* bridge head protons), 4.36-4.06 (m, 26H, OCH_2 and CH_2 ester protons), 3.57 (br s, 5H, OCH_3 of PMMA and NCH_2), 3.18 (br s, 2H, C*H*-C*H* bridge protons), 2.69 (q, 2H, $NCH_2CH_2CH_2O$), 1.88-0.81 (m, 71H, $CBr(CH_3)$, $C(CH_3)$, CH_2 and CH_3 along polymer backbone).

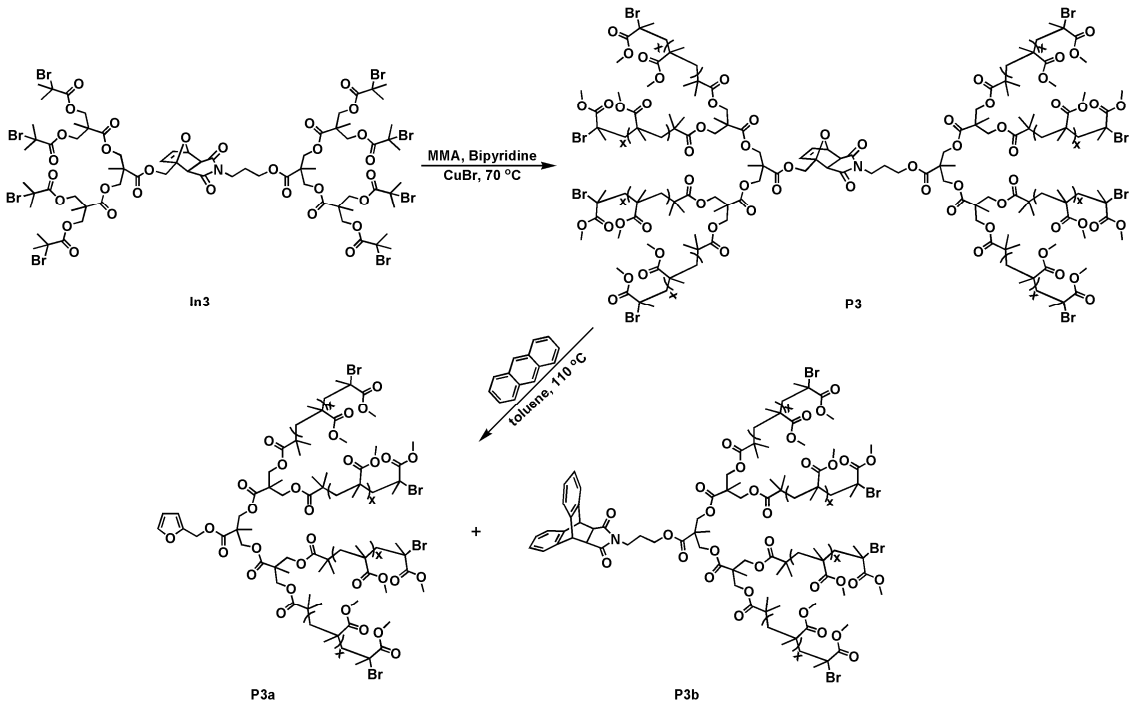

Figure 4.8. Synthesis of 8-arm PMMA polymer and retro of it

4.2.10. Synthesis of 16-arm PMMA Polymer (P4)

16-arm PMMA was prepared by ATRP of MMA. In 10 mL Shlenk tube, MMA (0.80 mL, 7.50 mmol), Bipyridine (0.023 mg, 0.150 mmol), CuBr (0.0108 g, 0.075 mmol), toluene (4.00 mL), and 16-arm initiator **(In4)** (0.020 g, 4.69 µmol) were added, and the reaction mixture was degassed, and left in niterogen. The tube was then placed in thermostated oil bath at 70 ^{o}C for 2 h. Polymerization mixture was diluted with THF, passed through a neutral alumina column to remove the catalyst, and precipitated in hexane. The polymer was dried for 24 h in vacuum line at ambient temperature. The 16-arm PMMA (**P4**) was obtained as white solid ($[M]_o/([I]_o$ = 1600, $[I]_o$:[CuBr]:[Bipyridine] = 1:16:32, conversion = 28%, $M_{n,theo}$ = 46,040, $M_{n,NMR}$ =73,580 , $M_{n,GPC}$ = 39,830, M_w/M_n = 1.23, relative to linear PS).

^{1}H NMR ($CDCl_3$, δ, ppm) 6.56 (br s, 1H, C*H* = CH), 6.42 (br s, 1H, CH = C*H*), 5.20 (br s, 1H, C*H* bridgehead proton), 4.91 (d, 1H, CH_2), 4.48 (d, 1H, CH_2), 4.35-4.06 (m, 56H, OCH_2 and CH_2 ester protons), 3.57 (br s, 5H, OCH_3 of PMMA and NCH_2), 2.99 (br s, 1H, C*H*-CH bridge proton), 2.95 (br s, 1H, CH-C*H* bridge proton), 2.69 (q, 2H, $NCH_2CH_2CH_2O$), 1.88-0.81 (m, 143H, CBr(CH_3), C(CH_3), CH_2 and CH_3 along polymer backbone).

4.2.11. Synthesis of P4a and P4b by Retro-Diels-Alder Reaction

The mixture of **P4** (16-arm PMMA) (40.0 mg, 1.00 µmol) and anthracene (0.71 mg, 4.00 µmol) were dissolved in toluene (0.5 ml) and refluxed at 110 ^{o}C for 16 h. ^{1}H NMR analysis and GPC result of resulting mixture indicated a cleavage of **P4** into **P4a** and **P4b**. ($M_{n,GPC}$ = 26,000, M_w/M_n = 1.23, relative to linear PS).

^{1}H NMR ($CDCl_3$, δ, ppm) 7.40 (br s, 1H, C*H*=CH), 7.36 (m, 4H, aromatic protons), 7.15 (m, 4H, aromatic protons), 6.41 (br s, 1H, C*H* = CH), 6.34 (br s, 1H, CH = C*H*), 5.08 (d, 2H, CH_2), 4.76 (br s, 2H, C*H*-C*H* bridge head protons), 4.38-4.05 (m, 48H, OCH_2 and CH_2 ester protons), 3.57 (br s, 5H, OCH_3 of PMMA and NCH_2), 3.18 (br s, 2H, C*H*-C*H* bridge protons), 2.69 (q, 2H, $NCH_2CH_2CH_2O$), 1.88-0.82 (m, 143H, CBr(CH_3), C(CH_3), CH_2 and CH_3 along polymer backbone).

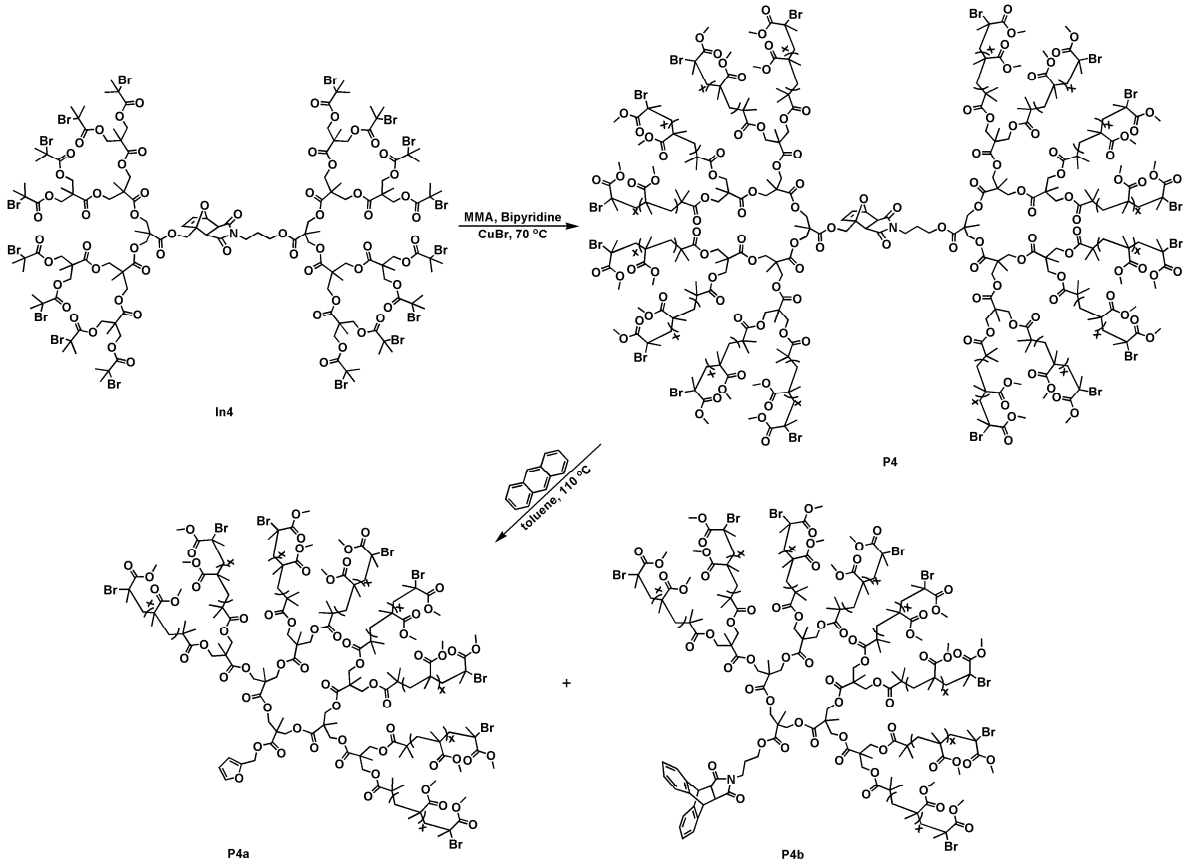

Figure 4.9. Synthesis of 16-arm PMMA polymer and retro of it

4.2.12. Synthesis of 32-arm PMMA Polymer (P5)

32-arm PMMA was prepared by ATRP of MMA. In 10 mL Shlenk tube, MMA (0.80 mL, 7.52 mmol), Bipyridine (0.023 mg, 0.150 mmol), CuBr (0.0108 g, 0.075 mmol), toluene (4.00 mL), and 32-arm initiator **(In5)** (0.020 g, 2.35 μmol) were added, and the reaction mixture was degassed, and left in niterogen. The tube was then placed in thermostated oil bath at 70 ^{o}C for 2 h. Polymerization mixture was diluted with THF, passed through a neutral alumina column to remove the catalyst, and precipitated in hexane. The polymer was dried for 24 h in vacuum line at ambient temperature. The 32-arm PMMA (**P5**) was obtained as white solid ($[M]_o/[I]_o$ = 3200, $[I]_o$:[CuBr]:[Bipyridine] = 1:32:64, conversion = 31%, $M_{n,theo}$ = 101,950 , $M_{n,NMR}$ = 148,800 , $M_{n,GPC}$ = 65,570, M_w/M_n = 1.25, relative to linear PS).

^{1}H NMR ($CDCl_3$, δ, ppm) 6.56 (br s, 1H, C*H* = CH), 6.42 (br s, 1H, CH = C*H*), 5.20 (br s, 1H, C*H* bridgehead proton), 4.97 (d, 1H, CH_2), 4.47 (d, 1H, CH_2), 4.34-4.04 (m, 122H, OCH_2 and CH_2 ester protons), 3.57 (br s, 5H, OCH_3 of PMMA and NCH_2), 2.99 (br

s, 1H, C*H*-CH bridge proton), 2.94 (br s, 1H, CH-C*H* bridge proton), 2.69 (q, 2H, $NCH_2CH_2CH_2O$), 2.03-0.82 (m, 287H, $CBr(CH_3)$, $C(CH_3)$, CH_2 and CH_3 along polymer backbone).

4.2.13. Synthesis of P5a and P5b by Retro-Diels-Alder Reaction

The mixture of **P5** (32-arm PMMA) (100 mg, 1.50 µmol) and anthracene (1.06 mg, 6.00 µmol) were dissolved in toluene (2ml) and refluxed at 110 ^oC for 16 h. ^1H NMR analysis and GPC result of resulting mixture indicated a cleavage of **P5** into **P5a** and **P5b**. ($M_{n,GPC}$ =42,060, M_w/M_n = 1.20, relative to linear PS).

^1H NMR ($CDCl_3$, δ, ppm) 7.40 (br s, 1H, C*H*=CH), 7.36 (m, 4H, aromatic protons), 7.15 (m, 4H, aromatic protons), 6.41 (br s, 1H, C*H* = CH), 6.33 (br s, 1H, CH = C*H*), 5.07 (d, 2H, CH_2), 4.75 (br s, 2H, C*H*-C*H* bridge head protons), 4.37-4.01 (m, 122H, OCH_2 and CH_2 ester protons), 3.57 (br s, 5H, OCH_3 of PMMA and NCH_2), 3.17 (br s, 2H, C*H*-C*H* bridge protons), 2.69 (q, 2H, $NCH_2CH_2CH_2O$), 2.04-0.82 (m, 287H, $CBr(CH_3)$, $C(CH_3)$, CH_2 and CH_3 along polymer backbone).

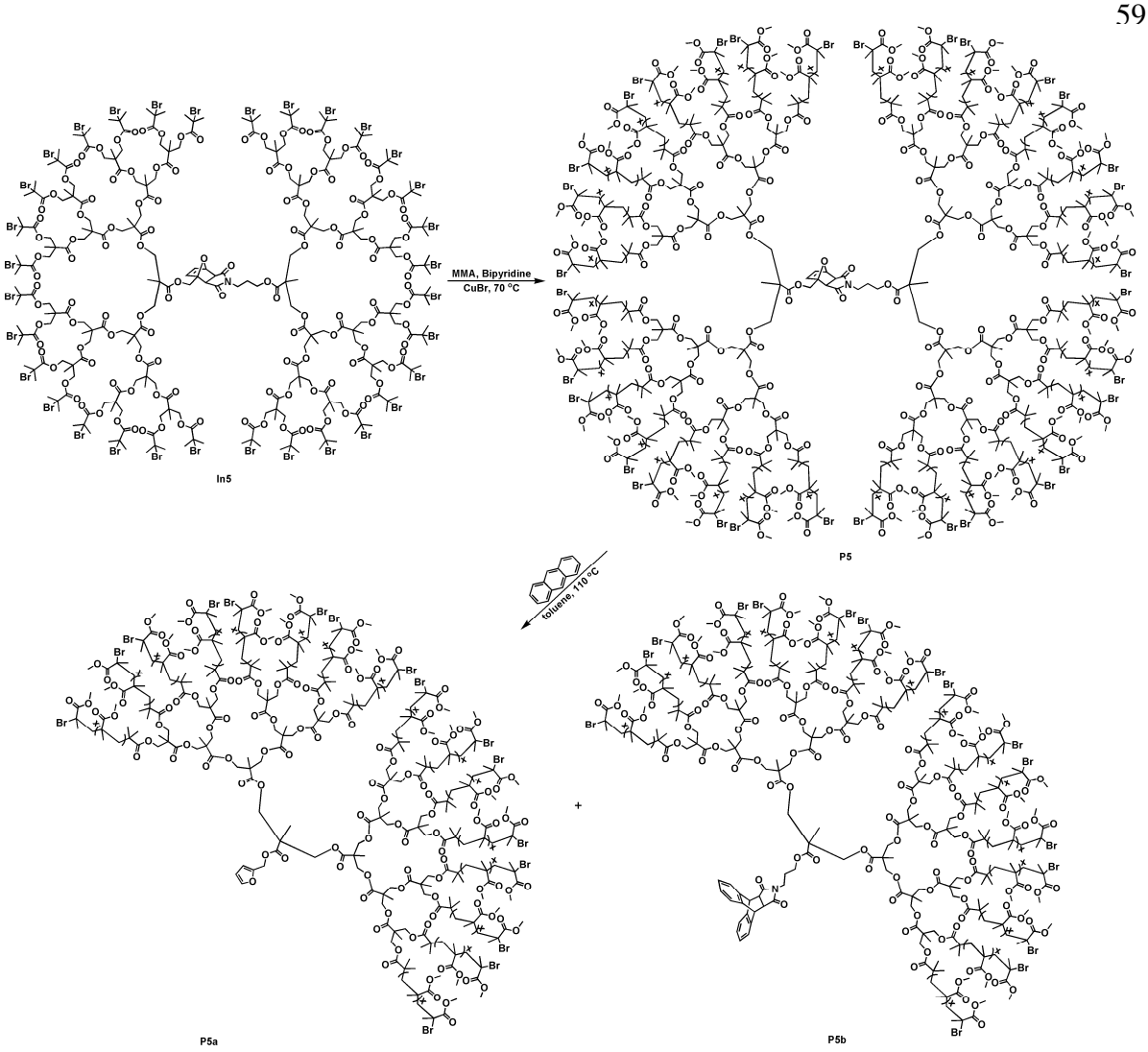

Figure 4.10. Synthesis of 32-arm PMMA polymer and retro of it

4.2.14. Synthesis of 3-arm PMMA Polymer (P9)

3-arm PMMA was prepared by ATRP of MMA. In 10 mL Shlenk tube, MMA (3.93 mL, 36.9 mmol), PMDETA (31 µL, 0.147 mmol), CuBr (0.0106 g, 0.0738 mmol), anisole (3.93 mL), and 3-arm initiator **(In1)** (0.020 g, 0.0246 mmol) were added, and the reaction mixture was degassed, and left in niterogen. The tube was then placed in thermostated oil bath at 70 ^{o}C for 2 h. Polymerization mixture was diluted with THF, passed through a neutral alumina column to remove the catalyst, and precipitated in hexane. The polymer was dried for 24 h in vacuum line at ambient temperature. The 3-arm PMMA (**P1**) was obtained as white solid ($[M]_o/[I]_o$ = 1500, $[I]_o$:[CuBr]:[PMDETA] = 1:3:6, conversion =

71%, $M_{n,theo}$ = 107,205, $M_{n,NMR}$ = 134,040 , $M_{n,GPC}$ = 85,790, M_w/M_n = 1.38, relative to linear PS).

^{1}H NMR ($CDCl_3$, δ, ppm) 6.54 (br s, 1H, C*H* = CH), 6.46 (d, 1H, CH = C*H*), 5.24 (br s, 1H, C*H* bridgehead proton), 4.91 (d, 1H, CH_2), 4.54 (d, 1H, CH_2), 4.32-4.07 (m, 6H, OCH_2 and CH_2 ester protons), 4.34 (t, 2H, OCH_2), 3.57 (br s, 5H, OCH_3 of PMMA and NCH_2), 2.97 (br s, 1H, C*H*-CH bridge proton), 2.89 (br s, 1H, CH-C*H* bridge proton), 2.69 (q, 2H, $NCH_2CH_2CH_2O$), 1.87-0.82 (m, 26H, CBr(CH_3), C(CH_3), CH_2 and CH_3 along polymer backbone).

4.2.15. Synthesis of P9a and P9b by Retro-Diels-Alder Reaction

The mixture of **P9** (3-arm PMMA) (100mg, 1.15 µmol) and anthracene (0.82 mg, 4.60 µmol) were dissolved in toluene (1 ml) and refluxed at 110 ^{o}C for 16 h. ^{1}H NMR analysis and GPC result of resulting mixture indicated a cleavage of **P9** into **P9a** and **P9b**. ($M_{n,GPC}$ = 54,400, M_w/M_n = 1.32, relative to linear PS).

^{1}H NMR ($CDCl_3$, δ, ppm) 7.39 (br s, 1H, C*H*=CH), 7.35 (m, 4H, aromatic protons), 7.15 (m, 4H, aromatic protons), 6.36 (br s, 1H, C*H* = CH), 6.32 (br s, 1H, CH = C*H*), 5.02 (d, 1H, CH_2), 4.96 (d, 1H, CH_2), 4.75 (br s, 2H, C*H*-C*H* bridge head protons), 4.34-4.08 (m, 6H, OCH_2 and CH_2 ester protons), 3.56 (br s, 5H, OCH_3 of PMMA and NCH_2), 3.17 (br s, 2H, C*H*-C*H* bridge protons), 2.69 (q, 2H, $NCH_2CH_2CH_2O$), 2.03-0.80 (m, 26H, CBr(CH_3), C(CH_3), CH_2 and CH_3 along polymer backbone).

4.2.16. Synthesis of 3-arm PMMA Polymer (P1)

3-arm PMMA was prepared by ATRP of MMA. In 10 mL Shlenk tube, MMA (0.786 mL, 7.38 mmol), Bipyridine (0.023 mg, 0.147 mmol), CuBr (0.0106 g, 0.0738 mmol), toluene (3.93 mL), and 3-arm initiator **(In1)** (0.020 g, 0.0246 mmol) were added, and the reaction mixture was degassed, and left in niterogen. The tube was then placed in thermostated oil bath at 70 ^{o}C for 2 h. Polymerization mixture was diluted with THF, passed through a neutral alumina column to remove the catalyst, and precipitated in hexane. The polymer was dried for 24 h in vacuum line at ambient temperature. The 3-arm PMMA (**P1**) was obtained as white solid ($[M]_o/[I]_o$ = 300, $[I]_o$:[CuBr]:[Bipyridine] = 1:3:6,

conversion = 26%, $M_{n,theo}$ = 8,020 , $M_{n,NMR}$ =11,190 , $M_{n,GPC}$ = 10450, M_w/M_n = 1.30, relative to linear PS).

^{1}H NMR ($CDCl_3$, δ, ppm) 6.54 (br s, 1H, C*H* = CH), 6.46 (d, 1H, CH = C*H*), 5.24 (br s, 1H, C*H* bridgehead proton), 4.91 (d, 1H, CH_2), 4.54 (d, 1H, CH_2), 4.32-4.07 (m, 6H, OCH_2 and CH_2 ester protons), 4.34 (t, 2H, OCH_2), 3.57 (br s, 5H, OCH_3 of PMMA and NCH_2), 2.97 (br s, 1H, C*H*-CH bridge proton), 2.89 (br s, 1H, CH-C*H* bridge proton), 2.69 (q, 2H, $NCH_2CH_2CH_2O$), 1.87-0.82 (m, 26H, CBr(CH_3), C(CH_3), CH_2 and CH_3 along polymer backbone).

4.2.17. Synthesis of P1a and P1b by Retro-Diels-Alder Reaction

The mixture of **P1** (3-arm PMMA) (30.0 mg, 2.88 µmol) and anthracene (1.54 mg, 8.64 µmol) were dissolved in toluene (0.4 ml) and refluxed at 110 ^{o}C for 16 h. ^{1}H NMR analysis and GPC result of resulting mixture indicated a cleavage of **P1** into **P1a** and **P1b**. ($M_{n,GPC}$ = 8330, M_w/M_n = 1.36, relative to linear PS).

^{1}H NMR ($CDCl_3$, δ, ppm) 7.39 (br s, 1H, C*H*=CH), 7.35 (m, 4H, aromatic protons), 7.15 (m, 4H, aromatic protons), 6.36 (br s, 1H, C*H* = CH), 6.32 (br s, 1H, CH = C*H*), 5.02 (d, 1H, CH_2), 4.96 (d, 1H, CH_2), 4.75 (br s, 2H, C*H*-C*H* bridge head protons), 4.34-4.08 (m, 6H, OCH_2 and CH_2 ester protons), 3.56 (br s, 5H, OCH_3 of PMMA and NCH_2), 3.17 (br s, 2H, C*H*-C*H* bridge protons), 2.69 (q, 2H, $NCH_2CH_2CH_2O$), 2.03-0.80 (m, 26H, CBr(CH_3), C(CH_3), CH_2 and CH_3 along polymer backbone).

4.2.18. Synthesis of P1a and P1c by Retro-Diels-Alder Reaction (without anthracene)

P1 (3-arm PMMA) (30.0 mg, 2.88 µmol) was dissplved in toluene (2ml) and refluxed at 110 ^{o}C for 16 h. ^{1}H NMR analysis and GPC result of resulting mixture indicated a cleavage of **P1** into **P1a** and **P1c**. ($M_{n,GPC}$ = 8700, M_w/M_n = 1.30, relative to linear PS).

^{1}H NMR ($CDCl_3$, δ, ppm) 7.39 (br s, 1H, C*H*=CH), 6.69 (br s, 2H, maleimide C*H*=CH), 6.35 (br s, 1H, CH = C*H*), 6.32 (br s, 1H, C*H* = C*H*), 5.02 (d, 1H, CH_2), 4.96 (d, 1H, CH_2), 4.32-4.09 (m, 6H, OCH_2 and CH_2 ester protons), 3.56 (br s, 5H, OCH_3 of PMMA and NCH_2), 2.66 (q, 2H, $NCH_2CH_2CH_2O$), 2.03-0.80 (m, 26H, CBr(CH_3), C(CH_3), CH_2 and CH_3 along polymer backbone) Figure 3.14.

4.3. Thermally Cleavable Miktoarm Star Polymers

4.3.1. Synthesis of 1OH:1Br ATRP and ROP Initiator (In1:1)

Furan-protected *N*-hydroxypropylmaleimide (2.00 g, 8.96 mmol) was added to a solution of triethylamine (1.58 mL, 15.68 mmol) and DMAP (0.16 g, 1.34 mmol) in THF (20 mL) under nitrogen. The mixture was cooled to 0 ^{o}C in ice bath. On the other side, 2-bromo-isobutyryl bromide (1.66 mL, 13.44 mmol) was diluted in THF (10 mL) and added into the former mixture drop wise (20 min). The obtained white suspension was stirred for 3 hours at 0 ^{o}C, warmed to room temperature and stirred for 16 h. The ammonia salt formed was filtered off and the residue was concentrated in *vacuo*. The product was obtained as a white solid **21** (3.07 g, 92% yield) after purification via column chromatography. Resulting compound **21** (1.00 g, 2.69 mmol) was dissolved in toluene (30 mL) and then refluxed for 24 h. The product **22** (0.79 g, 97% yield) was obtained as pure colorless liquid after concentrated in vacuo. **22** (0.5 g, 1.64 mmol) was then dissolved in benzene (20 mL) and to this solution furfuryl alcohol (0.21 mL, 2.46 mmol) was added with syringe. The resulting mixture was refluxed for 24 h. The crude product was purified by column chromatography to obtain white solid **In1:1** (0.55 g, 83% yield).

^{1}H NMR ($CDCl_3$, δ, ppm) 6.59-6.46 (m, 2H, C*H* = C*H*). 5.09 (d, 1H, *J* = 1.5 Hz , C*H* bridgehead proton), 4.97 (s, 1H, O*H*), 4.11-3.97 (m, 3H), 3.68 (dd, 1H, *J* = 12.6, 4.1 Hz), 3.43 (t, 2H, *J* = 6.8 Hz, NCH_2), 3.04 (d, 1H, *J* = 6.4 Hz, C*H*-CH bridge proton), 2.88 (d, 1H, *J* = 6.4 Hz, CH-C*H* bridge proton), 1.91 (s, 6H, CBr(CH_3)), 1.78 (q, 2H, $NCH_2CH_2CH_2O$).

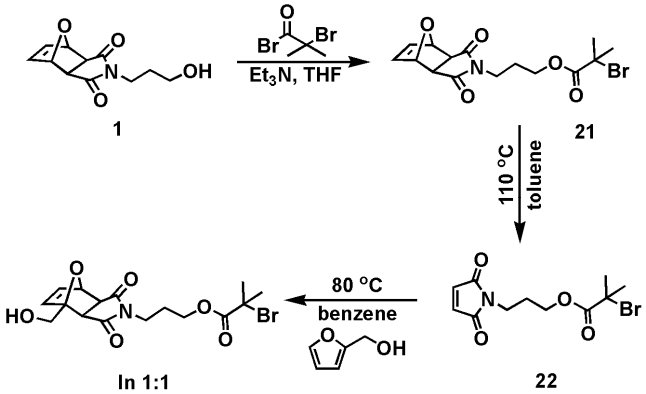

Figure 4.11. Synthesis of **In1:1** ATRP and ROP initiator

4.3.2. Synthesis of 1OH:2Br ATRP and ROP Initiator (In1:2)

To a solution of **7** (6.66 g, 20.16 mmol) in dry CH_2Cl_2 (80 mL), **1** (3.00 g, 13.44 mmol), DMAP (0.65 g, 5.37 mmol) and pyridine (2.44 mL, 30.24 mmol) was added. The mixture was stirred at ambient temperature for 16 h followed by quenching of excess anhydride with water (2.44 mL) for 5 h. Crude product was purified according to the literature procedures [53] to give 4.54 g of **16** as a white solid (89% yield). Compound **16** (3.00 g, 7.91 mmol) was dissolved in MeOH (60 mL) and to this solution Dowex H^+ resin was added with a tip of spatula. The resulting mixture was stirred at ambient temperature until the consumption of **16** was observed via TLC. The resin was filtered of and washed with MeOH. The crude product was then purified by recrystallization with CH_2Cl_2. The product obtained by filtration to give a white solid **23** (2.60 g, 97% yield). Then **23** (2.00 g, 5.89 mmol) was added to a solution of triethylamine (2.87 mL, 20.62 mmol) and DMAP (0.23 g, 1.76 mmol) in THF (30 mL) under nitrogen. The mixture was cooled to 0 ^oC in ice bath. On the other side, 2-bromo-isobutyryl bromide (2.18 mL, 17.67 mmol) was diluted in THF (10 mL) and added into the former mixture drop wise (30 min). The obtained white suspension was stirred for 3 hours at 0 ^oC, warmed to room temperature and stirred for 16 h. The ammonia salt formed was filtered off and the residue was concentrated in *vacuo*. The product was obtained as a white solid **24** (3.15 g, 84% yield) after purification via column chromatography. Resulting compound **24** (2.00 g, 3.14 mmol) was dissolved in toluene (80 mL) and then refluxed for 24 h. The product **25** (1.62 g, 91% yield) was obtained as pure colorless liquid after concentrated in vacuo. **25** (1.00 g, 1.76 mmol) was then dissolved in benzene (30 mL) and to this solution furfuryl alcohol (0.23 mL, 2.63 mmol) was added with syringe. The resulting mixture was refluxed for 24 h. The crude product was purified by column chromatography to obtain white solid **In1:2** (0.95 g, 81% yield).

^1H NMR ($CDCl_3$, δ, ppm) 6.58 (d, 1H, J = 5.7 Hz, C*H* = CH), 6.53 (dd, 1H, J = 5.7, 1.7 Hz, CH = C*H*), 5.22 (d, 1H, J = 1.7 Hz , C*H* bridgehead proton), 4.41 (dd, 2H, J = 10.8, 2.6), 4.31 (d, 2H, J = 10.8 Hz), 4.12-3.98 (m, 4H), 3.58 (dt, 2H, J = 6.7, 3.3 Hz, NCH_2), 2.98 (d, 1H, J = 6.5 Hz, C*H*-CH bridge proton), 2.95 (d, 1H, J = 6.5 Hz, CH-C*H* bridge proton), 2.75-2.69 (m, 1H), 1.89-1.87 (m, 14H, $NCH_2CH_2CH_2$, $CBr(CH_3)$), 1.35 (s, 3H, CH_3).

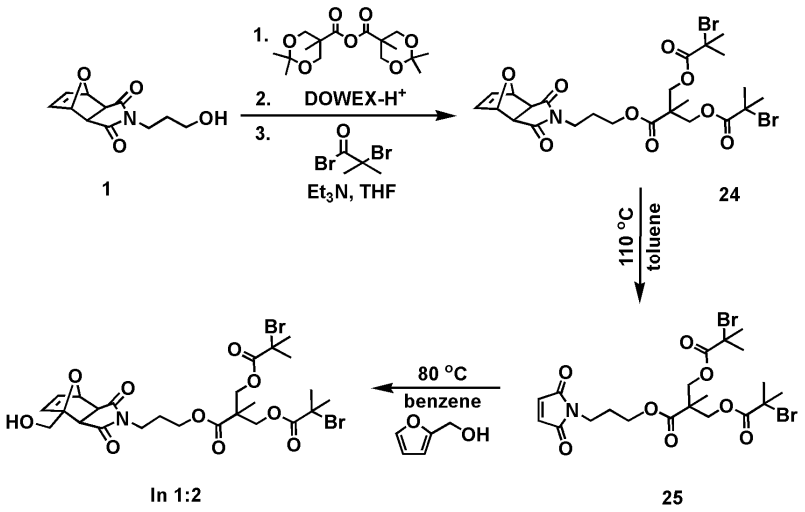

Figure 4.12. Synthesis of **In1:2** ATRP and ROP initiator

4.3.3. Synthesis of 2OH:2Br ATRP and ROP Initiator (In2:2)

To a solution of **7** (0.37 g, 1.12 mmol) in dry CH_2Cl_2 (30 mL), **In1:2** (0.5 g, 0.75 mmol), DMAP (0.036 g, 0.3 mmol) and pyridine (0.14 mL, 1.68 mmol) was added. The mixture was stirred at ambient temperature for 16 h followed by quenching of excess anhydride with water (0.14 mL) for 3 h. Crude product was purified according to the literature procedures [53] to give 0.51 g of **26** as a white solid (83% yield). Compound **26** (0.5 g, 0.61 mmol) was dissolved in MeOH (20 mL) and to this solution Dowex H^+ resin was added with a tip of spatula. The resulting mixture was stirred at ambient temperature until the consumption of **26** was observed via TLC. The resin was filtered of and washed with MeOH. The crude product was then purified by column chromatography. The product obtained by filtration to give a colorless liquid **(In2:2)** (0.47 g, 93% yield).

^{1}H NMR ($CDCl_3$, δ, ppm) 6.56 (d, 1H, J = 5.7 Hz, C*H* = CH), 6.47 (d, 1H, J = 5.7, Hz, CH = C*H*), 5.25 (d, 1H, J = 1.3 Hz , C*H* bridgehead proton), 4.78 (d, 1H, J = 12.3 Hz), 4.60 (d, 1H, J = 12.3 Hz), 4.41 (dd, 2H, J = 11.1, 0.9), 4.32 (d, 2H, J = 11.1 Hz), 4.13-4.02 (m, 2H), 3.89-3.65 (m, 4H), 3.57 (tt, 2H, J = 8.2, 4.3 Hz, NCH_2), 3.02-2.84 (m, 4H, O*H* and bridge protons), 1.97-1.84 (m, 14H, NCH$_2$CH_2CH$_2$, CBr(CH_3)), 1.35 (s, 3H, CH_3), 1.09 (s, 3H, CH_3).

