Novel Approaches To The Synthesis of Clicked Block Copolymers

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ABSTRACT

Block copolymers are widely used in both the academic and industrial communities due to their unique properties. With the development of living polymerization techniques, the synthesis of block copolymers with controlled molecular weights and unique architectures has reached an all time high. Here a novel approach to the synthesis of block copolymers, namely polystyrene-*b*-polyisoprene, using azide-alkyne click chemistry techniques is investigated. Both azido and alkyne-terminated polystyrene were synthesized using ATRP. Azido-terminated polystyrene was synthesized via a substitution reaction between NaN_3 and bromo-terminated polystyrene. Alkyne-functionalized polystyrene was synthesized using propargyl 2-bromoisobutyrate as a functional initiator. ^{1}H NMR and SEC were used to analyze the degree of polymer functionalization. Anionic polymerization techniques were used to synthesize polyisoprene. Polyisoprenyl lithium was reacted with propylene oxide to obtain hydroxyl-terminated polyisoprene. Functionalization of ≥ 90% was demonstrated via flash column chromatography. The aforementioned hydroxyl-terminated polyisoprene was reacted with both 11-chloroundecanoyl bromide and 11-chloroundecanoyl chloride to synthesize halogen-terminated polyisoprene. As with polystyrene, a substitution reaction with NaN_3 afforded azido-terminated polyisoprene. Alkyne-functionalized polystyrene was coupled with azido-terminated polyisoprene via click chemistry to create said block copolymers. The reactions were investigated using ^{1}H and ^{13}C NMR, SEC, IR and in some cases TEM. The clicked block copolymers should provide precedent for the synthesis of supramolecular block copolymers.

Dedicated to my family for their support and encouragement. None of this would have been possible without you.

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I Introduction

Over the years polymers have boomed into one of the most industrial relevant chemical discoveries. In fact you are almost certainly wearing at least a few polymers as you read this thesis. From the fibers in your clothes to the rubber in your shoes, polymers are everywhere. One of most important class of polymers are thermoplastic elastomers, which show the advantages typical of rubbery and plastic materials.

One of the most popular classes of thermoplastic elastomers is the styrenic block copolymers. A prime example of this is Kraton, which is a synthetic alternative to rubber. Kraton is a block copolymer consisting of polystyrene and polyisoprene or polybutadiene. It offers the same advantages as rubber but with increased resistance to heat and chemicals. Styrenic block copolymers are typically made using living anionic techniques in which the second monomer is added to the polymer anion of the first monomer. A novel approach to synthesizing styrene isoprene block copolymers by combining ATRP, anionic polymerization and click chemistry are herein discussed.

II Historical

II.1.0 Conventional Free Radical Polymerization

Free radical polymerizations are the most common type of addition polymerization. Free radical polymerizations are one of the most industrially successful polymerization routes for several reasons. First, free radical mechanisms are well established and easily applied to new monomers. Second, several widely available monomers are capable of undergoing free radical polymerization. Lastly, free radical polymerizations can take place in bulk or solution. Free radical polymerization occurs via four distinct steps (Scheme 1):

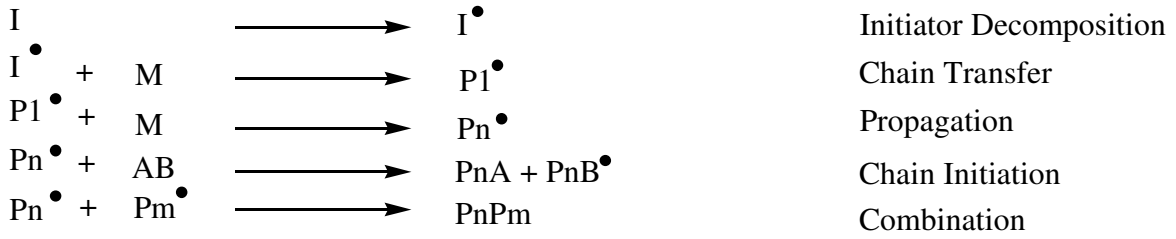
Initiation: In this first step a reactive center is formed. This typically occurs when an initiator decomposes to form a free radical. There are three types of free radical initiators: organic compounds that undergo hemolytic cleavage (peroxides, azo compounds), photosensitive molecules and redox-systems which transfer an electron during the reaction.

Propagation: Once the polymerization is initiated, monomer molecules are added to the active chain end. The reactive site is reformed after each addition of monomer.

Chain Transfer: Transfer occurs when the active center is transferred to an independent molecule such as solvent. This transfer results in a new radical site that is capable of propagation and a terminated molecule. (see termination step)

Termination: Termination typically occurs in two ways, combination and disproportionation. Combination occurs when two reactive sites couple, thus "killing" the propagating radical. Disproportionation is a type of atom transfer between active chains, typically involving hydrogen atoms.

Scheme 1: Free radical polymerization mechanism (I represents initiator species, M denotes monomer, P_n represents propagating radical chain and AB is a chain transfer agent.)



In a free radical polymerization chain initiation is not 100 %. This is due to inefficient synthesis of the radical species and side reactions. An efficiency factor (*f*) describes the effective radical concentration and typically varies from 0.3 to 0.8. As a result of inefficient chain initiatior, molecular weights are difficult to control and molecular weight distributions can be quite broad. Thankfully, new methods of radical polymerization named living radical polymerizations have been developed. Living radical polymerizations will be discussed later in this thesis.

II.1.1 Living Polymerizations

The term "living" designates the absence of chain termination or chain transfer. [1,2] However, since we are dealing with a radical process, some level of termination is inevitable. Therefore the term "living" is not strictly true and care should be used when addressing polymers as "living". Nevertheless, the scientific community has accepted the term "living polymerizations" with the assumption that some form of termination exists. Consequently the term "living" will be freely used in this thesis. Living polymerizations are defined by linear chain growth with time thus leading to controlled molecular weights and molecular weight distributions. Living polymers retain their active centers after complete polymerization, thereby allowing a new batch of monomer to be subsequently added to the existing chains. [3] Living polymerizations can be used to synthesize well-defined polymers with high degrees of compositional homogeneity. As such, living polymerizations provide an ideal method for synthesizing block copolymers.

Living polymerizations were first demonstrated by Michael Szwarc in 1956 with the anionic polymerization of styrene with an alkali metal in THF.[4] Over the years several new methods of living polymerizations were developed, including cationic polymerizations, stable free radical mediated polymerization (SFRP), reversible addition-fragmentation chain transfer polymerization (RAFT), and atom transfer radical polymerization (ATRP).

Being among the first discovered living polymerization techniques, anionic polymerization has been extensively studied. In the absence of impurities the carbanion will still be present at the chain end after complete consumption of monomer. Termination by coupling does not occur due to unfavorable electrostatic interactions between the two identical charges. The active carbanion is capable of adding another monomer or being converted to various end-group functionalities.

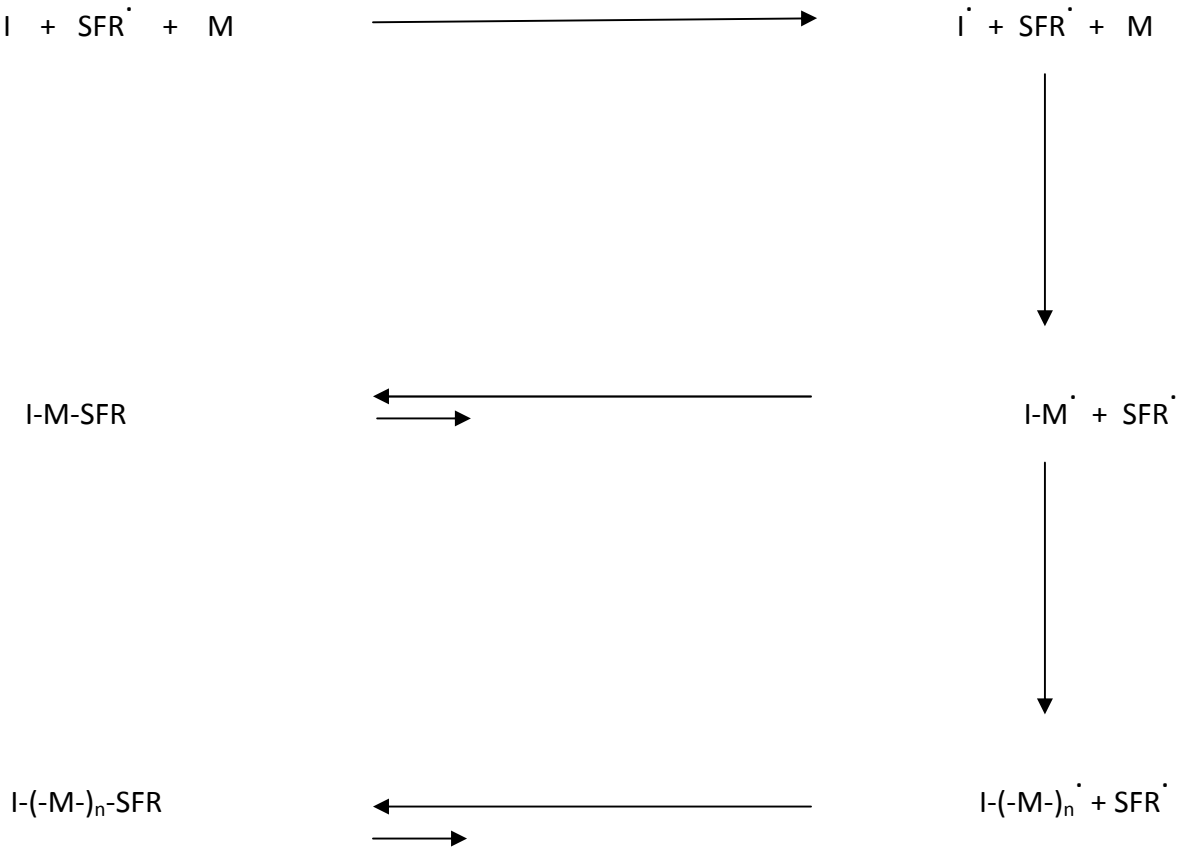
One of the major problems in anionic polymerizations lies in the experimental difficulty of polymerization. Carbanions are very reactive; as such the system must be void of moisture, oxygen or any other potential impurities. Furthermore, most anionic polymerization mechanisms have not been fully studied. Consequently, there is no general polymerization mechanism on which to base experiments. [5] As a result, the initiating mechanism must be determined in advance to ensure a successful polymerization. Due to the experimental difficulty involved, anionic polymerization methods are not typically used industrially.

Living polymerizations were first attempted with free radical systems in 1982 by Otsu et al. by the use of "iniferters", initiator-transfer-agent-terminators. [6] These initiators act as both primary radicals for polymerization as well as radical chain terminators. The ability to keep the radical concentration low allowed for the linear increase of molar mass with time and converstion. However, these systems displayed significant loss of active end groups on the

growing polymers. [7] As such these systems showed relatively large polydispersities (M_w/M_n) and large amounts of homopolymers being formed in attempted block copolymerizations.

Stable free radical polymerizations (SFRP), often referred to as nitroxide mediated polymerizations (NMP), were discovered in 1994 by Georges et al. [8] SFRP was discovered in the investigation of a free radical polymerization using a radical scavenger called TEMPO. When a stable free radical such as TEMPO couples with a polymer radical reversibly, the radical concentration can be limited to low concentrations. Maintaining a low concentration of radicals is the key equilibrium step in SFRP which allows for controlled polymerizations, because termination is minimized. The general SFRP mechanism can be seen in Scheme 2.

Scheme 2: SFRP mechanism (I (initiator), SFR (stable free radical), M (monomer)



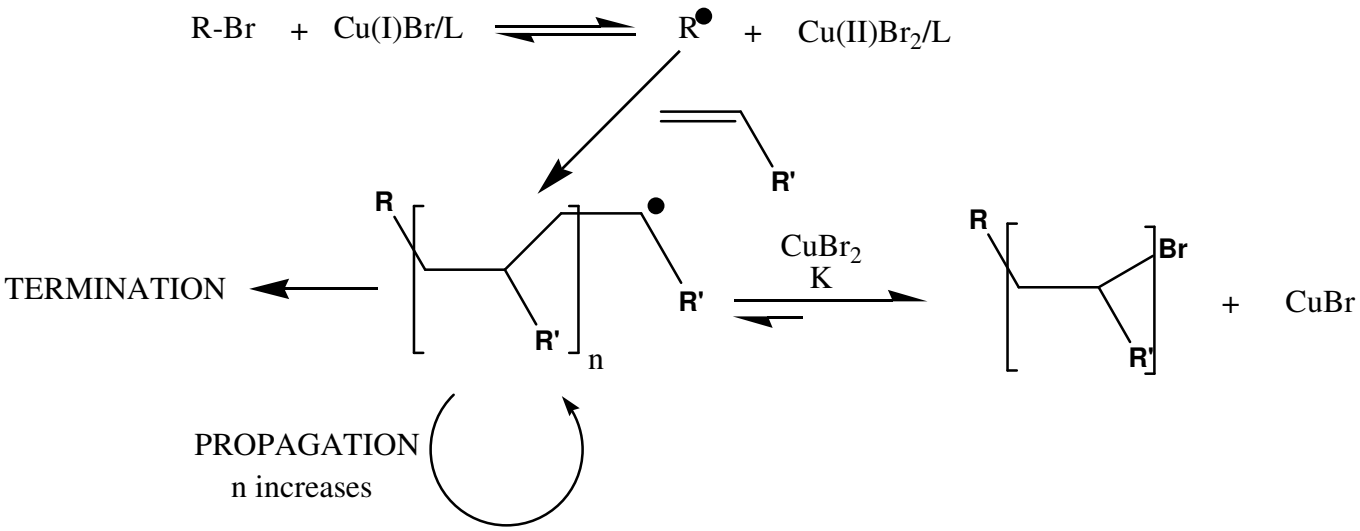
SFRP began as a very limited technique for controlled polymerizations. SFRP was limited to an extremely small range of monomers such as styrene and styrene derivatives. Polymerization of acrylates was only possible by copolymerization with styrene. [9] Over the years the development of novel nitroxides greatly enlarged the applications of SFRP. [10,11] As a result, controlled polymerizations of acrylates and acrylamides have been achieved. As early as

1997 Hawker and coworkers demonstrated the SFRP synthesis of polymer brushes following the "grafting to" approach. [12] In 1999 Hawker et al. used SFRP techniques to synthesize polymer brushes of styrene using the "grafting from" approach. [13]

A second approach to control radical polymerization resides in atom transfer radical polymerization (ATRP). ATRP was first reported by Matyjaszewski et al. in 1995. [14] ATRP involves forming a carbon-carbon bond through a transition metal catalyst. As the name implies the atom transfer step is the key step in the control of the polymer chain growth. The coordination complex reversibly abstracts a halide atom from the polymer chain end, thereby providing a reversible mechanism between a dormant and an active propagating species. By reversibly abstracting a halide atom from the chain end, the radical concentration is maintained at a low level. Akin to SFRP, the low radical concentration allows for controlled polymerizations, because of the minimizing of side reactions and termination.

ATRP is one of the most attractive living polymerization techniques for the synthesis of controlled polymers with chain-end functionality. [15] ATRP polymers contain a terminal halogen due to the alkyl halide initiator. This halogen end-group allows for further transformations through traditional organic chemistry procedures. A general mechanism can be seen in Scheme 3.

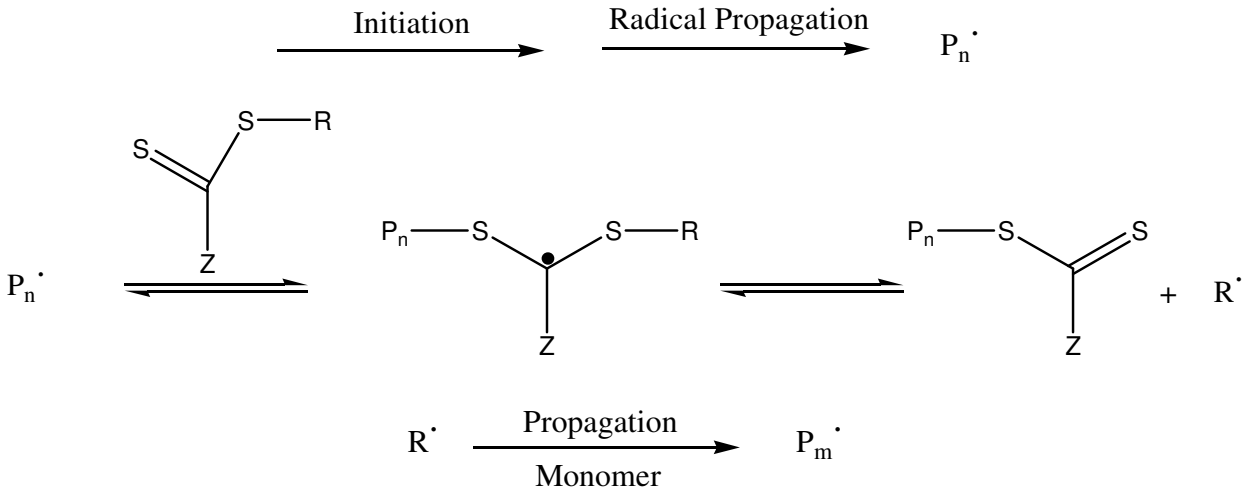
Scheme 3: ATRP mechanism (L = ligand)



One of the most recent developments in living free radical polymerization was reported by Thang et al. and Haddleton et al. [16,17] Reversible addition-fragmentation chain transfer polymerization (RAFT) is performed by a free radical polymerization in the presence of a RAFT agent (a dithio compound). The RAFT agent mediates the polymerization via a reversible chain-transfer process. As with other living techniques, RAFT operates by a rapid switching