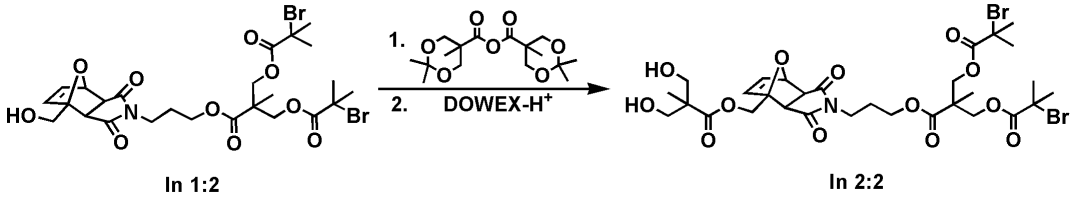

Figure 4.13. Synthesis of **In2:2** ATRP and ROP initiator

4.3.4. Synthesis of 1OH:4Br ATRP and ROP Initiator (In1:4)

To a solution of **7** (5.84 g, 17.67 mmol) in dry CH_2Cl_2 (30 mL), **23** (2.00 g, 5.89 mmol), DMAP (0.57 g, 4.71 mmol) and pyridine (2.14 mL, 26.50 mmol) was added. The mixture was stirred at ambient temperature for 16 h followed by quenching of excess anhydride with water (2.14 mL) for 5 h. Crude product was purified according to the literature procedures [53] to give 3.07 g of **28** as a white solid (80% yield). Compound **28** (3.00 g, 4.60 mmol) was dissolved in MeOH (80 mL) and to this solution Dowex H^+ resin was added with a tip of spatula. The resulting mixture was stirred at ambient temperature until the consumption of **28** was observed via TLC. The resin was filtered of and washed with MeOH. The crude product was then purified by column chromatography. The product obtained by filtration to give a white solid **29** (2.52 g, 96% yield). Then **29** (2.50 g, 4.37 mmol) was added to a solution of triethylamine (4.26 mL, 30.59 mmol) and DMAP (0.32 g, 2.62 mmol) in THF (50 mL) under nitrogen. The mixture was cooled to 0 ^oC in ice bath. On the other side, 2-bromo-isobutyryl bromide (3.24 mL, 26.22 mmol) was diluted in THF (15 mL) and added into the former mixture drop wise (30 min). The obtained white suspension was stirred for 3 hours at 0 ^oC, warmed to room temperature and stirred for 24 h. The ammonia salt formed was filtered off and the residue was concentrated in *vacuo*. The product was obtained as a white solid **30** (4.49 g, 88% yield) after purification via column chromatography. Resulting compound **30** (3.00 g, 2.57 mmol) was dissolved in toluene (100 mL) and then refluxed for 24 h. The product **31** (2.34g, 83% yield) was obtained as pure yellowish liquid after concentrated in vacuo. **31** (2.00 g, 1.82 mmol) was then dissolved in benzene (60 mL) and to this solution furfuryl alcohol (0.24 mL, 2.73 mmol) was added with syringe. The resulting mixture was refluxed for 24 h. The crude product was purified by column chromatography to obtain yellowish liquid **In1:4** (1.72 g, 79% yield).

^{1}H NMR ($CDCl_3$, δ, ppm) 6.58 (d, 1H, J = 5.7 Hz, C*H* = CH), 6.52 (d, 1H, J = 5.7 Hz, CH = C*H*), 5.22 (d, 1H, J = 1.4 Hz , C*H* bridgehead proton), 4.40-4.23 (m, 12H), 4.08-4.02 (m, 4H), 3.58 (t, 2H, J = 6.7 Hz, NCH_2), 2.99 (d, 1H, J = 6.5 Hz, C*H*-CH bridge proton), 2.96 (d, 1H, J = 6.4 Hz, CH-C*H* bridge proton), 2.75 (t, 1H, J = 7.2 Hz), 1.97-1.86 (m, 26H, $NCH_2CH_2CH_2$, $CBr(CH_3)$), 1.55 (s, 3H, CH_3), 1.31 (d, 6H, J = 5.0 Hz, CH_3).

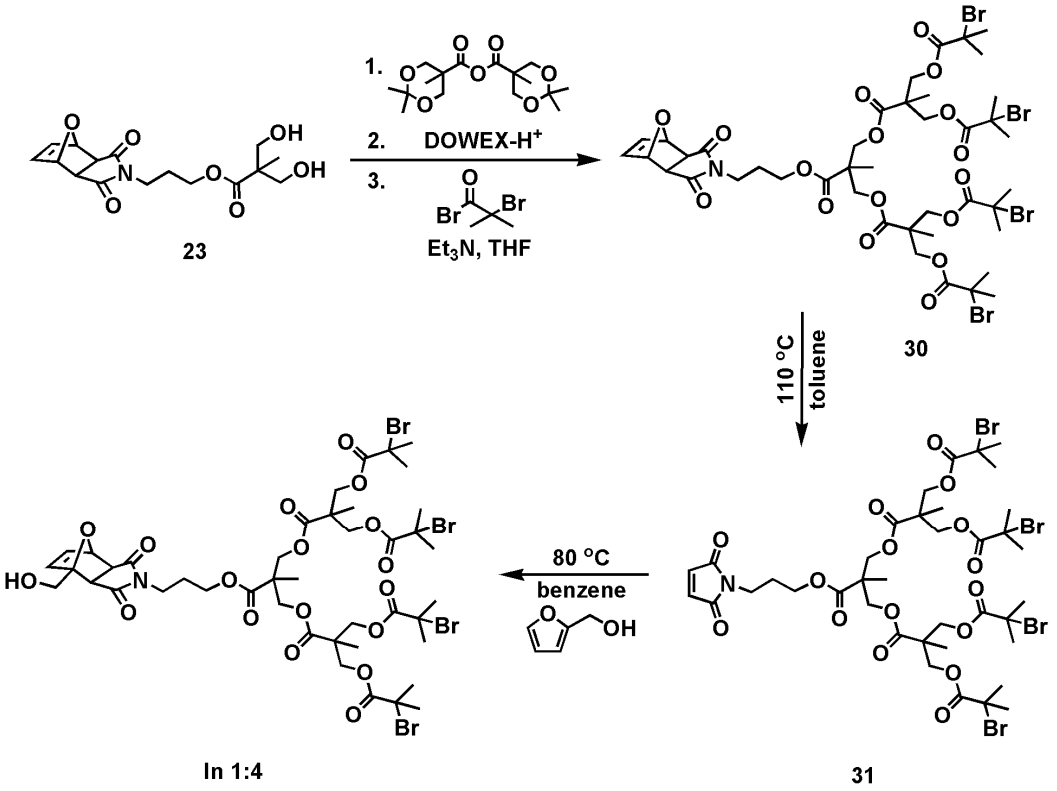

Figure 4.14. Synthesis of **In1:4** ATRP and ROP initiator

4.3.5. Synthesis of 2OH:4Br ATRP and ROP Initiator (In2:4)

To a solution of **7** (0.41 g, 1.25 mmol) in dry CH_2Cl_2 (50 mL), **In1:4** (1.00 g, 0.83 mmol), DMAP (0.041 g, 0.33 mmol) and pyridine (0.15 mL, 1.88 mmol) was added. The mixture was stirred at ambient temperature for 16 h followed by quenching of excess anhydride with water (0.15 mL) for 3 h. Crude product was purified according to the literature procedures [53] to give 0.96 g of **32** as a white solid (85% yield). Compound **32** (0.96 g, 0.71 mmol) was dissolved in MeOH (40 mL) and to this solution Dowex H^+ resin

was added with a tip of spatula. The resulting mixture was stirred at ambient temperature until the consumption of **32** was observed via TLC. The resin was filtered of and washed with MeOH. The crude product was then purified by column chromatography to give a colorless liquid **(In2:4)** (0.83 g, 89% yield).

^{1}H NMR ($CDCl_3$, δ, ppm) 6.56 (d, 1H, J = 5.6 Hz, C*H* = CH), 6.47 (d, 1H, J = 5.7, Hz, CH = C*H*), 5.25 (s, 1H, C*H* bridgehead proton), 4.78 (d, 1H, J = 12.4 Hz), 4.59 (d, 1H, J = 12.3 Hz), 4.41-4.24 (m, 12H, J = 11.1), 4.05 (t, 2H, J = 6.1 Hz), 3.93-3.64 (m, 4H), 3.57 (t, 2H, J = 6.6 Hz, NCH_2), 3.01 (d, 1H, J = 6.4 Hz), 3.97 (d, 1H, J = 6.4 Hz), 2.89 (s, 1H, O*H*), 2.77 (s, 1H, O*H*), 1.97-1.84 (m, 26H, $NCH_2CH_2CH_2$, $CBr(CH_3)$), 1.57 (s, 3H, CH_3), 1.30 (s, 6H, CH_3), 1.09 (s, 3H, CH_3).

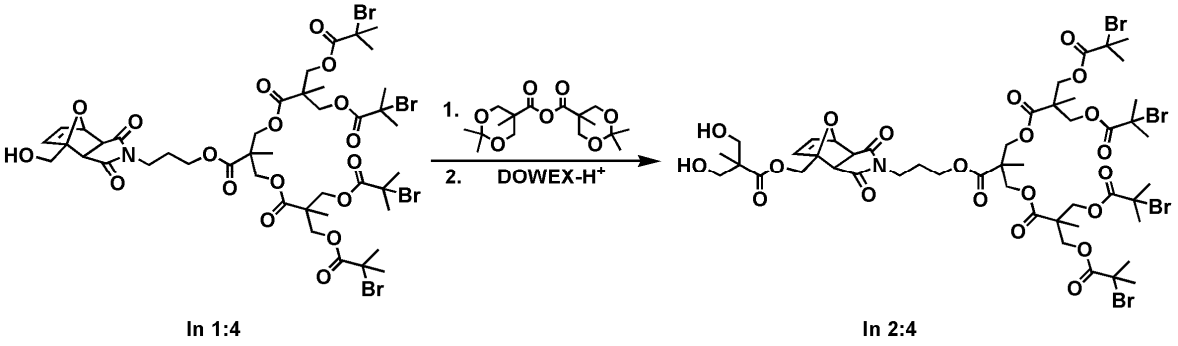

Figure 4.15. Synthesis of **In2:4** ATRP and ROP initiator

4.3.6. Synthesis of 4OH:4Br ATRP and ROP Initiator (In4:4)

To a solution of **7** (0.23 g, 0.68 mmol) in dry CH_2Cl_2 (30 mL), **In2:4** (0.3 g, 0.23 mmol), DMAP (0.022 g, 0.18 mmol) and pyridine (0.083 mL, 1.03 mmol) was added. The mixture was stirred at ambient temperature for 16 h followed by quenching of excess anhydride with water (0.083 mL) for 2 h. Crude product was purified according to the literature procedures [53] to give 0.29 g of **33** as a white solid (80% yield). Compound **33** (0.29 g, 0.18 mmol) was dissolved in MeOH (20 mL) and to this solution Dowex H^+ resin was added with a tip of spatula. The resulting mixture was stirred at ambient temperature until the consumption of **33** was observed via TLC. The resin was filtered of and washed with MeOH. The crude product was then purified by column chromatography to give a colorless liquid **(In4:4)** (0.24 g, 88% yield).

^{1}H NMR ($CDCl_3$, δ, ppm) 6.58-6.54 (m, 1H, C*H* = CH), 6.45 (dd, 1H, *J* = 7.8, 5.8 Hz, CH = C*H*), 5.25 (s, 1H, C*H* bridgehead proton), 4.81 (dd, 1H, *J* = 19.6, 12.5 Hz), 4.55 (d, 1H, *J* = 14.7, 12.7 Hz), 4.40-4.26 (m, 12H), 4.05 (t, 2H, *J* = 6.1 Hz), 3.88-3.60 (m, 12H), 3.57 (t, 2H, *J* = 6.6 Hz, NCH_2), 3.14-2.92 (m, 5H, C*H* bridgehead proton, O*H*), 2.17 (s, 1H, O*H*), 1.99-1.87 (m, 26H, $NCH_2CH_2CH_2$, $CBr(CH_3)$), 1.59 (s, 6H, CH_3), 1.31 (s, 9H, CH_3), 1.05 (s, 3H, CH_3).

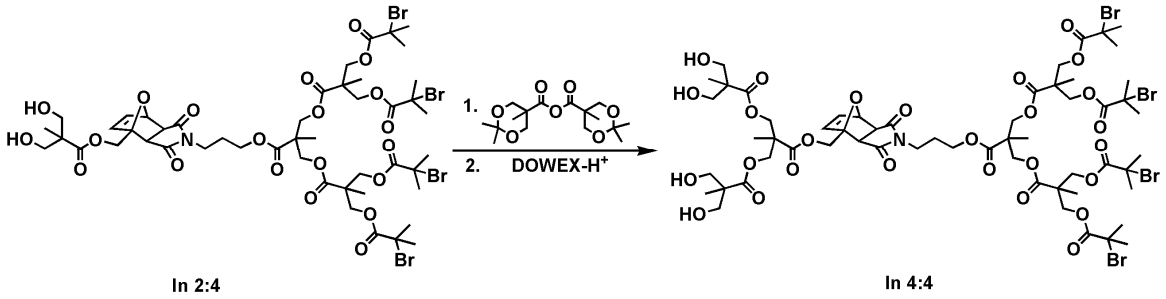

Figure 4.16. Synthesis of **In4:4** ATRP and ROP initiator

4.3.7. Synthesis of 1OH:1PMMA Homopolymer

1OH:1PMMA was prepared by ATRP of MMA. In 10 mL Shlenk tube, MMA (1.06 mL, 9.94 mmol), Bipyridine (0.031 mg, 0.1988 mmol), CuBr (0.0142 g, 0.0994 mmol), anisole (5.30 mL), and **In1:1** (0.040 g, 0.0994 mmol) were added, and the reaction mixture was degassed, and left in niterogen. The tube was then placed in thermostated oil bath at 70 ^oC for 1 h. Polymerization mixture was diluted with THF, passed through a neutral alumina column to remove the catalyst, and precipitated in hexane. The polymer was dried for 24 h in vacuum line at ambient temperature. **1OH:1PMMA** was obtained as white solid ($[M]_o/[I]_o$ = 100, $[I]_o$:[CuBr]:[Bipyridine] = 1:1:2, conversion = 64%, $M_{n,theo}$ = 6,665, $M_{n,NMR}$ = 9,930, $M_{n,GPC}$ = 7,730, M_w/M_n = 1.26, relative to linear PS).

^{1}H NMR ($CDCl_3$, δ, ppm) 6.59 (s, 1H, C*H* = CH), 6.53 (s, 1H, CH = C*H*), 5.23 (s, 1H, C*H* bridgehead proton), 4.07 (d, 1H, CH_2), 3.56 (br s, 5H, OCH_3 of PMMA and NCH_2), 2.97 (d, 2H, C*H*-C*H* bridge proton), 2.04-0.71 (m, 13H, $NCH_2CH_2CH_2O$, $CBr(CH_3)$, CH_2 and CH_3 along polymer backbone).

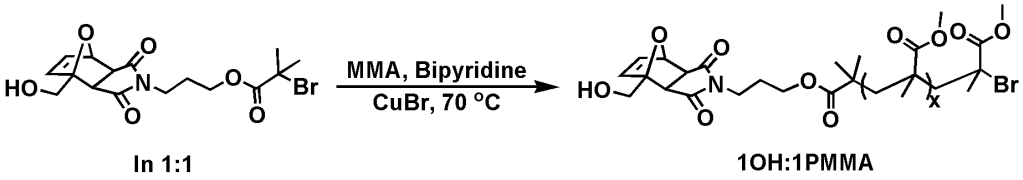

Figure 4.17. Synthesis of **1OH:1PMMA** polymer

4.3.8. Synthesis of 1OH:2PMMA Homopolymer

1OH:2PMMA was prepared by ATRP of MMA. In 10 mL Shlenk tube, MMA (1.28 mL, 11.98 mmol), Bipyridine (0.037 mg, 0.239 mmol), CuBr (0.017 g, 0.1198 mmol), anisole (6.40 mL), and **In1:2** (0.040 g, 0.0599 mmol) were added, and the reaction mixture was degassed, and left in niterogen. The tube was then placed in thermostated oil bath at 70 ^{o}C for 1 h. Polymerization mixture was diluted with THF, passed through a neutral alumina column to remove the catalyst, and precipitated in hexane. The polymer was dried for 24 h in vacuum line at ambient temperature. **1OH:2PMMA** was obtained as white solid ($[M]_o/[I]_o$ = 200, $[I]_o$:[CuBr]:[Bipyridine] = 1:2:4, conversion = 62%, $M_{n,theo}$ = 12,828, $M_{n,NMR}$ = 17,400, $M_{n,GPC}$ = 14,070, M_w/M_n = 1.39, relative to linear PS).

^{1}H NMR ($CDCl_3$, δ, ppm) 6.56 (s, 1H, C*H* = CH), 6.48 (s, 1H, CH = C*H*), 5.25 (s, 1H, C*H* bridgehead proton), 4.79 (d, 1H, J = 12.5 Hz, CH_2), 4.57 (d, 1H, J = 12.5 Hz, CH_2), 4.20-4.00 (m, 6H, OCH_2 ester protons, OCH_2), 3.56 (br s, 5H, OCH_3 of PMMA and NCH_2), 3.00 (d, 1H, J = 6.3 Hz, C*H*-CH bridge proton), 2.96 (d, 1H, J = 6.2 Hz, CH-C*H* bridge proton), 2.07-0.71 (m, 25H, $NCH_2CH_2CH_2O$, $CBr(CH_3)$, CH_2 and CH_3 along polymer backbone).

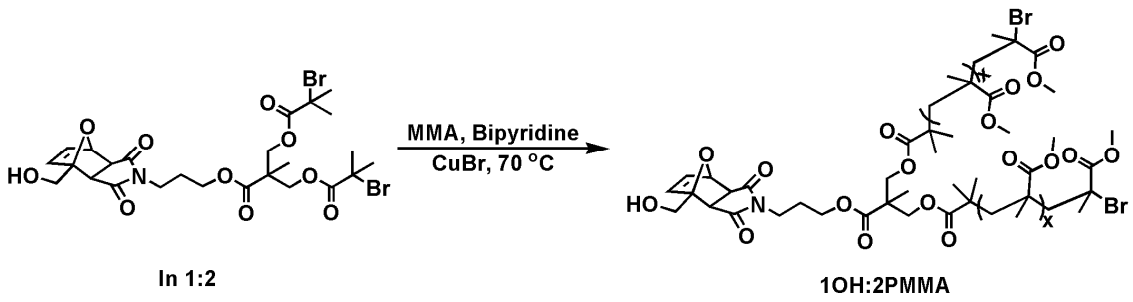

Figure 4.18. Synthesis of **1OH:2PMMA** polymer

4.3.9. Synthesis of 2OH:2PMMA Homopolymer

2OH:2PMMA was prepared by ATRP of MMA. In 10 mL Shlenk tube, MMA (1.08 mL, 10.20 mmol), Bipyridine (0.032 mg, 0.204 mmol), CuBr (0.015 g, 0.102 mmol), anisole (5.40 mL), and **In2:2** (0.040 g, 0.0510 mmol) were added, and the reaction mixture was degassed, and left in niterogen. The tube was then placed in thermostated oil bath at 70 ^{o}C for 1 h. Polymerization mixture was diluted with THF, passed through a neutral alumina column to remove the catalyst, and precipitated in hexane. The polymer was dried for 24 h in vacuum line at ambient temperature. **2OH:2PMMA** was obtained as white solid ($[M]_o/[I]_o$ = 200, $[I]_o$:[CuBr]:[Bipyridine] = 1:2:4, conversion = 66%, $M_{n,theo}$ = 13,733, $M_{n,NMR}$ = 16,250, $M_{n,GPC}$ = 15,340, M_w/M_n = 1.24, relative to linear PS).

^{1}H NMR ($CDCl_3$, δ, ppm) 6.56 (s, 1H, C*H* = CH), 6.48 (s, 1H, CH = C*H*), 5.25 (s, 1H, C*H* bridgehead proton), 4.79 (d, 1H, *J* = 12.5 Hz, CH_2), 4.58 (d, 1H, *J* = 12.5 Hz, CH_2), 4.21-3.97 (m, 6H, OCH_2 ester protons, OCH_2), 3.87-3.32 (m, 9H, OCH_3 of PMMA, OCH_2 of ester proton and NCH_2), 3.15-2.90 (m, 4H, C*H*-C*H* bridge protons and O*H*), 2.22-0.68 (m, 25H, $NCH_2CH_2CH_2O$, $CBr(CH_3)$, CH_2 and CH_3 along polymer backbone).

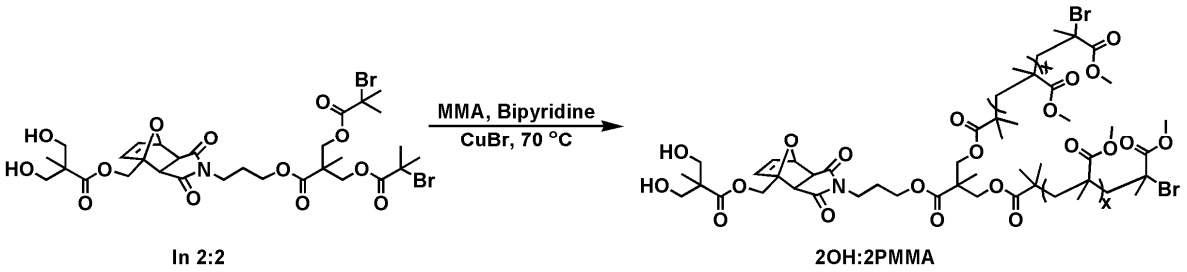

Figure 4.19. Synthesis of **2OH:2PMMA** polymer

4.3.10. Synthesis of 1OH:4PMMA Homopolymer

1OH:4PMMA was prepared by ATRP of MMA. In 10 mL Shlenk tube, MMA (1.42 mL, 13.36 mmol), Bipyridine (0.042 mg, 0.267 mmol), CuBr (0.019 g, 0.134 mmol), anisole (7.10 mL), and **In1:4** (0.040 g, 0.0334 mmol) were added, and the reaction mixture was degassed, and left in niterogen. The tube was then placed in thermostated oil bath at 70 ^{o}C for 1 h. Polymerization mixture was diluted with THF, passed through a neutral alumina

column to remove the catalyst, and precipitated in hexane. The polymer was dried for 24 h in vacuum line at ambient temperature. **1OH:4PMMA** was obtained as white solid ($[M]_o/[I]_o$ = 400, $[I]_o$:[CuBr]:[Bipyridine] = 1:4:8, conversion = 57%, $M_{n,theo}$ = 23,510, $M_{n,NMR}$ = 32,810, $M_{n,GPC}$ = 27,360, M_w/M_n = 1.30, relative to linear PS).

^{1}H NMR ($CDCl_3$, δ, ppm) 6.59 (s, 1H, C*H* = CH), 6.54 (s, 1H, CH = C*H*), 5.22 (s, 1H, C*H* bridgehead proton), 4.13 (dd, 10H, *J* = 57.2, 28.0 Hz, OCH_2 ester protons, OCH_2), 3.58 (d, 7H, OCH_3 of PMMA, CH_2, NCH_2), 3.00 (d, 1H, *J* = 6.6 Hz, C*H*-CH bridge proton), 2.95 (d, 1H, *J* = 6.4 Hz, CH-C*H* bridge proton), 2.10-0.54 (m, 38H, $NCH_2CH_2CH_2O$, $CBr(CH_3)$, CH_2 and CH_3 along polymer backbone).

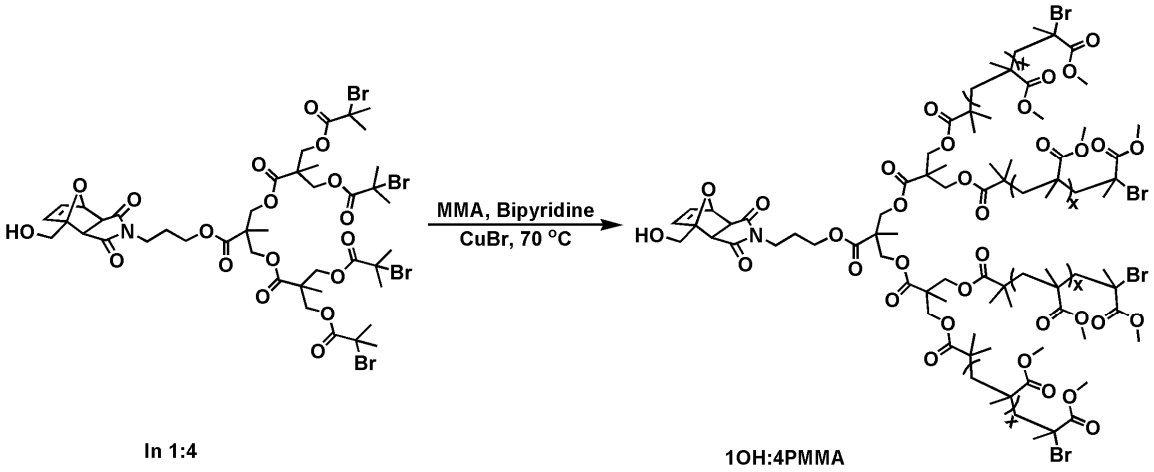

Figure 4.20. Synthesis of **1OH:4PMMA** polymer

4.3.11. Synthesis of 2OH:4PMMA Homopolymer

2OH:4PMMA was prepared by ATRP of MMA. In 10 mL Shlenk tube, MMA (1.30 mL, 12.16 mmol), Bipyridine (0.038 mg, 0.243 mmol), CuBr (0.017 g, 0.122 mmol), anisole (6.50 mL), and **In2:4** (0.040 g, 0.0304 mmol) were added, and the reaction mixture was degassed, and left in niterogen. The tube was then placed in thermostated oil bath at 70 ^oC for 1 h. Polymerization mixture was diluted with THF, passed through a neutral alumina column to remove the catalyst, and precipitated in hexane. The polymer was dried for 24 h in vacuum line at ambient temperature. **2OH:4PMMA** was obtained as white solid

($[M]_o/[I]_o$ = 400, $[I]_o$:[CuBr]:[Bipyridine] = 1:4:8, conversion = 57%, $M_{n,theo}$ = 23,576, $M_{n,NMR}$ = 29,690, $M_{n,GPC}$ = 24,880, M_w/M_n = 1.22, relative to linear PS).

^{1}H NMR ($CDCl_3$, δ, ppm) 6.57 (s, 1H, C*H* = CH), 6.49 (s, 1H, CH = C*H*), 5.24 (s, 1H, C*H* bridgehead proton), 4.79 (d, 1H, J = 12.2 Hz, CH_2), 4.57 (d, 1H, J = 11.3 Hz, CH_2), 4.30-3.99 (m, 10H, OCH_2 ester protons, OCH_2), 3.58 (d, 11H, OCH_3 of PMMA, CH_2, NCH_2), 3.02 (s, 1H, C*H*-CH bridge proton), 2.97 (s, 1H, CH-C*H* bridge proton), 2.07-0.61 (m, 41H, $NCH_2CH_2CH_2O$, $CBr(CH_3)$, CH_2 and CH_3 along polymer backbone).

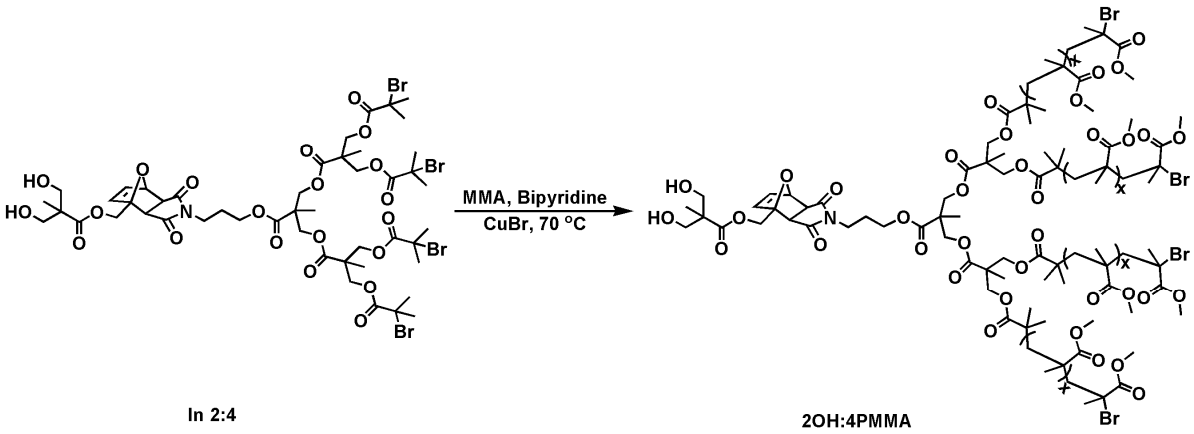

Figure 4.21. Synthesis of **2OH:4PMMA** polymer

4.3.12. Synthesis of 4OH:4PMMA Homopolymer

4OH:4PMMA was prepared by ATRP of MMA. In 10 mL Shlenk tube, MMA (1.10 mL, 10.35 mmol), Bipyridine (0.032 mg, 0.207 mmol), CuBr (0.015 g, 0.103 mmol), anisole (5.50 mL), and **In4:4** (0.040 g, 0.0259 mmol) were added, and the reaction mixture was degassed, and left in niterogen. The tube was then placed in thermostated oil bath at 70 ^oC for 1 h. Polymerization mixture was diluted with THF, passed through a neutral alumina column to remove the catalyst, and precipitated in hexane. The polymer was dried for 24 h in vacuum line at ambient temperature. **4OH:4PMMA** was obtained as white solid ($[M]_o/[I]_o$ = 400, $[I]_o$:[CuBr]:[Bipyridine] = 1:4:8, conversion = 63%, $M_{n,theo}$ = 26,204, $M_{n,NMR}$ = 35,720, $M_{n,GPC}$ = 29,850, M_w/M_n = 1.21, relative to linear PS).

^{1}H NMR ($CDCl_3$, δ, ppm) 6.56 (s, 1H, C*H* = CH), 6.46 (s, 1H, CH = C*H*), 5.23 (s, 1H, C*H* bridgehead proton), 4.81 (t, 1H, J = 12.3 Hz, CH_2), 4.50 (d, 1H, J = 12.4 Hz, CH_2), 4.36-3.96 (m, 10H, OCH_2 ester protons, OCH_2), 3.58 (d, 15H, OCH_3 of PMMA, CH_2, NCH_2), 3.01 (s, 1H, C*H*-CH bridge proton), 2.95 (s, 1H, CH-C*H* bridge proton), 2.01-0.67 (m, 47H, $NCH_2CH_2CH_2O$, $CBr(CH_3)$, CH_2 and CH_3 along polymer backbone).

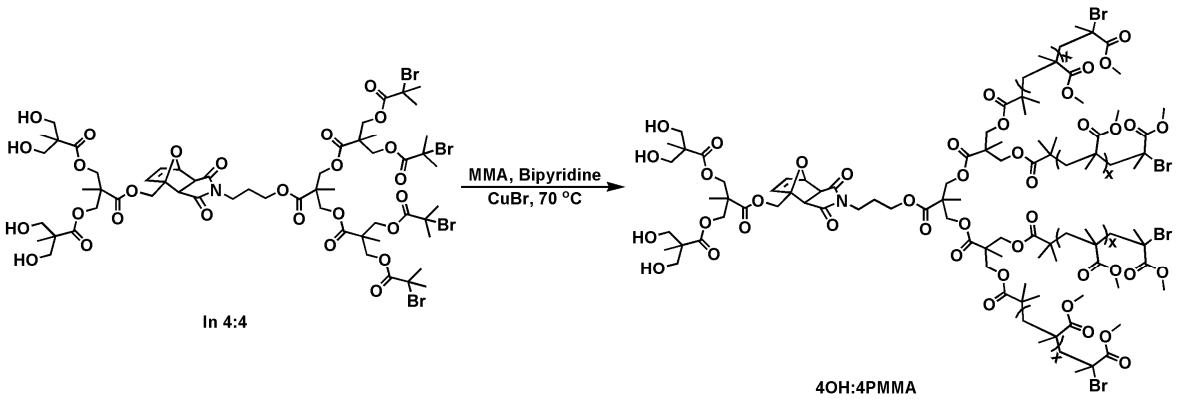

Figure 4.22. Synthesis of **4OH:4PMMA** polymer

4.3.13. Synthesis of 1PLA:1PMMA Linear Diblock Copolymer

1OH:1PMMA (200 mg 0.026 mmol) and D-LA (450 mg, 2.11 mmol) were dried under vacuum for 20 hours after three times azeotropic distillation with toluene. Thiourea co-catalyst (19.2 mg, 0.052 mmol) was added. This solid mixture was dissolved in dry CH_2Cl_2 (6.5 mL) under nitrogen atmosphere. DBU (3.9 µL, 0.026 mmol) was injected to the solution to initiate the polymerization. Reaction mixture was quenched with benzoic acid (5 mg, 0.042 mmol) after 90 min. After termination of the polymerization, solvent was evaporated and precipitated in the cold methanol. The polymer **1PLA:1PMMA** was obtained as white solid ($[M]_o/[I]_o$ = 120, conversion = 85 %. $M_{n,theo}$ = 24,400, $M_{n,NMR}$ = 26,290, $M_{n,GPC}$ = 14,060, M_w/M_n = 1.31, relative to PS).

^{1}H NMR ($CDCl_3$, δ, ppm) 6.53 (s, 1H, C*H* = CH), 6.38 (s, 1H, CH = C*H*), 5.24-5.06 (m, 2H, C*H* bridgehead proton and C*H*-O of lactide), 4.34 (dt, 1H, J = 13.9, 7.1 Hz, CH_2), 3.80-3.33 (m, 5H, OCH_3 of PMMA, NCH_2), 2.95 (s, 1H, C*H*-CH bridge proton), 2.87 (s, 1H, CH-C*H* bridge proton), 2.06-0.70 (m, 10H, $NCH_2CH_2CH_2O$, $HOC(CH_3)$ of PLA, $CBr(CH_3)$, CH_2 and CH_3 along PMMA backbone).

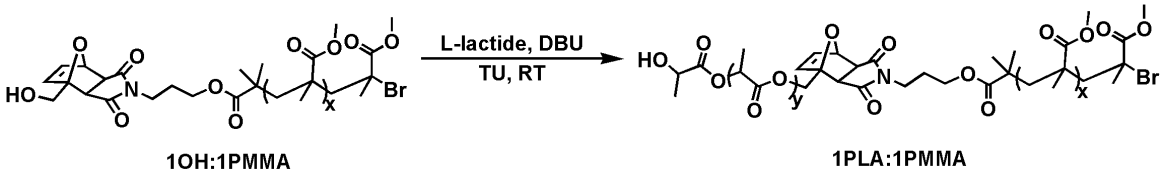

Figure 4.23. Synthesis of **1PLA:1PMMA** copolymer

4.3.14. Synthesis of 1PLA:2PMMA Miktoarm Polymer

1OH:2PMMA (200 mg 0.014 mmol) and D-LA (243 mg, 1.69 mmol) were dried under vacuum for 20 hours after three times azeotropic distillation with toluene. Thiourea co-catalyst (10.4 mg, 0.028 mmol) was added. This solid mixture was dissolved in dry CH_2Cl_2 (4.43 mL) under nitrogen atmosphere. DBU (2.1 μL, 0.014 mmol) was injected to the solution to initiate the polymerization. Reaction mixture was quenched with benzoic acid (2.7 mg, 0.022 mmol) after 90 min. After termination of the polymerization, solvent was evaporated and precipitated in the cold methanol. The polymer **1PLA:2PMMA** was obtained as white solid ($[M]_o/[I]_o$ = 120, conversion = 84 %. $M_{n,theo}$ = 34,700, $M_{n,NMR}$ = 29,144, $M_{n,GPC}$ = 22,520, M_w/M_n = 1.27, relative to PS).

^{1}H NMR ($CDCl_3$, δ, ppm) 6.52 (s, 1H, C*H* = CH), 6.37 (s, 1H, CH = C*H*), 5.24-5.08 (m, 2H, C*H* bridgehead proton and C*H*-O of lactide), 4.38-4.00 (m, 8H, CH_2), 3.79-3.32 (m, 5H, OCH_3 of PMMA, NCH_2), 2.96 (s, 1H, C*H*-CH bridge proton), 2.89 (s, 1H, CH-C*H* bridge proton), 2.08-0.70 (m, 23H, NCH$_2$CH_2CH$_2$O, HOC(CH_3) of PLA, CBr(CH_3), CH_2 and CH_3 along PMMA backbone).

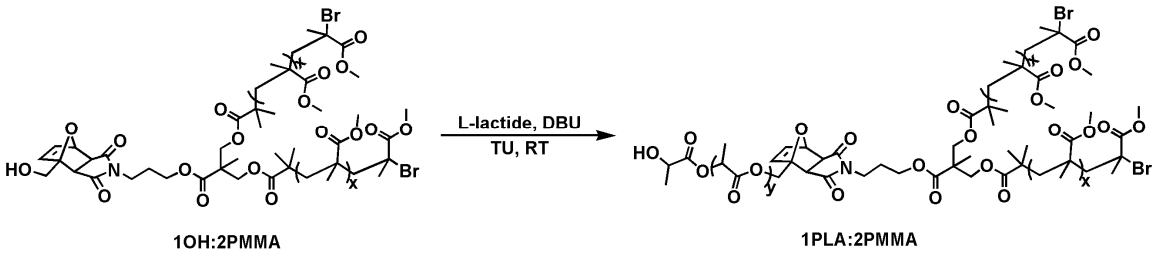

Figure 4.24. Synthesis of **1PLA:2PMMA** miktoarm polymer

4.3.15. Synthesis of 2PLA:2PMMA Miktoarm Polymer

2OH:2PMMA (200 mg 0.013 mmol) and D-LA (451 mg, 3.13 mmol) were dried under vacuum for 20 hours after three times azeotropic distillation with toluene. Thiourea co-catalyst (19.3 mg, 0.052 mmol) was added. This solid mixture was dissolved in dry CH_2Cl_2 (6.5 mL) under nitrogen atmosphere. DBU (3.9 µL, 0.026 mmol) was injected to the solution to initiate the polymerization. Reaction mixture was quenched with benzoic acid (5 mg, 0.042 mmol) after 90 min. After termination of the polymerization, solvent was evaporated and precipitated in the cold methanol. The polymer **2PLA:2PMMA** was obtained as white solid ($[M]_o/[I]_o$ = 240, conversion = 80 %. $M_{n,theo}$ = 40,672, $M_{n,NMR}$ = 46,373, $M_{n,GPC}$ = 32,770, M_w/M_n = 1.26, relative to PS).

^{1}H NMR ($CDCl_3$, δ, ppm) 6.54 (s, 1H, C*H* = CH), 6.39 (s, 1H, CH = C*H*), 5.26-5.05 (m, 2H, C*H* bridgehead proton and C*H*-O of lactide), 4.38-4.00 (m, 12H, CH_2), 3.58 (s, 5H, OCH_3 of PMMA, NCH_2), 2.98 (s, 1H, C*H*-CH bridge proton), 2.90 (s, 1H, CH-C*H* bridge proton), 2.10-0.72 (m, 26H, NCH_2CH_2CH_2O, HOC(CH_3) of PLA, CBr(CH_3), CH_2 and CH_3 along PMMA backbone).

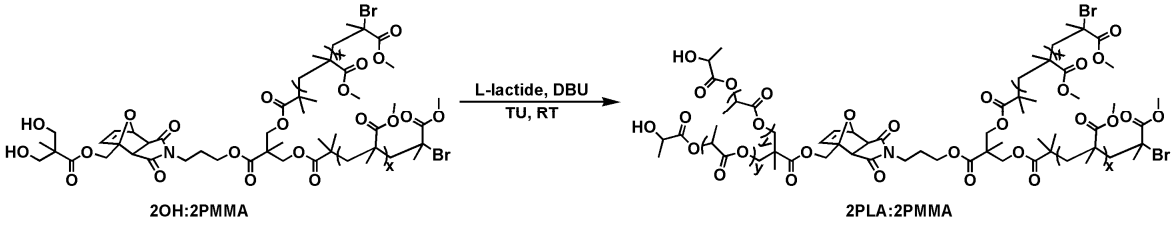

Figure 4.25. Synthesis of **2PLA:2PMMA** miktoarm polymer

4.3.16. Synthesis of 1PLA:4PMMA Miktoarm Polymer

1OH:4PMMA (200 mg 0.0073 mmol) and D-LA (126 mg, 0.877 mmol) were dried under vacuum for 20 hours after three times azeotropic distillation with toluene. Thiourea co-catalyst (5.4 mg, 0.015 mmol) was added. This solid mixture was dissolved in dry CH_2Cl_2 (3.3 mL) under nitrogen atmosphere. DBU (1.1 µL, 0.0073 mmol) was injected to the solution to initiate the polymerization. Reaction mixture was quenched with benzoic

acid (1.42 mg, 0.0116 mmol) after 90 min. After termination of the polymerization, solvent was evaporated and precipitated in the cold methanol. The polymer **1PLA:4PMMA** was obtained as white solid ($[M]_o/[I]_o$ = 120, conversion = 75 %. $M_{n,theo}$ = 37,580, $M_{n,NMR}$ = 48,030, $M_{n,GPC}$ = 27,880, M_w/M_n = 1.31, relative to PS).

^{1}H NMR ($CDCl_3$, δ, ppm) 6.56 (s, 1H, C*H* = CH), 6.38 (s, 1H, CH = C*H*), 5.28-5.03 (m, 2H, C*H* bridgehead proton and C*H*-O of lactide), 4.38-4.00 (m, 14H, CH_2), 3.58 (s, 5H, OCH_3 of PMMA, NCH_2), 3.00 (s, 1H, C*H*-CH bridge proton), 2.92 (s, 1H, CH-C*H* bridge proton), 2.10-0.67 (m, 41H, $NCH_2CH_2CH_2O$, $HOC(CH_3)$ of PLA, $CBr(CH_3)$, CH_2 and CH_3 along PMMA backbone).

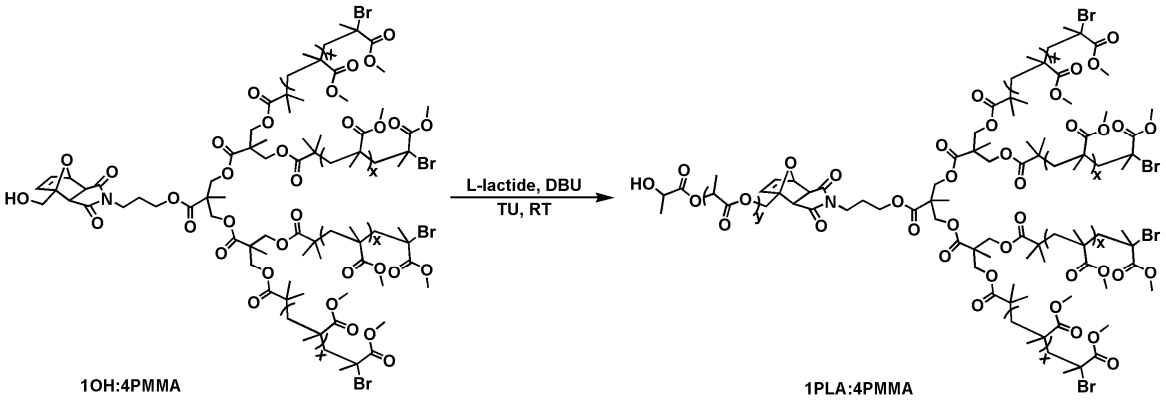

Figure 4.26. Synthesis of **1PLA:4PMMA** miktoarm polymer

4.3.17. Synthesis of 2PLA:4PMMA Miktoarm Polymer

2OH:4PMMA (200 mg 0.008 mmol) and D-LA (278 mg, 1.93 mmol) were dried under vacuum for 20 hours after three times azeotropic distillation with toluene. Thiourea co-catalyst (12 mg, 0.032 mmol) was added. This solid mixture was dissolved in dry CH_2Cl_2 (4.8 mL) under nitrogen atmosphere. DBU (2.4 µL, 0.016 mmol) was injected to the solution to initiate the polymerization. Reaction mixture was quenched with benzoic acid (3.2 mg, 0.025 mmol) after 90 min. After termination of the polymerization, solvent was evaporated and precipitated in the cold methanol. The polymer **2PLA:4PMMA** was obtained as white solid ($[M]_o/[I]_o$ = 240, conversion = 81 %. $M_{n,theo}$ = 51,420, $M_{n,NMR}$ = 56,400, $M_{n,GPC}$ = 33,850, M_w/M_n = 1.28, relative to PS).

^{1}H NMR ($CDCl_3$, δ, ppm) 6.55 (s, 1H, C*H* = CH), 6.38 (s, 1H, CH = C*H*), 5.29-4.98 (m, 2H, C*H* bridgehead proton and C*H*-O of lactide), 4.39-3.96 (m, 18H, CH_2), 3.58 (s, 5H, OCH_3 of PMMA, NCH_2), 2.99 (s, 1H, C*H*-CH bridge proton), 2.89 (s, 1H, CH-C*H* bridge proton), 2.12-0.70 (m, 41H, NCH$_2$CH_2CH$_2$O, HOC(CH_3) of PLA, CBr(CH_3), CH_2 and CH_3 along PMMA backbone).

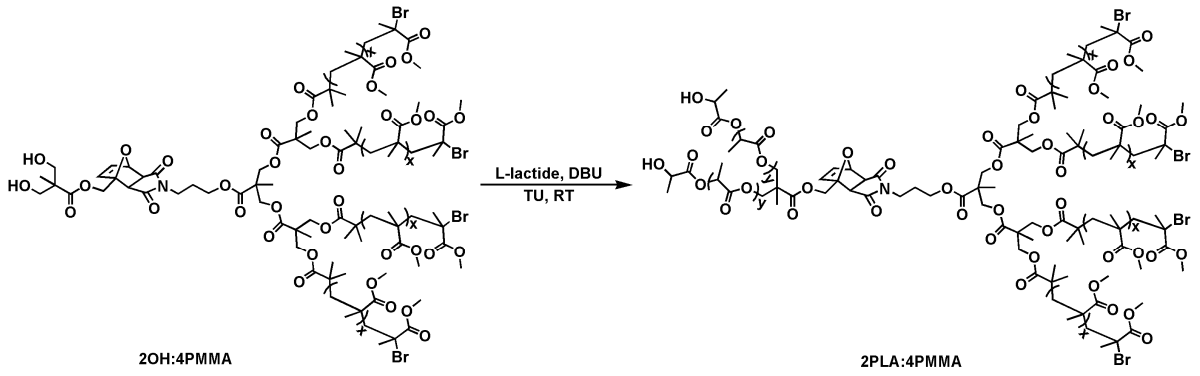

Figure 4.27. Synthesis of **2PLA:4PMMA** miktoarm polymer

4.3.18. Synthesis of 4PLA:4PMMA Miktoarm Polymer

4OH:4PMMA (200 mg 0.007 mmol) and D-LA (463 mg, 3.20 mmol) were dried under vacuum for 20 hours after three times azeotropic distillation with toluene. Thiourea co-catalyst (20 mg, 0.053 mmol) was added. This solid mixture was dissolved in dry CH_2Cl_2 (6.6 mL) under nitrogen atmosphere. DBU (4 µL, 0.026 mmol) was injected to the solution to initiate the polymerization. Reaction mixture was quenched with benzoic acid (5.2 mg, 0.042 mmol) after 90 min. After termination of the polymerization, solvent was evaporated and precipitated in the cold methanol. The polymer **4PLA:4PMMA** was obtained as white solid ($[M]_o/[I]_o$ = 480, conversion = 77 %. $M_{n,theo}$ = 80,774, $M_{n,NMR}$ = 80,850, $M_{n,GPC}$ = 43,520, M_w/M_n = 1.44, relative to PS).

^{1}H NMR ($CDCl_3$, δ, ppm) 6.53 (s, 1H, C*H* = CH), 6.37 (s, 1H, CH = C*H*), 5.29-4.98 (m, 2H, C*H* bridgehead proton and C*H*-O of lactide), 4.39-3.96 (m, 22H, CH_2), 3.57 (s, 5H, OCH_3 of PMMA, NCH_2), 2.98 (s, 1H, C*H*-CH bridge proton), 2.91 (s, 1H, CH-C*H*

bridge proton), 2.07-0.51 (m, 47H, $NCH_2CH_2CH_2O$, $HOC(CH_3)$ of PLA, $CBr(CH_3)$, CH_2 and CH_3 along PMMA backbone).

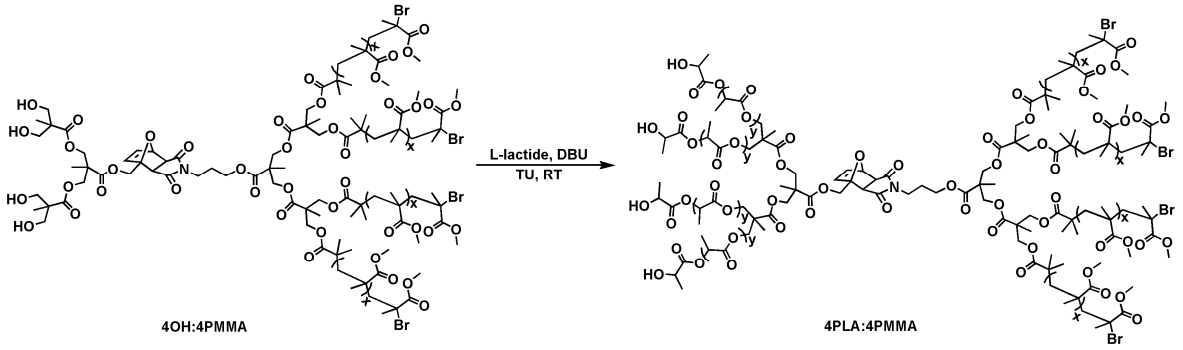

Figure 4.28. Synthesis of **4PLA:4PMMA** miktoarm polymer

4.3.19. Synthesis of 1PLA and 1PMMA by Retro-Diels-Alder Reaction

The mixture of **1PLA:1PMMA** (100 mg, 7.14 μmol) and anthracene (5.0 mg, 28 μmol) were dissolved in toluene (1.0 ml) and refluxed at 110 ^oC for 9 h. ^1H NMR analysis and GPC result of resulting mixture indicated a cleavage of **1PLA:1PMMA** into **1PLA** and **1PMMA**. ($M_{n,GPC}$ = 9,880, M_w/M_n = 1.62, relative to linear PS).

^1H NMR ($CDCl_3$, δ, ppm) 7.41-7.33 (m, 4H, aromatic protons), 6.39 (s, 1H, C*H* = CH), 6.34 (s, 1H, CH = C*H*), 5.31-5.04 (m, CH_2 and C*H*-O of lactide), 4.78 (s, 2H, C*H*-C*H* bridge head protons), 4.42-4.14 (m, 1H, OCH_2), 3.59 (s, 5H, OCH_3 of PMMA and NCH_2), 3.19 (s, 2H, C*H*-C*H* bridge protons), 2.00-0.74 (m, 16H, $NCH_2CH_2CH_2O$, $HOC(CH_3)$ of PLA, $CBr(CH_3)$, CH_2 and CH_3 along PMMA backbone).

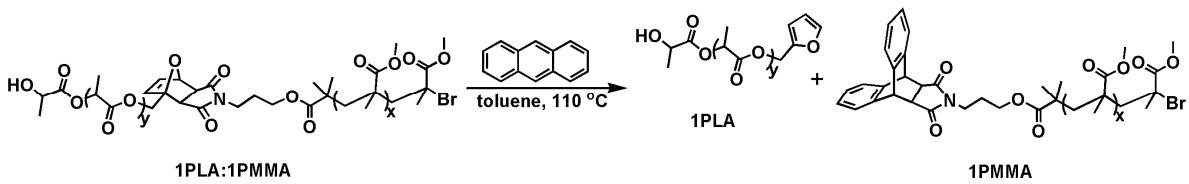

Figure 4.29. Synthesis of **1PLA** and **1PMMA** via rDA

4.3.20. Synthesis of 1PLA and 2PMMA by Retro-Diels-Alder Reaction

The mixture of **1PLA:2PMMA** (100 mg, 4.76 µmol) and anthracene (3.4 mg, 19 µmol) were dissolved in toluene (1.0 ml) and refluxed at 110 ^{o}C for 9 h. ^{1}H NMR analysis and GPC result of resulting mixture indicated a cleavage of **1PLA:2PMMA** into **1PLA** and **2PMMA**. ($M_{n,GPC}$ = 11,860, M_w/M_n = 1.68, relative to linear PS).

^{1}H NMR ($CDCl_3$, δ, ppm) 7.43 (d, 1H), 7.37 (s, 4H, aromatic protons), 7.13 (d, 4H, aromatic protons), 6.37 (s, 1H, C*H* = CH), 6.32 (s, 1H, CH = C*H*), 5.36-4.96 (m, CH_2 and C*H*-O of lactide), 4.76 (s, 2H, C*H*-C*H* bridge head protons), 4.39-4.01 (m, 4H, OCH_2), 3.81-3.34 (m, 5H, OCH_3 of PMMA and NCH_2), 3.18 (s, 2H, C*H*-C*H* bridge protons), 2.08-0.58 (m, 25H, $NCH_2CH_2CH_2O$, HOC(CH_3) of PLA, CBr(CH_3), CH_2 and CH_3 along PMMA backbone).

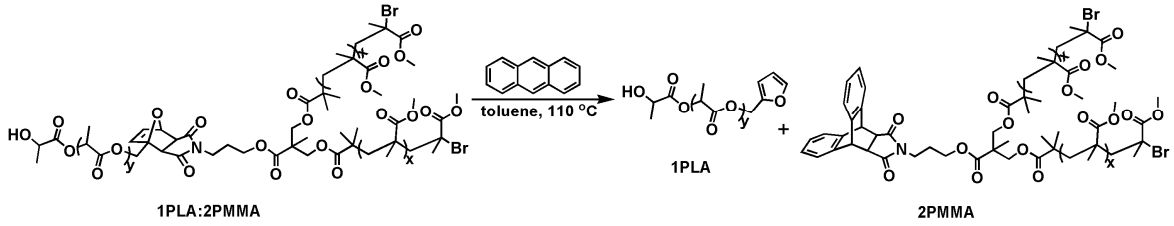

Figure 4.30. Synthesis of **1PLA** and **2PMMA** via rDA

4.3.21. Synthesis of 2PLA and 2PMMA by Retro-Diels-Alder Reaction

The mixture of **2PLA:2PMMA** (100 mg, 3.06 µmol) and anthracene (2.2 mg, 12 µmol) were dissolved in toluene (1.0 ml) and refluxed at 110 ^{o}C for 9 h. ^{1}H NMR analysis and GPC result of resulting mixture indicated a cleavage of **2PLA:2PMMA** into **2PLA** and **2PMMA**. ($M_{n,GPC}$ = 18,250, M_w/M_n = 1.30, relative to linear PS).

^{1}H NMR ($CDCl_3$, δ, ppm) 7.43 (s, 1H), 7.37 (s, 4H, aromatic protons), 7.14 (d, 4H, aromatic protons), 6.38 (s, 1H, C*H* = CH), 6.32 (s, 1H, CH = C*H*), 5.33-4.97 (m, CH_2 and C*H*-O of lactide), 4.76 (s, 2H, C*H*-C*H* bridge head protons), 4.35-4.03 (m, 6H, OCH_2), 3.57 (s, 5H, OCH_3 of PMMA and NCH_2), 3.19 (s, 2H, C*H*-C*H* bridge protons), 2.06-0.61 (m, 28H, $NCH_2CH_2CH_2O$, HOC(CH_3) of PLA, CBr(CH_3), CH_2 and CH_3 along PMMA backbone).

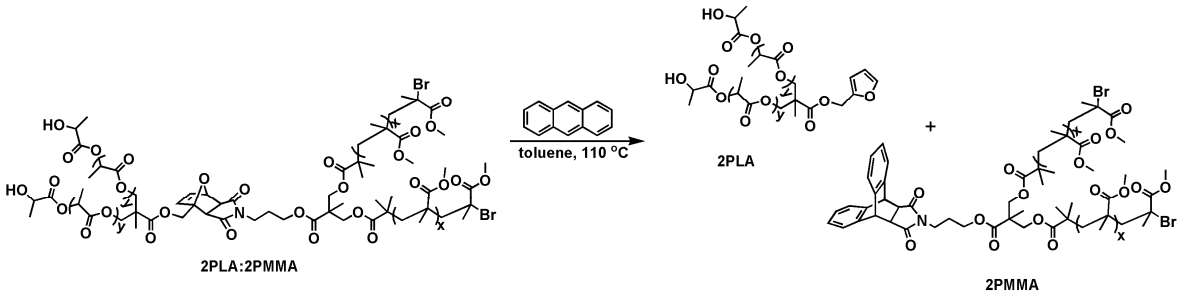

Figure 4.31. Synthesis of **2PLA** and **2PMMA** via rDA

4.3.22. Synthesis of 1PLA and 4PMMA by Retro-Diels-Alder Reaction

The mixture of **1PLA:4PMMA** (100 mg, 3.59 µmol) and anthracene (2.6 mg, 14.4 µmol) were dissolved in toluene (1.0 ml) and refluxed at 110 ^{o}C for 9 h. ^{1}H NMR analysis and GPC result of resulting mixture indicated a cleavage of **1PLA:4PMMA** into **1PLA** and **4PMMA**. ($M_{n,GPC}$ = 22,000, M_w/M_n = 1.44, relative to linear PS).

^{1}H NMR ($CDCl_3$, δ, ppm) 7.43 (s, 1H), 7.37 (s, 4H, aromatic protons), 7.14 (d, 4H, aromatic protons), 6.38 (s, 1H, C*H* = CH), 6.32 (s, 1H, CH = C*H*), 5.33-4.97 (m, CH_2 and C*H*-O of lactide), 4.76 (s, 2H, C*H*-C*H* bridge head protons), 4.35-4.03 (m, 14H, OCH_2), 3.57 (s, 5H, OCH_3 of PMMA and NCH_2), 3.19 (s, 2H, C*H*-C*H* bridge protons), 2.06-0.61 (m, 41H, $NCH_2CH_2CH_2O$, HOC(CH_3) of PLA, CBr(CH_3), CH_2 and CH_3 along PMMA backbone).

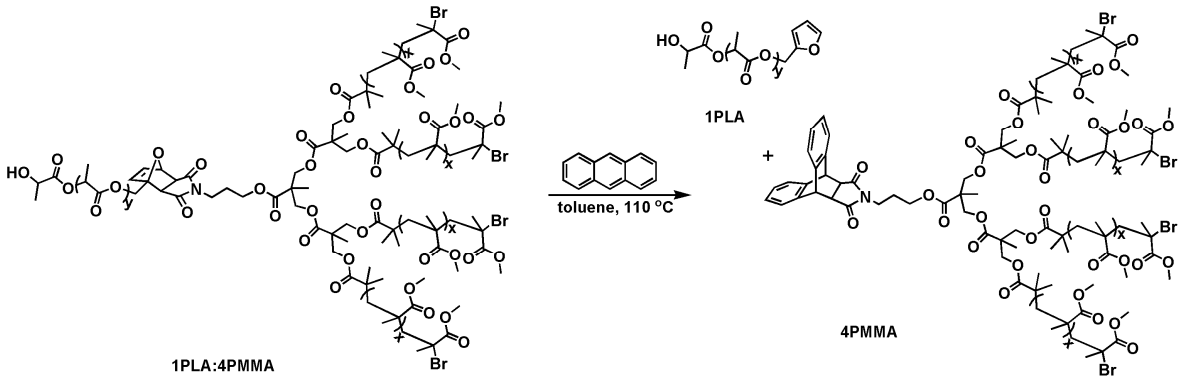

Figure 4.32. Synthesis of **1PLA** and **4PMMA** via rDA

4.3.23. Synthesis of 2PLA and 4PMMA by Retro-Diels-Alder Reaction

The mixture of **2PLA:4PMMA** (100 mg, 1.48 µmol) and anthracene (1.1 mg, 5.9 µmol) were dissolved in toluene (1.0 ml) and refluxed at 110 ^{o}C for 9 h. ^{1}H NMR analysis and GPC result of resulting mixture indicated a cleavage of **2PLA:4PMMA** into **2PLA** and **4PMMA**. ($M_{n,GPC}$ = 24,570, M_w/M_n = 1.23, relative to linear PS).

^{1}H NMR ($CDCl_3$, δ, ppm) 7.43 (s, 1H), 7.37 (s, 4H, aromatic protons), 7.12 (d, 4H, aromatic protons), 6.37 (s, 1H, C*H* = CH), 6.32 (s, 1H, CH = C*H*), 5.45-4.97 (m, CH_2 and C*H*-O of lactide), 4.76 (s, 2H, C*H*-C*H* bridge head protons), 4.35-4.03 (m, 14H, OCH_2), 3.56 (s, 5H, OCH_3 of PMMA and NCH_2), 3.18 (s, 2H, C*H*-C*H* bridge protons), 2.08-0.57 (m, 44H, $NCH_2CH_2CH_2O$, HOC(CH_3) of PLA, CBr(CH_3), CH_2 and CH_3 along PMMA backbone).

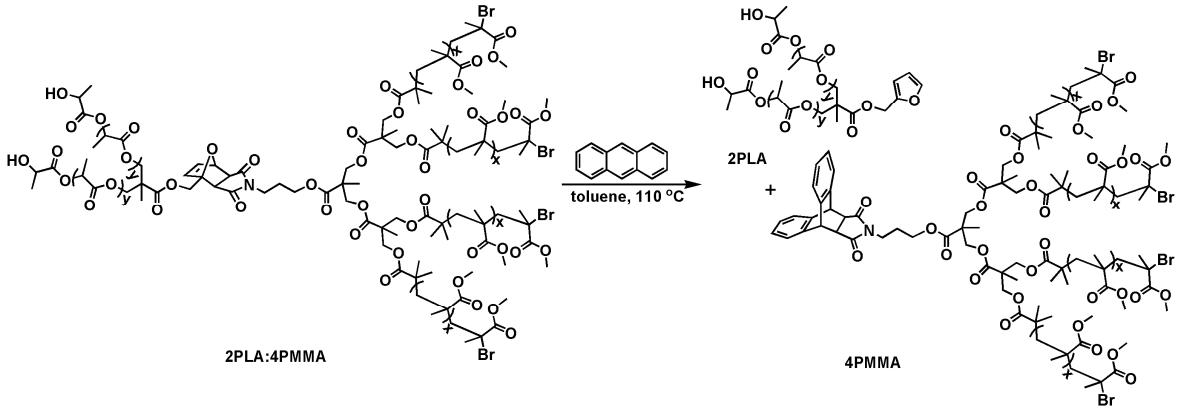

Figure 4.33. Synthesis of **2PLA** and **4PMMA** via rDA

4.3.24. Synthesis of 4PLA and 4PMMA by Retro-Diels-Alder Reaction

The mixture of **4PLA:4PMMA** (100 mg, 2.30 µmol) and anthracene (1.6 mg, 9.2 µmol) were dissolved in toluene (1.0 ml) and refluxed at 110 ^{o}C for 9 h. ^{1}H NMR analysis and GPC result of resulting mixture indicated a cleavage of **4PLA:4PMMA** into **4PLA** and **4PMMA**. ($M_{n,GPC}$ = 30,120, M_w/M_n = 1.26, relative to linear PS).

^{1}H NMR ($CDCl_3$, δ, ppm) 7.43 (s, 1H), 7.37 (s, 4H, aromatic protons), 7.15 (s, 4H, aromatic protons), 6.38 (s, 1H, C*H* = CH), 6.32 (s, 1H, CH = C*H*), 5.27-4.98 (m, CH_2 and C*H*-O of lactide), 4.76 (s, 2H, C*H*-C*H* bridge head protons), 4.29 (m, 28H, OCH_2), 3.57 (s,

5H, OCH_3 of PMMA and NCH_2), 3.18 (s, 2H, CH-CH bridge protons), 2.10-0.72 (m, 50H, $NCH_2CH_2CH_2O$, HOC(CH_3) of PLA, CBr(CH_3), CH_2 and CH_3 along PMMA backbone).

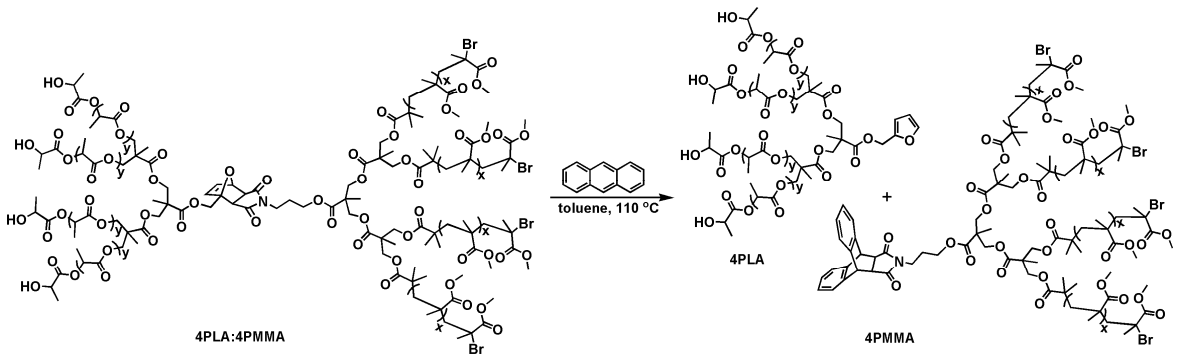

Figure 4.34. Synthesis of **4PLA** and **4PMMA** via rDA

5. CONCLUSION

In the first study, thermally cleavable multiarm star polymers were synthesized using a novel Diels-Alder/retro Diels-Alder strategy. Thermoreverisble furan-maleimide core containing dendritic initiators (3arm, 4arm, 8 arm, 16 arm, and 32 arm) from generation one through fourth were synthesized via divergent synthesis of poly(ester) dendron. Atom transfer radical polymerization (ATRP) of methyl methacrylate was successfully performed with all symmetrical and unsymmetrical initiators. Thermal cleavage of all the prepared multiarm star polymers were accomplished via retro Diels-Alder reaction of star polymers by heating to the 110 ^{o}C in the presence of anthracene as a maleimide unit scavenger. All multiarm star polymers have been cleaved successfully by showing the relative molecular weight decrease. Moreover, the reassembly of the cleaved star polymers were tested via Diels-Alder reaction at a lower temperature.

In the second study, miktoarm star polymers containing thermoreversible furan-maleimide unit at the core have been synthesized using Diels-Alder/retro Diels-Alder reaction again. Linear and dendritic initiators were prepared (1OH:1Br, 1OH:2Br, 2OH:2Br, 1OH:4Br, 2OH:4Br, and 4OH:4Br) which contains atom transfer radical polymerization (ATRP) and ring opening polymerization (ROP) initiating units, halide and hydroxyl functional groups respectively. ATRP of methyl methacrylate were synthesized from all the initiators firstly and then ROP of L-lactide were carried out with hydroxyl group bearing PMMA macroinitiators successfully. Finally, thermal cleavage of miktoarm star polymers were performed by heating at the 110 ^{o}C in the presence of anthracene as maleimide group scavenger. All linear and miktoarm star polymers were seen to be cleaved after the retro Diels-Alder reaction.

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APPENDIX

^{1}H NMR spectrums of newly synthesized products are included.