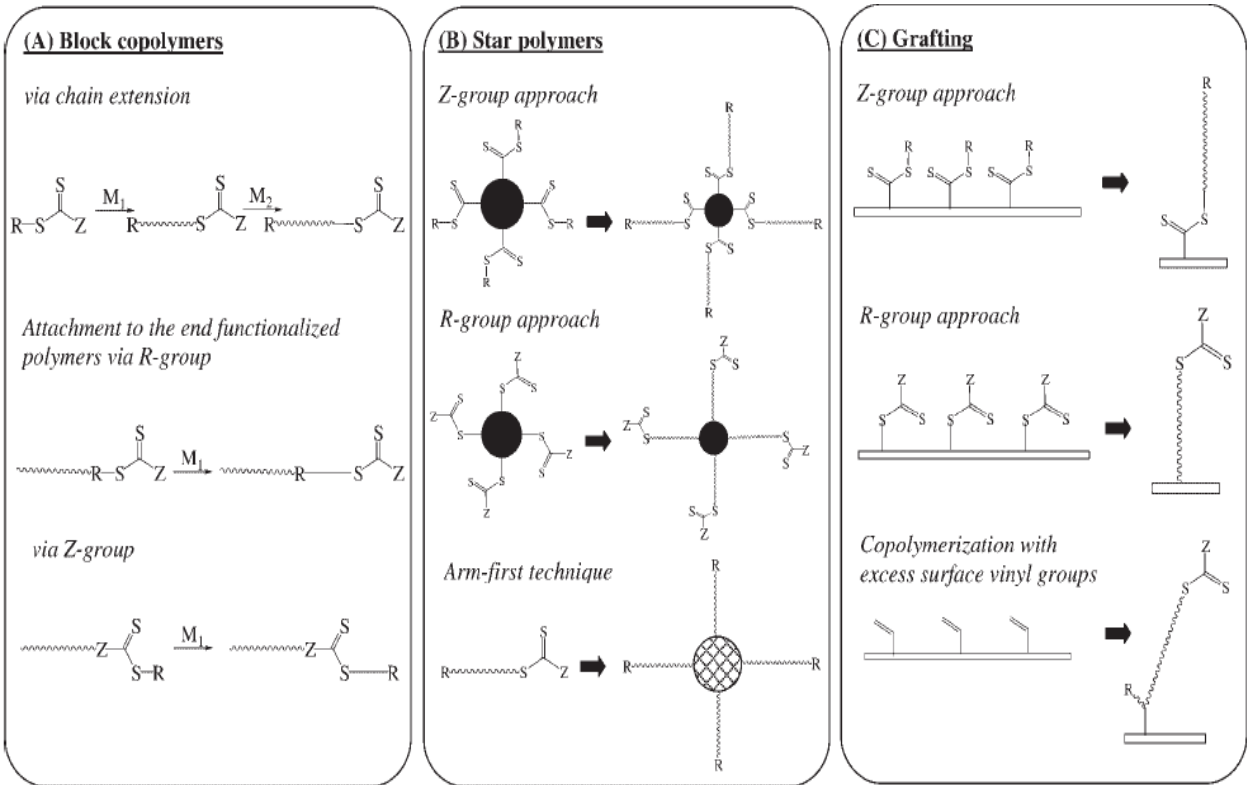
mechanism between dormant and active chain ends. The propagating chain adds to the C=S bond creating a stabilized radical intermediate. The stable radical intermediate does not undergo termination, but rather reforms a C=S bond, causing fragmentation of a radical. The fragmented radical is capable of initiation or propagation with monomer (Scheme 4).[18]

Scheme 4: RAFT mechanism



RAFT technology has the benefits of readily synthesizing polymers with narrow molecular weight distributions and predetermined molecular weights, while covering a large range of monomers. Monomers with reactive terminal groups can be easily manipulated with complex architectures. [19] Furthermore, RAFT can be used in solution, emulsion and suspension polymerizations. [20] Lastly, RAFT polymerizations also have the unique attributes of various modes of attaching the RAFT group to the functional moiety. The nature of the RAFT agent allows for two distinct approaches to the synthesis of complex architectures commonly referred to as the R and Z approaches (Scheme 5). [21] The Z and R approaches occur on preformed polymers. In the Z group approach, the RAFT agent stays bound to the scaffold surface via its stabilizing Z group. Consequently, the core will not contain any propagating radical functions. In other words propagation occurs only in the solution surrounding the core. Because the RAFT agent is permanently attached to the surface, this approach resembles a "grafting to" approach. However, in the R-group approach the RAFT agent leaves the core structure, leaving the core to become a radical species. Therefore, the core itself can undergo reactions leading to macromolecular formations. The R group approach is similar to grafting to a "grafting from" approach.

Scheme 5: General synthetic approaches for the synthesis of complex architectures. A.)Block copolymers performed by conventional chain extension; B) Star polymers by Z or R-group approaches; C) Surface grafting by Z or R-group approaches.



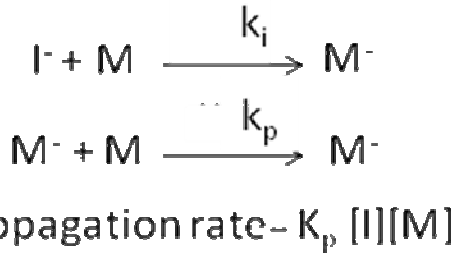
Each of the aforementioned techniques provides the opportunity to synthesize a large range of polymers. ATRP in particular has received massive recent interest in a wide range of applications. All of the living radical techniques provide suitable methods for the synthesis of block copolymers. Block copolymers can simply be prepared by addition of a second monomer to the reaction after complete consumption of the original monomer. Block copolymers may also be prepared by using the obtained macromolecule as a macroinitiator.

II.1.2 Living Anionic Polymerization

The discovery of living anionic polymerization in 1956 my Szwarc et al was one of the major discoveries in the field of polymer science. Szwarc performed detailed investigations into electron transfer between the anion of naphthalene and styrene in an aprotic solvent. Through these investigations, Szwarc was able to establish that the electron transfer formed a dianion which very quickly added to styrene, forming a living polymer. Szwarc began to investigate the mechanism of the polymerization and was able to determine the thermodynamics and kinetics of the polymerization in great depth. Szwarc also investigated structural properties of many different radical ions.[4] The aforementioned work had a profound effect on the future of polymer synthesis as the living polymers provided unprecedented control over architecture, molecular weight and polydispersity.

The general reaction mechanism for living anionic polymerization can be seen in Scheme 6. Since termination is absent in living polymerizations the rate of propagation is equal to the rate of polymerization and the concentration of the propagating species is equal to the concentration of the initiator. In order to study the kinetics of anionic polymerization, five techniques are generally used: stop-flow, capillary flow, sampling, dilatometry and near-infrared (NIR) spectroscopy. Of the aforementioned techniques, NIR is the only technique that allows for real time analysis without the use of designated systems while still avoiding the difficult and monotonous nature involved with the other techniques.[22] Although a NIR probe must be present in the reaction flask, Long et al. were able to investigate the kinetics of styrene and isoprene while maintaining the "living" nature of the polymers.[23] More recent work has demonstrated the ability to study isobutylene and styrene in the mid-infrared (MIR) region.[24,25]

Scheme 6: Living anionic polymerization reaction mechanism (I- = initiator, M = monomer, M- = propagating anion, k_i = initiation rate constant, k_p = propagation rate constant).



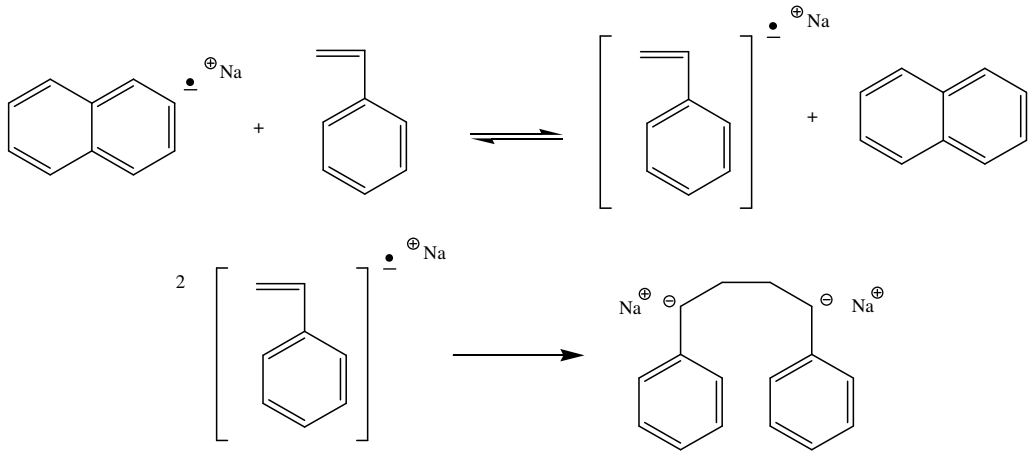
Anionic polymerization is applicable to both vinyl and cyclic monomers. For cyclic monomers the ring must be chosen such that it can open by reaction with nucleophiles. For vinyl monomers, a suitable reaction pathway must exist to allow the polymerization to proceed spontaneously. This typically implies that there must be substituents on the double bond that

can stabilize the negative charge that occurs in the transition state for the monomer addition. The aforementioned substituent must also not react with the anionic chain end. Therefore, strongly electrophilic groups and proton donating groups should not be used unless they are first protected.[26] Popular choices for the stabilizing group include ester, carbonyl, cyano, sulfone, nitro, aromatic rings and double bonds. It should be noted that very polar substituents such as carbonyl and nitro groups typically undergo side reactions and control over the polymerization may be lost. A general relationship between monomer reactivity and the stability of the anion formed can be determined from the pK_a value for the conjugate acid of the anion. As a result the monomers that form the most stable anions (lowest pK_a for conjugate acid) are the most reactive monomers in anionic polymerization. For less reactive monomers, more reactive initiators must be used. Typically, the initiator should have reactivity similar to the propagating anion.[5]

There are many different types of initiators that can be used for anionic polymerization. Some of the earliest reported initiators are the alkali metals. In 1911 Strange and Mathews reported the use of metallic sodium in the polymerization of isoprene.[27] The mechanism for alkali metal initiated polymerizations has been described by Szwarc and colleagues.[28] Szwarc described the process as heterogeneous, occurring on the surface of the metal. This heterogeneous initiation reaction continually generates new chain ends during propagation. As a result, there is little control over the molecular weight or molecular weight distribution. The microstructures of alkali metal initiated polyisoprene have all been studied. It is interesting to note that polyisoprene with a high degree of 1,4-microstructure can only be prepared using lithium as the counter ion.

Radical anions have also been used as initiators for anionic polymerization. Several aromatic hydrocarbons react with alkali metals in polar solvents to form radical anions. The naphthalene radical anion is perhaps the most studied radical anion initiator. Radical anions react with monomers through a reversible electron transfer to form the monomer radical anion (Scheme 7). This initiation is very efficient as the monomer radical anion undergoes dimerization very rapidly. With radical anions it is important to consider that they can only be formed in polar aprotic solvents such as THF.

Scheme 7: Sodium naphthalene initiation



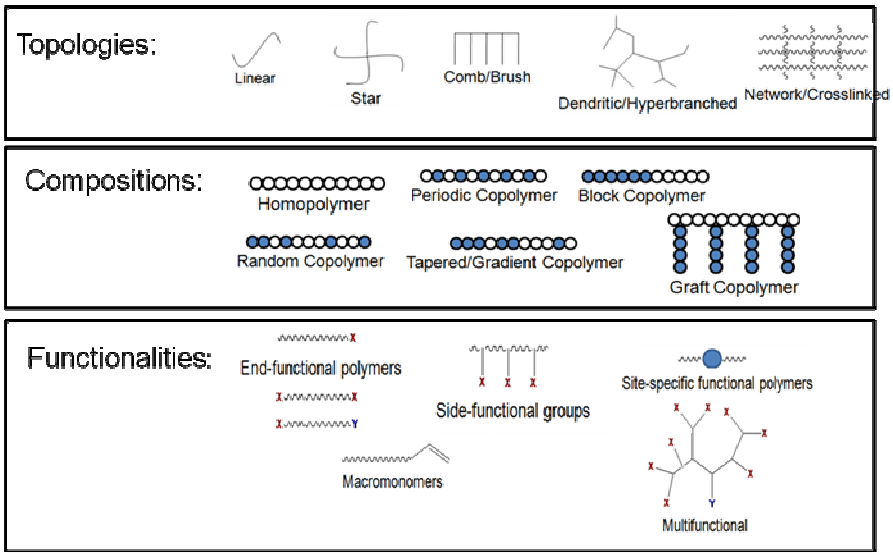
A third type of initiator for anionic polymerizations is the alkyllithium family. Alkyllithium compounds differ by their reactivity and degree of aggregation in solution. The reactivity of alkyllithium compounds as initiators is closely related to their average degree of association. The more associated alkyllithiums are less reactive initiators. Solvents that decrease the degree of association, such as aromatics, increase the initiation rate.[29] Alkyllithium initiators are typically used to polymerize dienes and styrenes. As previously mentioned, the lithium-based initiators produce polydienes with a high degree of 1,4-microstructure. *sec*-butyllithium and *n*-butyllithium are the two most commonly used alkyllithium initiators.[30]

It is possible to use both mono and di-functional initiators for anionic polymerization. Difunctional initiators are of special interest for the synthesis of advanced polymer structures such as telechelic polymers and macrocyclic polymers. Aromatic radical anions have been used as difunctional initiators.[31] However, the need for polar solvents with these initiators limits their synthetic value. Sanderson et al. report the synthesis of the hydrocarbon-soluble initiator 2,2-*bis*[3-(1-lithio-2,3-dimethylpentyl)-4-methoxyphenyl]propane. Using the aforementioned difunctional initiator, the authors were able to effectively polymerize 1,3-butadiene with predictable molecular weights and narrow molecular weight distributions.[32] Alkyllithium initiators containing functional groups have been used to synthesize end-functional polymers. Since the functional group is present on the initiator chain end, functional initiators allow for the preparation of star and block copolymers on the anionic chain end, while still maintaining the functional group on the initiating chain end.

II.1.3 ATRP

ATRP has become one of the most rapidly developed areas of chemistry since its discovery in 1995. There have been over 1000 publications relating to ATRP by Matyjaszewski and coworkers alone. One of the main reasons for the rapid development of ATRP is that one can readily synthesize controlled polymers with chain end functionality using this technique.[33] ATRP allows for the synthesis of many different polymer topologies, compositions and functionalities (Scheme 8).[34] As a result, many materials have already been synthesized using this technique.

Scheme 8: ATRP topologies, composition and functionalities



ATRP allows for many different approaches to polymer functionality. Due to the fact that ATRP polymers contain a terminal halogen, chain end functionality is readily available.[35] Functional initiators and monomers may also be used in ATRP.[36,37] By virtue of the large number of approaches to polymer functionality, ATRP has been extensively studied for the synthesis of advanced polymer architectures. Several examples of brushes, hyperbranched and star polymers have been reported.[38,39,40]

When using functionalized initiators it is of great importance that the initiator does not interact with alkyl halide or the catalyst. As such, initiators which contain carboxylic acid groups for example, are very difficult to use as they have been shown to poison the catalyst.[41] However, by simply protecting the carboxylic acid, a number of successful polymerizations have been reported.[42] Initiators containing functional groups such as amide, sulfonyl halides, thiophene, alkynes etc. have been demonstrated.[43,44,45,46] Furthermore, Destarac et al. reported

that some activated initiators can behave bifunctionally, such as α,α–dichloroacetophenone.[47] When designing a functional initiator, the rate of addition of the initiator to monomer must be similar or greater than the propagation rate. This allows for fast quantitative initiation and thus greater control of the polymerization.

A recent study by Singha et al. demonstrates the polymerization of methyl methacrylate using an amino-adamantane functionalized initiator.[48] Amantadine is used in anti-influenza drugs and polymers bearing such drug molecules are of great importance in the field of medicinal chemistry.[49] Although the polymerization rate was slow compared to standard initiators, the authors were able to successfully synthesize functionalized poly(methyl methacrylate) with controlled molecular weights, low PDI's and well-defined end groups.

When a successful ATRP is performed, the halogen end group is preserved throughout the polymerization. The halogen chain end allows for further transformations using traditional organic chemistry. Displacement of the terminal halogen by free radical chemistry, electrophilic addition and nucleophilc substitution has been demonstrated.[50,51] Nucleophilic substitution of the halogen end group by an azide ion is a well established and efficient reaction.[52] One attraction of organic azides resides in "click chemistry". This will be discussed in greater detail later in this thesis. It should also be noted that the halogen atom can be completely removed if desired. The dehalogenation reaction with trialkyltin hydrides is a conventional technique for said removal.[53]

ATRP also allows for the synthesis of a variety of monomers. The polymerization of methacrylates, styrenes, acrylonitrile, dienes and methacrylamides has been demonstrated.[54.55] Since each monomer has its own equilibrium constant for its active and dormant species ($K_{eq}=k_a/k_{da}$) , the equilibrium rates must be carefully considered. For example, if the equilibrium constant is too large, a high radical concentration can arise leading to a large amount of termination.[56] The rate of the equilibrium also depends on the reactivity of the transition metal catalyst. Therefore, when designing an ATRP experiment careful thought should be given to the equilibrium rates.

Due to the ability of ATRP to operate with a wide range of monomers with control over molecular weight and polydispersity plus the ability to control functionality, ATRP is a popular technique for the synthesis of block copolymers. A large variety of diblock and triblock copolymers have been synthesized exclusively by ATRP.[57] These block copolymers can be prepared by either sequential monomer addition or by using the functional polymers as macroinitiators. Bifunctional macroinitiators have also been demonstrated for the synthesis of block copolymers. In 2004 Vlček et al. reported the synthesis of poly(*t*-BuA-*b*-MMA-*b*-*t*-BuA) copolymers using a 1,3-*bis*{1-methyl-1-[(2,2,2-trichloroethoxy)carbonylamino]ethyl}benzene as a bifunctional initiator in ATRP.[58] This work was later expanded upon by Ritz et al. to include the

synthesis of various styrene-acrylate block copolymers from the aforementioned bifunctional initiator.[59]

Block copolymers may also be synthesized by combining ATRP with various other polymerization techniques. Successful ATRP macroinitiators have been synthesized by anionic, cationic, ring opening, step growth and conventional radical polymerization techniques.[60,61,62] The aforementioned techniques have been used to synthesize graft copolymers, star polymers and hyperbranched polymers.[63]

ATRP is one of the most valuable techniques for the synthesis and design of novel materials. ATRP allows for the polymerization of a wide range of monomers while providing access to numerous compositions, functionalities and topologies. The explosive growth of ATRP in the development of novel compounds is a testament to its synthetic strength.

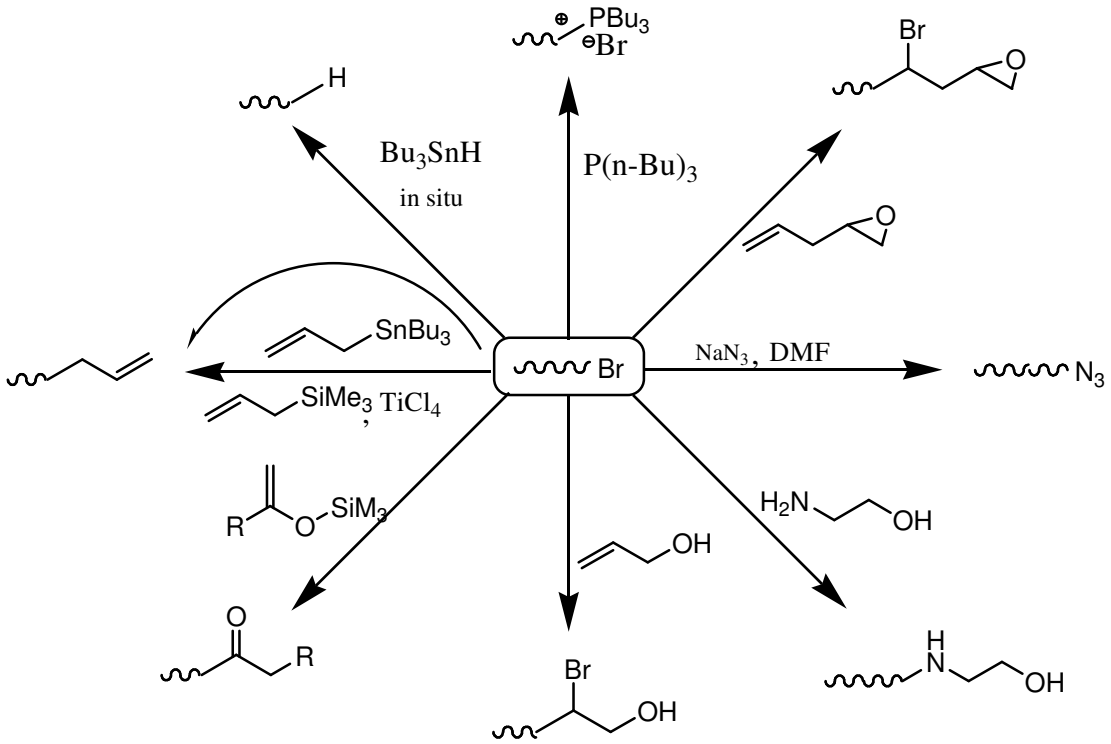
II.1.4 Polymer Functionalization

ATRP and living anionic polymerization are two of the most useful techniques for polymer functionalization reactions. Due to the "living" character of these techniques, controlled molecular weights and narrow molecular weight distributions are obtained. Furthermore, greater control of polymer end groups is obtained as termination steps such as chain transfer and chain termination do not occur. This absence of termination allows for termination methods to be determined by researchers. Both techniques allow for two distinct approaches to polymer functionalization: post polymerization chain end functionalization and initiator functionalization. Although both ATRP and anionic polymerization provide the same approaches to polymer functionalization, very different criteria must be met for successful polymerization. The advantages and limitations of both techniques are herein discussed.