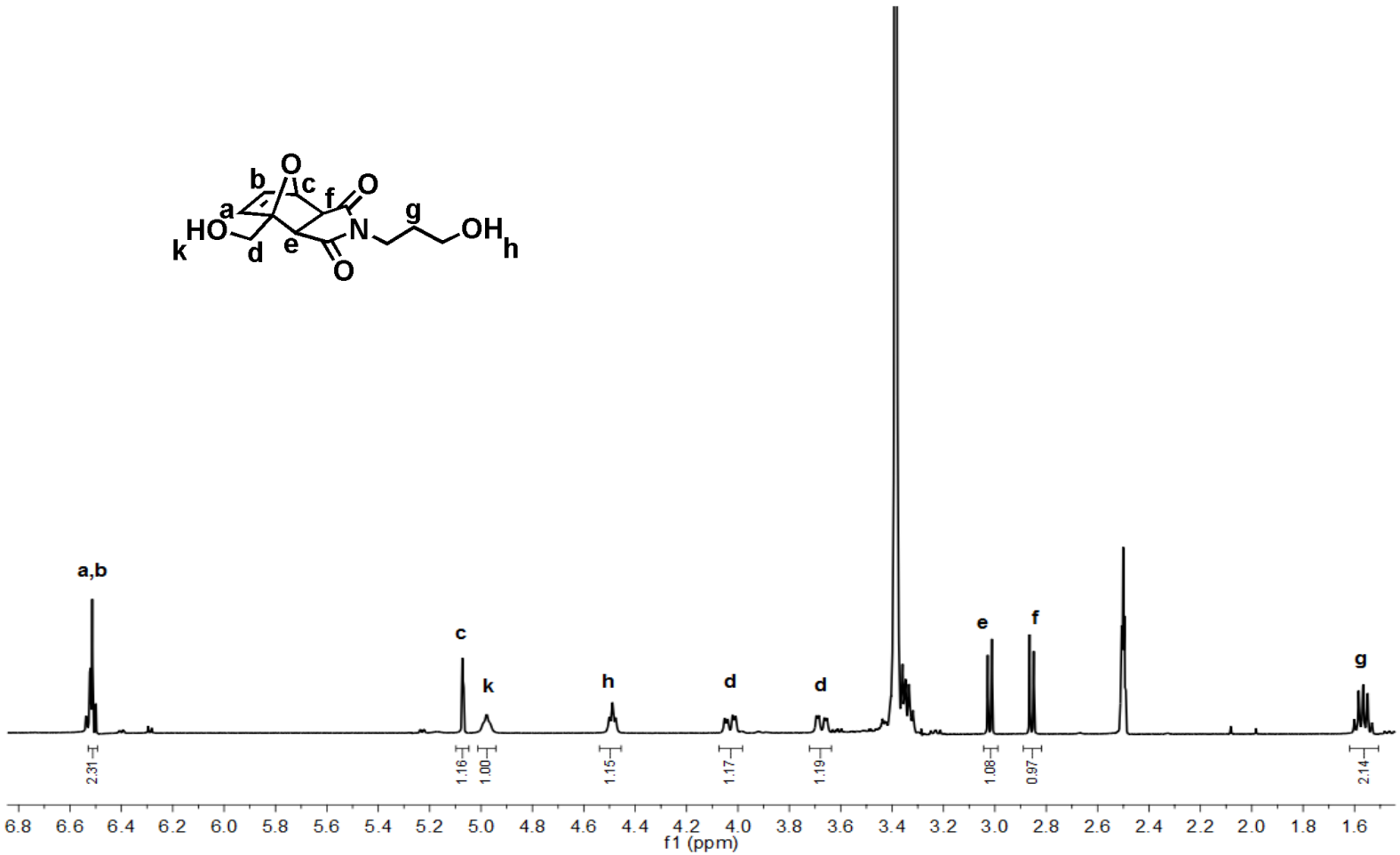

Figure A.1. ^{1}H NMR spectrum of diol core **3**

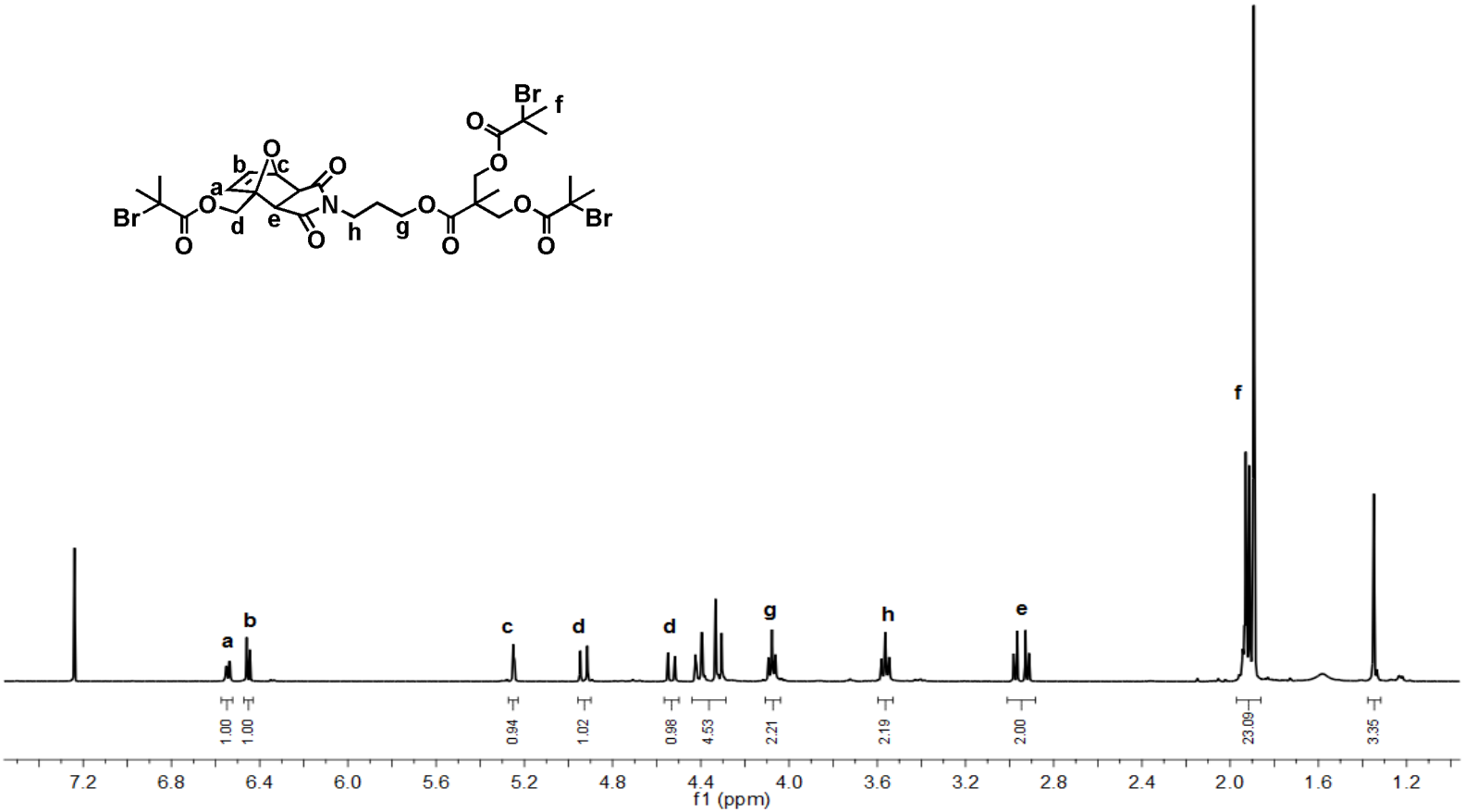

Figure A.2. ^{1}H NMR spectrum of 3arm initiator **(In1)**

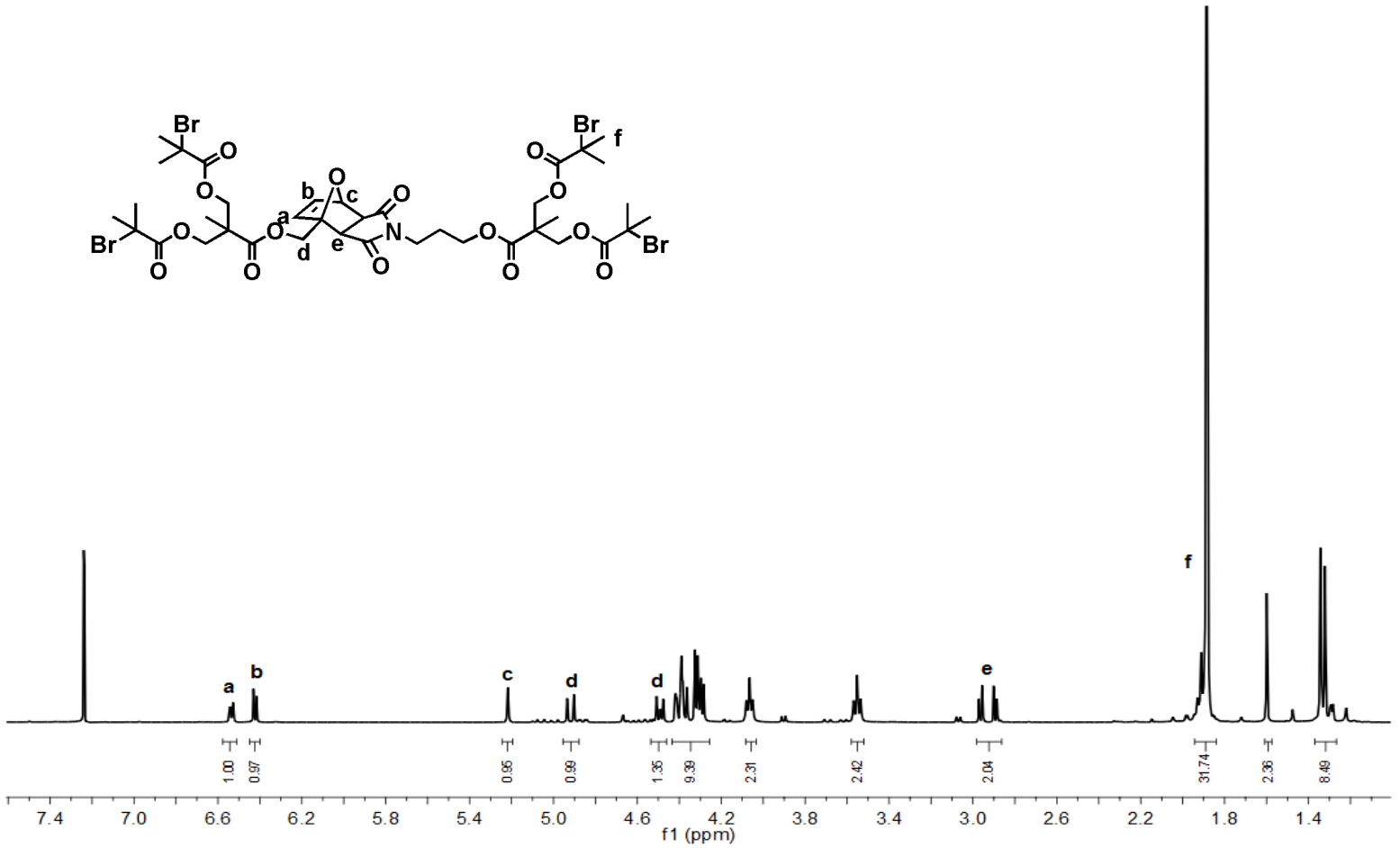

Figure A.3. ^{1}H NMR spectrum of 4arm initiator **(In2)**

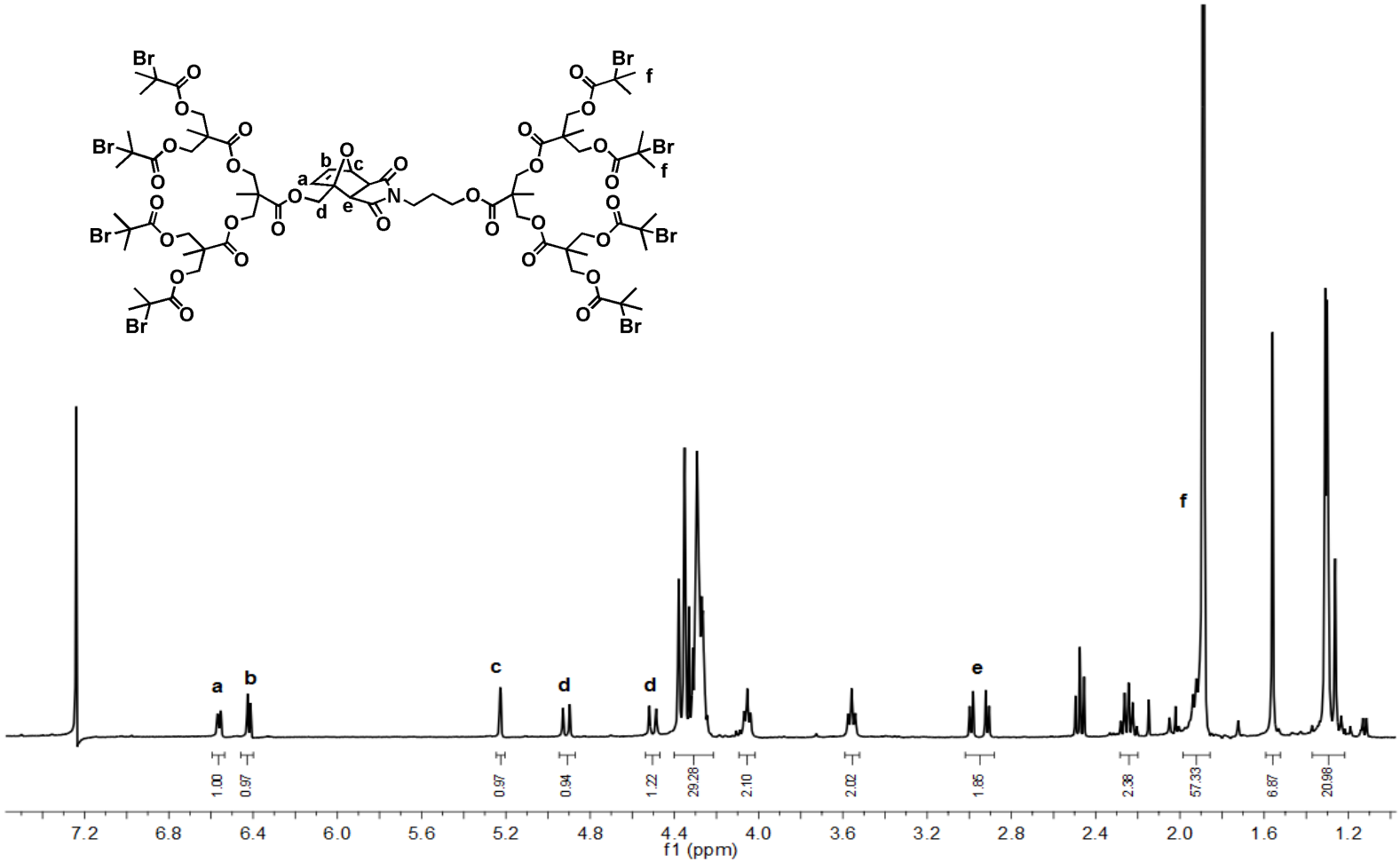

Figure A.4. ^{1}H NMR spectrum of 8arm initiator **(In3)**

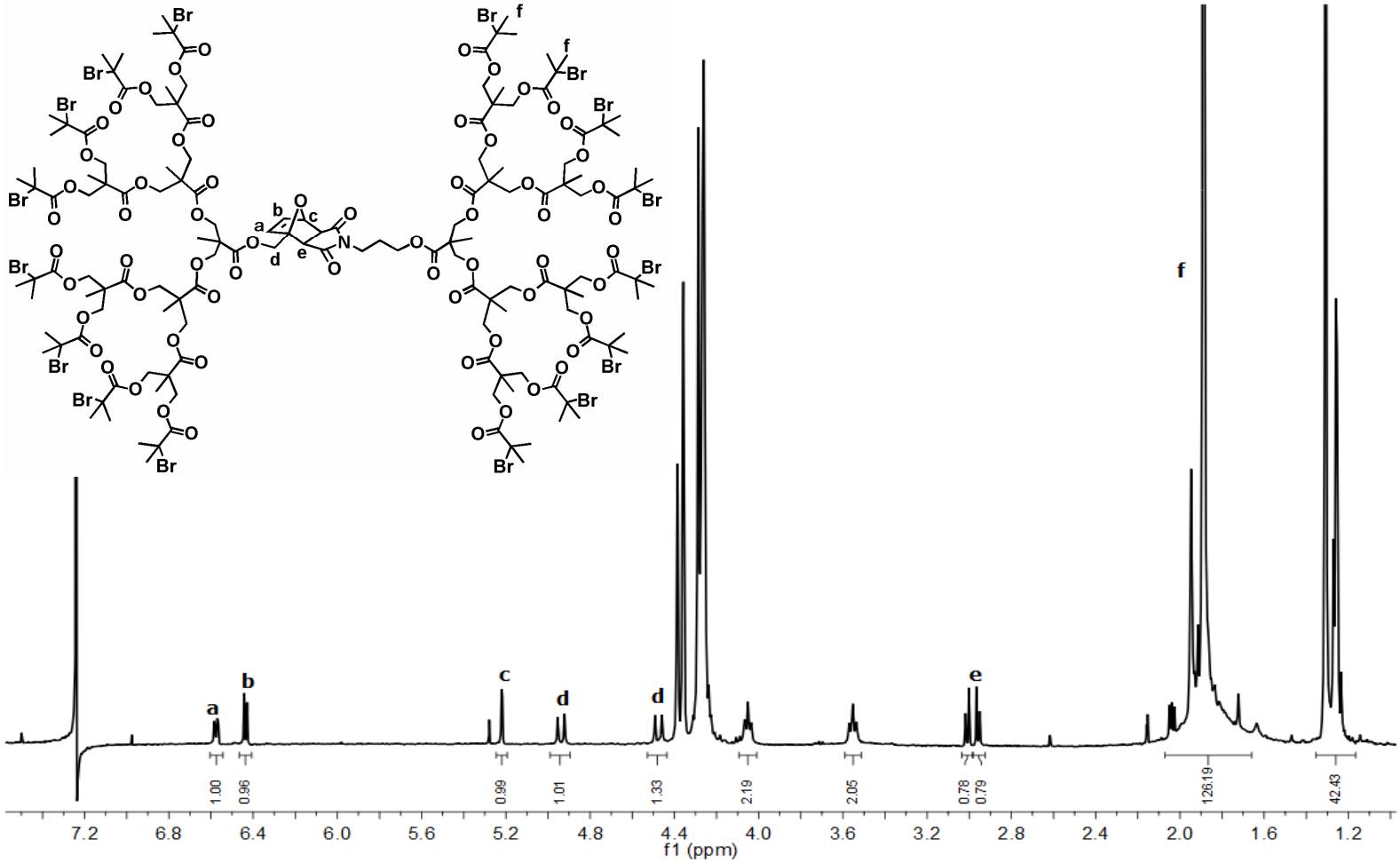

Figure A.5. ^{1}H NMR spectrum of of 16arm initiator **(In4)**

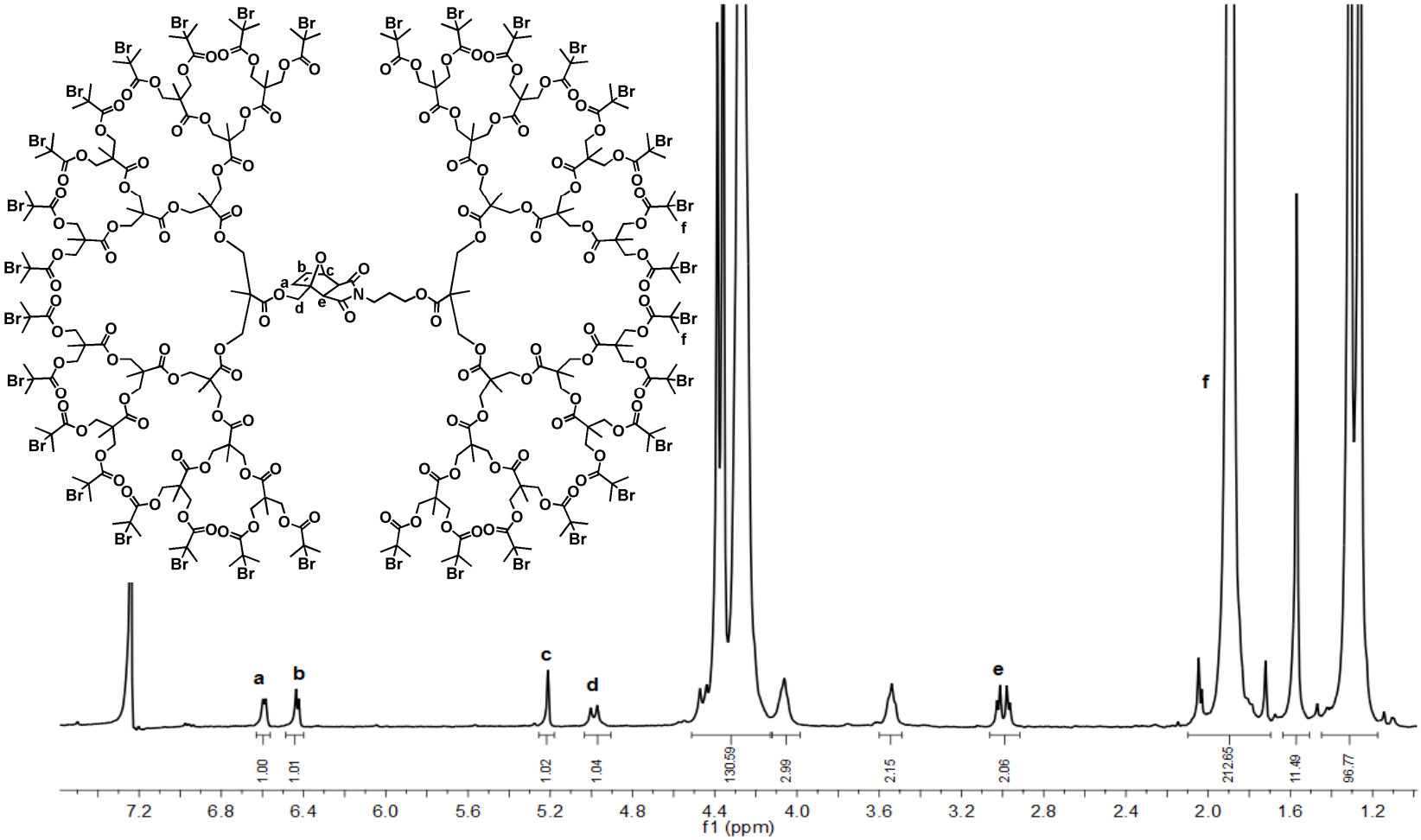

Figure A.6. ^{1}H NMR spectrum of 32arm initiator **(In5)**

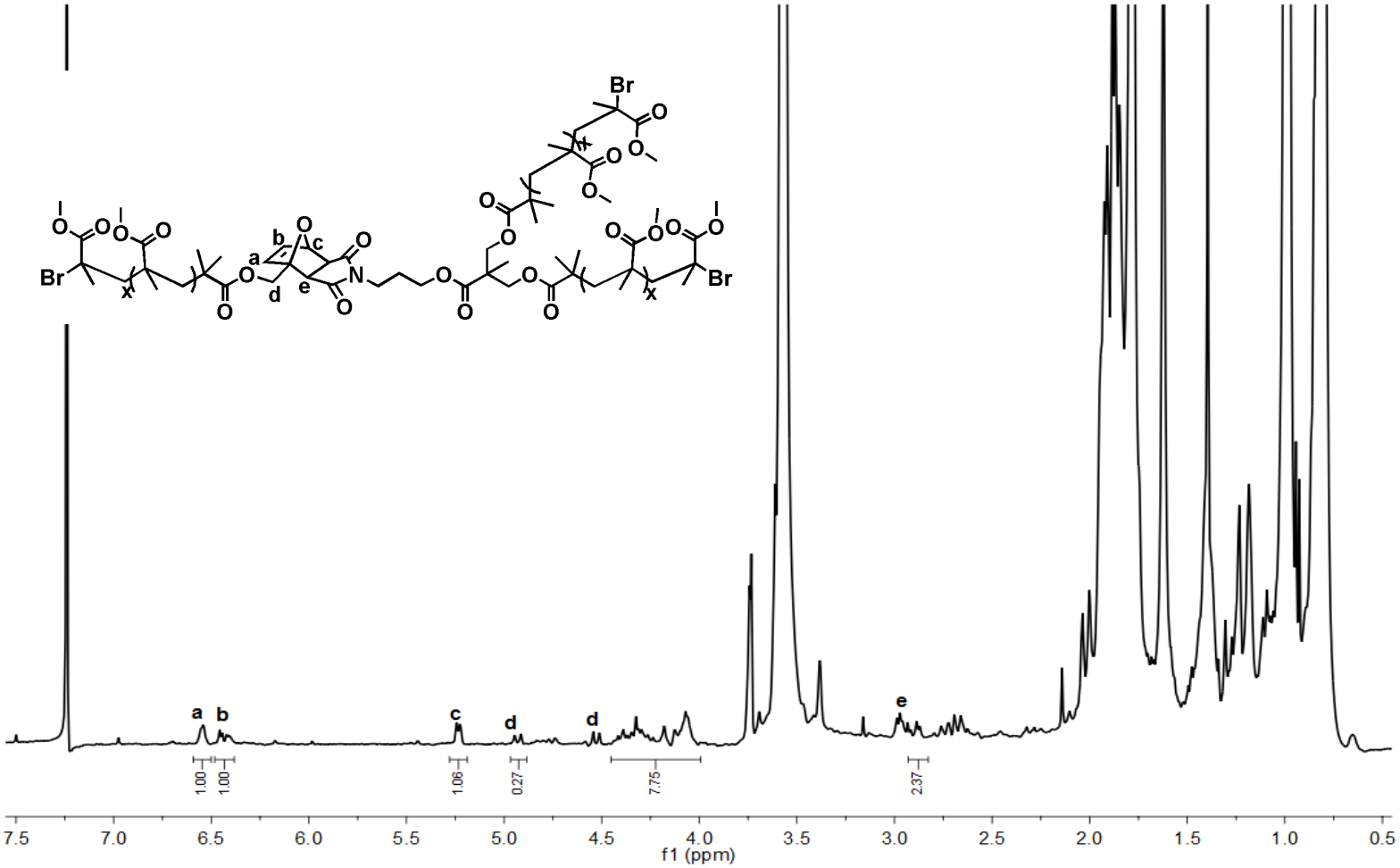

Figure A.7. ^{1}H NMR spectrum of **P1**

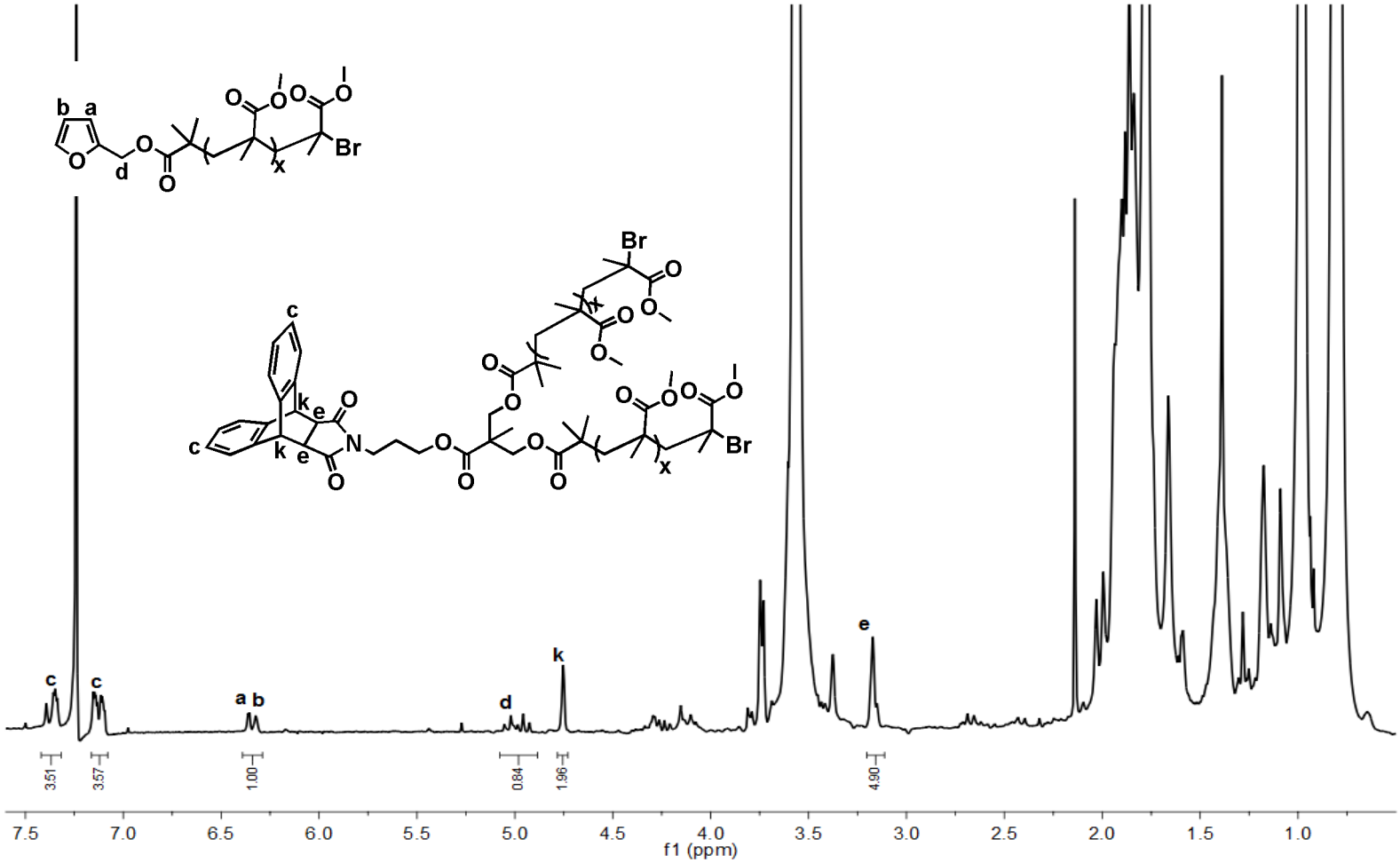

Figure A.8. ^{1}H NMR spectrum of **P1a** and **P1b**

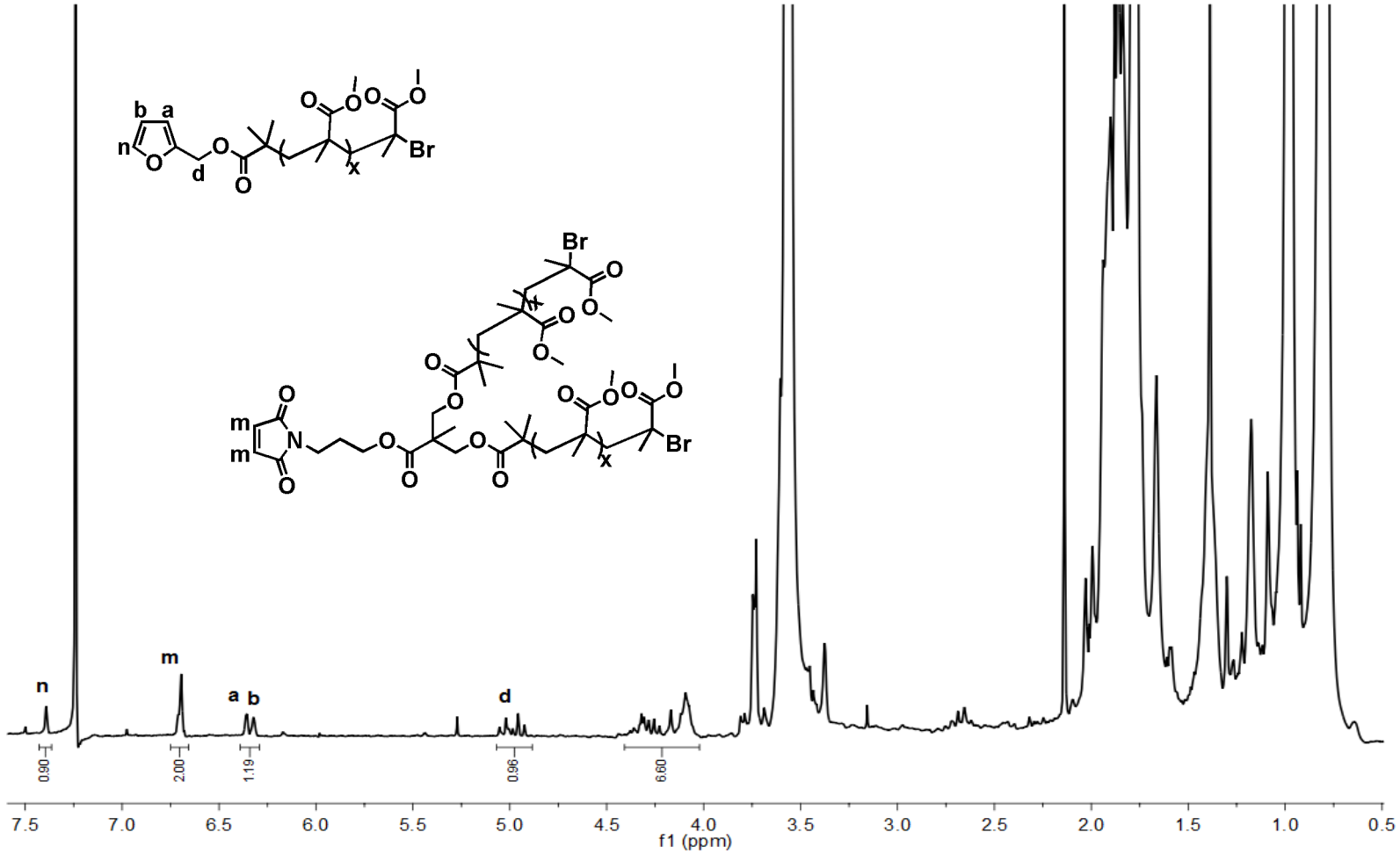

Figure A.9. ^{1}H NMR spectrum of **P1a** and **P1c**

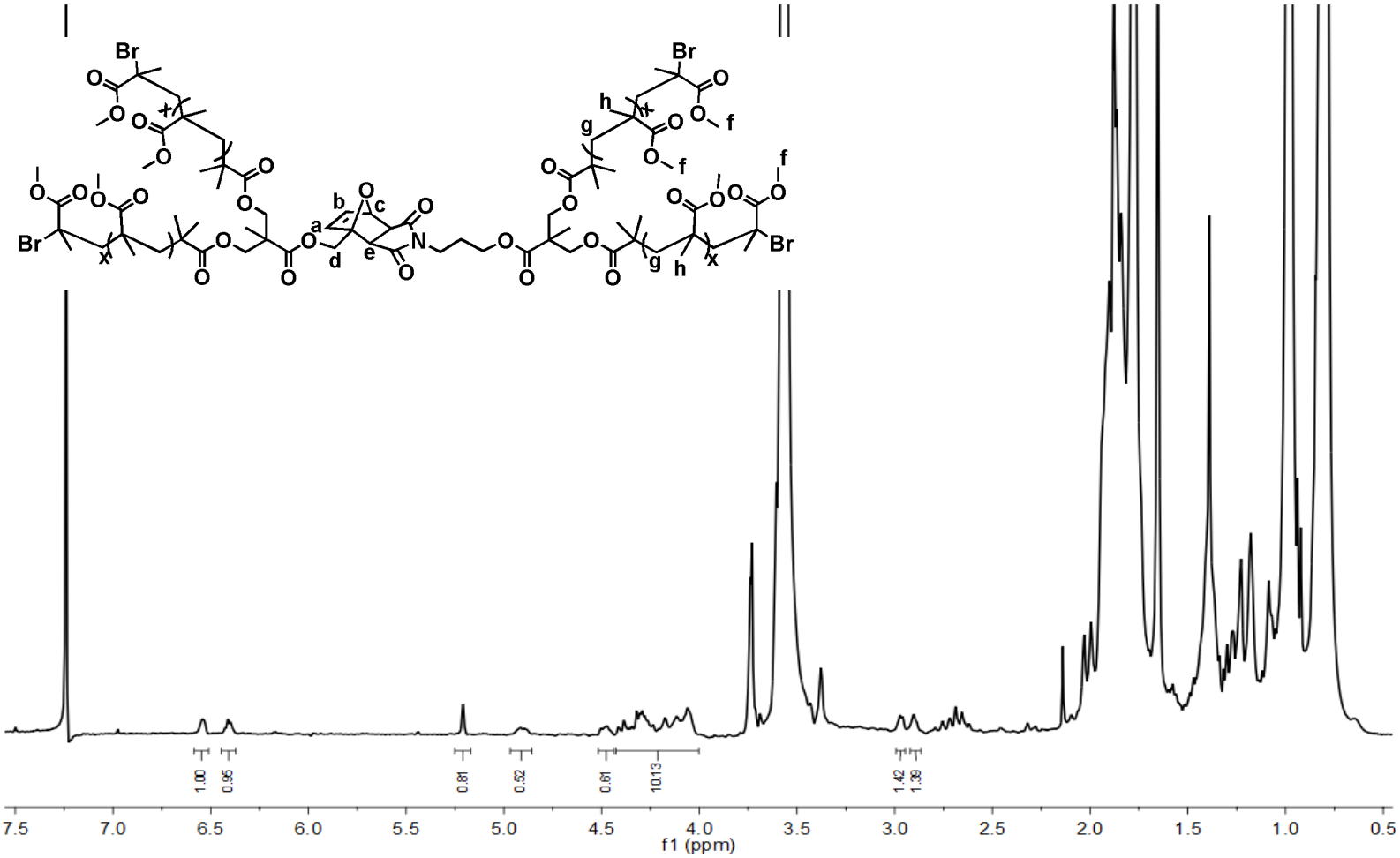

Figure A.10. ^{1}H NMR spectrum of **P2**

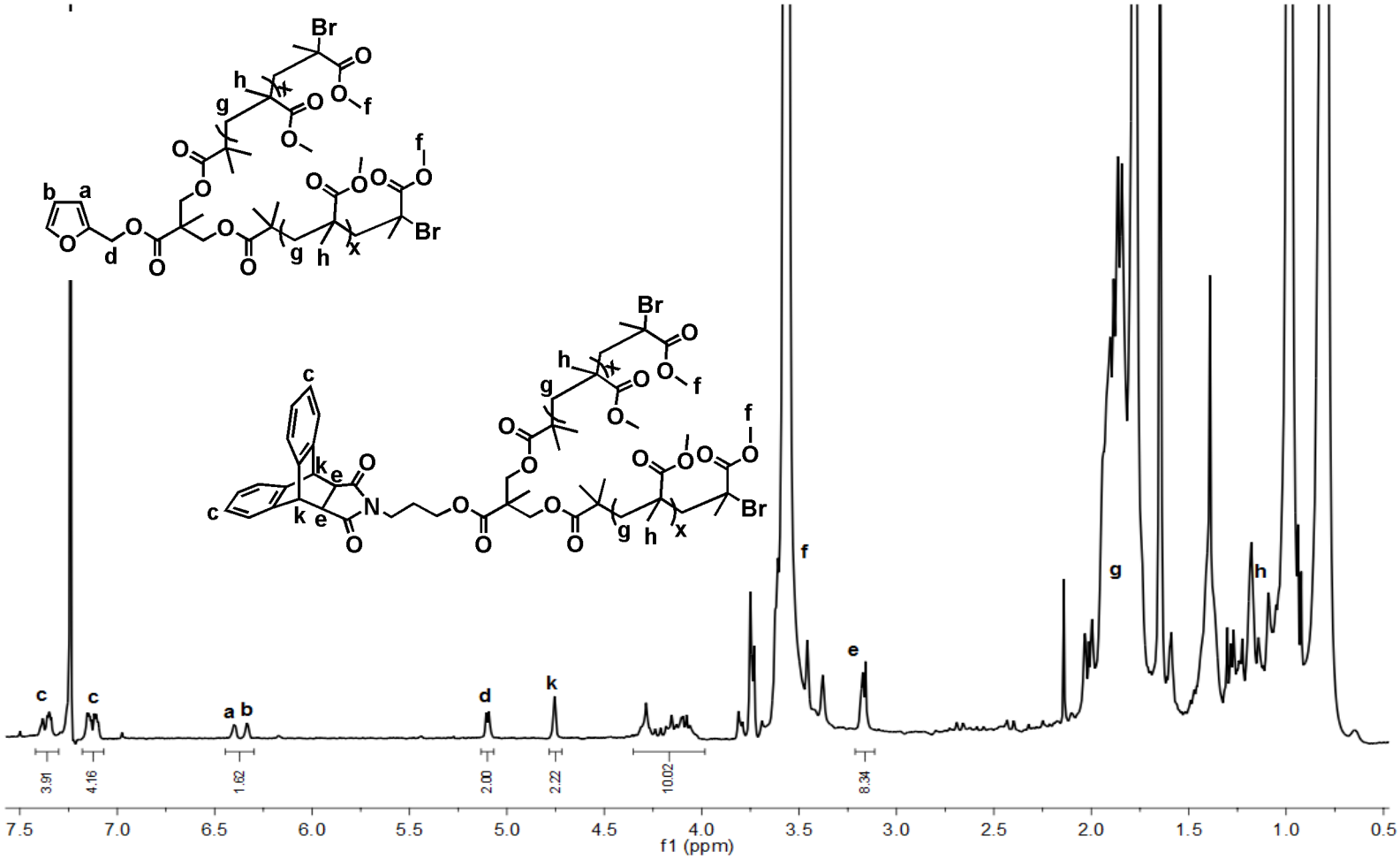

Figure A.11. ^{1}H NMR spectrum of **P2a** and **P2b**

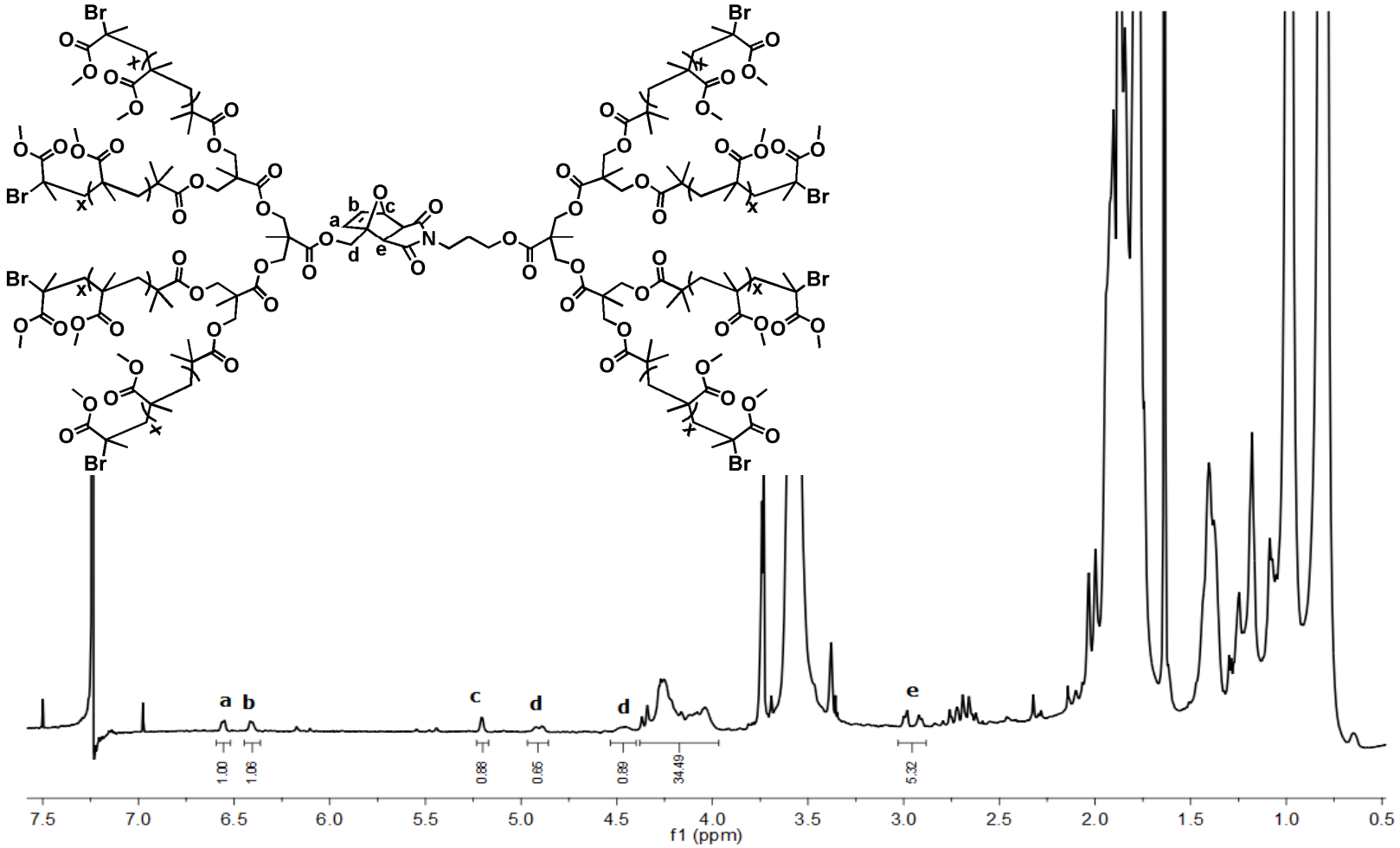

Figure A.12. ^{1}H NMR spectrum of **P3**

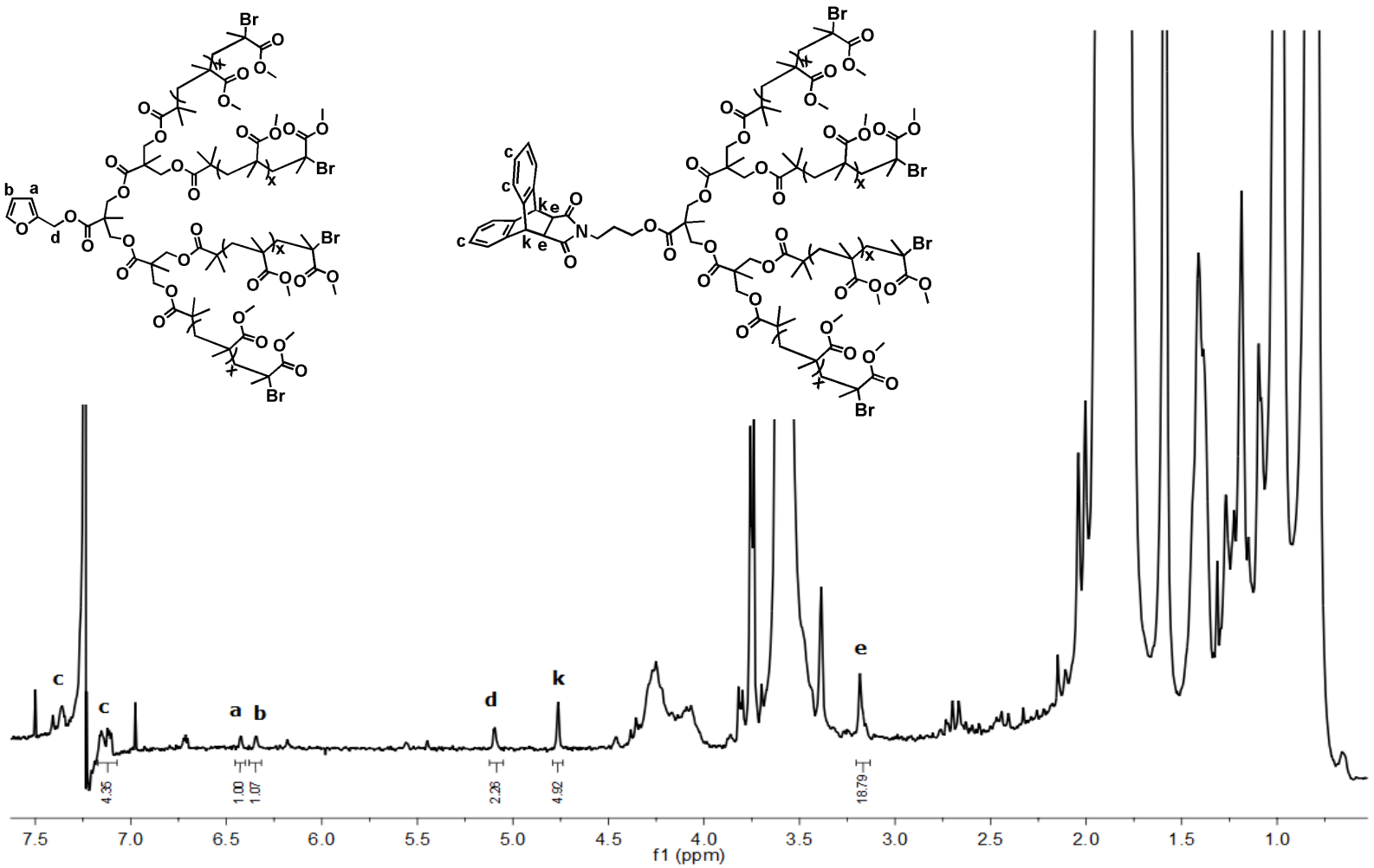

Figure A.13. ^{1}H NMR spectrum of **P3a** and **P3b**

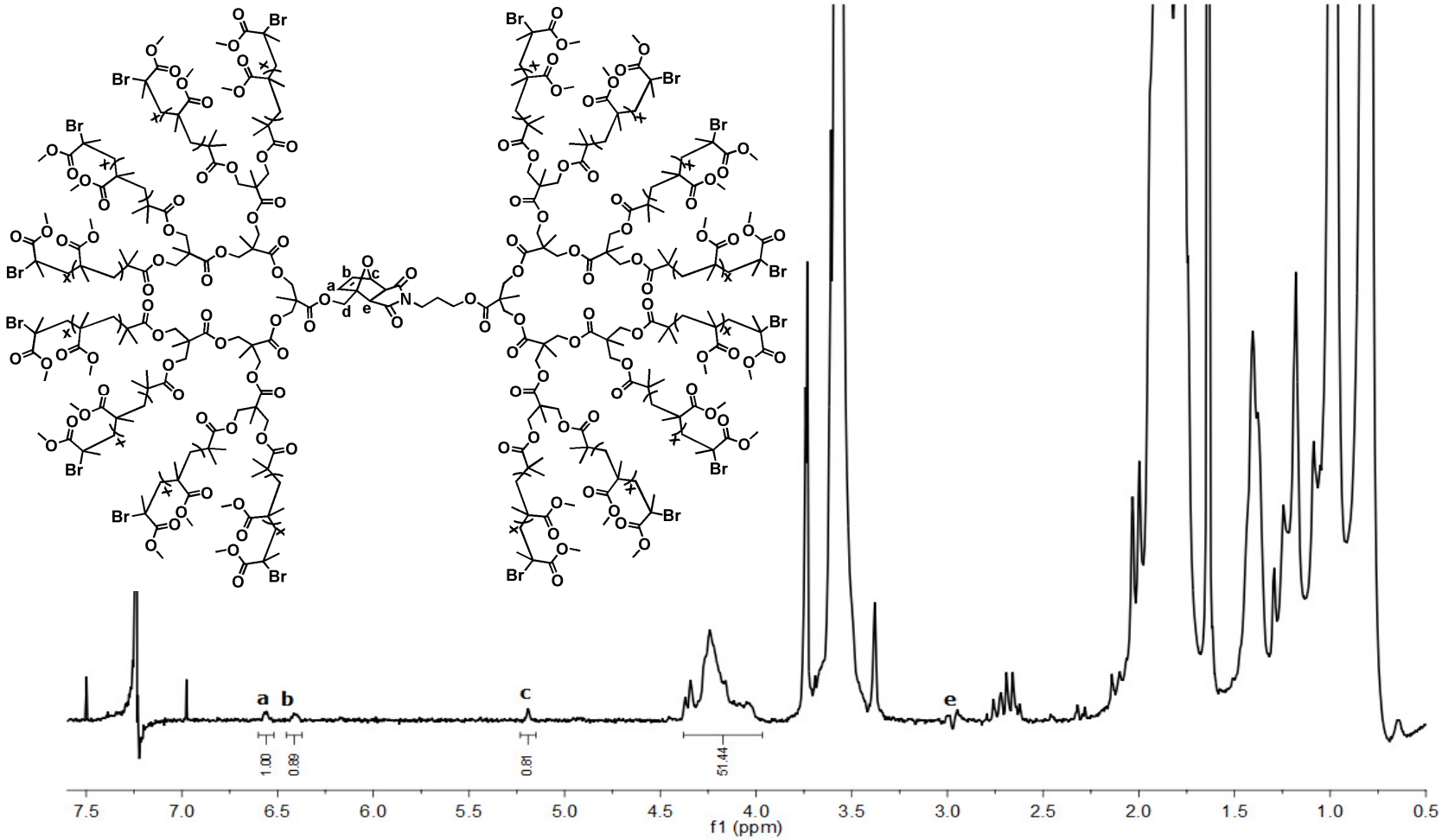

Figure A.14. ^{1}H NMR spectrum of **P4**

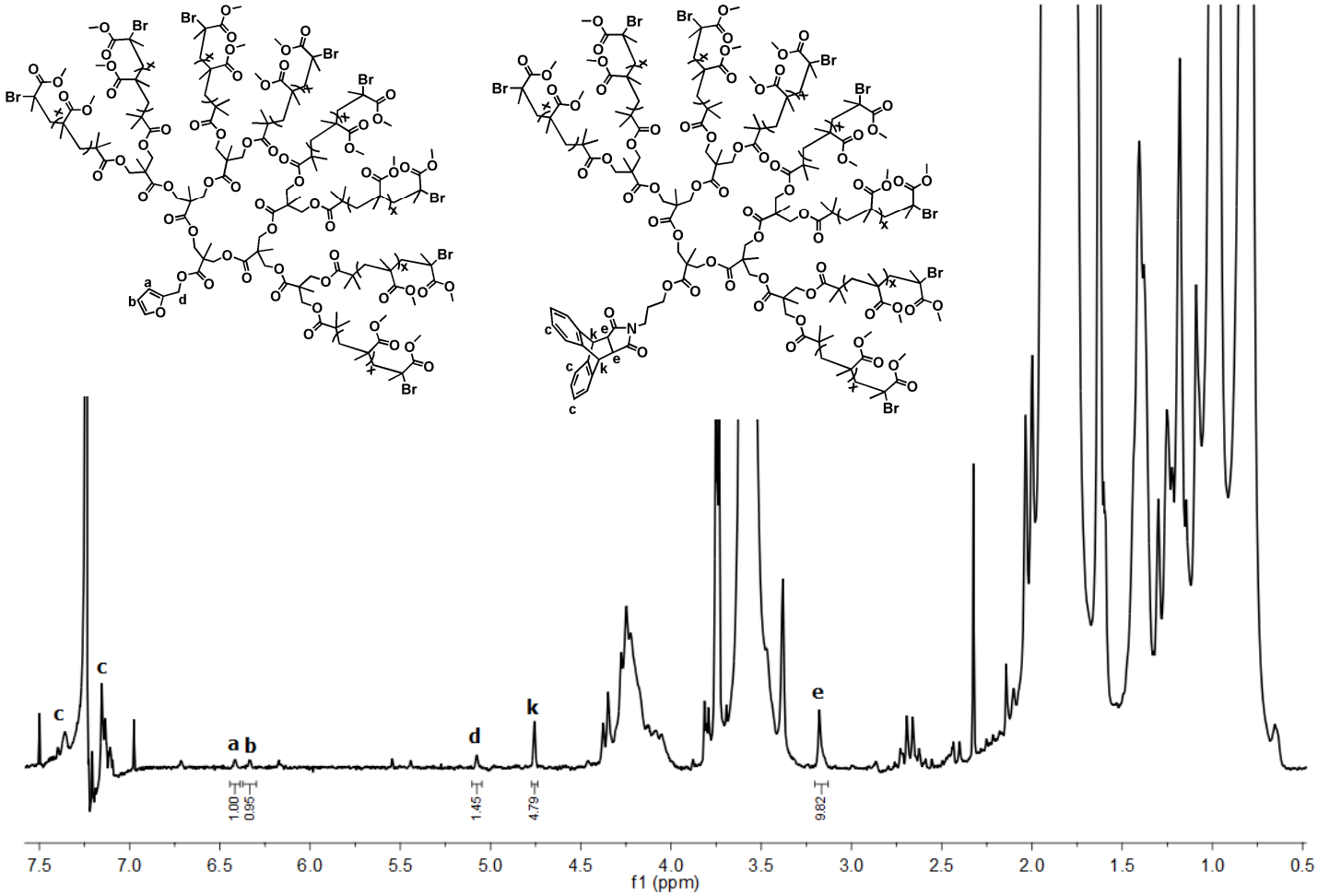

Figure A.15. ^{1}H NMR spectrum of **P4a** and **P4b**

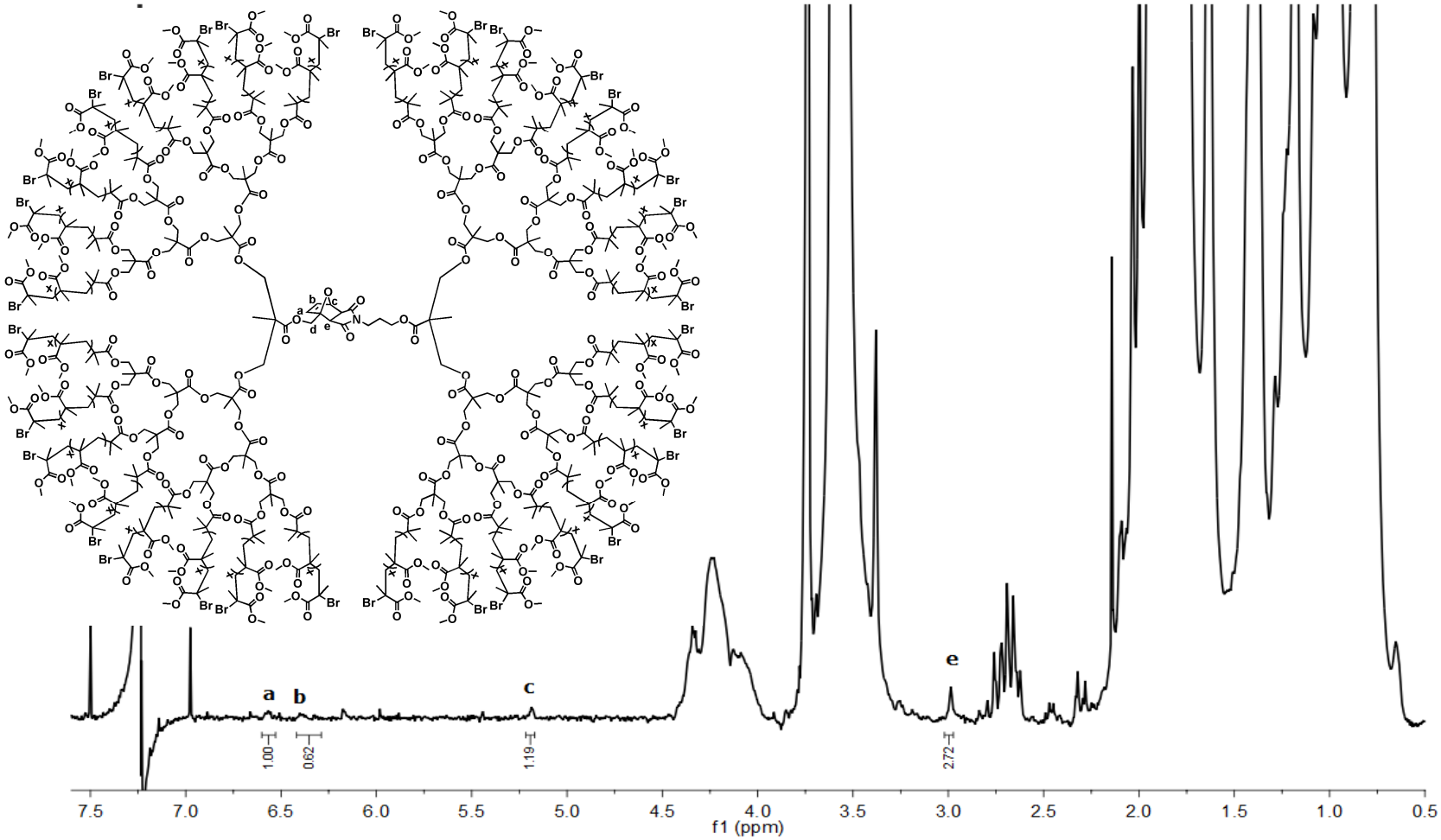

Figure A.16. ^{1}H NMR spectrum of **P5**

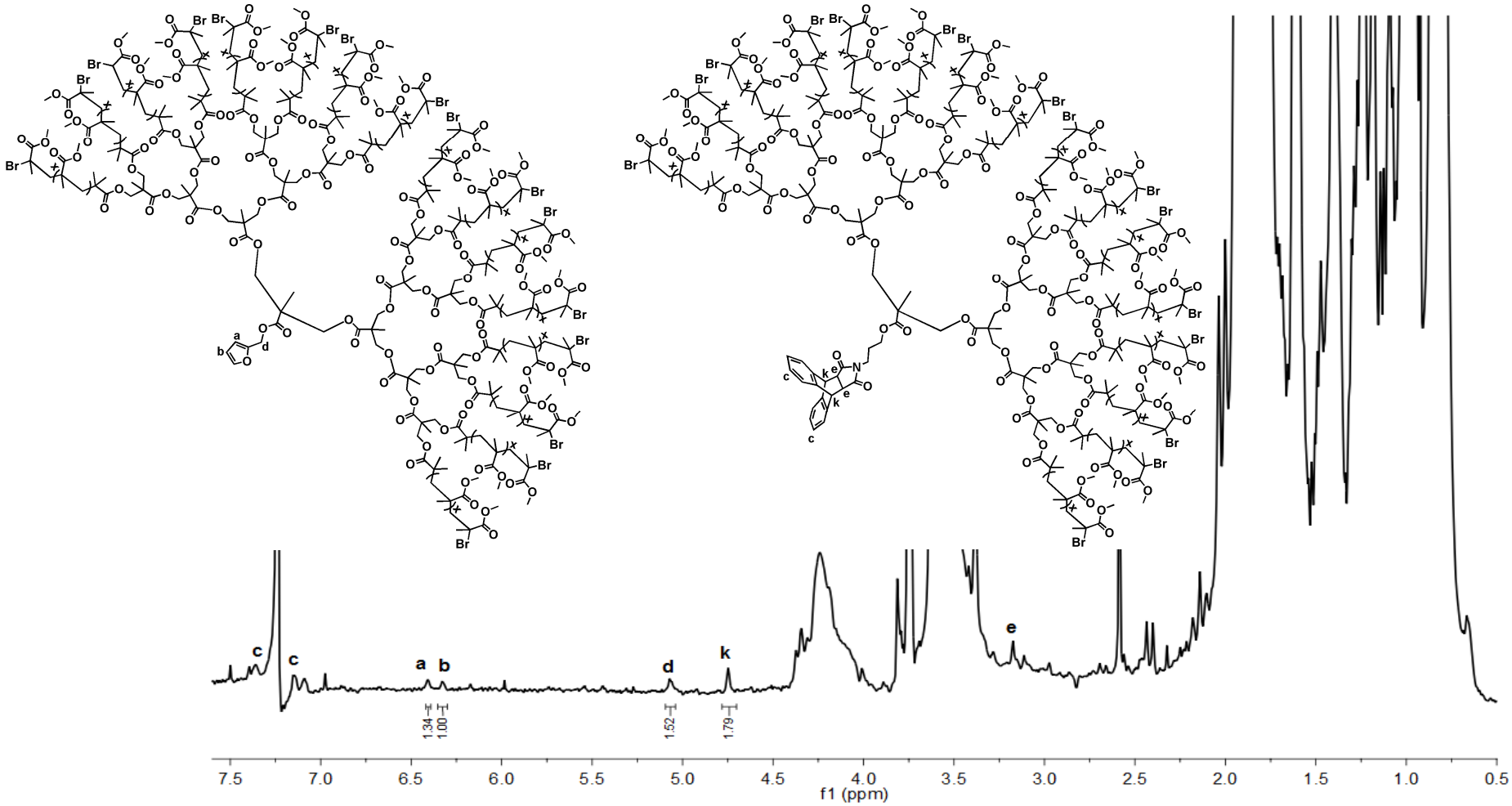

Figure A.17. ^{1}H NMR spectrum of **P5a** and **P5b**

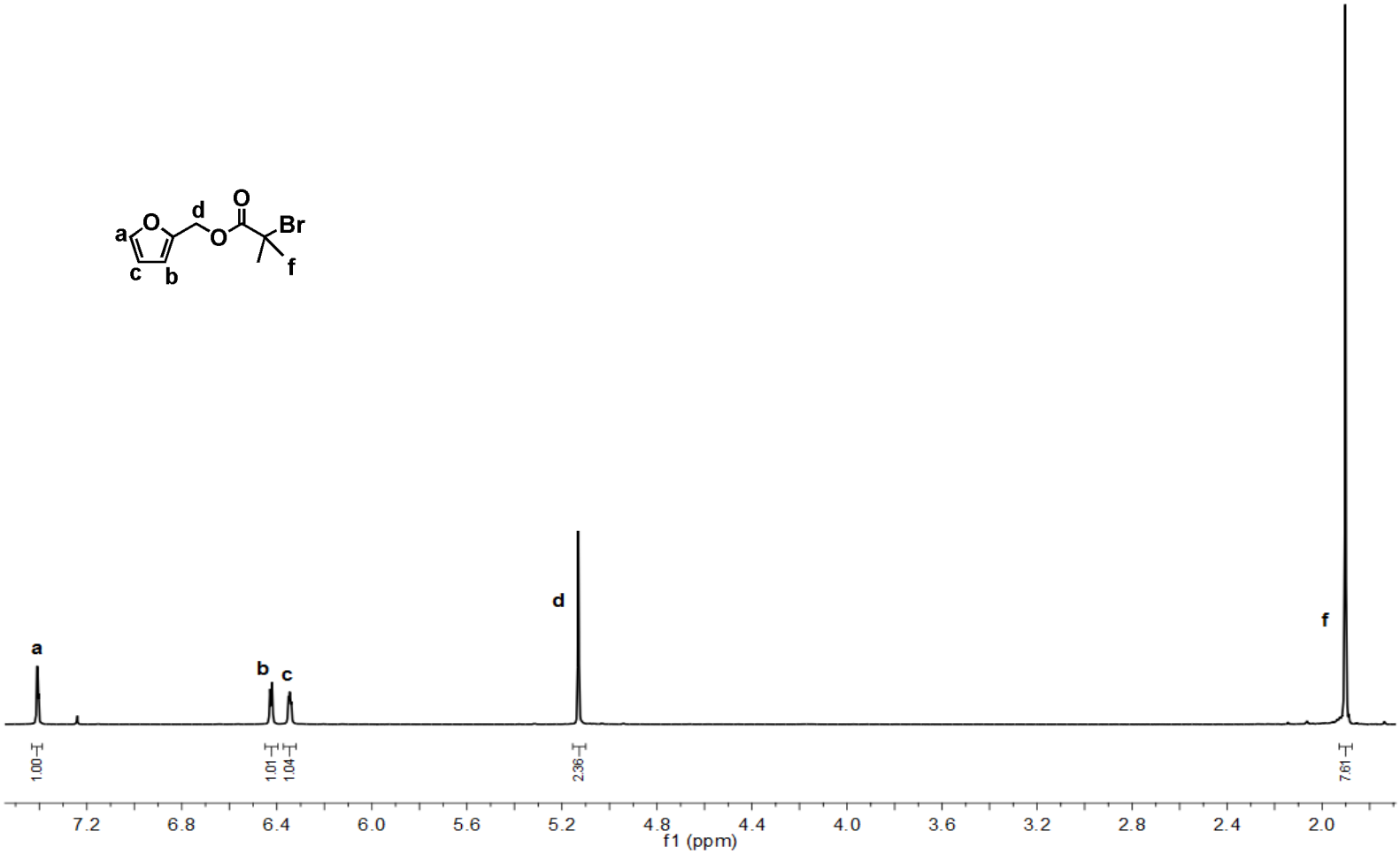

Figure A.18. ^{1}H NMR spectrum of compound **19**

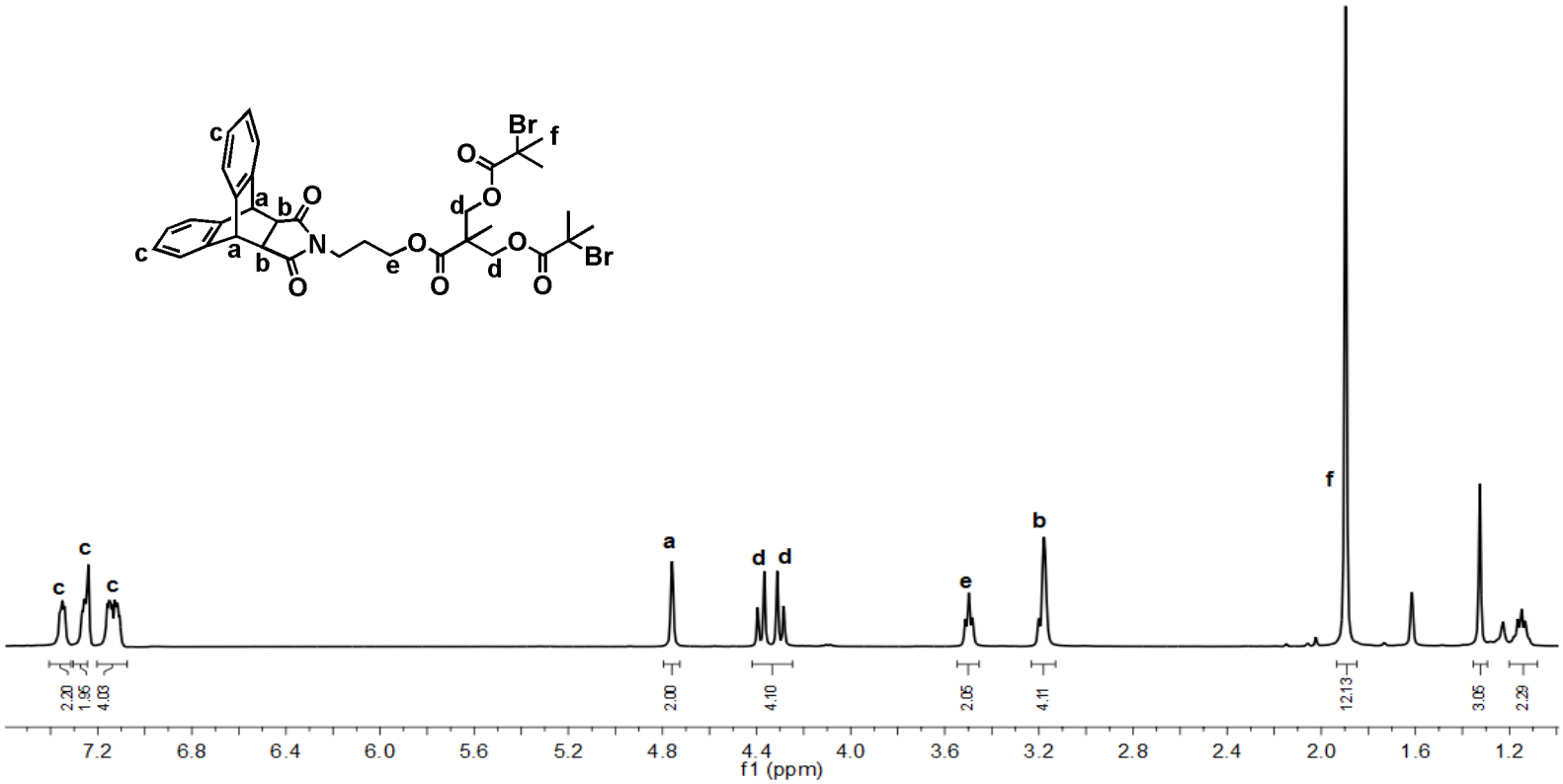

Figure A.19. [1]HNMR spectrum of **20**