When designing a functionalized initiator for ATRP it is necessary to account for several factors. Initiation is typically accomplished through homolytic cleavage of an activated halogen containing compound, followed by addition of the resulting radical to an alkene. The stabilizing group for the radical must reside on the α-carbon or contain weak bonding with a heteroatom. Therefore, acyl halides or haloarenes, for example, are poor ATRP initiators. Several different functionalized initiators for ATRP have been reported.[64,37,65]

In ATRP, preservation of the halogen end group is critical to obtain a living polymer. The halogen atom allows for further manipulation through standard organic chemistry procedures. The aforementioned chain end manipulation lends itself to a wide variety of chemistries including nucleophilic, electrophilic and radical transformations (Scheme 9).[34] In recent years a large number of reports have investigated the use of azide-alkyne click reactions to synthesize block copolymers.[36] The halogen end group in ATRP allows for direct synthesis of azide terminated polymers through nucleophilic displacement.[66] Furthermore, alkyne functionalized initiators have been demonstrated.[36] Further investigations into the previously mentioned click reactions will be discussed later in this thesis.

Scheme 9: ATRP end group transformations



Living anionic polymerizations provide "living" polymeric anion end groups, which have been used for a variety of functionalization reactions.[67,68] The most studied end group reactions involve electrophilic reagents (Scheme 10). Carbonation, hydroxylation, sulfonation, amination and oxidation are just a few examples of reactions utilizing the aforementioned technique.[69,70] There are, however, several drawbacks to post polymerization functionalization reactions. Great care must be given to reactivities and solvent conditions. Due to the relatively high reactivity of the end group anion, potential side reactions must be accounted for. It is also important to account for potential reactions with the solvent. For example, several polymeric anion end groups are able to abstract a proton from the methyl group on toluene. Whenever possible, unreactive solvents such as benzene should be used. Furthermore, the reaction system must be void of all moisture; this includes moisture present in air.

Scheme 10: Living anionic polymers reactions with electrophiles (X-Y)

Functionalized initiators provide several advantages over end functionalization reactions. Each initiator molecule creates one macromolecule. Therefore, each initiator

molecule will generate a functionalized polymer regardless of the molecular weight. Furthermore, stability of the chain end is of no concern when using a functionalized initiator. However, many functional groups are not stable in the presence of organolithium reagents. For that reason, protecting groups are typically needed when using functionalized initiators.

Work discussed later in this thesis attempts to use azide and alkyne functionalized polymers from both ATRP and anionic polymerization to synthesize polystyrene-polyisoprene block copolymers. Living anionic polymerization techniques are used as they provide a means to synthesize living polyisoprene. ATRP is utilized to provide straight-forward syntheses of azide and alkyne terminated polystyrene.

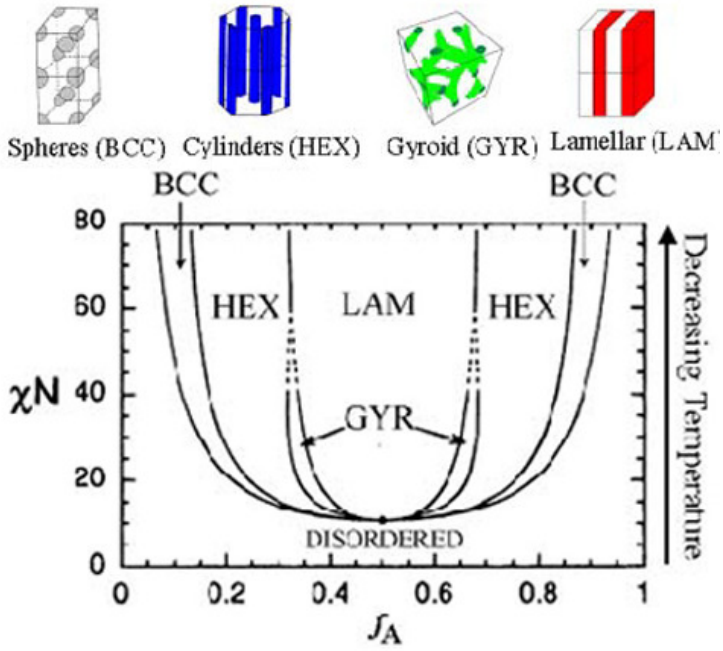
II.1.5 Block copolymers

Block copolymers are composed of a polymer unit linked to a polymer unit of a different type. The blocks can be connected in a wide variety of ways such as A-B diblock copolymers or ABA triblock copolymers (Scheme 11). The blocks may be arranged in several ways such as linear and star for example. Block copolymers are widely used in the industrial world due to their ability to phase separate, thus providing very interesting properties.

Scheme 11: AB diblock and ABA triblock structures

When two polymers are mixed together a polymer blend is obtained. However, most polymers do not mix. This is due to the second law of thermodynamics which, in its most general form states that the world acts to minimize potentials (or to maximize entropy). In other words, the entropy of the world always increases. In an amorphous polymer entropy is very high due to the random and chaotic state of the polymer. Therefore, adding a second polymer does not typically increase entropy and mixing is disfavored. So when two polymers are mixed, phase separation can occur. The polymer phases can separate into morphologies such as spheres, cylinders, lamellar and gyroid (Scheme 12).[71] Block copolymer morphology cay be readily characterized by small-angle x-ray scattering (SAXS) or by scanning electron microscopy(SEM).

Scheme 12: AB diblock phase diagrams. f_a = volume fraction of a block, c = Flory interaction parameter, N = degree of polymerization.



When polymers phase separate interesting properties may be observed. Phase separation can allow you to combine the properties of the two different polymers. For example polystyrene and polybutadiene phase separate at the proper molecular weights. Polystyrene is a stiff material but it's rather brittle. If polybutadiene, a rubbery polymer, is added to the polystyrene, the resulting copolymer is tougher and more ductile then the individual polymers. Polystyrene and polybutadiene copolymers are sold as high impact polystyrene (HIPS). Other examples of immiscible polymer blends include poly(ethylene terephthalate) and poly(vinyl alcohol).

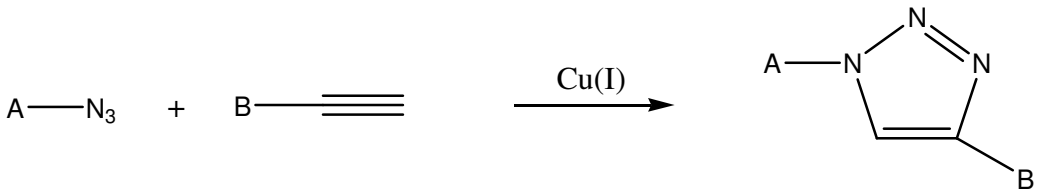
Due to the interesting properties of block copolymers and recent advances in synthetic chemistry interest in block copolymers has increased significantly in the last few decades. Shell Chemical Company and Phillips Petroleum Company have commercialized thermoplastic elastomers (TPEs).[72] These are block copolymers of styrene and butadiene or styrene and isoprene prepared via anionic processes. The tensile strength of TPEs is dependent on the ability of the hard block (polystyrene) to resist deformation under stress. As a result, the strength decreases as the glass transition is approached. Hard blocks with higher $T_{g's}$ such as poly(methylstyrene) or poly(methyl methacrylate) (PMMA) have been investigated. However the use of different hard blocks presents problems. For example, the controlled synthesis of PMMA-b-PBD is difficult due to the difficult purification of MMA and side reactions that can occur during propagation of PMMA.

Recent literature has shown the synthesis of novel block copolymer materials prepared by dual polymerization methods such as polycondensation followed by ATRP.[73] An ABA tri-block copolymer with a polysulfone block and butyl acrylate blocks prepared in the aforementioned duel polymerization method showed unique properties such as molecular selfassembly.[74] Huang et al. provide a second example of using dual polymerization methods with the use of free radical and ring opening polymerizations.[75] The use of free radical and ring opening polymerizations provided a viable technique for the synthesis of a wide variety of block copolymers. The use of various polymerization techniques to synthesize block copolymers will be investigated later in this thesis.

II.1.6 Click Chemistry

Click chemistry was first introduced in 2001 by K. Berry Sharpless.[76] Click chemistry is used to describe reactions that join molecules together quickly and reliably. One of the most famous click reactions is the azide alkyne Huisgen cycloaddition reaction. Rolf Huisgen was the first to describe this organic reaction.[77,78] The Huisgen cycloaddition reaction is a reaction between an alkyne and an azide to produce a 1,2,3-triazole. This reaction gives a mixture of the 1,4 and 1,5 adducts. However, in 2002 Meldel et al. reported a copper catalyzed version of the azide alkyne cycloaddition (CuAAC) reaction to synthesize peptidotriazoles.[79] Using the copper catalyst this click reaction was shown to afford the 1,4 regioisomer exclusively (Scheme 13).

Scheme 13: Cu catalyzed azide-alkyne Huisgen cycloaddition reaction.



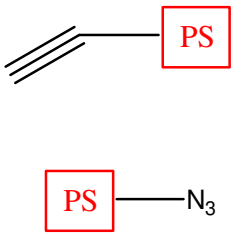
The copper catalyzed azide-alkyne cycloaddition has gained widespread use in the field of polymer synthesis. This is partially due to the fact that these click reactions give near quantitative yield with low susceptibility to side reactions. In addition, controlled radical polymerization techniques such as ATRP provide functional end groups which can be transformed into "clickable" end groups such as azides. Matyjaszewski et al. provide a prime example of the use of CRP techniques coupled with CuAAC to synthesize novel polymers.[46] An alkyne functional initiator was used to synthesize α-alkyne-ω-bromo-terminated polystyrene. The resulting polymer was reacted with NaN_3 to yield α-alkyne-ω-azide-terminated polystyrene. A click coupling reaction was performed on the alkyne-azide polystyrene to synthesize polystyrene containing 1,2,3-triazole linkages. The aforementioned techniques have been extended to synthesize a wide variety of architectures such as block and star polymers.[80]

The recent surge of interest in azide-alkyne click reactions with polymer synthesis has resulted in the establishment of effective routes to the synthesis of complex polymer architectures with 1,2,3-triazole linkages regularly distributed in said polymers.[81] However, interest in click coupling of two separate polymers together has been limited. Urein and collegues demonstrated a synthetic approach to clicking polystyrene with α,ω-ethynyl poly(3-hexylthiophenes).[82] There are several other examples of using click chemistry to link two separate polymers. However, no example of clicking high molecular weight polymers (≥ 30 kDa) has been demonstrated. Attempts to synthesize clicked block copolymers combining two separate CRP techniques are discussed later in this thesis.

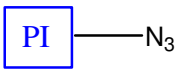
III Objectives

The objectives of this report are to investigate the synthesis of novel polyisoprene-polystyrene "clicked" block copolymers. The ultimate goal of this research is to compare said clicked block copolymers with supramolecular block copolymers from the Gibson group. However, the supramolecular block copolymers are yet to be synthesized. As a result, a variety of synthetic routes to "clicked" block copolymers are herein discussed.

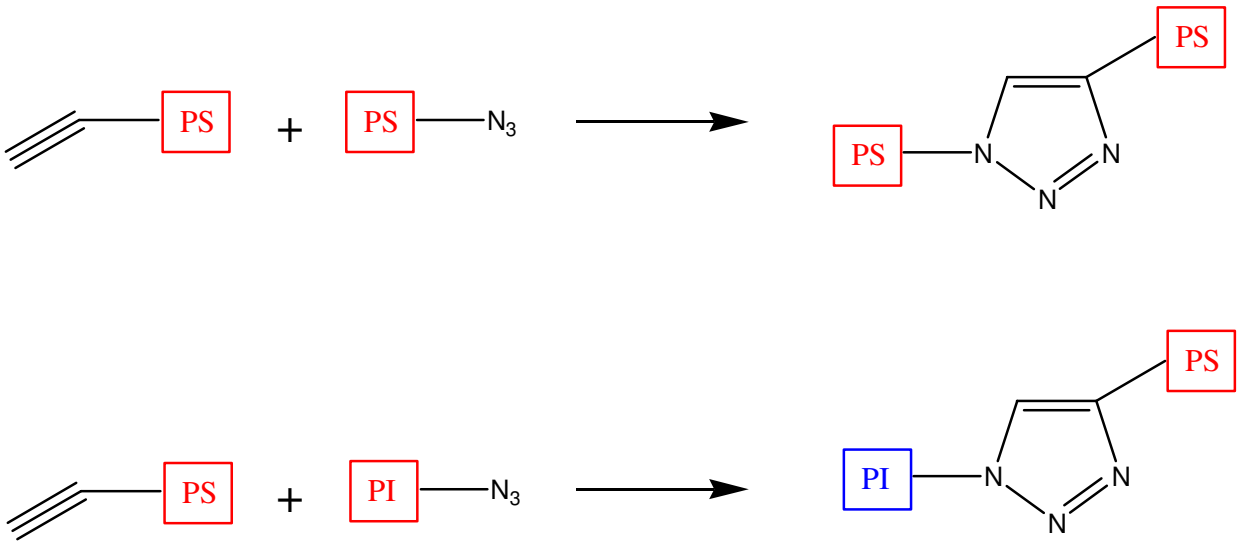
ATRP



Anionic Polymerization



Click



IV ATRP

IV.1.0 Experimental

All products were analyzed with either a Varian Unity 400 MHz or a JEOL Eclipse+ 500 MHz. $M_{n(NMR)}$ was determined using the ratio of polymer end group protons to the starting monomer protons. SEC was run with polystyrene standards using chloroform as the eluting solvent and a refractive index detector.

Bromo-terminated polystyrene [1] with 1-phenylethyl bromide initiator (Scheme 14)

Cu(I)Br (0.125 g, 0.87 mmol), and PMDTA (0.4 mL, 3 mmol) were added to a 25 mL round bottom flask. The contents of the flask were degassed by flowing nitrogen through the flask for 15 min. Previously distilled styrene (5 mL, 0.04 mol) and 1-phenylethyl bromide (0.16 g, 0.87 mmol) were degassed separately and added to the flask. The solution was stirred at 110 ^{o}C for 1.5 h under N_2. The mixture was dissolved in chloroform and run through a neutral alumina column to remove the copper complex and then concentrated by rotoevaporation. The polymer was precipitated into excess methanol (3x) and filtered. The polymer was dried at 40 ^{o}C under vacuum. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.13-1.15 (3H), 1.21-2.10 (m, 121H), 4.15 (1H), 6.21-7.25 (m, 218H) (PNMR 1). Polymerization analogously performed to produce a wide variety of molecular weights (Table 1).

Azido-terminated polystyrene [2] (Scheme 14)[66]

NaN_3 (0.55 g, 8.5 mmol) was added to a solution of **[1]** (5.0 g, 0.85 mmol) in DMF (25 mL). The solution was stirred under N_2 for 24 h. The polymer was purified by extraction with water/chloroform. The organic phase was dried over Na_2SO_4 and evaporated. The polymer was precipitated from chloroform into methanol (3x) and dried at 40^{o}C under vacuum: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.91 (3H), 1.20-2.20 (m, 151H), 4.12 (1H), 6.25-7.26 (m, 238H) (PNMR 2). IR (cm^{-1}): 2300 (N_3), 3100 (C-H, aromatic), 1700 – 1900 (aromatic overtones), 1400 – 1600 (C=C, aromatic). Reactions performed on all molecular weights of **[1]** (Table 1).

Amino-terminated polystyrene [3] (Scheme 14)[83]

$LiAlH_4$ (0.05 g, 1 mmol) and dry diethyl ether (2 mL) were added to a dry round bottom flask under N_2. A solution of **[2]** (0.72 g, 0.13 mmol) in diethyl ether (9 mL) was added with vigorous stirring. The mixture was stirred at reflux for 5 h. In order to quench the mixture, water (0.04 mL) was added followed by NaOH (0.04 mL, 15 %) and a second addition of water (0.02 mL). The solution was filtered and precipitated into methanol (3x). ^{1}H NMR (500 MHz, $CDCl_3$) δ

(ppm): 1.05 (3H), 1.25-2.25 (m, 150H), 6.30-7.30 (m, 255H) (PNMR 3). Reaction performed on all molecular weights of **[2]** (Table 1).

Alkyne-terminated polystyrene via N-acylation [4] (Scheme 14)

Propiolic acid (11 mg, 0.16 mmol), DMAP (2.4 mg, 0.02 mmol) and **[3]** (0.43 g, 0.08 mmol) were dissolved in dry THF (10 mL) and cooled in an ice bath. DCC (33 mg, 1.6 mmol) in THF (3 mL) was slowly added to the solution which turned orange followed by red. The reaction mixture was stirred at room temperature for 18 h. The mixture was precipitated into methanol (3 x) and dried. ^{1}H NMR spectroscopy showed only starting materials. The same results were obtained when the reaction was run at higher concentrations.