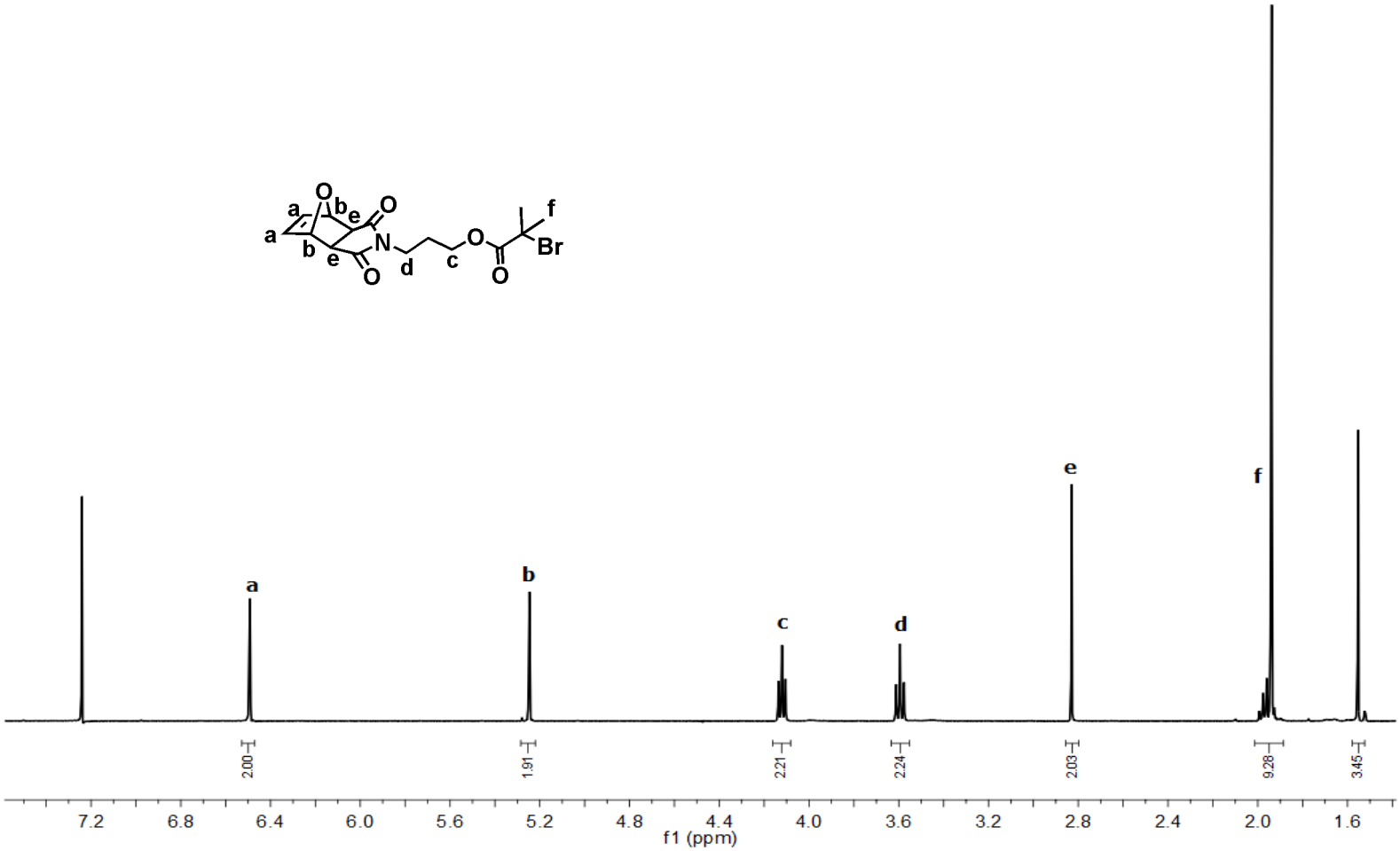

Figure A.20. ^{1}H NMR spectrum of compound **21**

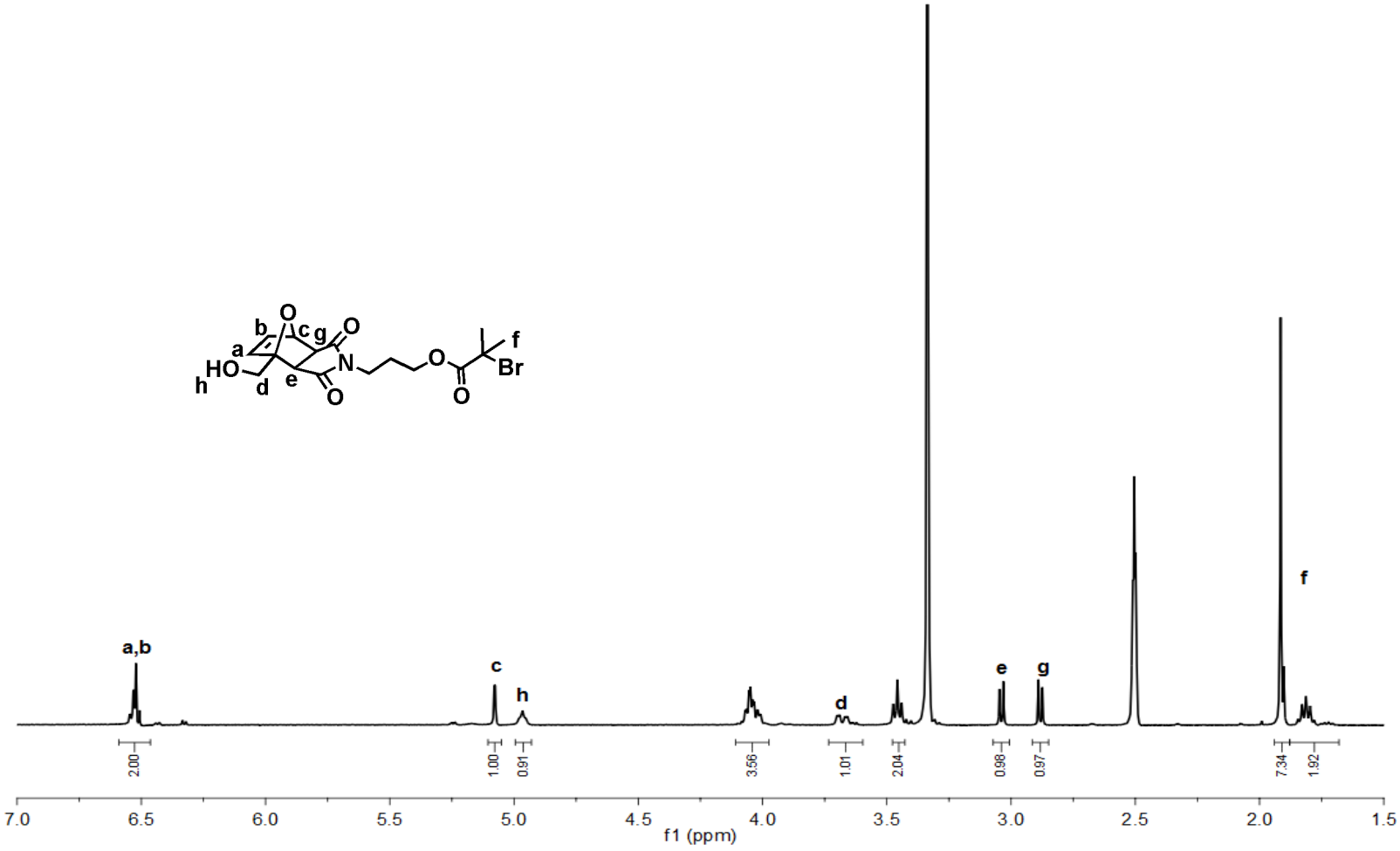

Figure A.21. ^{1}H NMR spectrum of **In1:1**

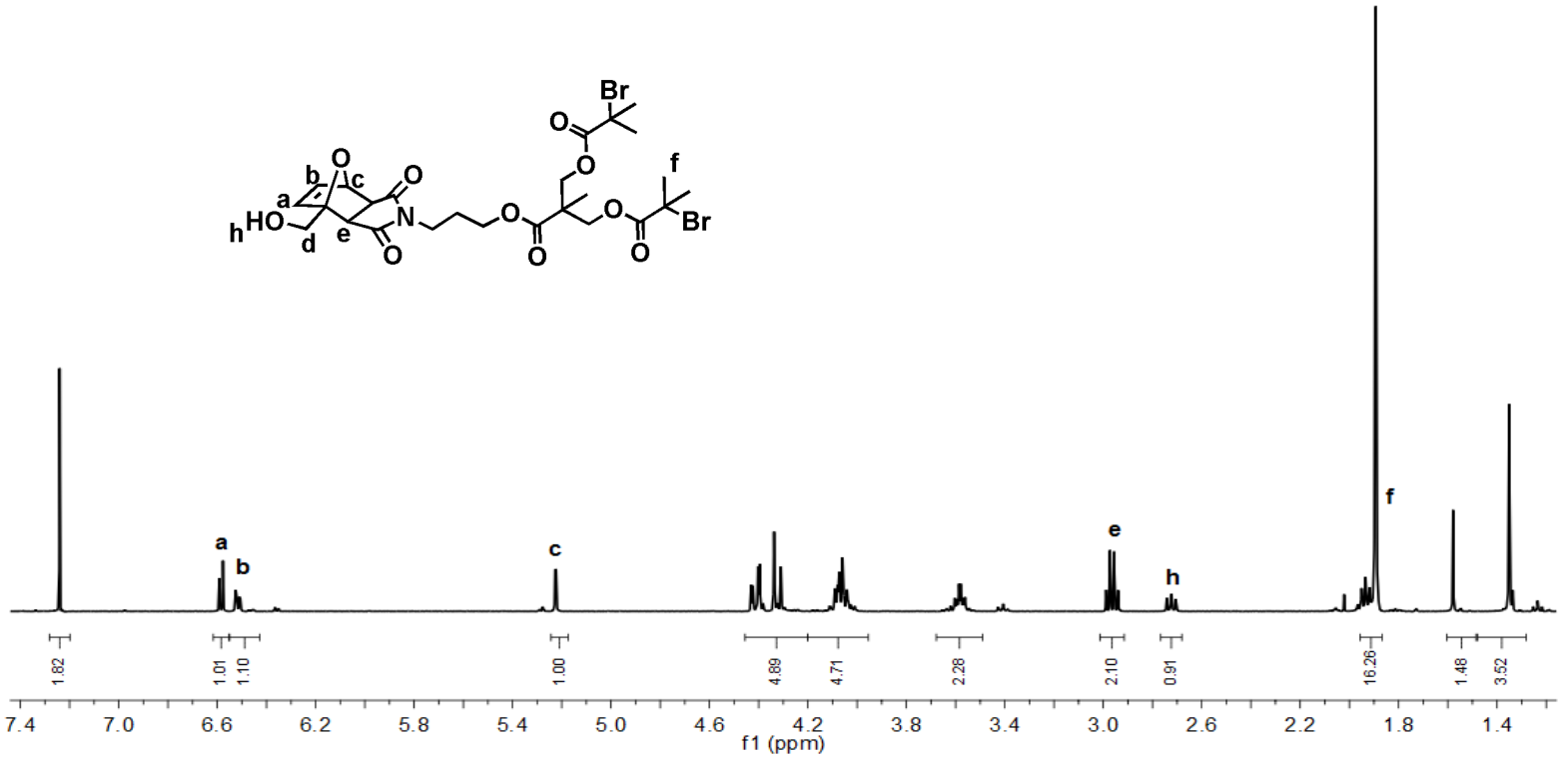

Figure A.22. ^{1}H NMR spectrum of **In1:2**

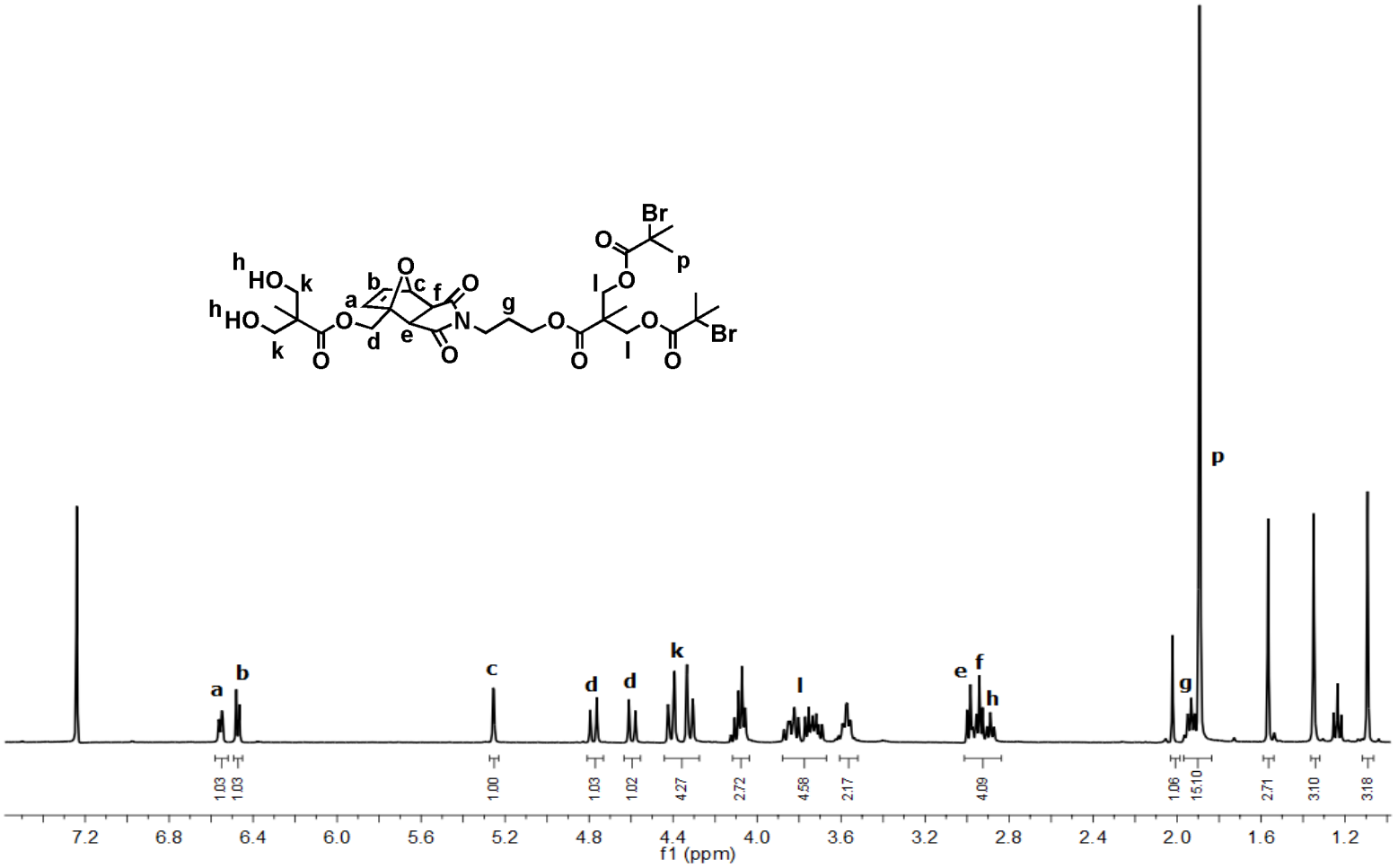

Figure A.23. ^{1}H NMR spectrum of **In2:2**

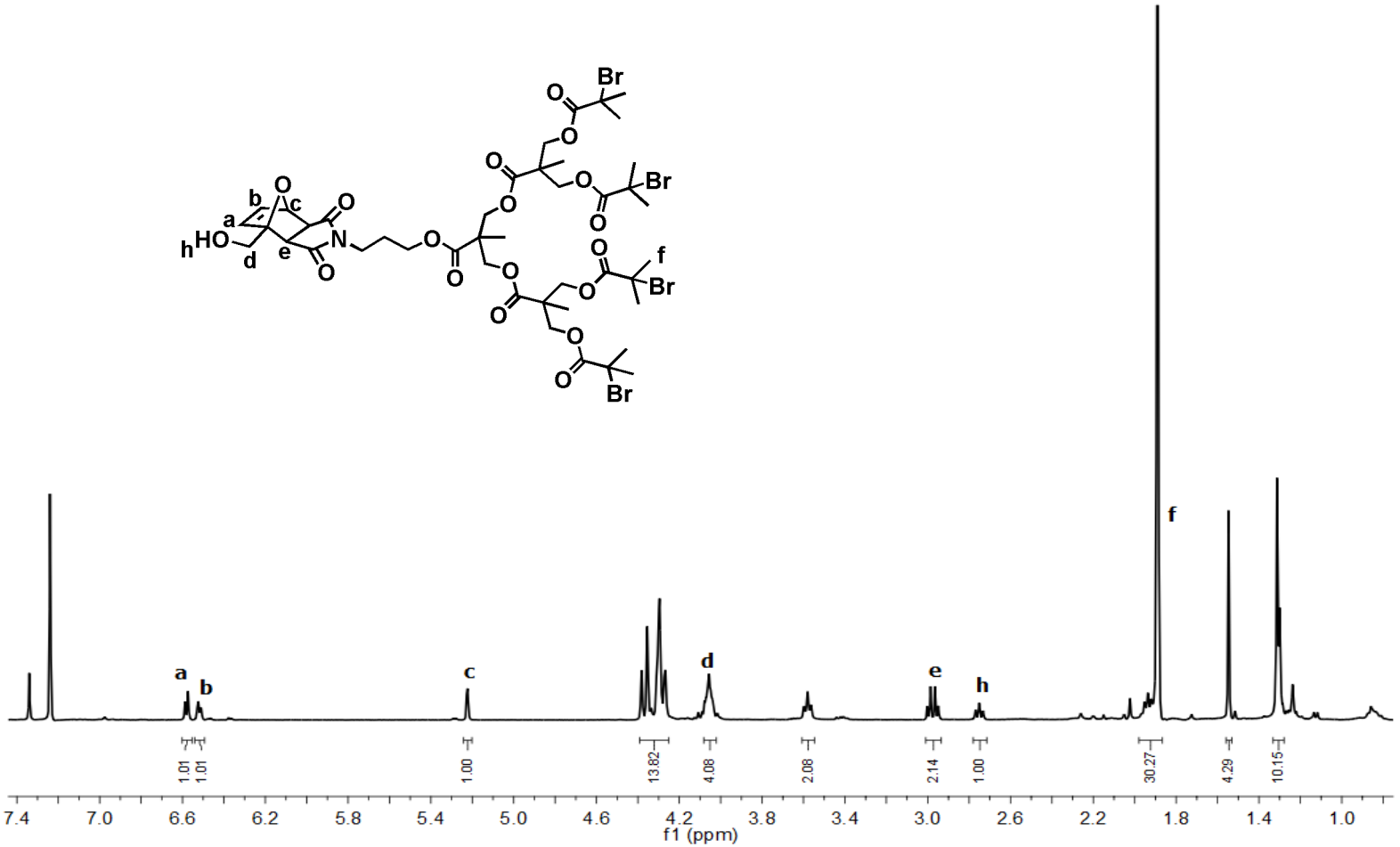

Figure A.24. ^{1}H NMR spectrum of **In1:4**

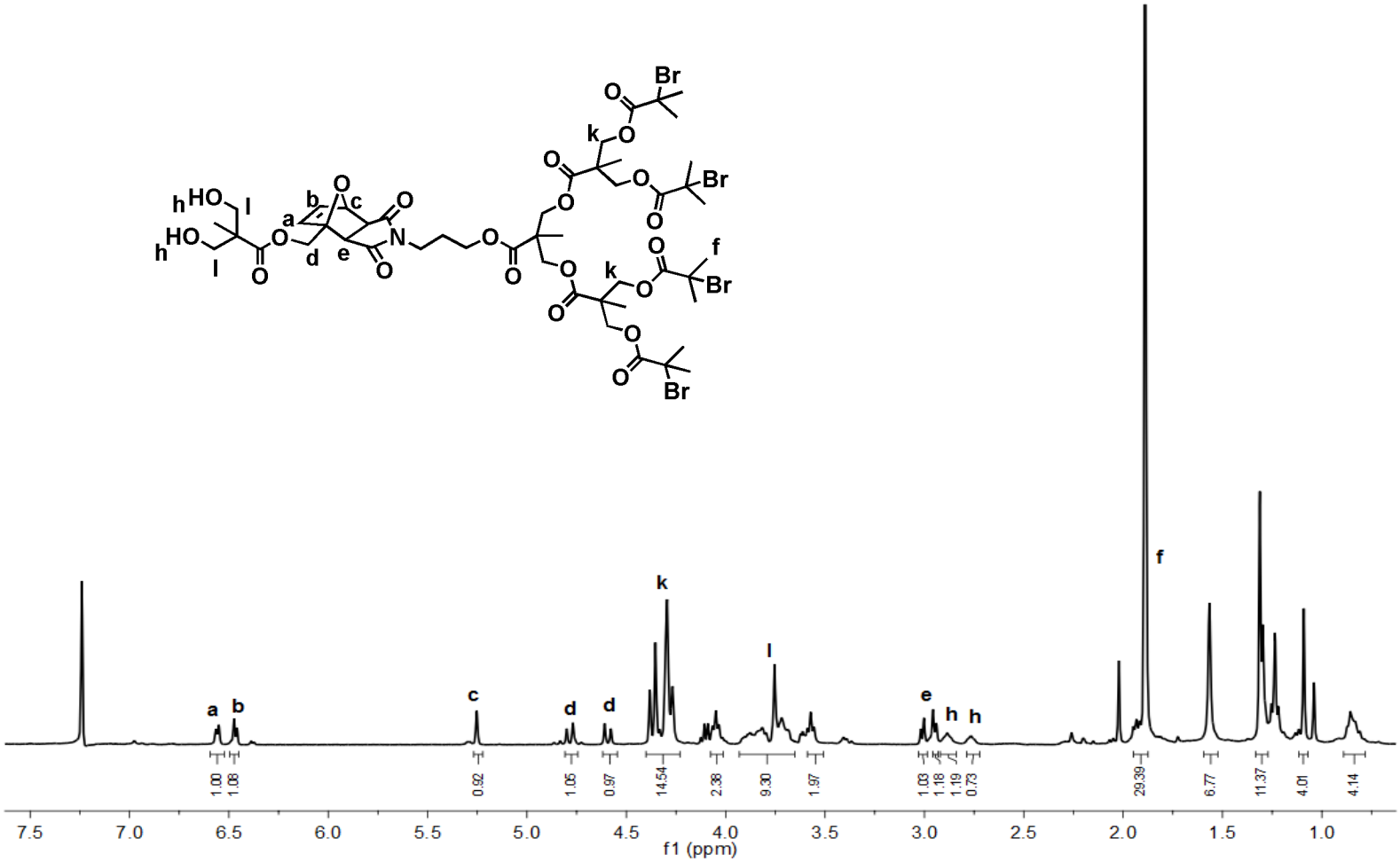

Figure A.25. ^{1}H NMR spectrum of **In2:4**

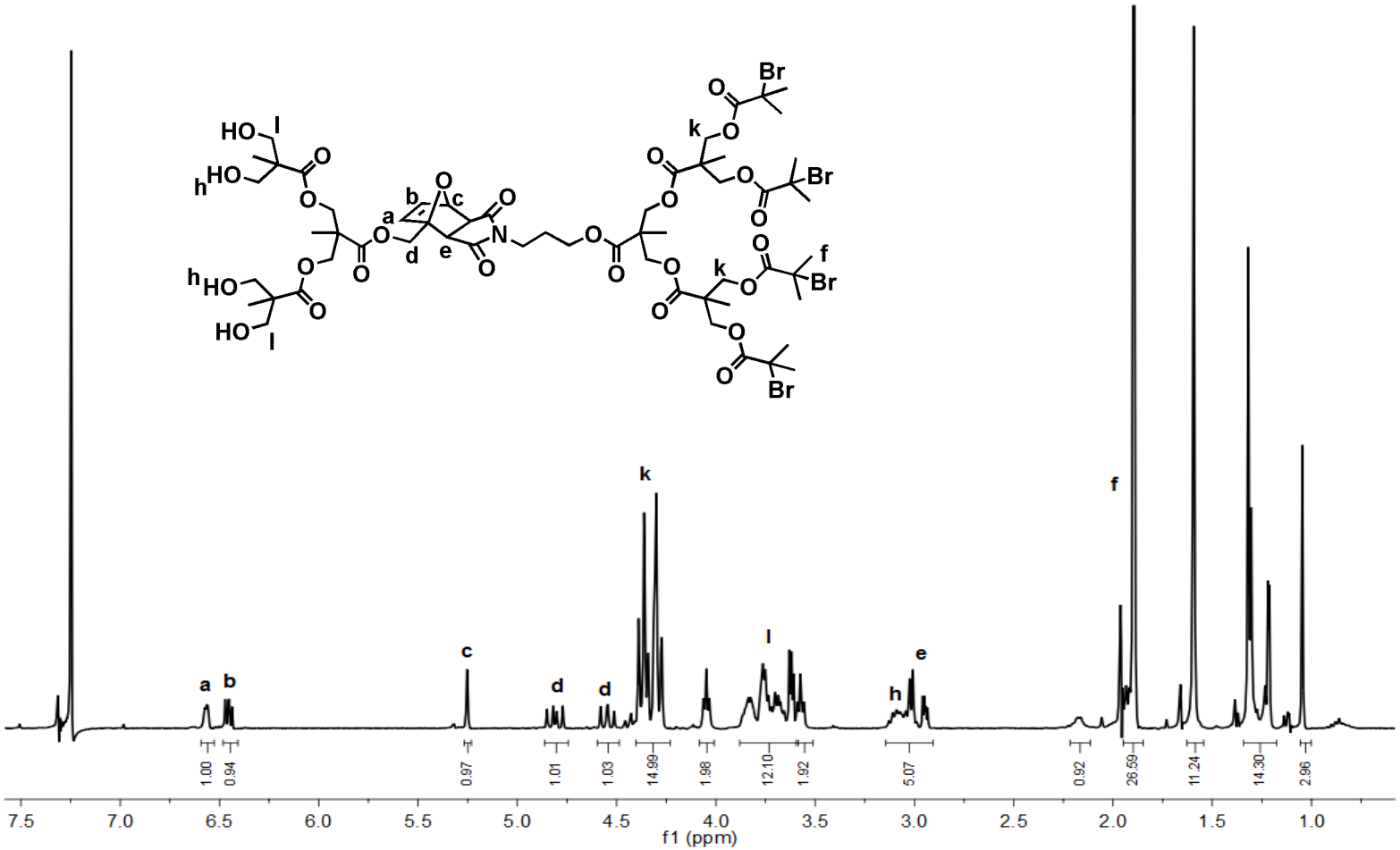

Figure A.26. ^{1}H NMR spectrum of **In4:4**

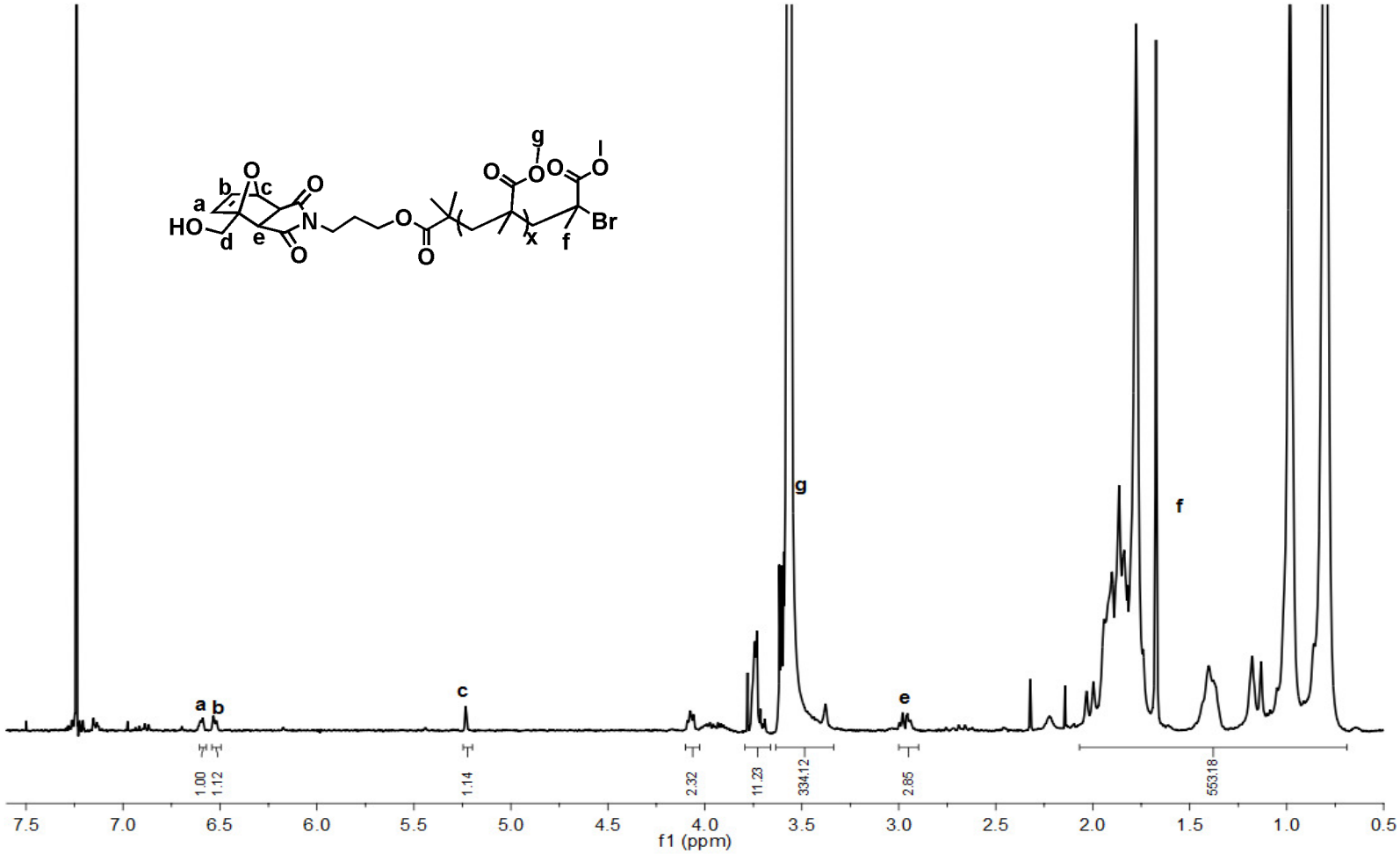

Figure A.27. ^{1}H NMR spectrum of **1OH:1PMMA**

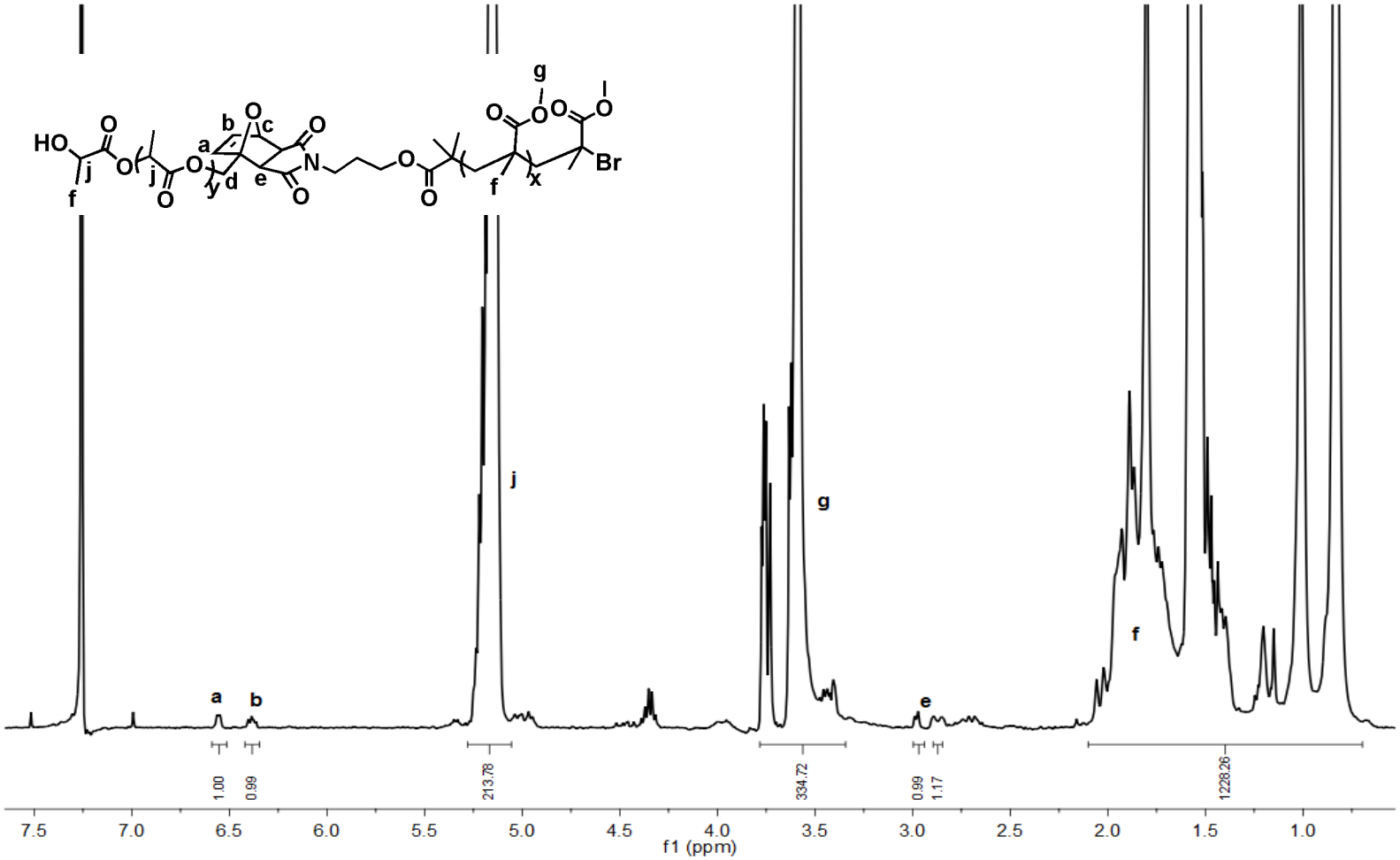

Figure A.28. ^{1}H NMR spectrum of **1PLA:1PMMA**

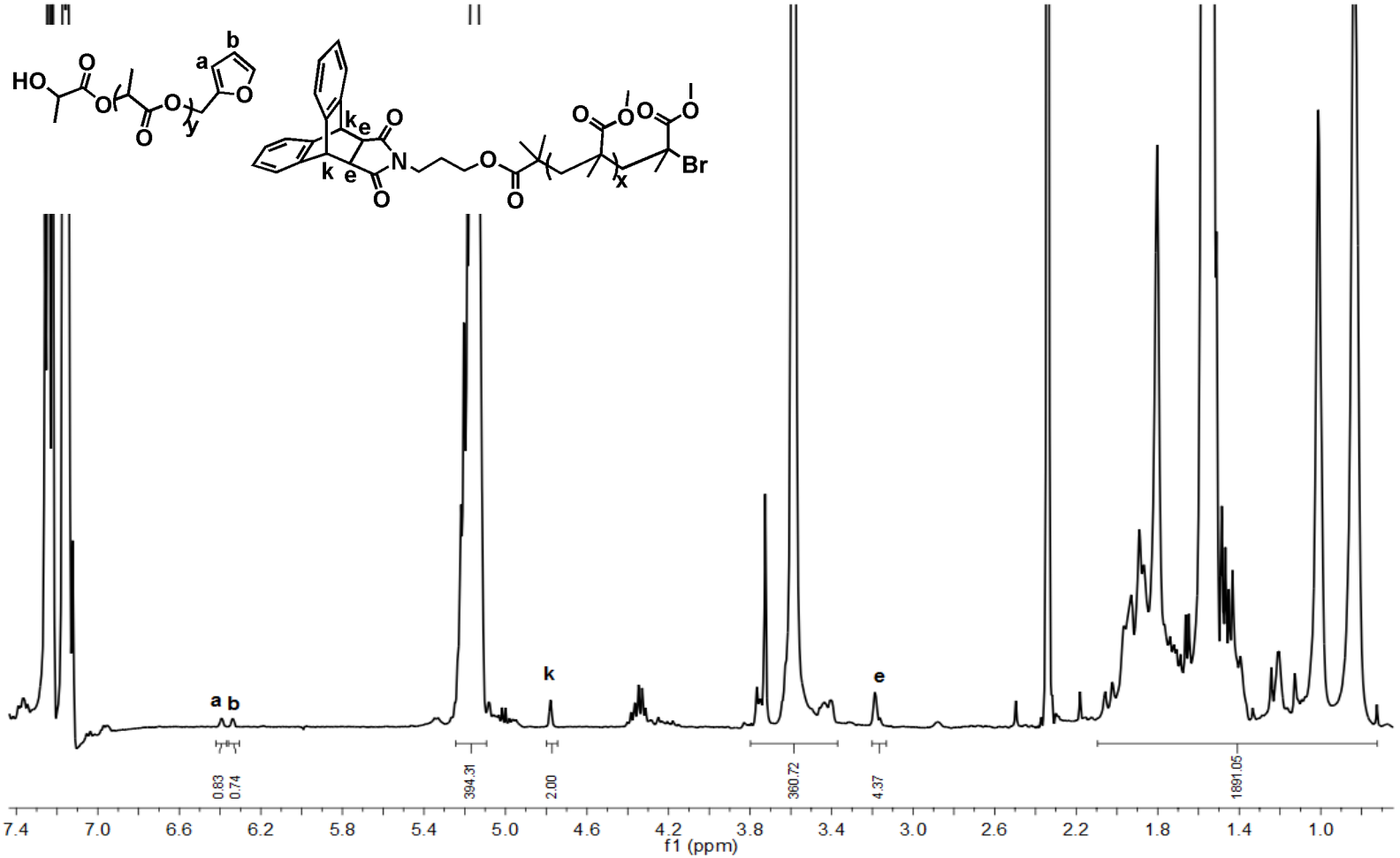