Scheme 14: ATRP polystyrene end-group manipulation

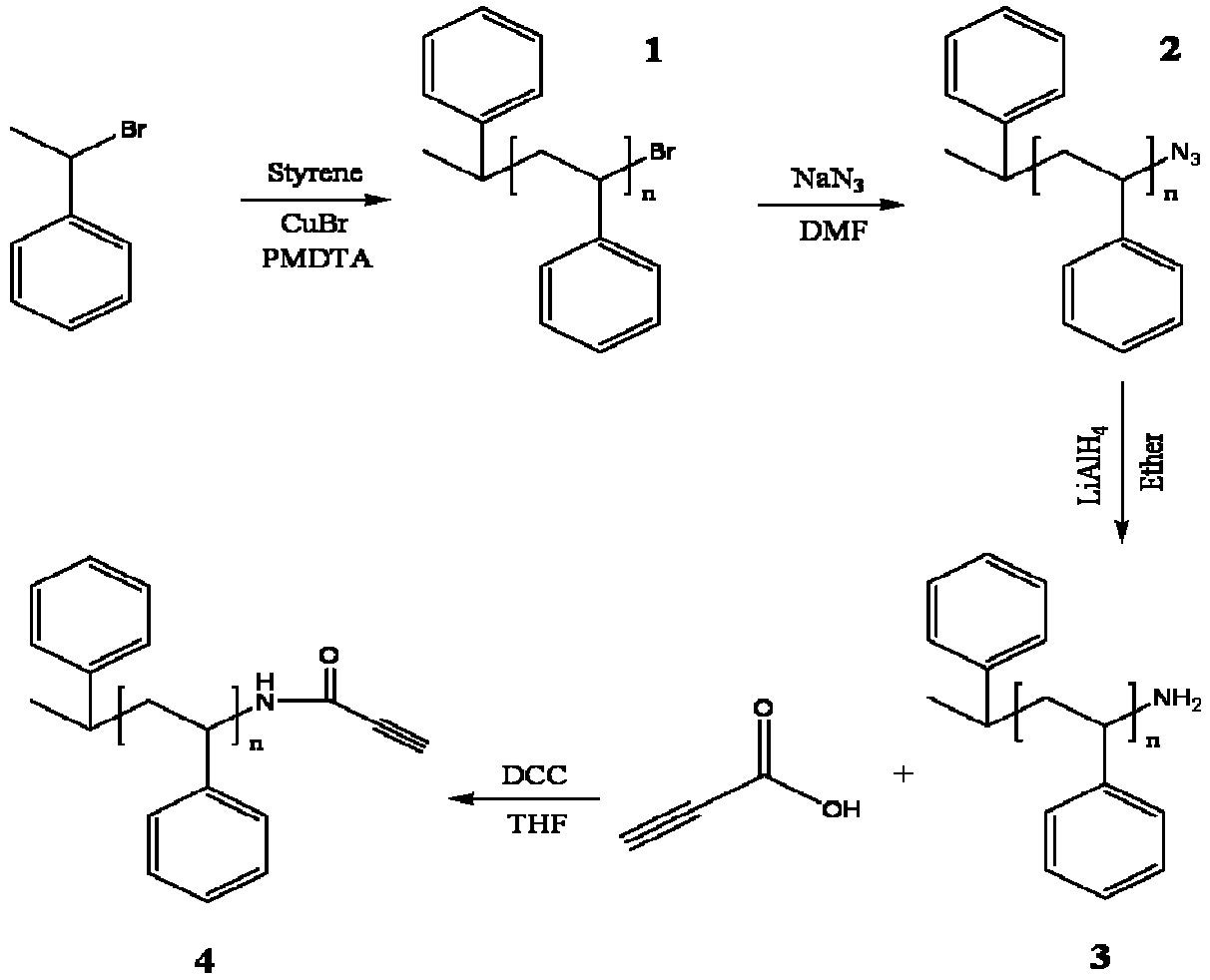


Table 1: Molecular weights (kDa) and PDIs of polymers [1], [2] and [3]

Polymer	$M_{n(NMR)}$ (kDa)	$M_{n(GPC)}$ (kDa)	M_w/M_n
[1]	5.2	5.8	1.29
	10.3	10.1	1.22
	23.1	26.8	1.33
[2]	5.7	5.8	1.30
	11.0	10.7	1.18
	22.4	27.1	1.34
[3]	5.4	5.6	1.44
	13.1	11.6	1.23
	28.0	25.2	1.41

Propargyl 2-bromoisobutyrate [5] (Scheme 15)[46]

2-Bromo-2-methylpropanoyl bromide (34.3 g, 0.15 mol) in 67 mL of ether was cooled to 0 ^{o}C under N_2. Propargyl alcohol (10 g, 0.18 mol) and pyridine (14.3 g, 0.18 mol) in 50 mL of ether were slowly added. The mixture was allowed to warm to room temperature and stir for 12 h under N_2. The product mixture was washed with water (2x), $NaHCO_3$ (3x), 5 % HCL (2x), and brine (2x), dried over Na_2SO_4 and concentrated. Distillation yielded 18.4 g (60 %) of **[5]**. Bp 86-88 ^{o}C (20 mm) [lit.[46] bp 84-87 ^{o}C (20 mm)]. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.96 (s, 6H), 2.50 (s, 1H), 4.78 (s, 2H) (PNMR 4).

Alkyne-functionalized polystyrene [6] (Scheme 15)[46]

Cu(I)Br (0.5 g, 3 mmol), and PMDTA (0.79 mL, 3.5 mmol) were added to a 25 mL round bottom flask. The contents of the flask were degassed by flowing nitrogen through the flask. Previously distilled styrene (20.0 mL, 174 mmol), **[5]** (0.51 g, 3.5 mmol) and diphenyl ether (2.5 mL) were degassed separately and added to the flask. The solution was stirred at 90 ^{o}C for 1.5 h under N_2. The mixture was dissolved in chloroform, passed through a neutral alumina column and concentrated via rotoevaporation. The polymer was precipitated from chloroform into excess methanol (3x) and filtered. The polymer was dried at 35 ^{o}C under vacuum. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 1.2-2.2 (m, 138H), 6.2-7.3 (m, 260H) (PNMR 5). Polymerization performed at several molecular weights (Table 2).

Scheme 15: ATRP alkyne-terminated polystyrene

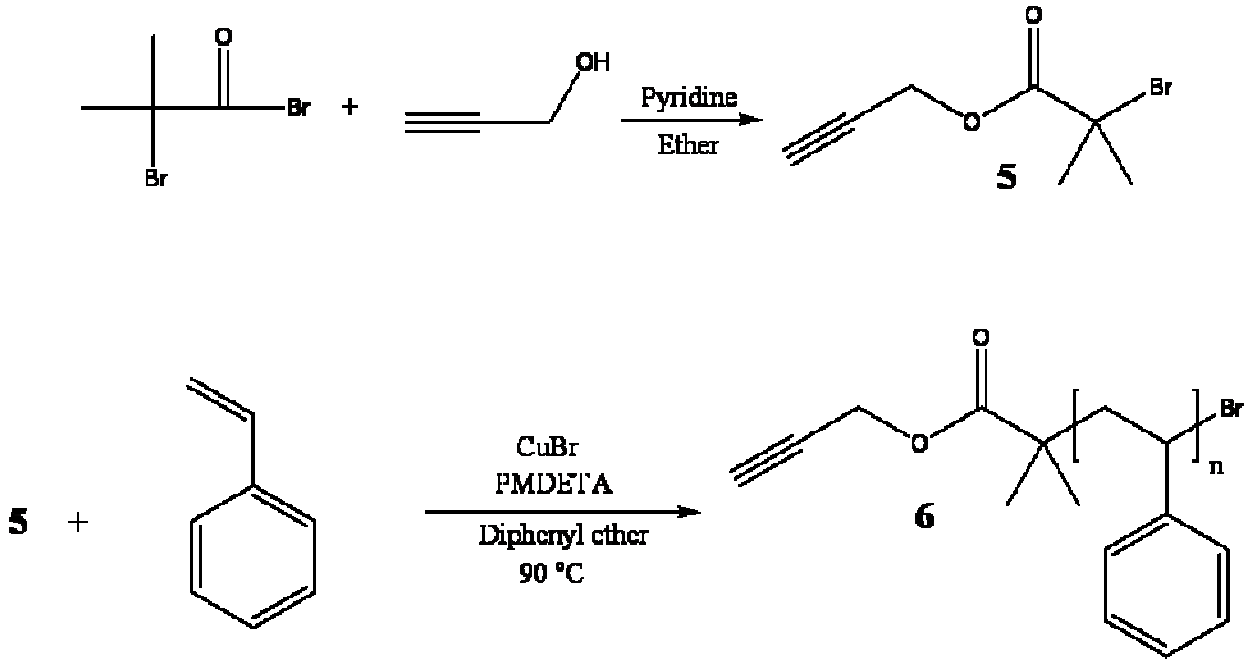


Table 2: Molecular weights and PDIs of alkyne-terminated polystyrene [6]

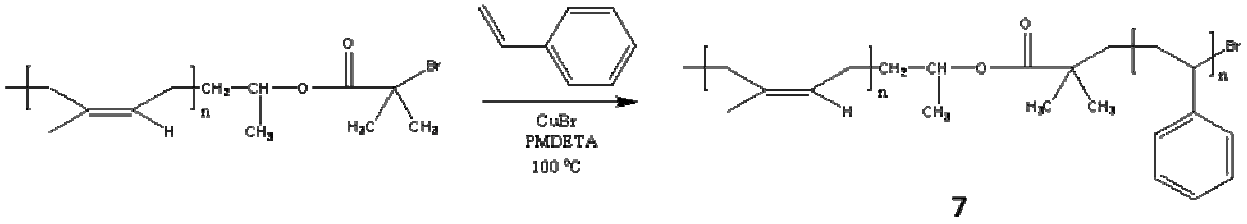
$M_{n(NMR)}$ (kDa)	$M_{n(GPC)}$ (kDa)	M_w/M_n
3.2	3.5	1.44
5.4	5.3	1.38
10.0	9.4	1.46
N/A	12.5	1.33
N/A	65.1	1.40

Styrene-Isoprene block copolymer via ATRP [7] (Scheme 16)

Styrene (5.0 g, 48 mmol), CuBr (0.1 g, 0.7 mmol) and PMDETA (0.13 g, 0.72 mmol) were added to a flame dried 25 mL round bottom flask. The mixture was purged with N_2. In a separate flask, tertiary bromo-terminated polyisoprene (1.2 g, 0.12 mmol) was added to diphenyl ether (1.5 mL) and purged with N_2. The initiator solution was added to the styrene solution via a

degassed syringe and the resulting mixture was heated at 100 ^{o}C under N_2 for 2.0 h. The mixture was dissolved in $CHCl_3$ and passed through an alumina column to remove residual CuBr. The polymer solution was concentrated via rotoevaporation and the polymer was precipitated from $CHCl_3$ into methanol (3x). Only starting material was recovered.

Scheme 16: ATRP polymerizations of polyisoprene-polystyrene block copolymers [7].



7

IV.1.1 Results and Discussion

ATRP produces polymers with halogen functional end groups. This functionalization has been exploited to produce "clickable" polymers. As previously mentioned, azide and alkyne functional polymers are required to achieve the desired "clicked" block copolymers.

In order to properly characterize the functional polymers, NMR, SEC and in some cases IR was used. SEC provides information on the molecular weight as well as the molecular weight distribution (PDI). NMR provides information on molecular weight and chemical structure. Lastly, IR spectroscopy was used to help characterize the polymer end groups.

Azido-terminated polystyrene was synthesized using a nucleophilic substitution reaction with sodium azide on bromo-terminated polystyrene. The aforementioned substitution occurs at room temperature with quantitative yields. Azido-terminated polystyrene was characterized by ^{1}H and ^{13}C NMR, IR and SEC. Several molecular weights of azido-terminated polystyrene were synthesized (Table 1). The livingness of bromo and azido-termianted polystyrene was demonstrated by SEC (PDI ≤ 1.50). The ^{1}H NMR spectrum of bromo-terminated polystyrene shows a signal at 4.75 ppm corresponding to the proton next to the bromine endgroup. The ^{1}H NMR spectrum of azido-terminated polystyrene shows a signal at 4.12 ppm resulting from the proton next to the azide end group. Furthermore, complete removal of the proton signal at 4.75 ppm is observed, thus suggesting complete azide substitution. The IR spectrum of azido-terminated polystyrene contains a signal at 2300 cm^{-1} corresponding to the N_3 vibrations.

The synthesis of alkyne-functionalization polystyrene requires a different approach than the synthesis of azido-functionalized polystyrene. Rather than post polymerization functionalization, as used for azido-terminated polystyrene, initiator functionalization was employed. The chosen initiation, propargyl 2-bromoisobutyrate, was synthesized from 2-bromo-2-methylpropanoyl bromide. Propargyl 2-bromoisobutyrate was characterized by ^{1}H NMR and Bp.

Alkyne-functionalized polystyrene was synthesized using the aforementioned functional initiator, propargyl 2-bromoisobutyrate. Diphenyl ether was required as a solvent in this polymerization. The solvent was required because the monomer and initiator are not soluble in one another. A second advantage to using a solvent is that gel effects can be minimized by keeping the viscosity low. Alkyne-functionalized polystyrene was characterized by SEC, ^{1}H NMR and ^{13}C NMR. Several molecular weights were synthesized (Table 2). A PDI ≤ 1.50 was obtained for all molecular weights of alkyne-functionalized polystyrene. The signal at 4.45 ppm corresponds to the protons adjacent to the alkyne endgroup. The signal at 4.75 corresponds to the proton next to the bromine endgroup.

Investigations into the synthesis of alkyne-functionalized polystyrene with the alkyne group on the polymer chain end rather than the initiator end were performed. Reduction of azido-terminated polystyrene to amino-terminated polystyrene was performed using $LiAlH_4$. Amino-terminated polystyrene was characterized by SEC and ^1H NMR spectroscopy. The ^1H NMR spectrum showed complete removal of the azido peaks, thus suggesting complete conversion. N-Acylation was then attempted using the previously mentioned amino-terminated with propiolic acid. DCC (dicyclohexylcarbodiimide) and DMAP (4-*N*-*N*-dimethylaminopyridine) were used to catalyze the reaction. DCC and the carboxylic acid react to form an acylisourea intermediate which offers increased reactivity with the amine. DMAP reacts with the acylisourea leading to an active ester. The active ester further increases reactivity. Even with the use of said catalyst, ^1H NMR spectroscopy showed only starting material. One possible explanation for the failure of the acylation reaction is the decreased reactivity of polymer chain ends. Shorter polystyrene chains or increased reaction temperature may aid the alkylation reaction.

V Anionic Polymerization

V.1.0 Experimental

Trimethylsilane (TMS)-terminated polystyrene [9] (Scheme 17)[84]

The synthesis of polystyryl lithium **[8]** was carried out in a flame dried flask under N_2. To a solution of styrene (3.0 g, 29 mmol) in benzene (10 mL) was added *n*-butyllithium (0.35 mL, 0.58 mmol) in cyclohexane. The red solution was stirred at room temperature for 12 h under N_2. TMSCl (2.27 mL, 18 mmol) was added to the reaction mixture and stirred for 48 h. The solution was quenched by addition of methanol and purified by precipitation from chloroform into methanol (3x). $M_{n(NMR)}$ = 4.1 kDa. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): -0.4-0.4 (m, 19H), 0.7-1.0 (m, 9H), 1.1-1.2 (m, 3H), 1.3-2.3 (m, 127H), 4.4-4.8 (m, 2H), 6.2-7.4 (m, 192H) (PNMR 6).

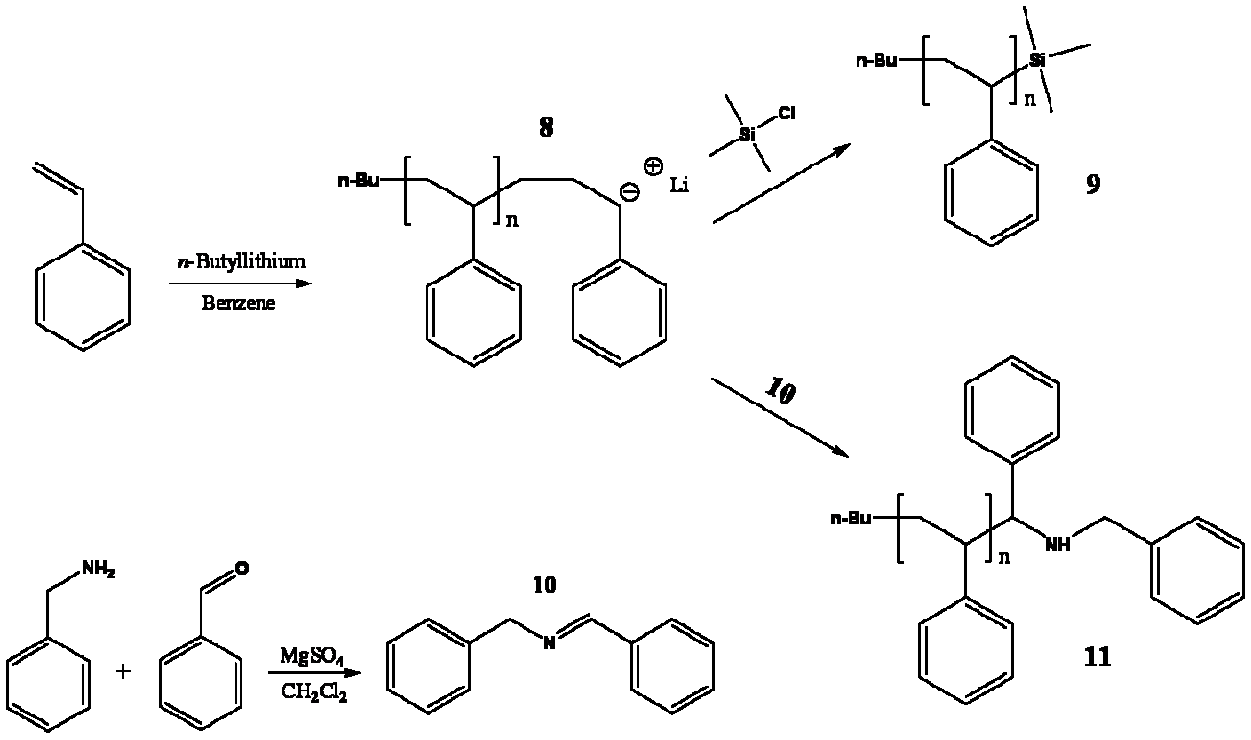
N-Benzylidenebenzylamine [10] (Scheme 17)[85]

To a flame dried flask filled with N_2 was added benzylamine (6.0 g, 56 mmol), $MgSO_4$ (10.0 g, 84 mmol) and CH_2Cl_2 (120 mL). After stirring for 5 minutes, benzaldehyde (6.0 g, 57 mmol) was added. The reaction mixture was stirred at room temperature for 28 h under N_2. The mixture was filtered through Celite and the Celite was washed with CH_2Cl_2. The solvent was removed via rotary evaporation. The imine was purified by vacuum distillation (155–156 ^{o}C at 5 mm Hg: lit. 119-120 ^{o}C at 0.1 mm Hg) to afford 8.4 g (77 %: lit.[85] 87 %) of **[10]**. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 4.70-4.90 (s, 2H), 7.20-7.30 (1H), 7.30-7.35 (4H), 7.35-7.45 (3H), 7.70-7.90 (s, 2H), 8.30-8.45 (s, 1H) (PNMR 7).

Dibenzylamino-terminated polystyrene [11] (Scheme 17)

The synthesis of polystyrene was carried out in a flame dried flask under N_2. To a solution of styrene (3.0 g, 29 mmol) in benzene (10 mL) was added *n*-butyllithium (0.35 mL, 0.58 mmol) in cyclohexane. The red solution was stirred at room temperature for 15 h under N_2. N-benzylidenebenzylamine **[10]** (0.23 g, 1.2 mmol) was added to the polystyryl anion **[8]** solution. The resulting yellow mixture was stirred for 48 h, quenched in methanol and precipitated from $CHCl_3$ into methanol (3x). $M_{n(GPC)}$ = 7.4 kDa, $M_{n(NMR)}$ = 7.1 kDa, PDI = 1.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 1.0-1.1 (3H), 1.2-2.4 (200H), 6.2-7.4 (345H) (PNMR 8).

Scheme 17: Synthesis of TMS-terminated polystyrene [9], N-benzylidenebenzylamine [10], and dibenzylamino-terminated polystyrene [11] from polystyryl lithium [8]



Hydroxyl-terminated polyisoprene [12] (Scheme 18)

Isoprene (150.0 g, 2.2 mol) was added to a flame dried flask containing benzene (150 mL) under N_2. The flask was cooled in a NaCl ice bath to -5 ^{o}C. *Sec*-butyllithium in hexane (8.46 mL, 11.0 mmol) was added via a degassed syringe. The reaction mixture was stirred at room temperature for 12 h under N_2. An aliquot was removed and quenched with methanol. The aliquot was purified by precipitation from chloroform into methanol (3x), dissolving in chloroform and washing with water (3x). $M_{n(GPC)}$: 13.5 KDa, M_w/M_n : 1.13. A 10-fold excess of propylene oxide (6.39 g, 0.11 mol) over the initiator was added to the polyisoprenyl lithium **[11]** using a degassed syringe. The mixture was stirred for 14 h under N_2 and quenched with methanol. The propylene oxide terminated polyisoprene **[12]** was purified by precipitation from chloroform into methanol (3x), dissolution in chloroform and washing with water (3x). The polymer solution was dried over Na_2SO_4. The chloroform was removed via rotoevaporation to obtain **[12]**. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 0.85-0.90 (3H), 1.15-1.50 (19H), 1.50-1.75 (296H), 1.80-2.12 (385H), 4.60-4.85 (25H), 5.0-5.25 (185H) (PNMR 9). The hydroxylation

reaction was performed at several molecular weights **(**Table 3**).** The ^{13}C NMR spectra of the unfunctionalized and functionalized polyisoprene side by side can be seen in appendix CNMR 10.

Chloro-terminated polyisoprene from 2-chloroacetyl chloride

Hydroxyl-terminated polyisoprene (7.0 g, 0.5 mmol) was dissolved in THF (10 mL). A 4-fold excess of 2-chloroacetyl chloride (0.24 g, 2.1 mmol) was added to the mixture. A 7-fold excess of K_2CO_3 (0.49 g, 3.5 mmol) was then added. The mixture was stirred at R.T for 96 h under N_2. The mixture was diluted with THF and filtered to remove residual K_2CO_3. The THF was removed via reduced pressure vaporization and the remaining polymer was dissolved in $CHCl_3$. The polymer was washed with H_2O (3x) and $NaHCO_3$ (2x). The polymer was precipitated from $CHCl_3$ into methanol (3x), dissolved in $CHCl_3$ and dried over $NaSO_4$. The $CHCl_3$ was removed via rotoevaporation to afford 4.04 g of polymer. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 0.8-0.85(3H), 1.2-1.5 (19H), 1.5-1.8 (295H), 1.8-2.2 (364H), 4.6-4.8 (27H), 5.0-5.2 (196H) (PNMR 11). The ^{13}C NMR spectrum can be seen in appendix CNMR 12. The same procedure was used to synthesize bromo-terminated polyisoprene using bromoisobutyryl bromide as the acylating agent. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 0.8-0.9 (3H), 1.2-1.5 (18H), 1.5-1.8 (290H), 1.8-2.15 (358H), 4.6-4.8 (22H), 5.0-5.2 (191H) (PNMR 13). The ^{13}C NMR spectrum can be seen in appendix CNMR 14. The reactions were attempted using pyridine as a base. Similar results were obtained.

Chloro-terminated polyisoprene [13] from 11-chloroundecanoyl chloride [14] (Scheme 18)

11-Chloroundecanoic acid (10.0 g, 0.042 mol) was dissolved in a 5-fold excess of thionyl chloride (25.0 g, 0.21 mol). The mixture was heated at reflux for 5 h under N_2. Excess thionyl chloride was removed via vacuum distillation. Acyl chloride **[14]** was used directly without further purification. Hydroxyl-terminated polyisoprene **[12]** (5.0 kDa, 8.1 kDa, and 50.1 kDa) in pyridine was added to **[14]**. The mixture was stirred at R.T under N_2 protection. Reaction times varied for the various molecular weights used. The 5.0 kDa reaction was run for 48 h, 8.1 kDa for 96 h and 50.1 kDa for 120 h. The mixture was diluted with THF, precipitated into methanol (3x), dissolved in chloroform and washed with H_2O (3x) and $NaHCO_3$ (2x). The zoomed ^1H NMR spectrum can be seen in appendix PNMR 15

Bromo-terminated polyisoprene [15] from 11-bromoundecanoyl chloride [16] (Scheme 18)

11-Bromoundecanoic acid (10.0 g, 0.038 mol) was dissolved in a 5-fold excess of thionyl chloride (22.4 g, 0.189 mol). The mixture was heated at reflux for 5 h under N_2. Excess thionyl chloride was removed via vacuum distillation. Acyl bromide **[16]** was used directly without further purification. Hydroxyl-terminated polyisoprene **[12]** (5.0 kDa, 8.1 kDa, and 50.1 kDa) in

pyridine was added to **[16]**. The mixture was stirred at R.T under N_2 protection. As with chloro-terminated polyisoprene **[13]**, reaction times varied for the various molecular weights used. The mixture was diluted with THF, precipitated into methanol (3x), dissolved in chloroform and washed with H_2O (3x) and $NaHCO_3$ (2x). The ^1H NMR spectrum can be seen in appendix PNMR 15.

Azido-terminated polyisoprene [17] (Scheme 18)

NaN_3 (0.41 g, 6.2 mmol) was added to a solution of bromide-terminated polyisoprene (4.0 g, 0.62 mmol) in DMF (2 mL). The solution was stirred at room temperature for 12 h (5.0 kDa), 48 h (8.1 kDa) and 96 h (50.1 kDa) under N_2. **[17]** was isolated by precipitation into water and purified via precipitation from chloroform into methanol (3x). Precipitation was followed by dissolution in chloroform and washing with water (3x). ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 0.8-0.9 (3H), 1.2-1.5 (17H), 1.5-1.8 (183H), 1.8-2.2 (241H), 4.6-4.8 (17H), 5.0-5.2 (101H) (PNMR 16).

Scheme 18: Polyisoprene chain-end manipulation

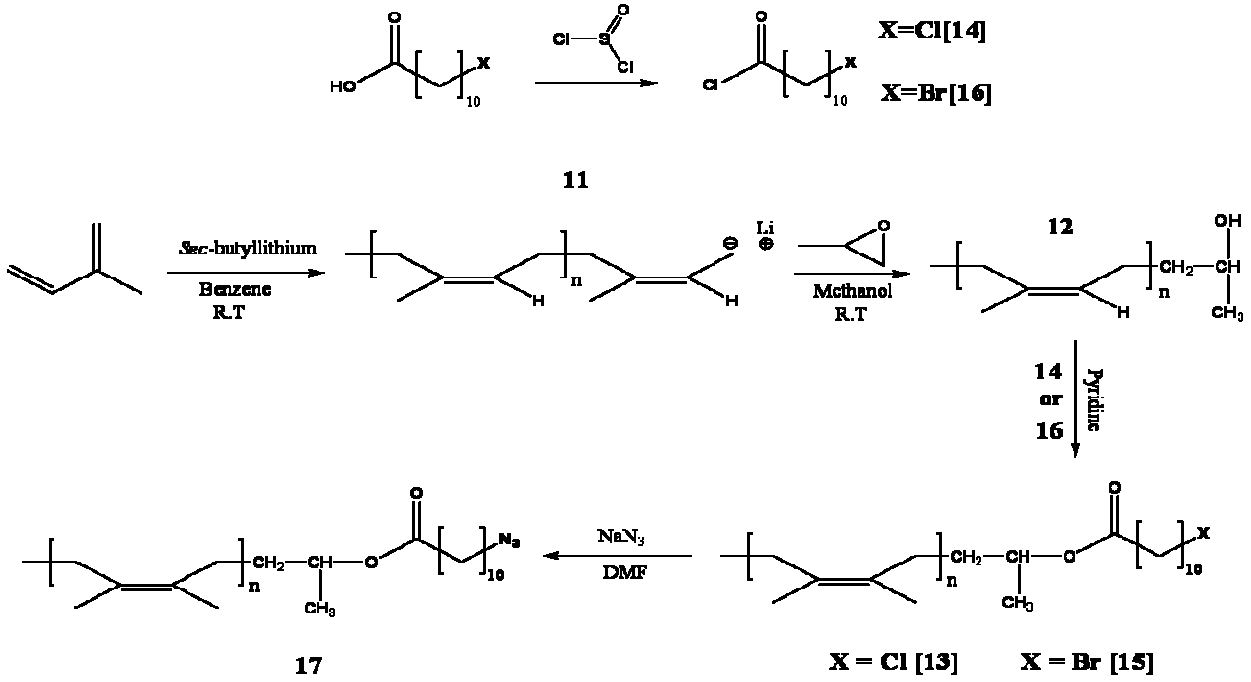


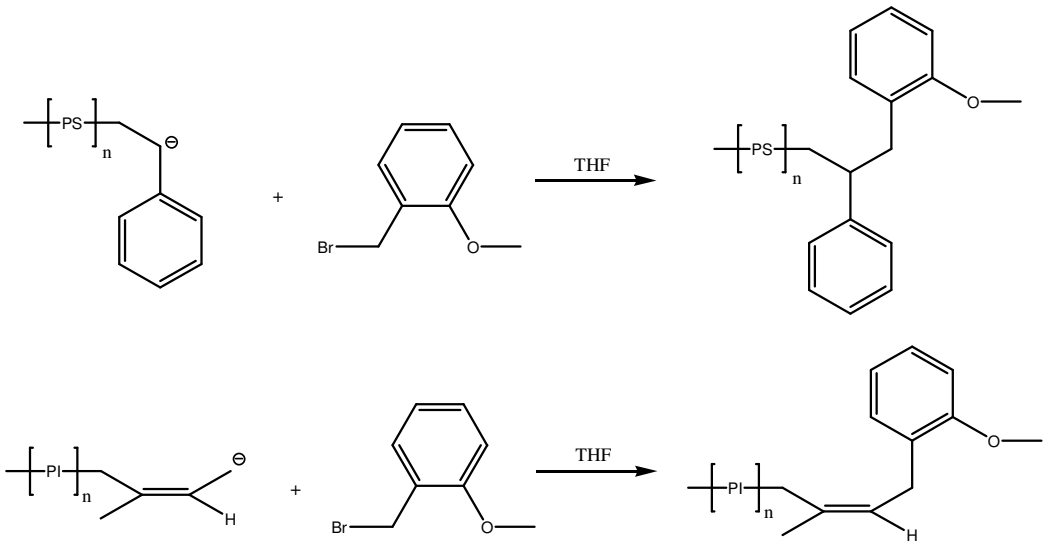
Table 3: Molecular weights ($M_{n(GPC)}$) of [12]

M_n (kDa) of base polymer	M_w/M_n	M_n (kDa) of functional Polymer	M_w/M_n
1.8	1.10	1.9	1.10
3.8	1.15	3.8	1.13
5.0	1.18	ND	ND
8.5	1.21	8.6	1.20
13.5	1.09	17.3	1.04
50.1	1.20	ND	ND

Anisole-terminated polymers (Scheme 19)

Isoprene (6.0 g, 88 mmol) was added to a flame dried flask containing benzene (10 mL) under N_2. *Sec*-butyllithium in hexane (0.12 g, 1.8 mmol) was added via a degassed syringe. The reaction mixture was stirred at room temperature for 12 h under N_2. An aliquot was removed and quenched with methanol. The aliquot was purified by precipitation from chloroform into methanol (3x), dissolving in chloroform and washing with water (3x). $M_{n(GPC)}$: 3.1 kDa, M_w/M_n : 1.08. A 10-fold excess of *o*-bromomethylanisole (3.54 g, 17.6 mmol) over the initiator was added to the living polyisoprene using a degassed syringe. The mixture was stirred for 14 h under N_2. The mixture was quenched with methanol. The anisole-terminated polyisoprene was purified by precipitation from chloroform into methanol (3x), dissolution in chloroform and washing with water (3x). The polymer solution was dried over Na_2SO_4. The chloroform was removed via rotoevaporation to obtain anisole-terminated polyisoprene. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 0.80-0.95 (3H), 1.20-1.50 (14H), 1.50-1.75 (87H), 1.80-2.12 (116H), 3.6-3.9 (3H), 4.60-4.85 (9H), 5.0-5.25 (66H) (PNMR 17). Anisole-terminated polystyrene (M_{nGPC} = 4.9 kDa, M_w/M_n : 1.21). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 0.7-0.8 (3H), 1.2-2.4 (121H), 3.65-3.95 (3H), 6.2-7.4 (211H) (PNMR 18). A second reaction was performed under the same conditions using polystryl lithium.

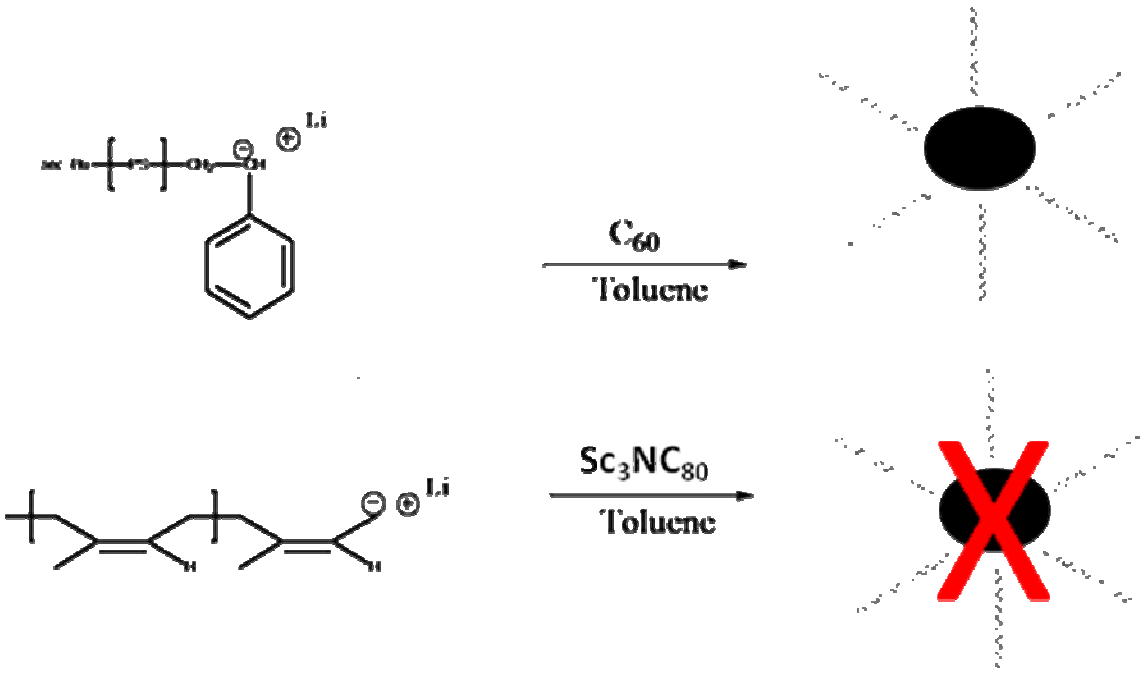
Scheme 19: Reaction of polymer anions with o-bromomethyl anisole



Fullerene centered star polymers (Scheme 20)[86,87]

Styrene (5.0 g, 48 mmol) was added to a flame dried flask containing benzene (15 mL) under N_2. *n*-Butyllithium in cyclohexane (0.307 g, 4.8 mmol) was added via a degassed syringe. The reaction was stirred at room temperature for 12 h under Ar. An aliquot was removed and quenched with methanol. The aliquot was purified by precipitation from chloroform into methanol (3x) ($M_{n(GPC)}$ = 1.3 kDa, M_w/M_n : 1.24). A 20-fold excess of the polystryl anion (2 mL in benzene) was added dropwise to a solution of C_{60} (23 mg, 0.032 mmol) in toluene (3 mL) under N_2. Upon addition of the polymer, the fullerene solution changed color from purple to dark brown. The mixture was stirred for 3 h under N_2. The mixture was quenched with methanol. Toluene was removed using reduced pressure vaporization and the crude product was dissolved in THF. Unreacted C_{60} was removed via centrifuge. The polymer was precipitated into methanol (3x) and dried under vacuum. Molecular weight was determined using GPC coupled with refractive index (M_{nGPC} = 8.8 kDa). A second reaction was performed under the same conditions using polyisoprenyl lithium. Molecular weight of polyisoprene aliquot (M_{nGPC} = 0.7 kDa) and polyisoprene star (M_{nGPC} = 4.3 kDa). All reactions on Sc_3NC_{80} yielded only starting material, thus proving unsuccessful.