Figure A.29. [1]H NMR spectrum of **1PLA** and **1PMMA** mixture after rDA

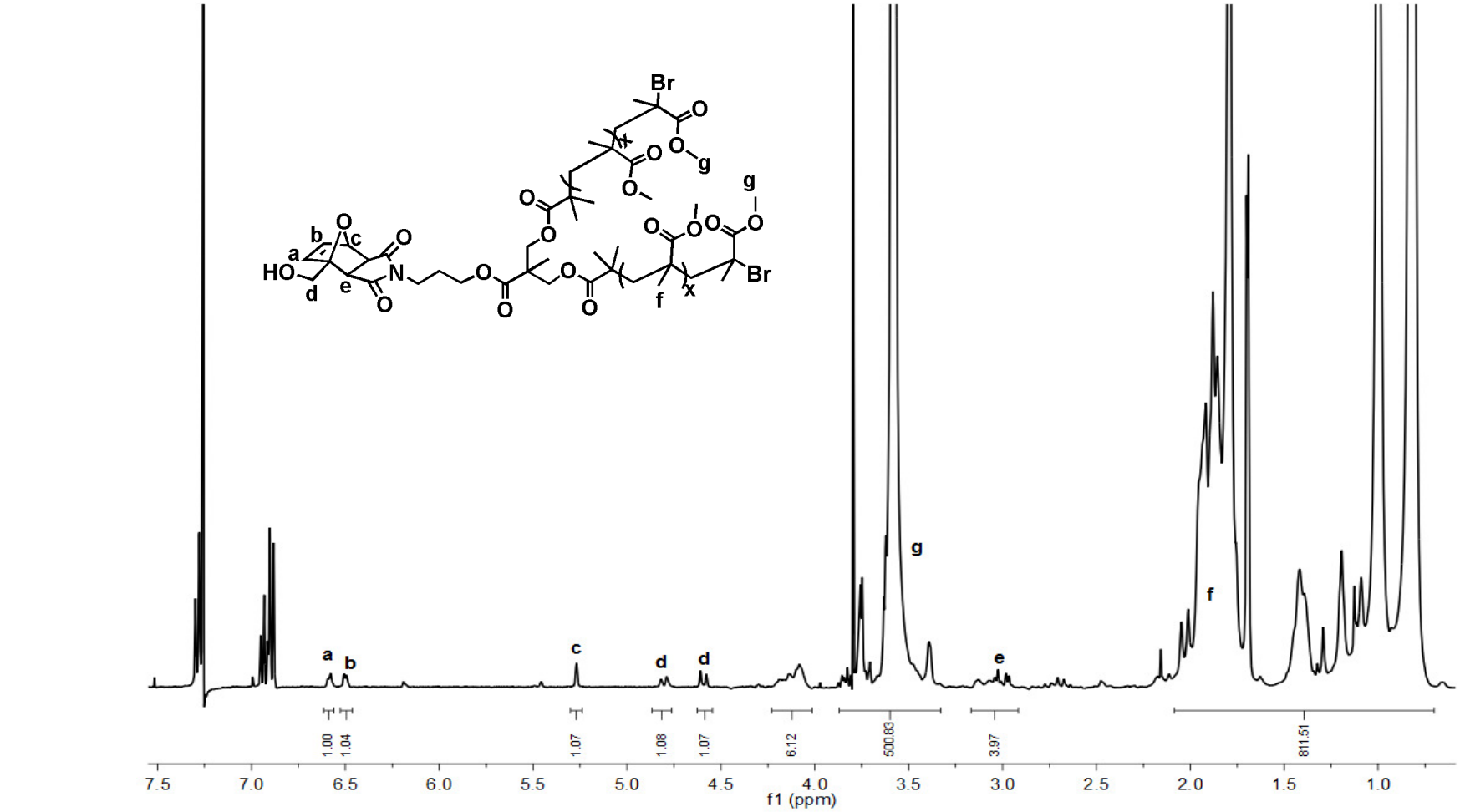

Figure A.30. ^{1}H NMR spectrum of **1OH:2PMMA**

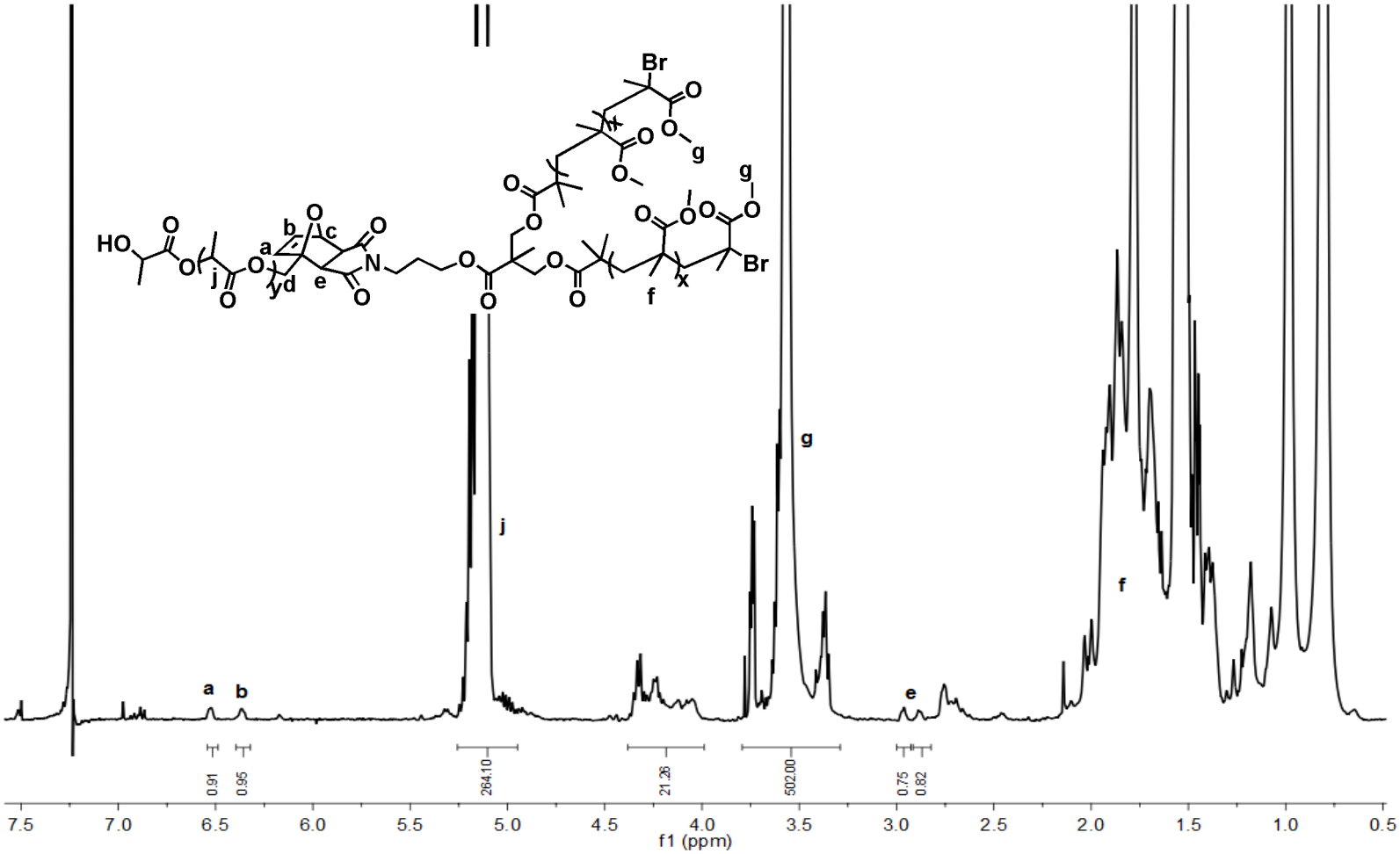

Figure A.31. ^{1}H NMR spectrum of **1PLA:2PMMA**

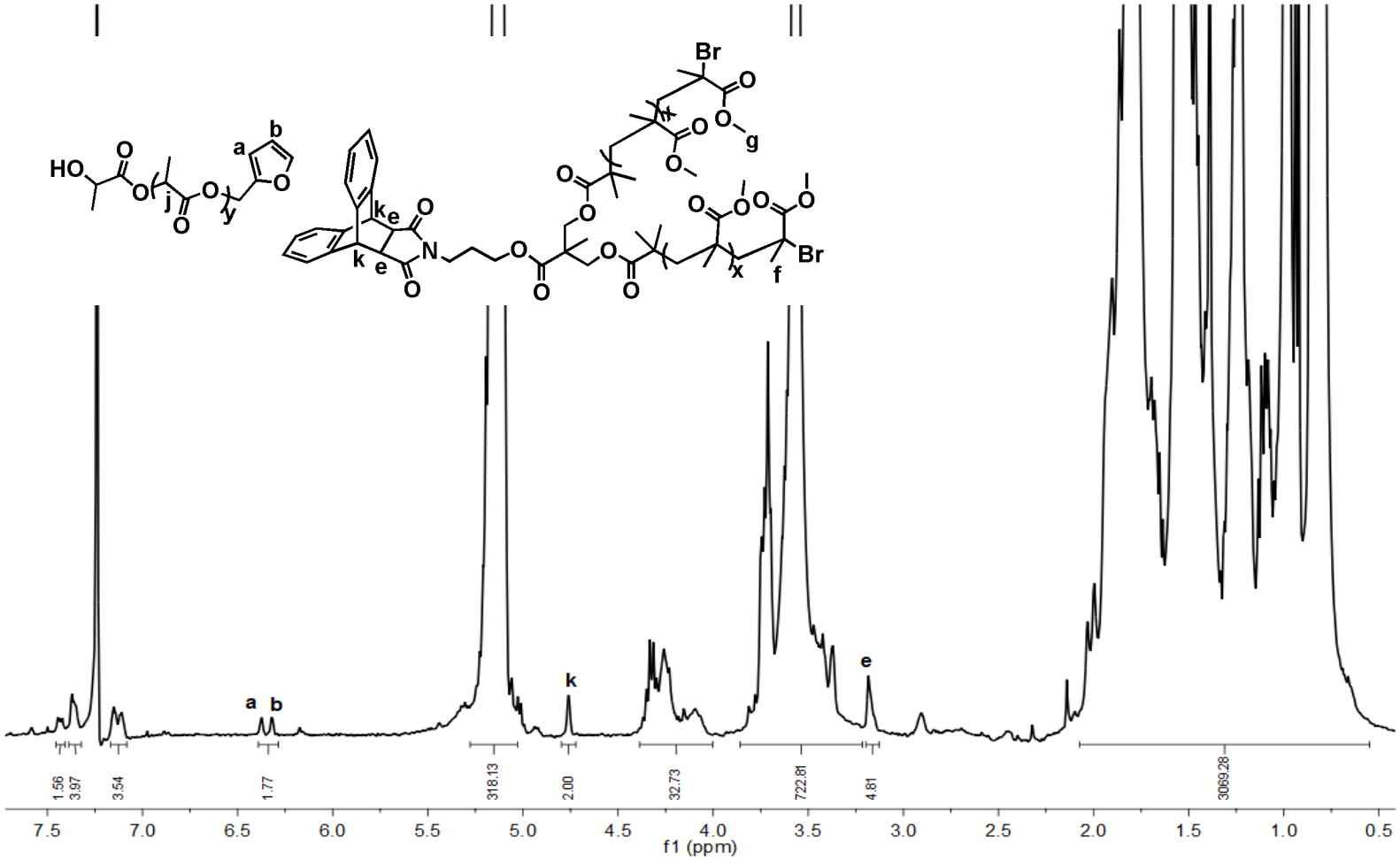

Figure A.32. ^{1}H NMR spectrum of **1PLA** and **2PMMA** mixture after rDA

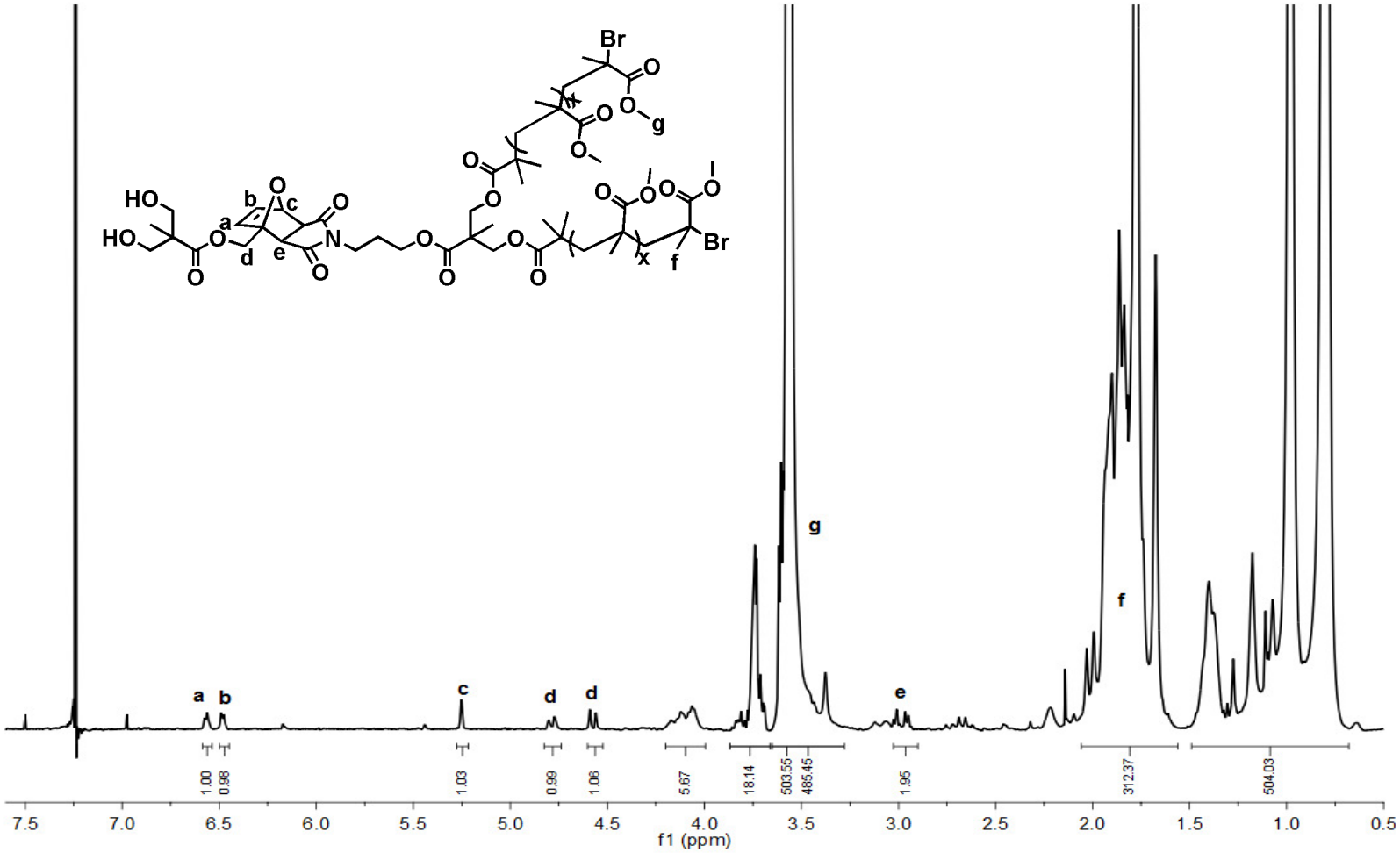

Figure A.33. ^{1}H NMR spectrum of **2OH:2PMMA**

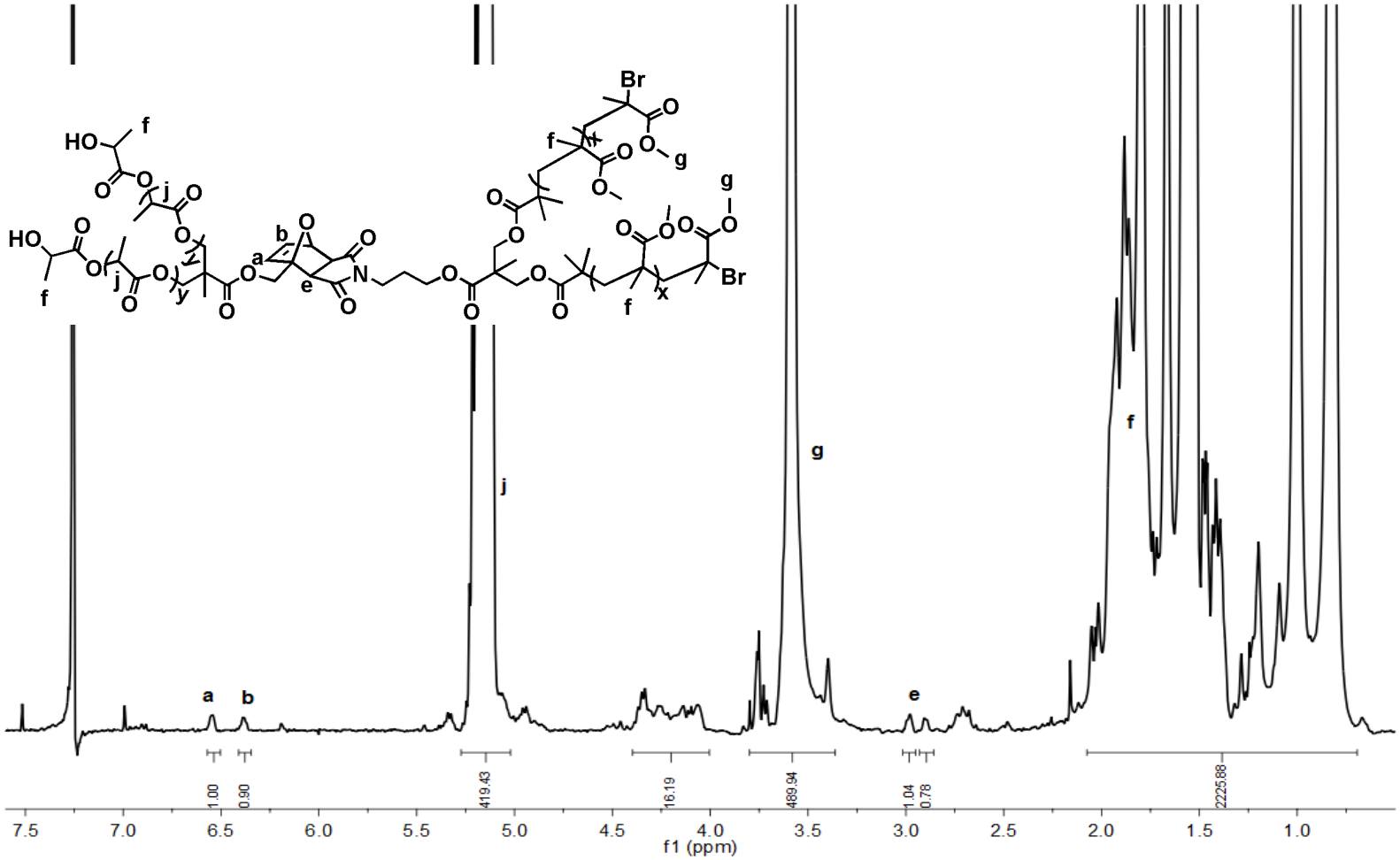

Figure A.34. ^{1}H NMR spectrum of **2PLA:2PMMA**

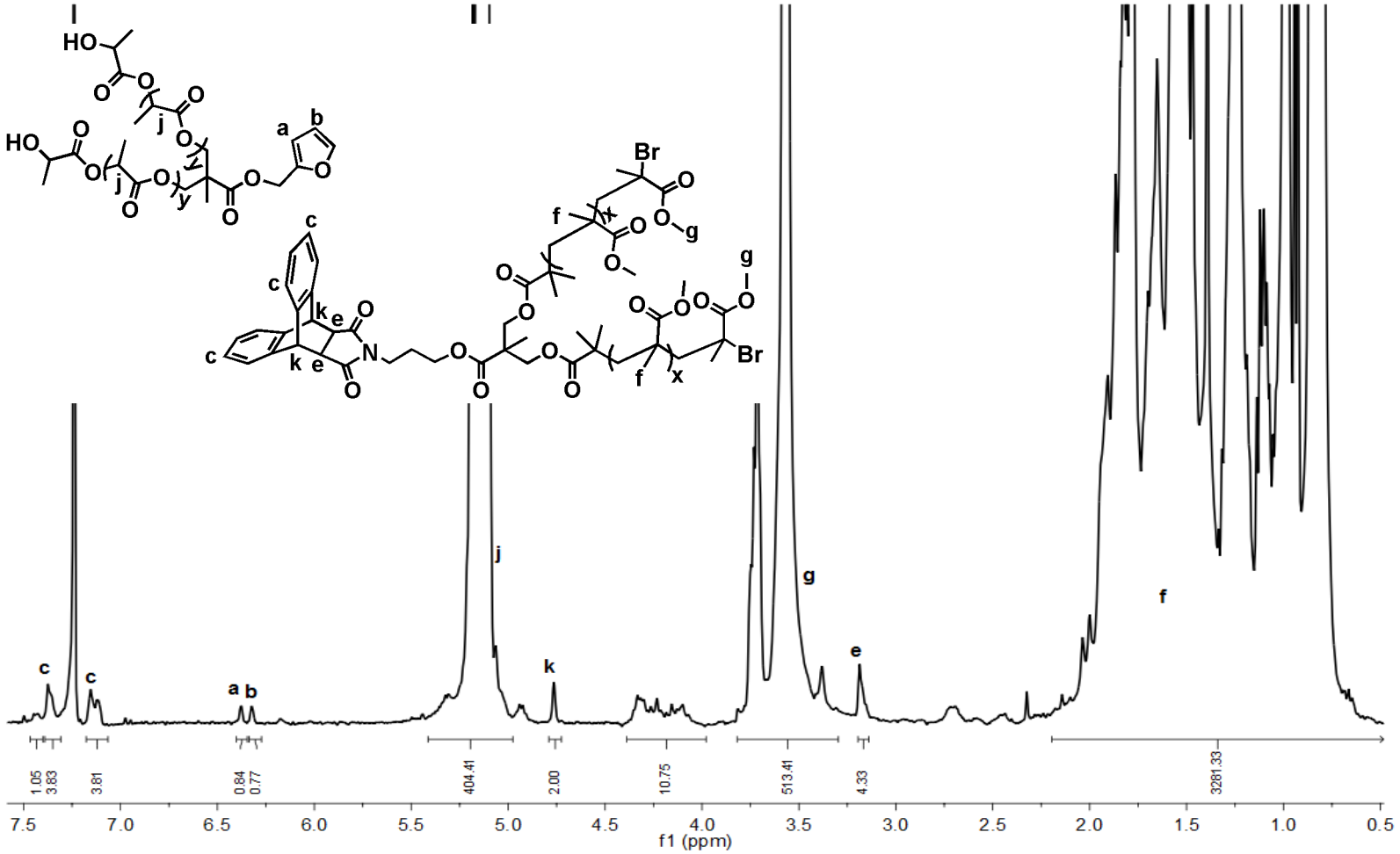

Figure A.35. ^{1}H NMR spectrum of **2PLA** and **2PMMA** mixture after rDA

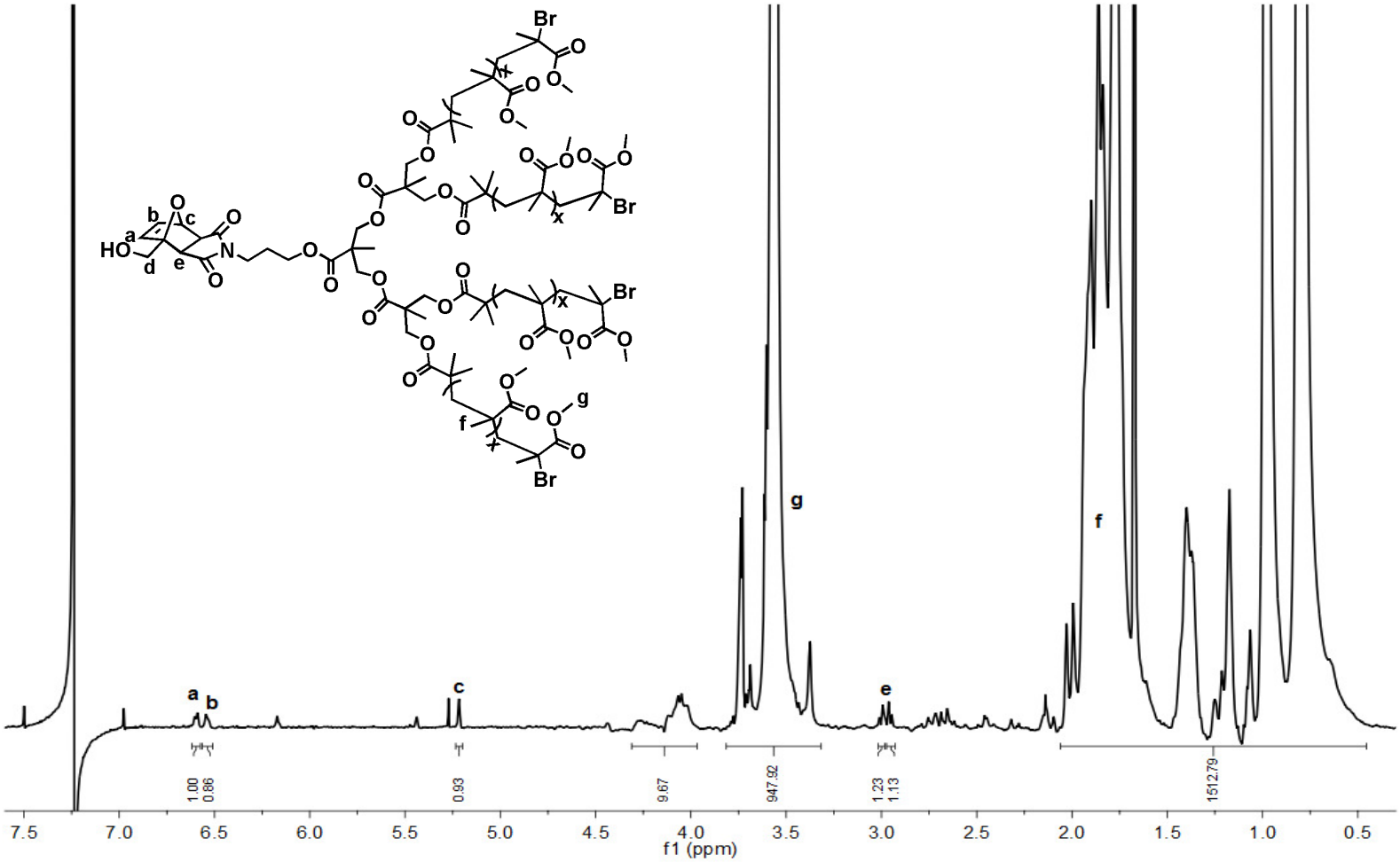

Figure A.36. ^{1}H NMR spectrum of **1OH:4PMMA**

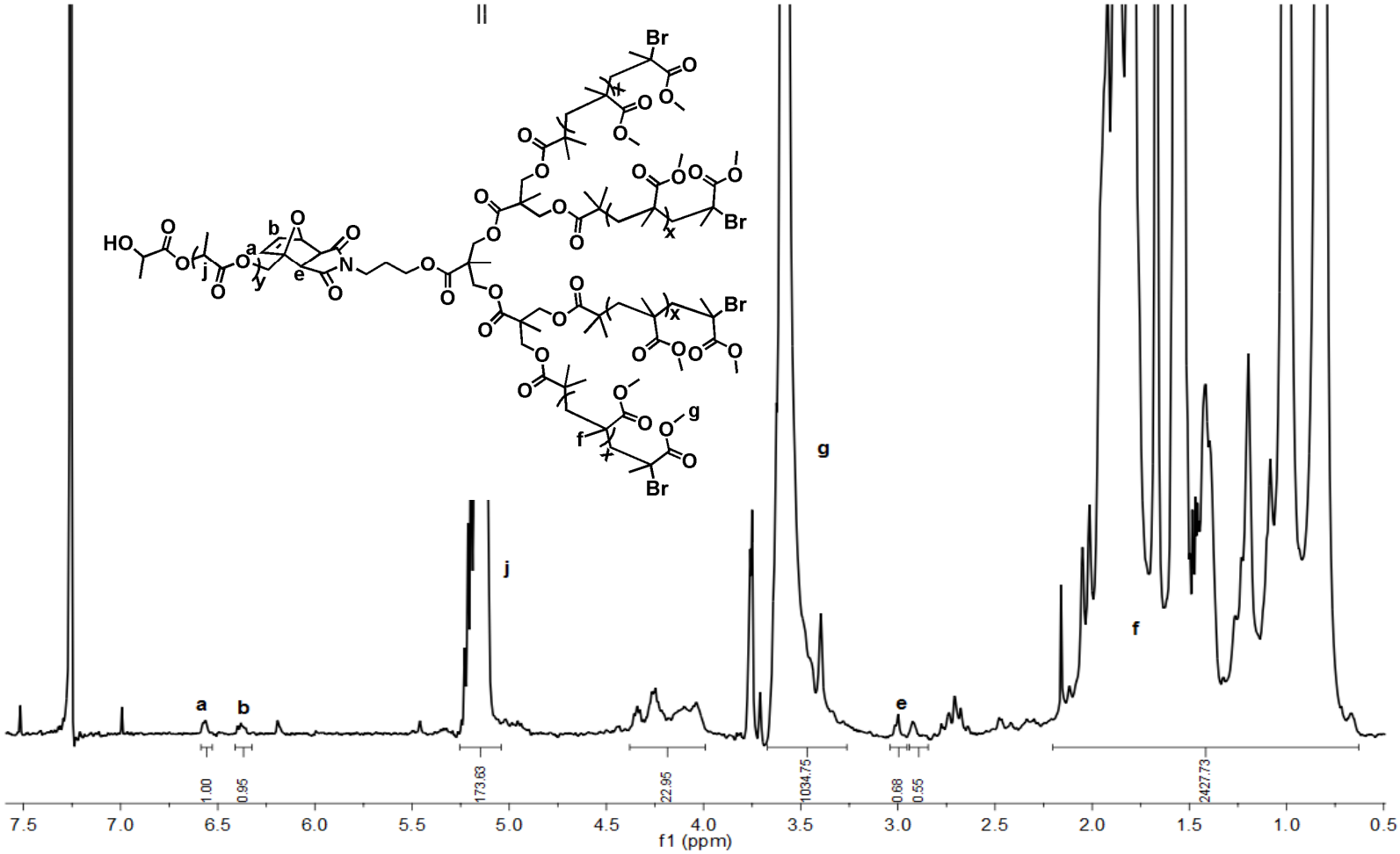

Figure A.37. ^{1}H NMR spectrum of **1PLA:4PMMA**

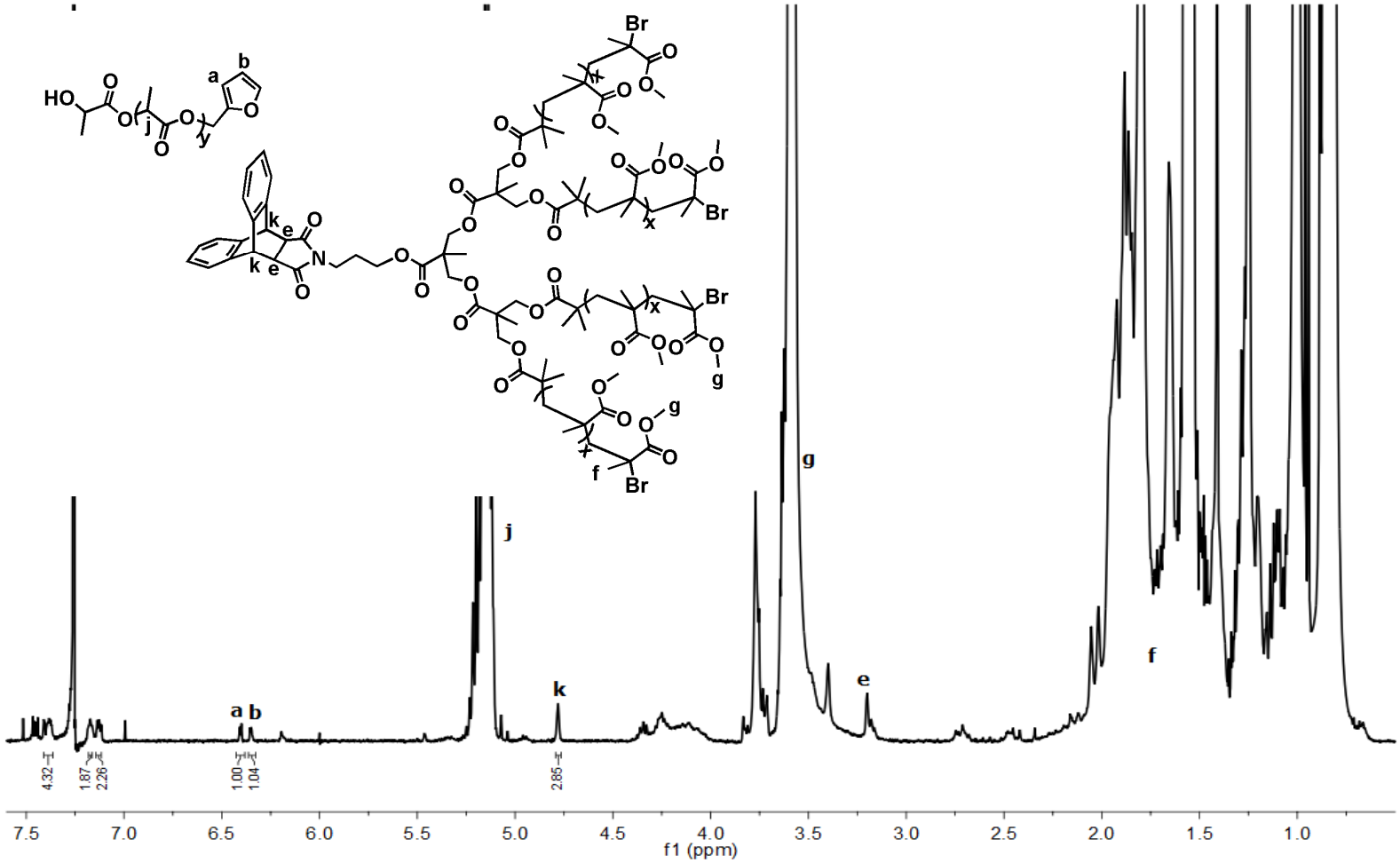