Scheme 20: Fullerene centered star polymers



Polystyrene-Polyisoprene block copolymer via anionic polymerization (Scheme 21)[88]

Styrene (15 g, 0.14 mol) was added to a flame dried flask containing benzene (15 mL) under Ar. *Sec*-butyllithium in hexane (31 mg, 0.48 mmol) was added via a degassed syringe. The mixture was stirred at room temperature for 12 h under Ar. An aliquot was removed and quenched with methanol. The aliquot was purified by precipitation from chloroform into methanol (3x) ($M_{n(GPC)}$ = 33.1 kDa, M_w/M_n : 1.11). Isoprene (32.70 g, 0.48 mol) in degassed benzene (30 mL) was added to the polystyryl anion via a degassed syringe. The reaction mixture was stirred at room temperature for 14 h. The mixture was quenched with methanol. The polymer was precipitated from chloroform into methanol (3x). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 0.7-0.8 (3H), 1.2-2.4 (4216H), 4.6-4.8 (148), 5.0-5.2 (942H), 6.2-7.3 (2463H) (PNMR 19). The ^{13}C NMR spectrum can be seen in appendix CNMR 20. M_{nGPC} = 102.1 kDa, T_{gDSC} = -74 ^{o}C and 91 ^{o}C. A variety of molecular weights were synthesized **(Table 4)**

Scheme 21: Polystyrene-polyisoprene block copolymer

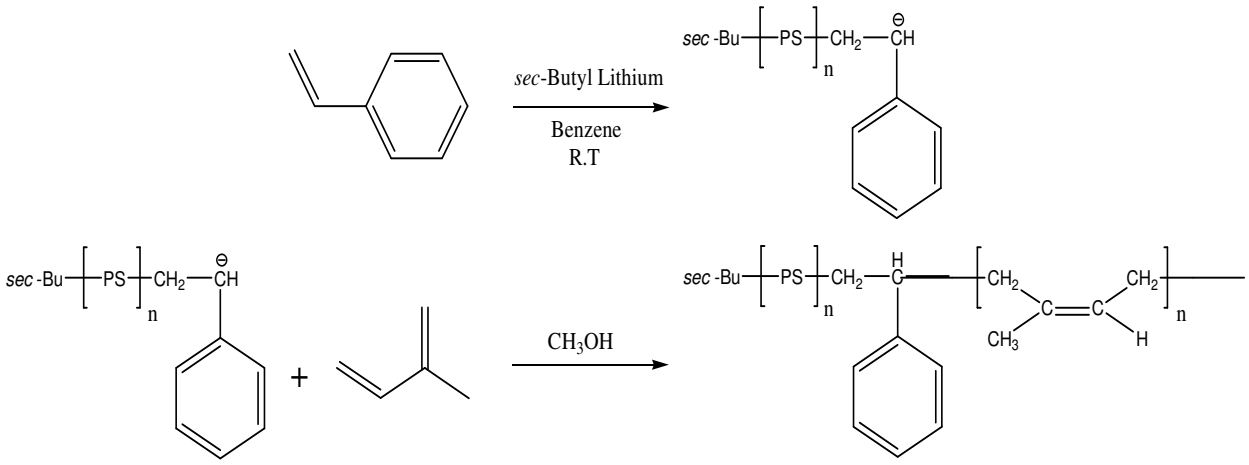


Table 4: Polystyrene-polyisoprene block copolymer molecular weights ($M_{n(GPC)}$)

Polystyrene:Polyisoprene (wt % ratio)	Polystyrene M_{nGPC} (kDa)	M_n (kDa)
86:14	18.0	21.2
22:78	4.3	18.3
31:69	33.1	102.1

V.1.1 Results and Discussions

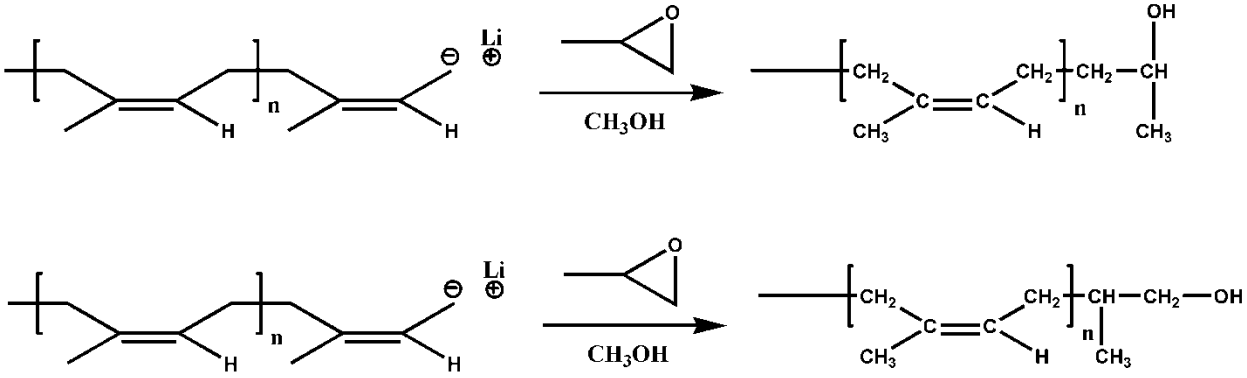
One of the drawbacks of ATRP is its inability to polymerize isoprene. As such, anionic polymerization was used to synthesize polyisoprene. Unlike ATRP, anionic polymerization does not result in halogen terminated polymers. Therefore, different approaches must be used to synthesize "clickable" polymers. Though anionic polymerization does not yield a halogen group with which perform chemical manipulation, anionic polymers do provide a reactive end-group in the form of an anion.

In order to fully understand anionic polymerization, several model reactions were performed. TMS-terminated polystyrene was synthesized in benzene using *n*-butylithium as the initiator. The aforementioned polymer was characterized by NMR and SEC. Benzene was used because non-polar solvents help to keep the ion pair "tight". The "tighter" the ion pair, the slower the rate of propagation. It's also worth noting that the size of the counter ion, lithium in this case, plays an important role in the rate of propagation. Lithium was chosen because it is a small counter ion and thus keeps the ion pair "tight" and helps to control the rate of propagation.

Dibenzylamino-terminated polystyrene was synthesized as a second model reaction. The endcapper, N-benzylidenebenzylamine, was synthesized in a 77 % yield and characterized by NMR and Bp. The imine was purified by vacuum distillation (155-156 ^{o}C (5 mm Hg) [lit. 119-120 ^{o}C (0.1 mm Hg)[85]]. The low yield was due to problems with bumping during the vacuum distillation. Polystyryl lithium was synthesized in the same manner as TMS-terminated polystyrene. N-Benzylidenebenzylamine was added to the polystyryl lithium anion and the resulting dibenzylamino-terminated polystyrene was characterized by NMR and SEC. M_{nNMR} = 7.1 kDa, M_{nGPC} = 7.4 kDa, M_w/M_n = 1.50.

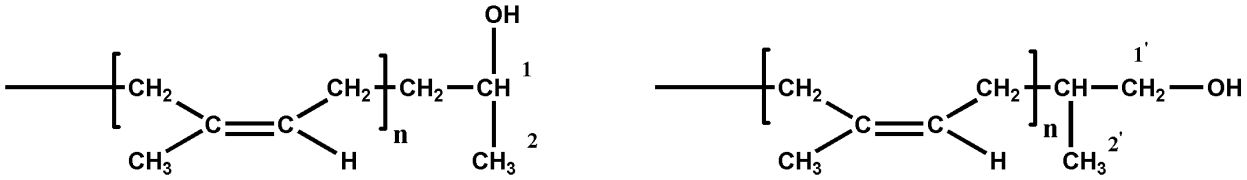
Various molecular weight hydroxyl-terminated polyisoprene were successfully synthesized using *sec*-butyllithium as the initiator and propylene oxide as the end-capper. An aliquot was removed prior to addition of propylene oxide for all polymers. SEC analysis was performed on all base polymers and hydroxylated polymers (Table 3). The degree of chain-end functionality was determined via flash column chromatography. Quantification of functional and unfunctional polymer was determined by collecting the fractions and weighing them.

Scheme 22: Two possible regiochemistries at the chain end in the reaction between poly(isoprenyl)lithium and propylene oxide



Further assessment of functionality was made by ^{1}H and ^{13}C NMR. It should be noted that Quirk et al. identified NMR peaks for propylene oxide terminated polystyrene, thereby providing precedent for NMR assessment on propylene oxide terminated polyisoprene.[89] The ^{1}H NMR spectrum of hydroxylated polyisoprene displays one broad peak at 3.75 ppm. The aforementioned signal corresponds to the methine proton on the carbon atom adjacent to the hydroxyl group. Although propylene oxide presents two different modes of attack (Scheme 22), the presence of only one broad signal at 3.75 suggests that only one regiochemistry was formed at the propylene oxide chain end. This is explained by steric hindrance of the methyl group on propylene oxide.[90] As a result, attack on the least substituted carbon is the preferred reaction pathway. Furthermore, a peak present 1.10-1.20 ppm is indicative of the methyl group on the propylene oxide chain end based on chemical shift and an integration value of 3. ^{1}H NMR chemical shift assignments can be seen in Table 5.

Table 5: ^{1}H and ^{13}C NMR chemical shift assignments



	^{1}H NMR Chemical Shift (ppm)	^{13}C NMR Chemical Shift (ppm)
1	3.75	65.9
2	1.10-1.20	23.3-24.6
1'	Overlapped	67.9
2'	Overlapped	14.3

The ^{13}C NMR spectrum of hydroxylated polyisoprene contains peaks at 14.3, 23.3-24.6, 65.9 and 67.6 ppm that do not appear in the spectrum of unfunctionalized polyisoprene. The peak present at 65.9 ppm is indicative of the methine carbon (1) adjacent to the hydroxyl group. The signal at 23.3-24.6 ppm corresponds to the methyl group (2) on the propylene oxide chain end. According to Quirk et al. the signals at 67.9 and 14.3 ppm represent the methylene carbon (1') and methyl group (2') on the propylene oxide chain end that results from the second mode of attach on the propylene oxide.[89] If two regiochemistries are present on the chain end, one would expect to see a second signal for the methylene protons (1') in the ^{1}H NMR spectrum at 3.7-3.8. It is possible that the expected second peak is overlapped with the broad methine proton from the preferred chain end regiochemistry. ^{13}C NMR shift assignments can be seen in Table 5.

Hydroxyl-terminated polyisoprene was used to synthesize chloro and bromo-terminated polyisoprene. Early attempts to synthesize halogen-terminated polyisoprene were attempted using 2-chloroacetyl chloride and bromoisobutyryl bromide. The ^{1}H and ^{13}C NMR spectra reveal side reactions, suggesting that the acylating agents were too reactive. As such, 11-chloroundecanoyl chloride and 11-bromoundecanoyl chloride were used as acylating agents. 11-Bromoundecanoyl chloride and 11-chloroundecanoyl chloride were synthesized from their corresponding carboxylic acids using thionyl chloride. The acyl chlorides were used for the esterification reaction with hydroxyl-terminated polyisoprene directly. The ^{1}H NMR spectra contain a signal at 3.8-3.9 ppm that represents the methine group adjacent to the carbonyl. The signals at 3.78 ppm and 3.65 ppm represent the methylene group adjacent to the chloride and bromide, respectively. The reaction time was increased with the increasing molecular weight polymers.

Using the aforementioned halogen-terminated polyisoprene, it becomes possible to synthesize azido-terminated polyisoprene. As with the ATRP polystyrene, substitution with sodium azide yielded azido-terminated polyisoprene. The azido-terminated polyisoprene was characterized by NMR, SEC and IR. SEC showed controlled molecular weights with PDI ≤ 1.50. The ^{1}H NMR spectra reveal the CH_2-N_3 signal at 3.5 and no signal resulting from the CH_2-Br (3.65) in the starting material. This lack of a CH_2-Br signal suggests complete end-group conversion. IR spectroscopy shows a signal at ~2300 cm^{-1} resulting from the N_3 vibration.

Test reactions of polystyryl and polyisoprenyl lithium anion with *o*-bromomethyl anisole were performed. These reactions were studied to determine the viability of reactions between living polymer anions with bromomethyl functionalized crown ethers. ^{1}H NMR spectroscopy was used to analyze the products. Although the results suggest that reactions on bromine functionalized crown ethers with anionic polymers are possible, no further reactions were performed.

Several molecular weight polystyrene-polyisoprene block copolymers were synthesized using traditional anionic polymerization techniques. A high molecular weight (M_{nGPC} = 102.1 kDa) polystyrene-polyisoprene block copolymer (46:54 wt. %) is of particular interest. The goal of the high molecular weight block copolymer was to witness phase separation. DSC showed T_g's at -74 ^oC and 91 ^oC for polyisoprene and polystyrene respectively. The ^1H NMR spectra possess both polystyrene and polyisoprene proton signals. A thin polymer film was made from solution (2 wt% in toluene) and the film was stained with OsO_4. TEM was performed on the resulting film. The TEM image shows well defined regions demonstrating lamellar morphology (PTEM 1).

The synthesis of C_{60} and Sc_3NC_{80} centered star polymers was attempted with polystyryl lithium and polyisoprenyl lithium. Mathis et al. demonstrated the synthesis of said star polymers on C_{60}.[87] The authors were able to demonstrate a maximum of 6 arms on the star polymer with some control over the number of grafts. However, there is no literature precedent for the use of Sc_3NC_{80} to create star polymers. When the aforementioned literature approach was attempted on Sc_3NC_{80}, only starting material was recovered. The failure of the reaction is most likely the result of the 6 electron transfer from the Sc_3N cluster inside the C_{80} cage. C_{60} acts as an electrophile due to the lack of electrons on the cage. As a result of the electron transfer, Sc_3NC_{80} is less of an electrophile then C_{60}. As such, the reaction conditions should be changed for the Sc_3NC_{80}. An increased reaction time may lead to reactions of the C_{80} cage

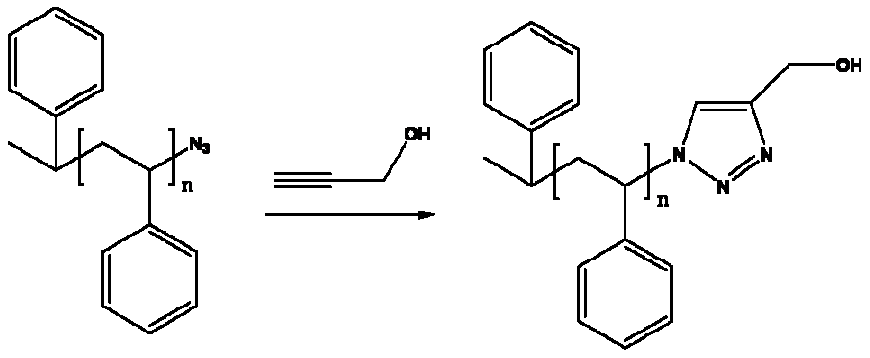
VI Click Reactions

VI.1.0 Experimental

Azido-terminated polystyrene [2] model click reaction (Scheme 23)

Azido-terminated polystyrene (3 kDa, 0.9 g, 0.3 mmol) **[2]**, CuBr (0.15 g, 1.0 mmol), and PMDETA (0.82 g, 2.0 mmol) were added to a dry round bottom flask under N_2. Previously degassed THF (9.0 mL) was added followed by degassed propargyl alcohol (0.06 g, 1 mmol). The reaction mixture was stirred overnight at room temperature. Polymer **[18]** was precipitated from THF into methanol (3x). M_{nGPC} = 3.0 kDa. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 1.05 (3H), 1.20-2.20 (155H), 6.30-7.30 (260H) (PNMR 21).

Scheme 23: Practice click reaction

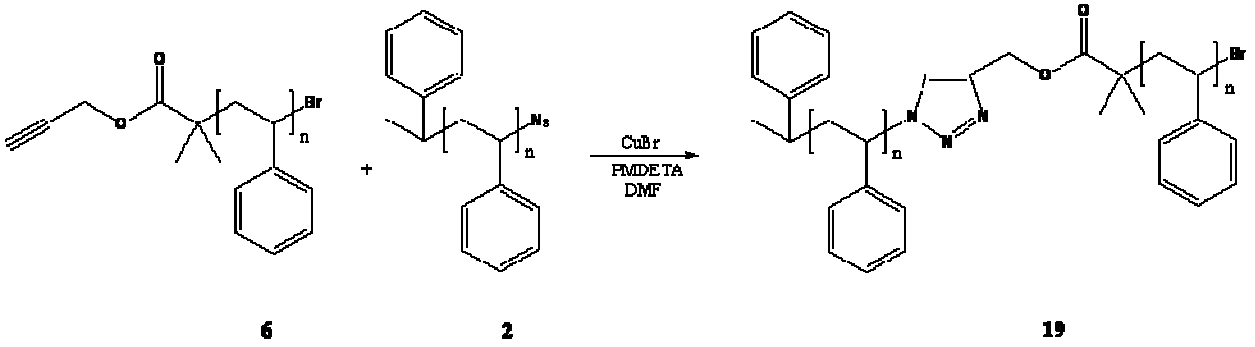


2 **18**

Polystyrene-Polystyrene click reaction [19] (Scheme 24)

Azido-terminated polystyrene (5.0 kDa) (1.0 g, 0.2 mmol) **[2**], CuBr (0.11 g, 0.6 mmol) and PMDETA (0.55 g, 1.2 mmol) were added to a dry round bottom under N_2. Previously degassed DMF (10 mL) was added followed by degassed alkyne-terminated polystyrene (4.6 kDa) (0.92 g, 0.2 mmol) **[6]**. The reaction mixture was stirred at room temperature under N_2 for 24 h. The polymer was precipitated into water and dissolved in THF. The polymer was then precipitated from THF into methanol (3x). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 1.00 (3H), 1.20-2.35 (325H), 6.25-7.40 (510H) (PNMR 22). A variety of molecular weights were synthesized (**Table 6**). All attempts to synthesize combined molecular weights of greater than 30 kDa proved unsuccessful.

Scheme 24: Polystyrene-polystyrene click reaction



6 2 19

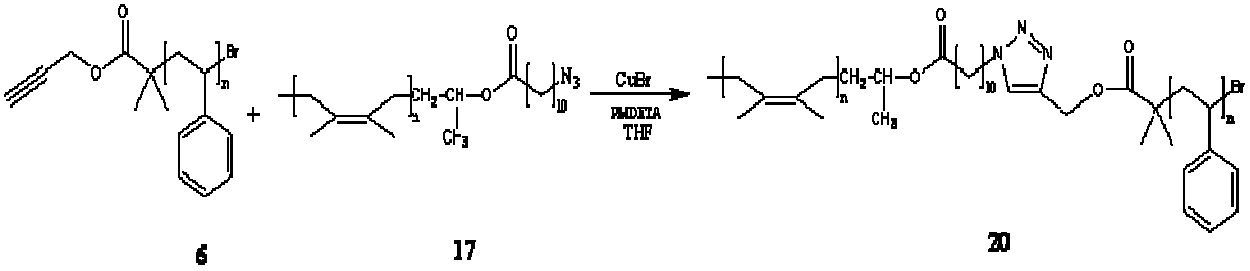
Table 6: Polystyrene-polystyrene $M_{n(GPC)}$

Polystyrene:Polystyrene (wt % ratio)	M_n of starting blocks (kDa)	M_n (kDa) of block copolymers
60:40	5.2:4.6	10.1
74:26	14.6:6.0	21.2

"Clicked" polyisoprene-polystyrene block copolymers (Scheme 25)

Alkyne-terminated polystyrene (12.5 kDa) (1 g, 0.08 mmol), CuBr (34 mg, 0.24 mmol) and azido-terminated polyisoprene (8.1 kDa) (0.65 g, 0.08 mmol) were dissolved in 5 mL of THF. PMDETA (41 mg, 0.24 mmol) was added to the reaction flask via a degassed syringe. The reaction mixture was stirred for 96 h under N_2 protection. The reaction mixture was precipitated from THF into methanol (3x), dissolved in chloroform and passed through an alumina column to remove residual CuBr. This reaction was attempted at several molecular weights (**Table 7**). Attempts to synthesize block copolymers with combined molecular weights of greater than 30 kDa proved unsuccessful. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 0.8-0.9 (3H), 1.2-2.4 (913H), 4.6-4.8 (19H), 5.0-5.2 (94H), 6.3-7.3 (678H) (PNMR 23).

Scheme 25: Polystyrene-polyisoprene click reaction



6 17 20

Table 7: Polystyrene-polyisoprene $M_{n(GPC)}$

Polystyrene:Polyisoprene (wt % ratio)	M_n (kDa) of starting blocks	M_n (kDa) of block copolymers
35:65	6.1:3.7	10.6
81:19	14.6:3.4	21.8
65:35	12.5:8.1	23.4

Small molecule "click" linker [21] (Scheme 26)

Propiolic acid (8.4 g, 0.14 mol) was added to a solution of 1,10-decanediol (10.0 g, 0.057 mol) in toluene (150 mL). The solution was heated at reflux for 5 days using a modified Dean Stark trap. Toluene was removed via reduced pressure vaporization. TLC (1:1/Hex:EA) showed decanediol as well as the mono and di aducts. Column chromatography (1:1/Hex:EA) was used to separate the adducts. A yield of 9.6 g (61 %) of off white crystals was obtained. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 1.20-1.45 (13), 1.60-1.80 (4H), 2.85-2.95 (2H), 4.19-4.35 (4H) (PNMR 24).

Chain extended polymers using "click" linker [21] (Scheme 26)

The reaction was performed on both polystyrene and polyisoprene at several different molecular weights (Table 8).

Polystyrene [22]: Alkyne-terminated polystyrene (10.8 kDa, 5.84 g, 0.54 mmol) and 1,4-bis(azidomethyl benzene[91] (0.05 g, 0.3 mmol) were dissolved in 3 mL of THF. CuBr(0.12 g, 0.81 mmol) and PMDETA (0.14 g, 0.81 mmol) were added to the flask via a degassed syringe. The reaction mixture was stirred for 72 h under N_2. The reaction mixture was precipitated from THF into methanol (3x), dissolved in chloroform and passed through a alumina column to remove

residual CuBr. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 0.9-1.1 (3H), 1.2-2.4 (374H), 4.6-4.8 (19H), 6.2-7.6 (641H) (PNMR 25). Molecular weights of the polymers can be seen in Table 7.

Polyisoprene [23]: Azido-terminated polyisoprene (8.0 kDa, 5.0 g, 0.62 mmol) and decane-1,10-diyl dipropiolate (86 mg, 0.31 mmol) were dissolved in 3 mL of THF. CuBr(0.13 g, 0.90 mmol) and PMDETA (0.16 g, 0.90 mmol) were added to the flask via a degassed syringe. The reaction mixture was stirred for 72 h under N_2. The reaction mixture was precipitated from THF into methanol (3x), dissolved in chloroform and passed through a alumina column to remove residual CuBr. The polymer solution was then washed with water (3x). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 0.8-0.9 (3H), 1.2-1.5 (17H), 1.5-1.8 (183H), 1.8-2.2 (241H), 4.15-4.35 (16H), 4.40-4.45 (31), 4.65-4.85 (42) 5.0-5.2 (121H) (PNMR 26). Molecular weights of the polymers can be seen in Table 7.

Scheme 26: Polymer "click" reactions with small molecule linker

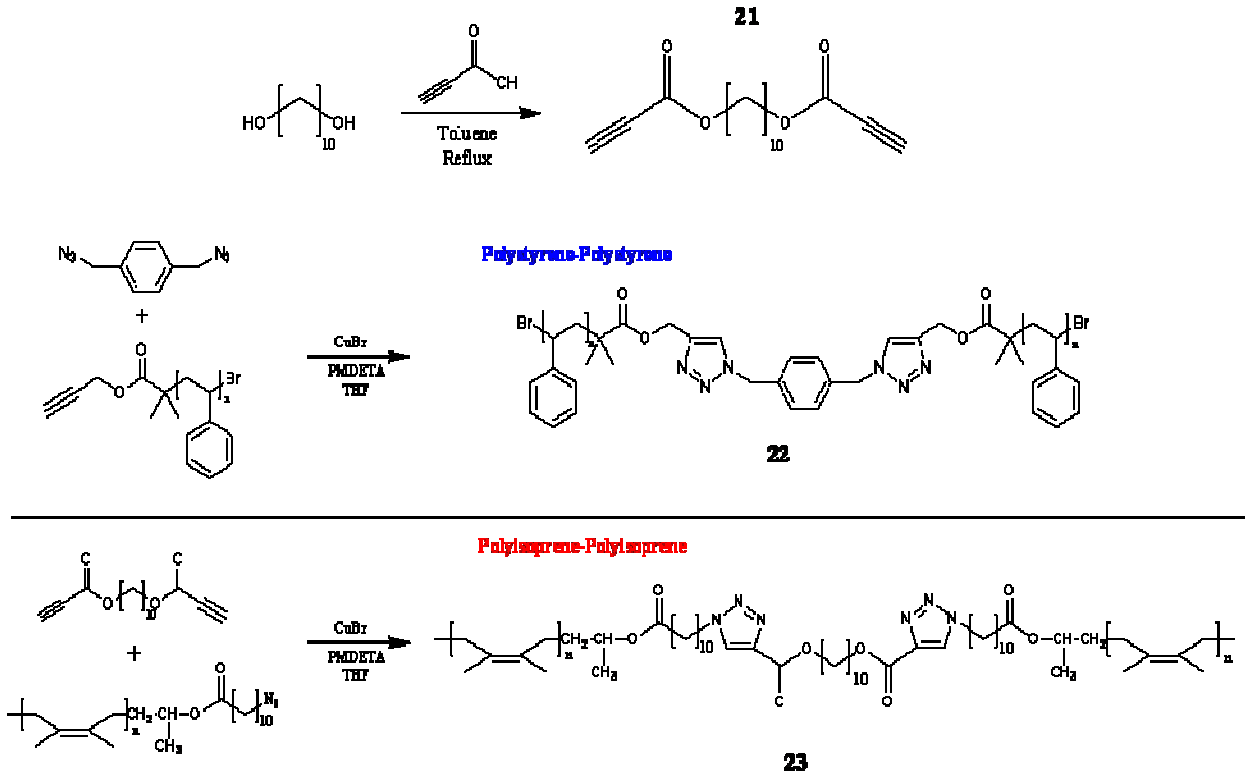


Table 8: $M_{n(GPC)}$ of chain extended hompolymers using "click" linker

Polymer	$M_{n(GPC)}$ (kDa) of starting polymer	$M_{n(GPC)}$ (kDa) of linked polymer
22	2.9	6.3
	5.2	9.8
	10.7	21.8
23	3.9	8.4
	6.0	13.9
	8.1	22.8

V.1.1 Results and Discussions

The final goal of this project is to synthesize "clicked" block copolymers**.** Having successfully synthesized alkyne and azide terminated polymers, click reactions to synthesize block copolymers becomes viable.

In order to properly evaluate the synthesis of "clicked" block copolymers, model reactions were performed. Azido-terminated polystyrene was reacted with propargyl alcohol to study the click reaction. Propargyl alcohol was chosen due to its relative ease of study when compared to polymer-polymer click reactions. CuBr was used to catalyze the click reaction giving the 1,4-regioisomer exclusively. PMDETA was used as a stabilizing ligand. The ^{1}H NMR spectrum of the model reaction product has a signal at 4.60 – 4.70 ppm corresponding to the proton adjacent to nitrogen on the triazole. A signal present at 5.0 – 5.15 ppm represents the proton next to the hydroxyl group. Furthermore the ^{1}H NMR spectrum shows no signals from the starting azide or alkyne. This lack of signals suggests a complete reaction with the polymer endgroup.

With a model click reaction between polymer-small molecule successfully performed, synthesis of "clicked" chain-extended homopolymers was investigated. Chain-extended polymers were investigated before block copolymers due to their relative ease of synthesis. Azido-terminated polystyrene was reacted with alkyne-terminated polystyrene to synthesize the aforementioned chain-extended homopolymer. Several molecular weights were synthesized and can be seen in Table 5. ^{1}H NMR was used to investigate the reaction products. The ^{1}H NMR spectrum showed a signal present at 4.80-4.90 ppm representing the proton adjacent to the nitrogen on the triazole. A peak present at 4.15-4.35 ppm represents the protons between the carbonyl and triazole. Since the proton adjacent to the bromine end group has a chemical shift between 4.1-4.4 ppm, it is difficult to differentiate the two signals. According to SEC, the molecular weight of the final product was approximately twice the molecular weight of the starting polymer. Furthermore, the proton signal next to the azide of the starting material does not appear in the spectrum for the products. This lack of signal suggests complete conversion to the triazole. Infrared spectroscopy was also used to investigate the chain-extended homopolymer. However, due to the relative size of the polymer compared with the functional group, IR does not allow for proper analysis.

Attempts to synthesize chain-extended homopolymers with a molecular weight ≥30 kDa proved unsuccessful. One possible explanation for the inability to synthesize high molecular weight "clicked" polymers is the inaccessibility of the polymer chain ends. It should also be noted that as the molecular weight of the polymer increased, reaction time had to be increased in order to achieve the desired clicked product.

With the results of the model click reactions in hand; the synthesis of "clicked" block copolymers was investigated. Alkyne-terminated polystyrene was reacted with azido-

terminated polyisoprene to synthesize block copolymers. As with the model reactions, all attempts to synthesize block copolymers with a molecular weight greater than 30 kDa proved unsuccessful. ^{1}H NMR spectroscopy demonstrated complete removal of the CH_2-N_3 proton peaks from the starting material as well as the signals appertaining to the protons adjacent to the triazole. As a result of the low molecular weight, DSC shows only one T_g at 73 ^{o}C, thus precluding phase separation.

In order to synthesize high molecular weight "clicked" block copolymers, a second route was investigated. Small molecule "click" linkers were used in an attempt to achieve higher molecular weights. 1,4-*Bis*(azidomethyl) benzene and decane-1,10-diyl dipropiolate were the chosen linkers. 1,4-*Bis*(azidomethyl) benzene was synthesized by Daniel Schoonover of the Gibson group. Decane-1,10-diyl dipropiolate was synthesized by the esterification reaction between 1,10-decanediol and propiolic acid. A Dean-Stark trap was used to help drive the reaction by removing the water side product. Even after exploiting the le Chatelier principle, column chromatography was required to separate the mono and di-adducts. The reaction could have been optimized to achieve higher yields. However, optimization was deemed unnecessary.

Azido-terminated polyisoprene was reacted with decane-1,10-diyl dipropiolate to synthesize chain extended polyisoprene. Alkyne-terminated polystyrene was reacted with 1,4-*bis*(azidomethyl) benzene to synthesize chain extended polystyrene. As with all previous click reactions, the synthesis of high molecular weight block copolymers proved unsuccessful. When high molecular weight polymers were used, ^{1}H NMR spectroscopy showed that only one side of the linker reacted. It is the belief of the author that the polymers react with one end of the linker first, thus creating a similar situation to the polymer click reactions previously performed. Inaccessible chain ends appear to be one of the main hurdles to synthesizing high molecular weight block copolymers by this method.

VII Conclusions and Future Work

In conclusion, a novel route to the synthesis of "clicked" polyisoprene-polystyrene block copolymers was successfully demonstrated. Azido-terminated polyisoprene can be synthesized using anionic polymerization methods coupled with end group manipulation. A new approach to the synthesis of hydroxyl-terminated polyisoprene using propylene oxide was established. The hydroxyl-terminated polyisoprene was then successfully reacted with both 11-chloroundecanoyl chloride and 11-bromoundecanoyl chloride to synthesize halide-terminated polyisoprene. With the aforementioned halide-terminated polyisoprene in hand, synthesis of azido-terminated polyisoprene was accomplished using a substitution reaction with NaN_3. ^1H NMR spectroscopy demonstrated complete end group conversion with NaN_3.

The synthesis of chain-extended "clicked" homo polymers was also demonstrated. Chain extended polymers can be synthesized using either a small molecule chain extender or by direct reaction of the functionalized polymers. With both the block copolymers and chain extended homopolymers, high molecular weight (≥ 30 kDa) was unobtainable. However, with lower molecular weight polymers, these methods prove an ideal route to the synthesis of "clicked" block and chain-extended polymers.

Future work is required to investigate the inability to synthesize high molecular weight block copolymers. High molecular weight "clicked" block copolymers could phase separate, thus providing interesting properties such as thermoelastisity. It is the belief of the author that inaccessible chain ends could be responsible for the failure to synthesize high molecular weights. Investigations into solvents that can unfold the polymers during the click reaction should be performed. Mass spectrometry, such as MALTI-TOF, should also be employed as a means of studying polymer end groups. Mass spectrometry should allow for a more in depth study of the polymer end groups.

Reactions of polymer anions with bromomethylanisole demonstrated the ability of the polymer anion to displace the bromine while leaving the methyl ester on the ring untouched. This may provide an ideal route to the synthesis of crown ether functionalized polymers. This direct and simple method would be very useful in the synthesis of supramolecular block copolymers.

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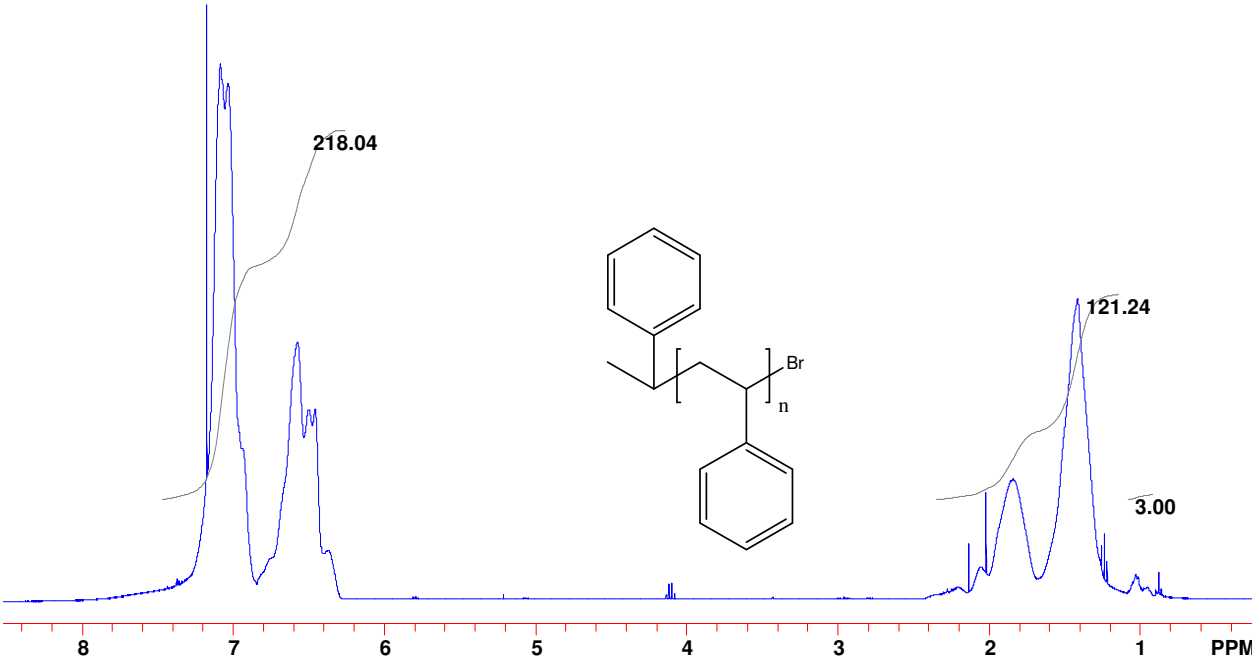
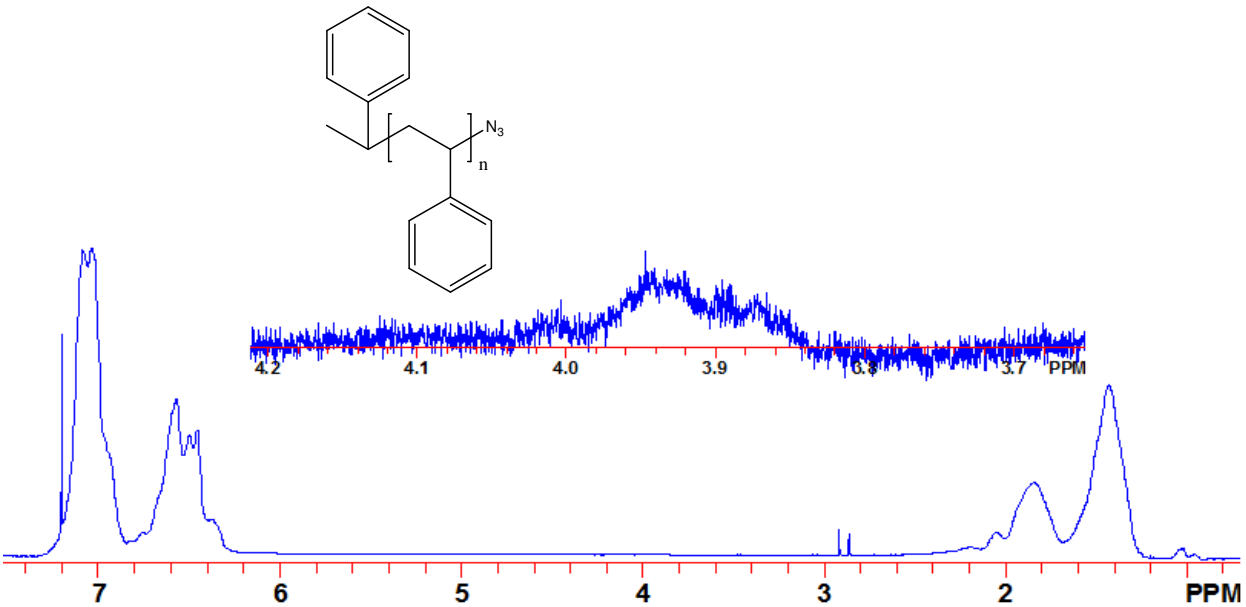
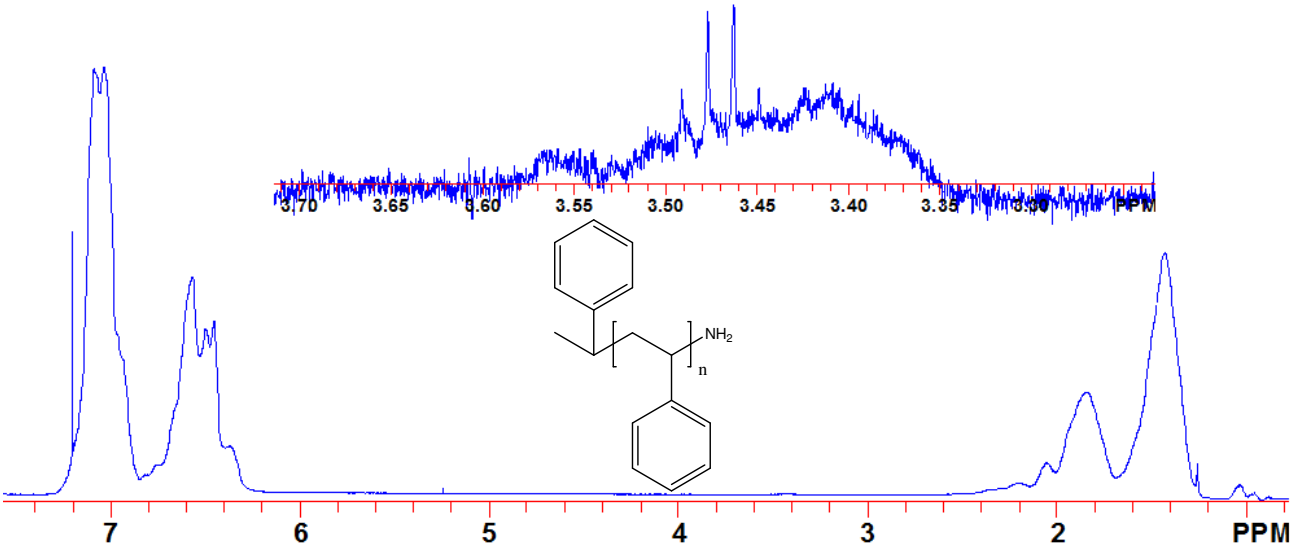
Appendix