Figure A.38. ^{1}H NMR spectrum of **1PLA** and **4PMMA** mixture after rDA

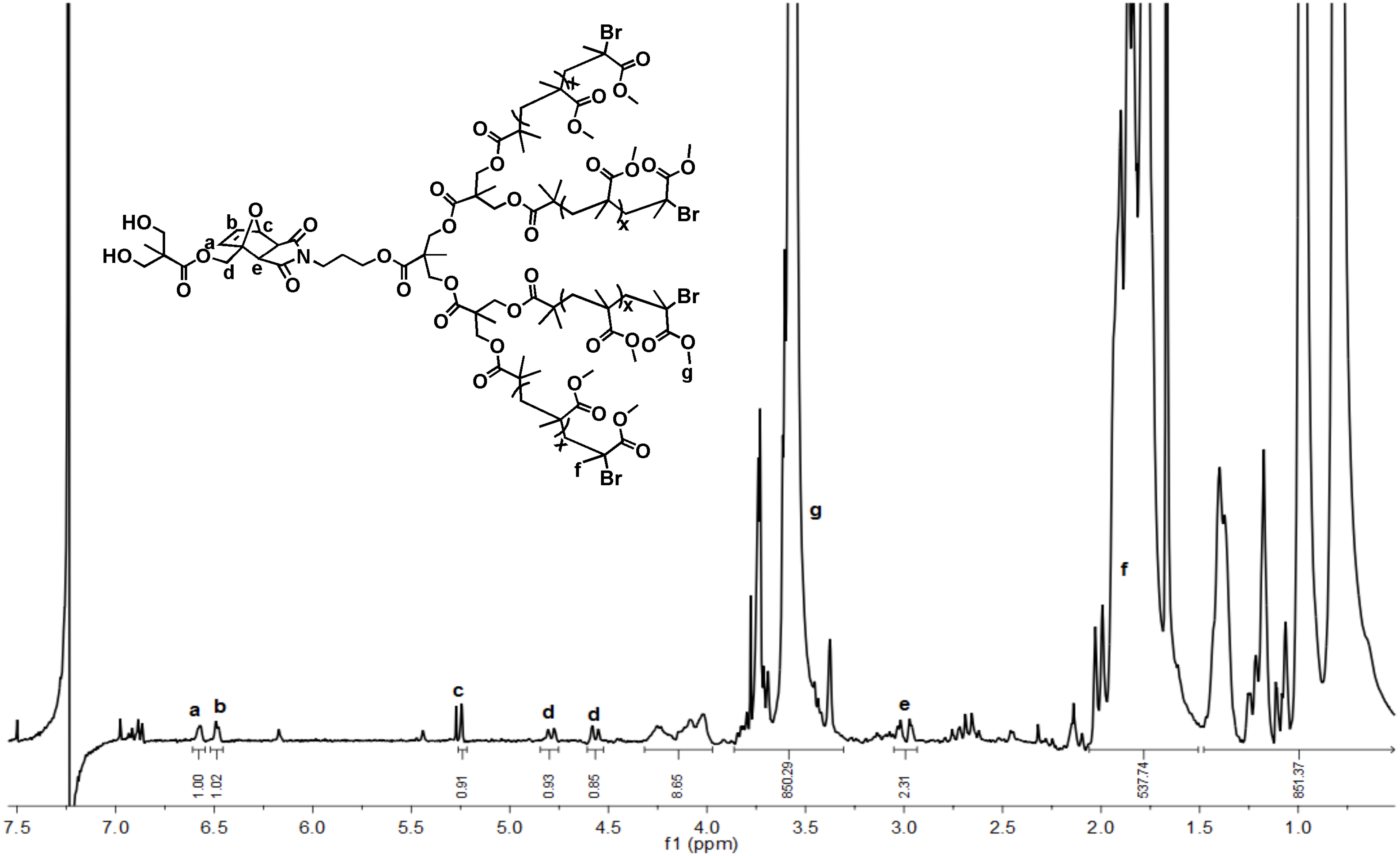

Figure A.39. [1]H NMR spectrum of **2OH:4PMMA**

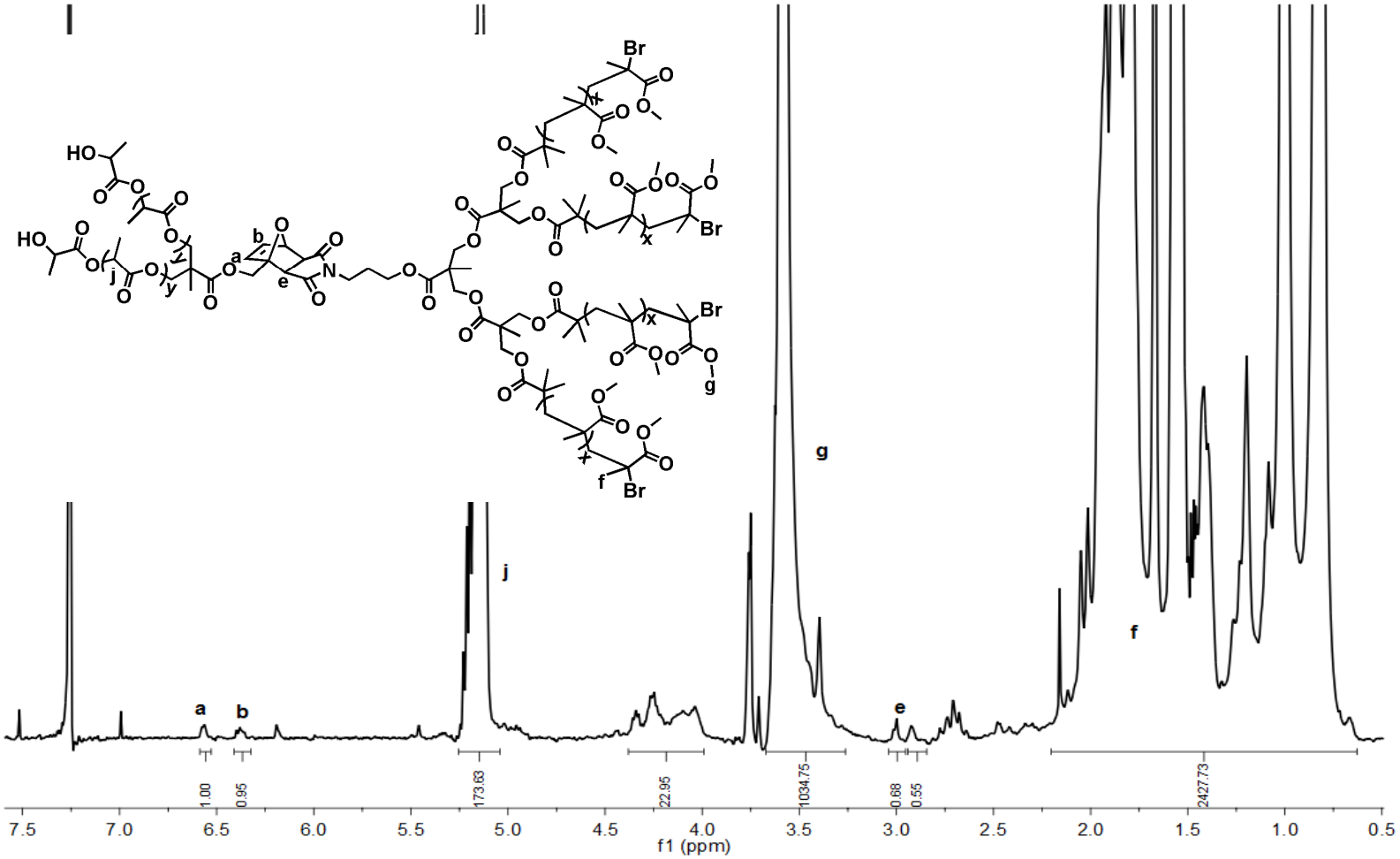

Figure A.40. ^{1}H NMR spectrum of **2PLA:4PMMA**

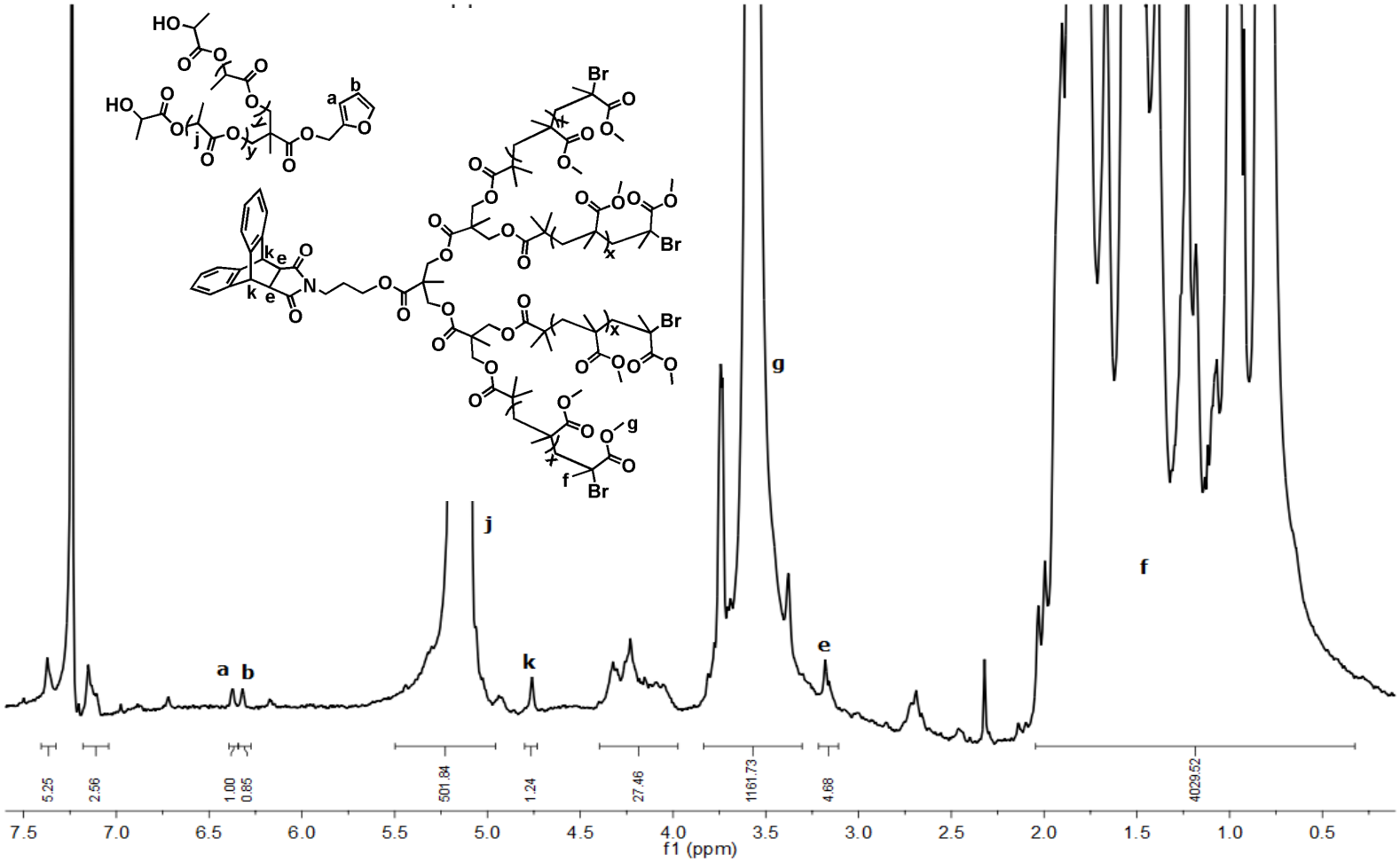

Figure A.41. ^{1}H NMR spectrum of **2PLA** and **4PMMA** mixture after rDA

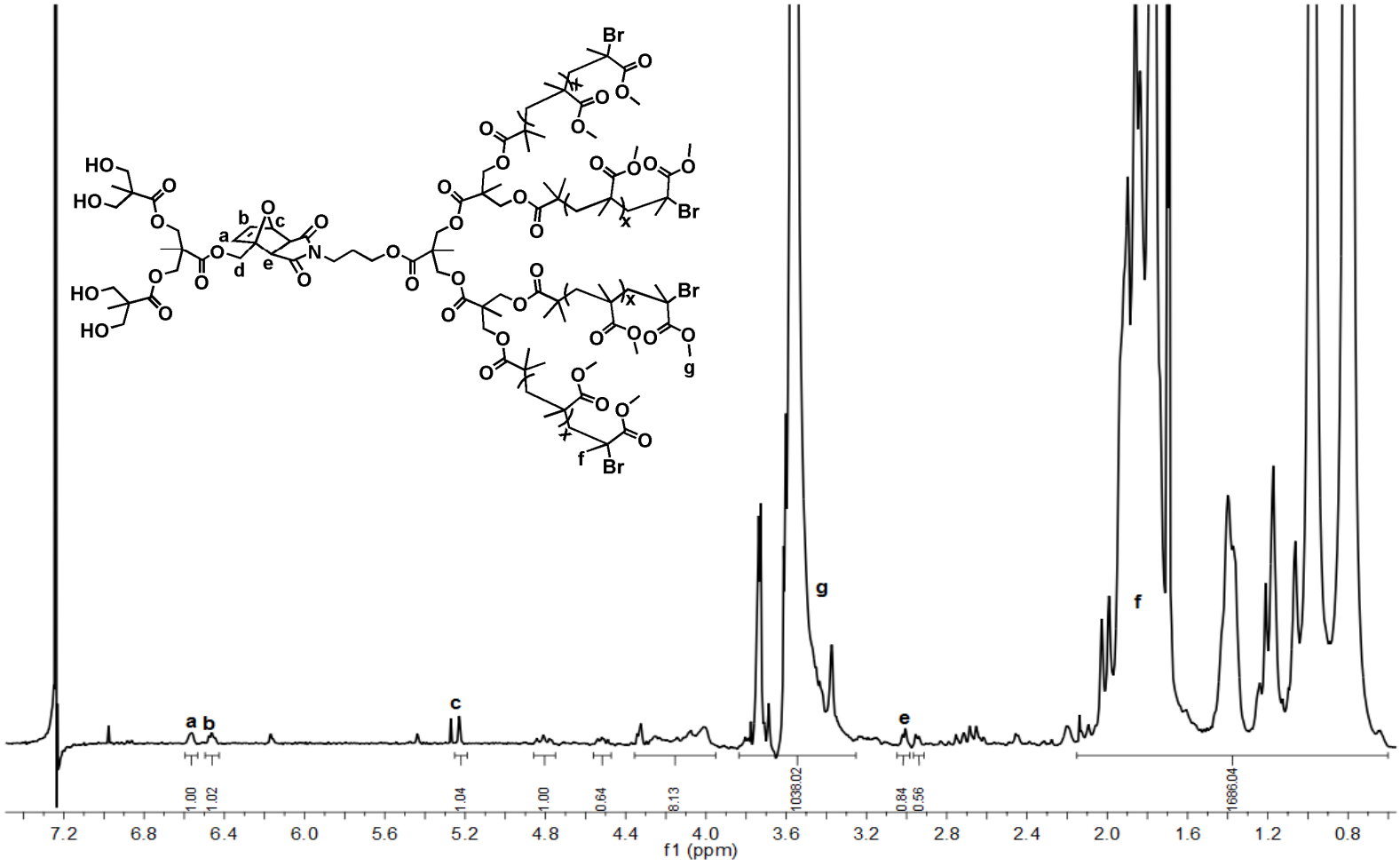

Figure A.42. ^{1}H NMR spectrum of **4OH:4PMMA**

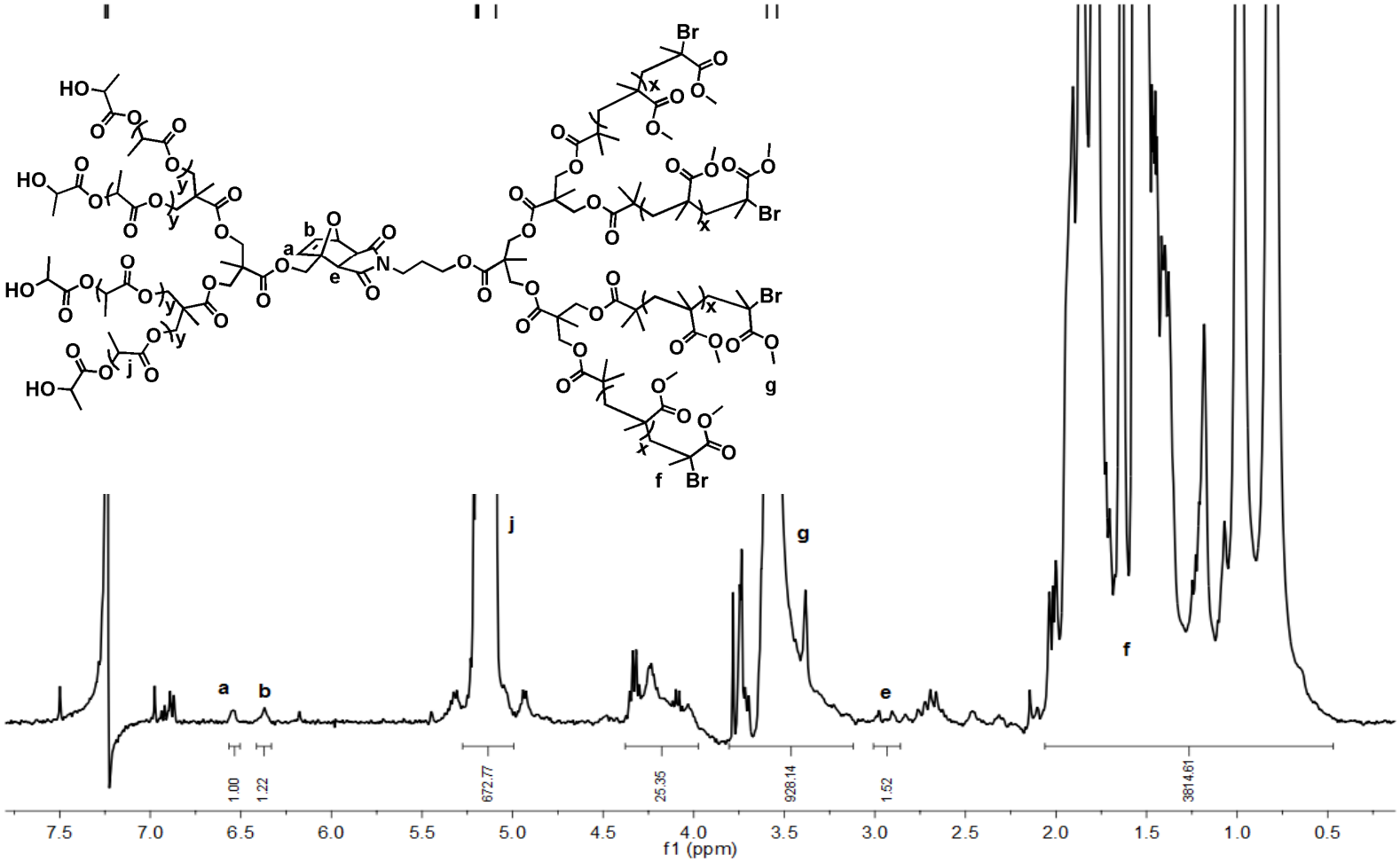

Figure A.43. ^{1}H NMR spectrum of **4PLA:4PMMA**

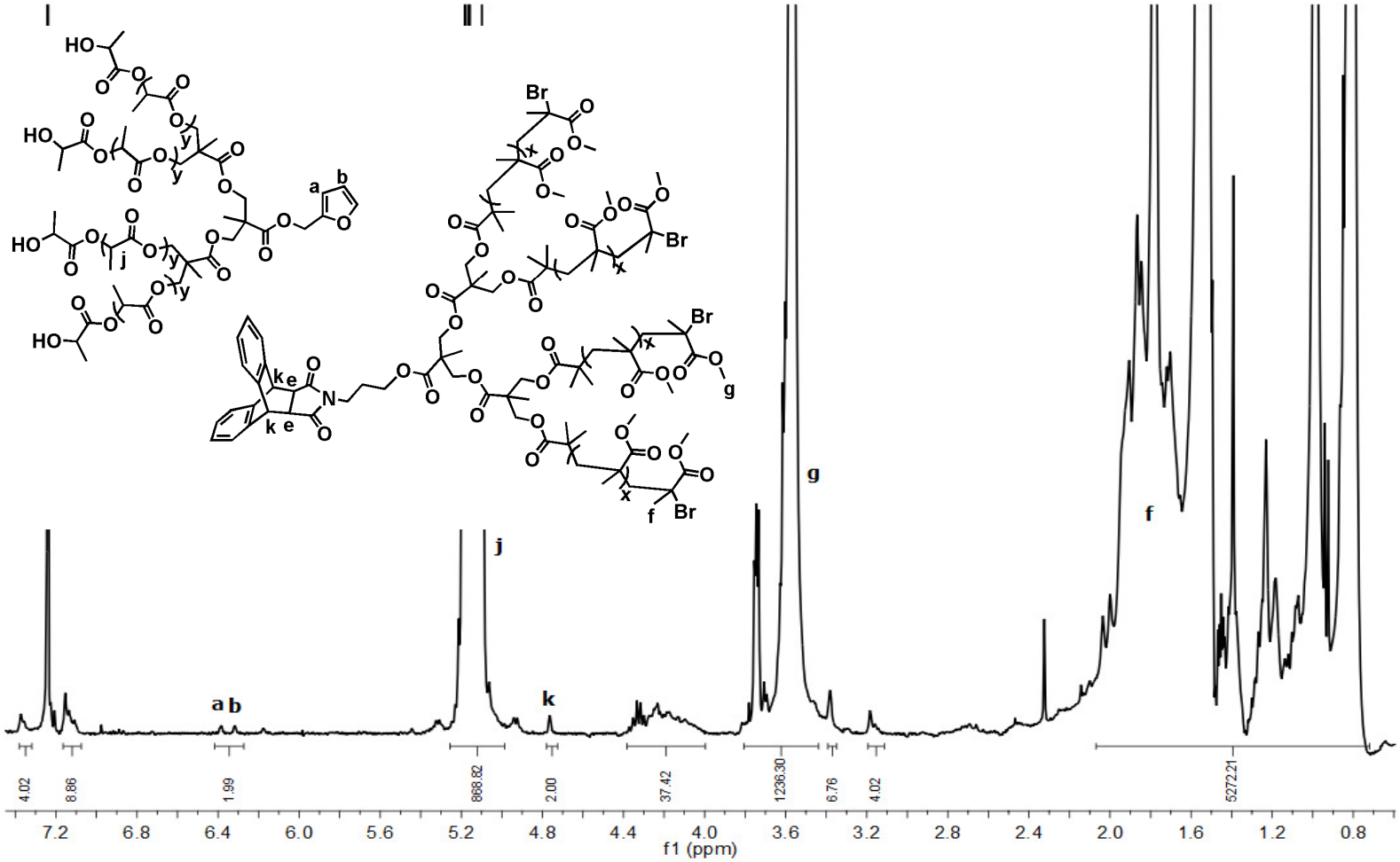

Figure A.44. ^{1}H NMR spectrum of **4PLA** and **4PMMA** mixture after rDA

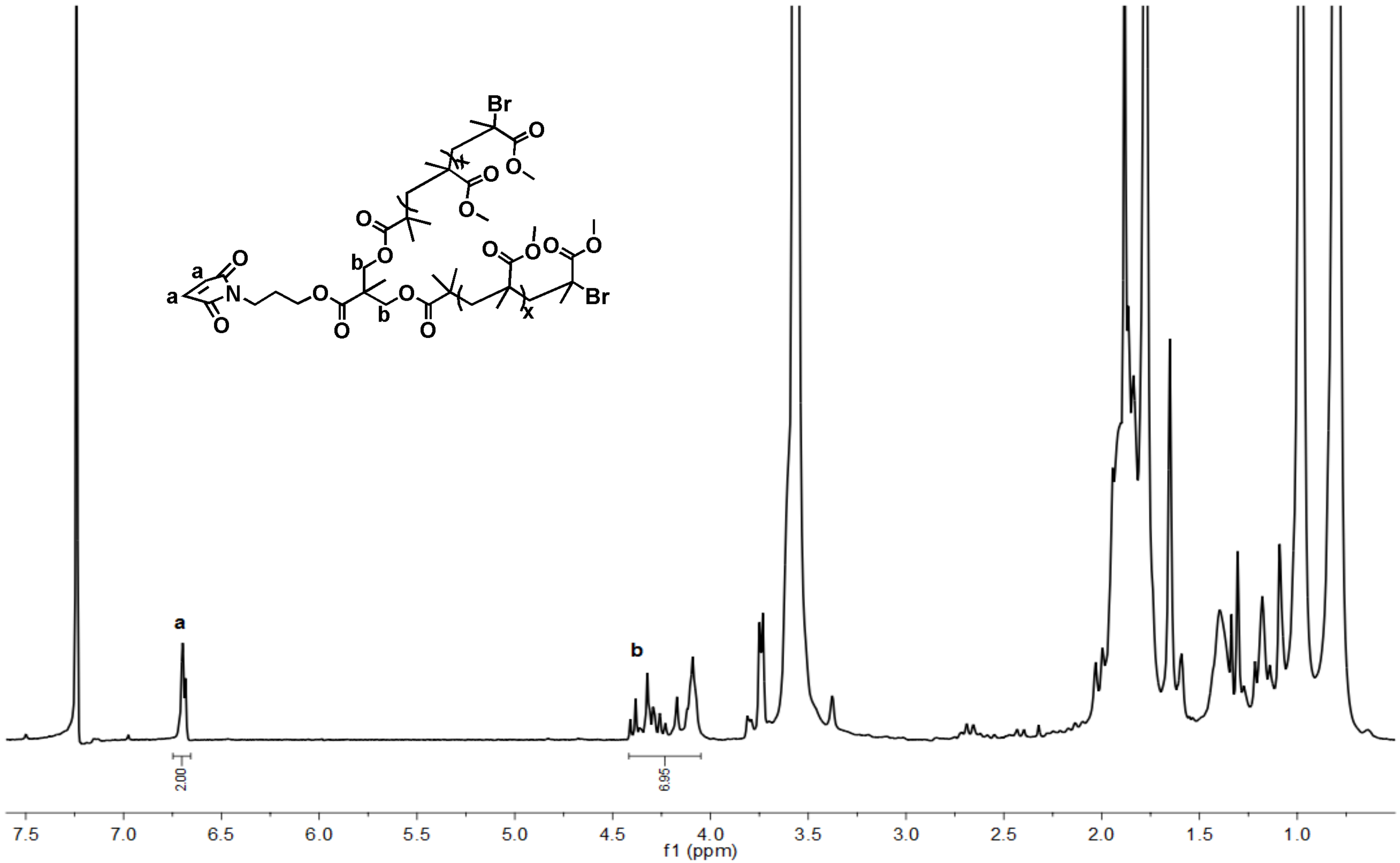

Figure A.45. [1]H NMR spectrum of **P6**

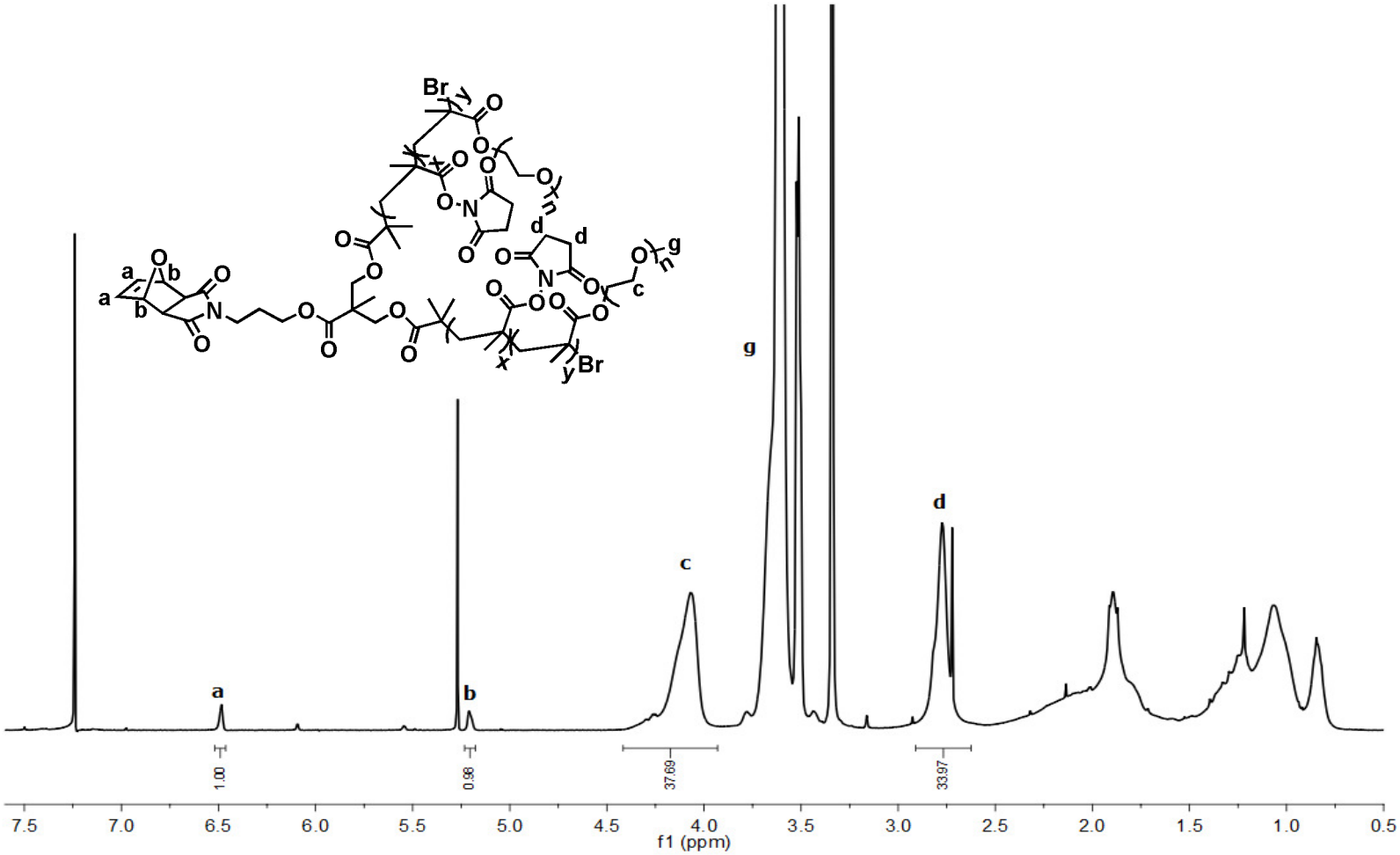

Figure A.46. ^{1}H NMR spectrum of **P11**

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