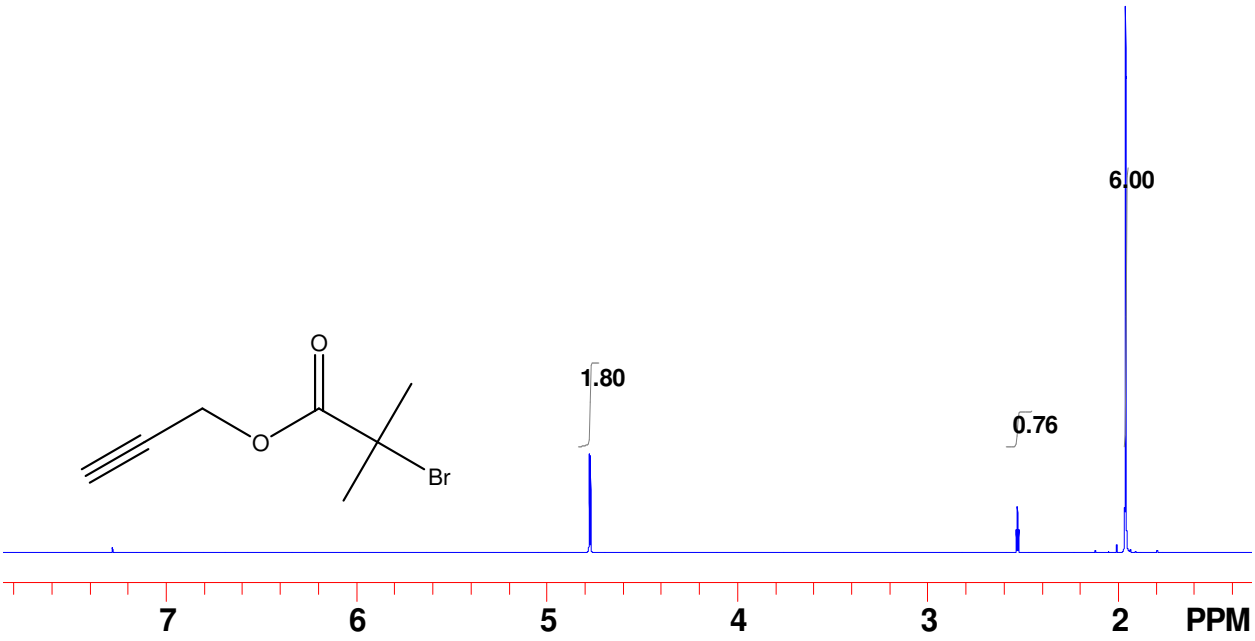
PNMR 1: 400 MHz ^{1}H NMR of polystyrene (4.5 kDa) in $CDCl_3$



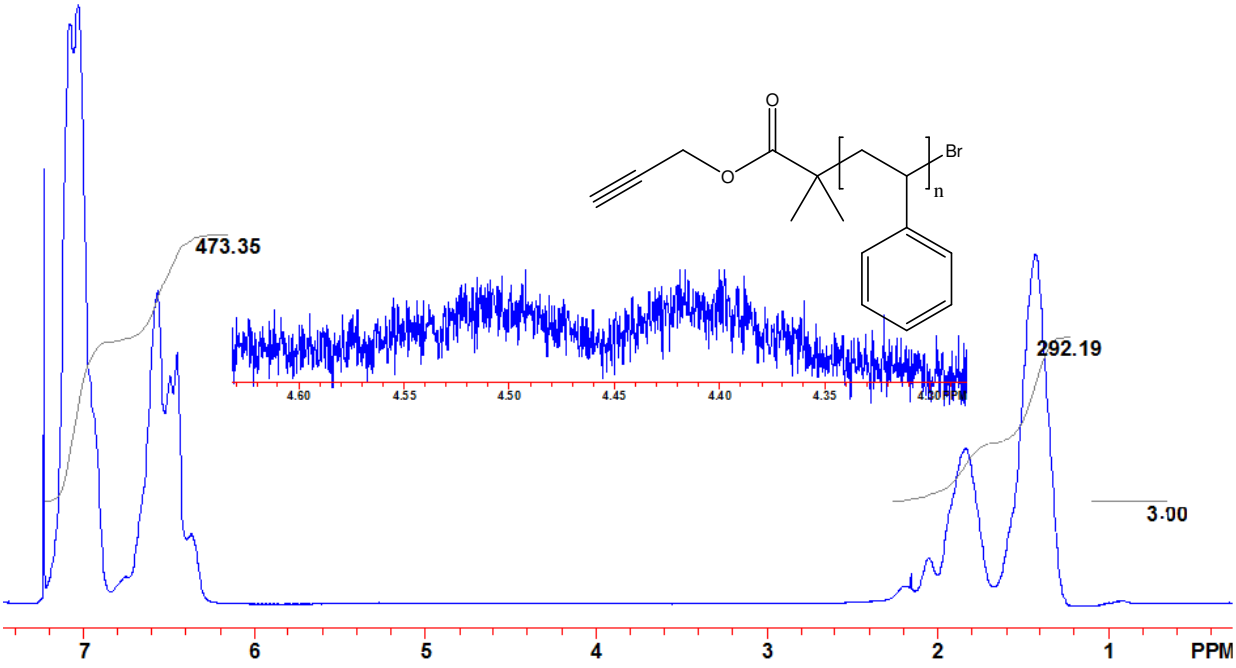
PNMR 2: 500 MHz ^{1}H NMR spectrum of azide-terminated polystyrene (4.7 kDa). Zoomed region corresponds to end group proton.



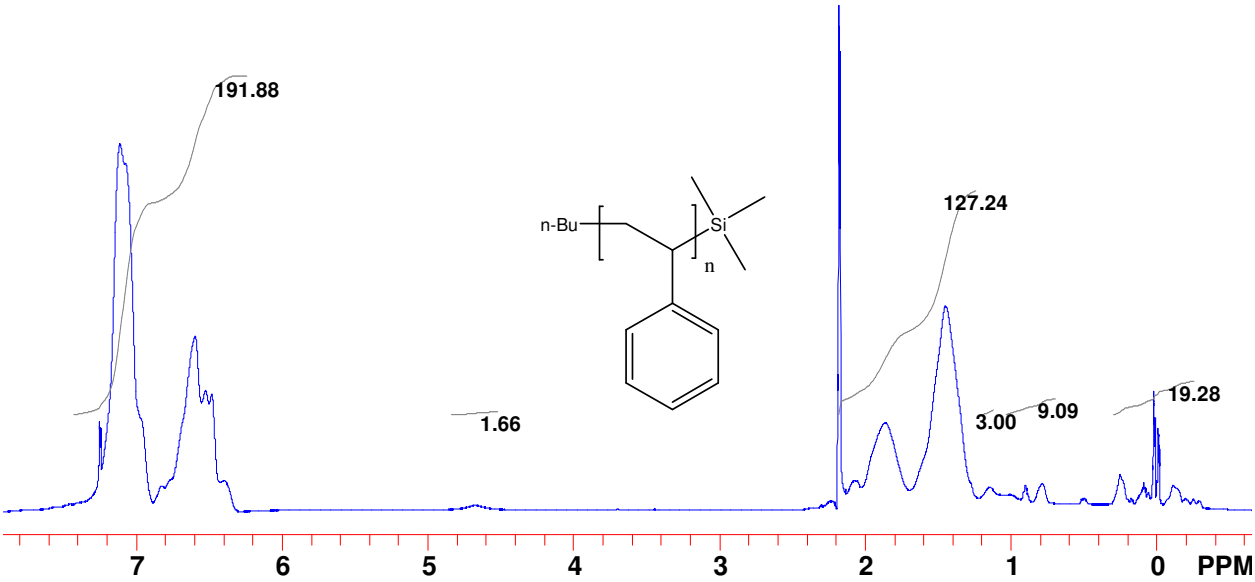
PNMR 3: 500 MHz ^{1}H NMR spectrum of amine-terminated polystyrene (5.1 kDa). Zoomed region corresponds to end group proton.



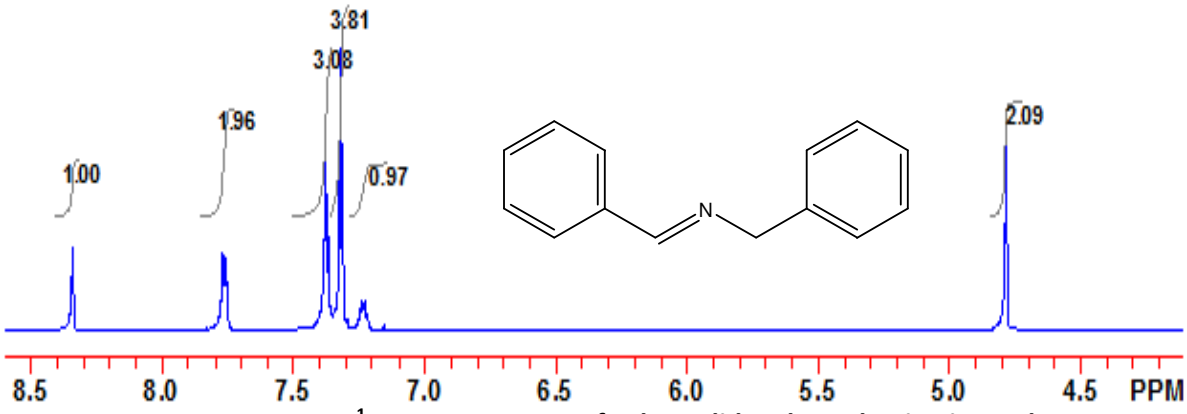
PNMR 4: 400 MHz ^{1}H NMR of propargyl 2-bromoisobutyrate in $CDCl_3$



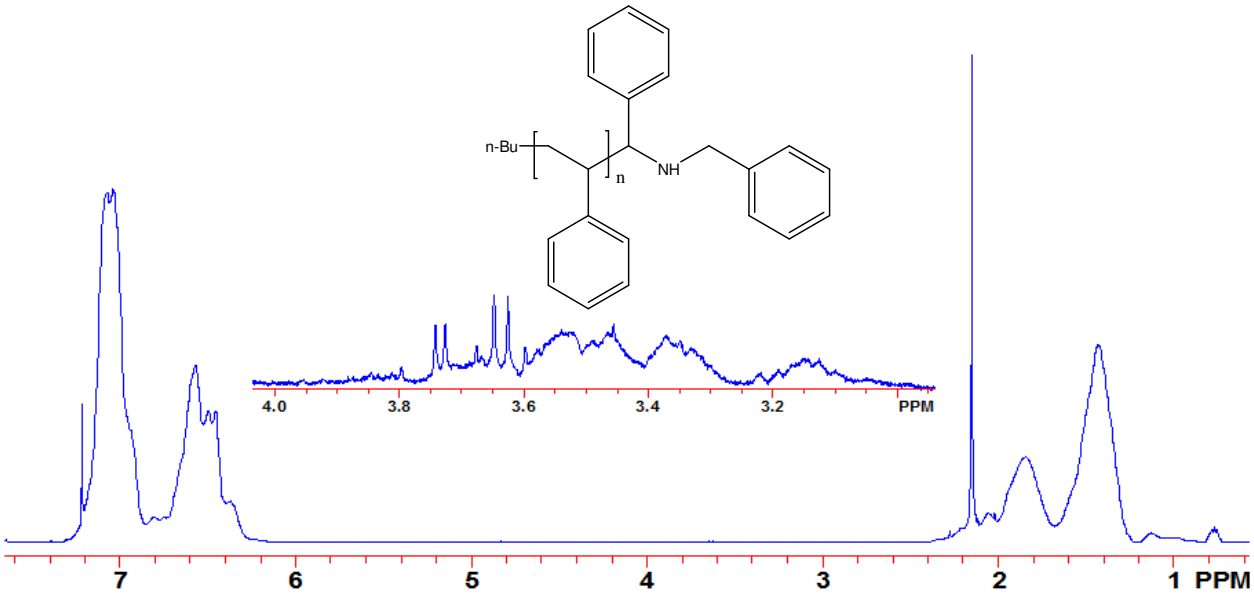
PNMR 5: 500 MHz ^{1}H NMR spectrum of alkyne-terminated polyisoprene (5.4 kDa) in $CDCl_3$.



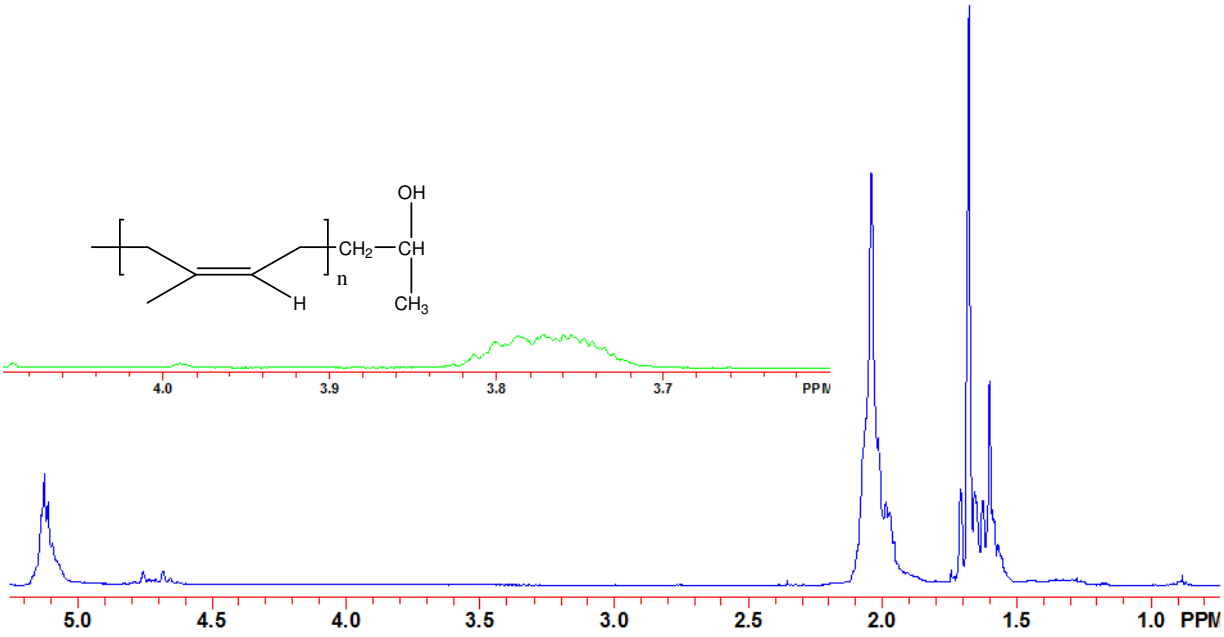
PNMR 6: 400 MHz ^{1}H NMR spectrum of TMS-terminated polystyrene (4.0 kDa) in $CDCl_3$.



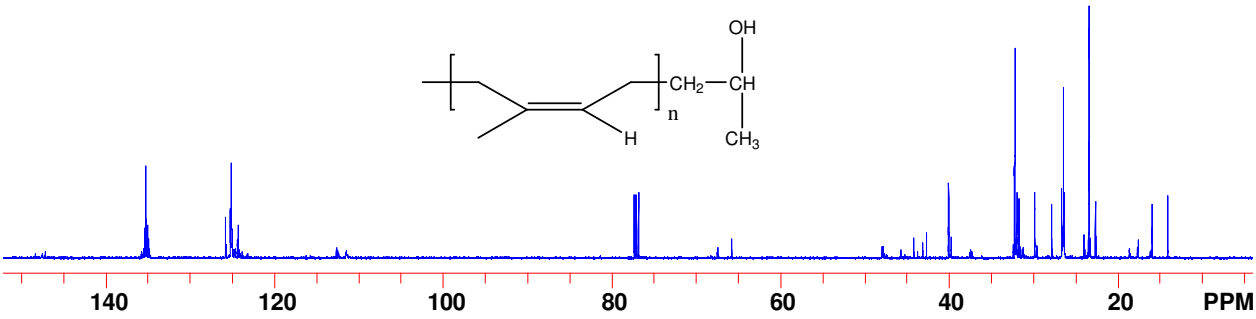
PNMR 7: 500 MHz ^{1}H NMR spectrum of N-benzylidenebenzylamine in $CDCl_3$



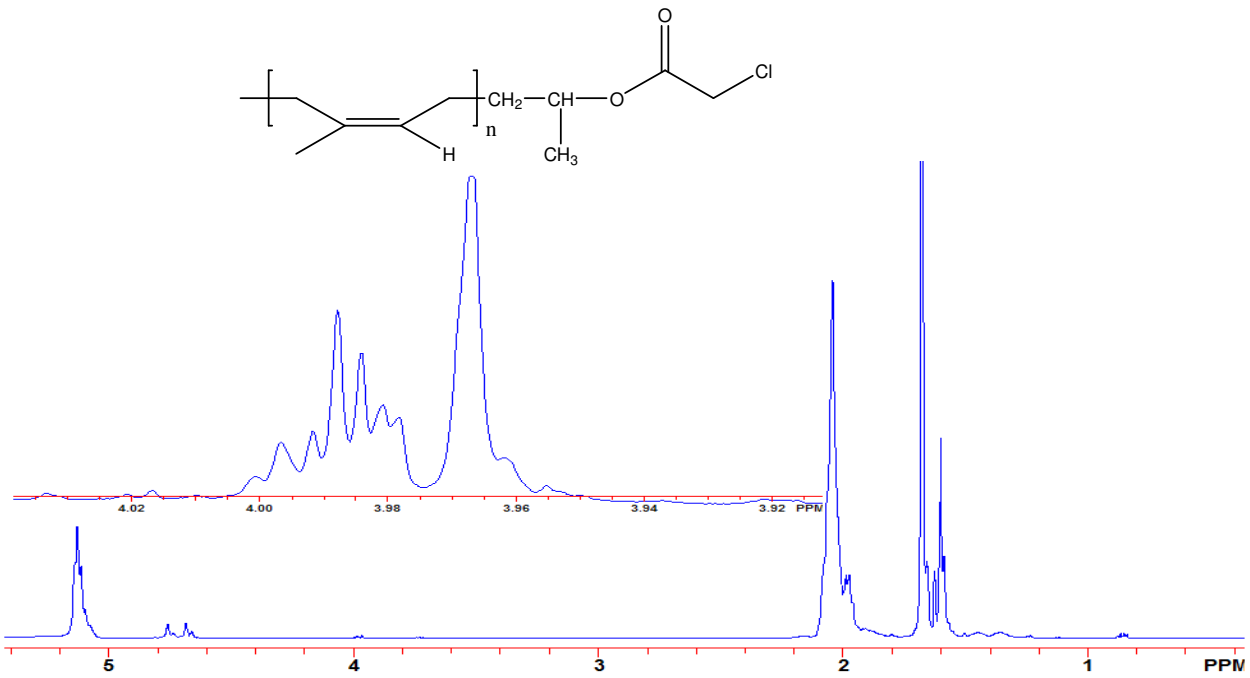
PNMR 8: 500 MHz ^{1}H NMR spectrum of dibenzylamino-terminated polystyrene (7.4 kDa) in $CDCl_3$. Zoomed region corresponds to dibenzylamino protons



PNMR 9: 500 MHz ^{1}H NMR spectra of hydroxyl-terminated polyisoprene (13.9 kDa) in $CDCl_3$.

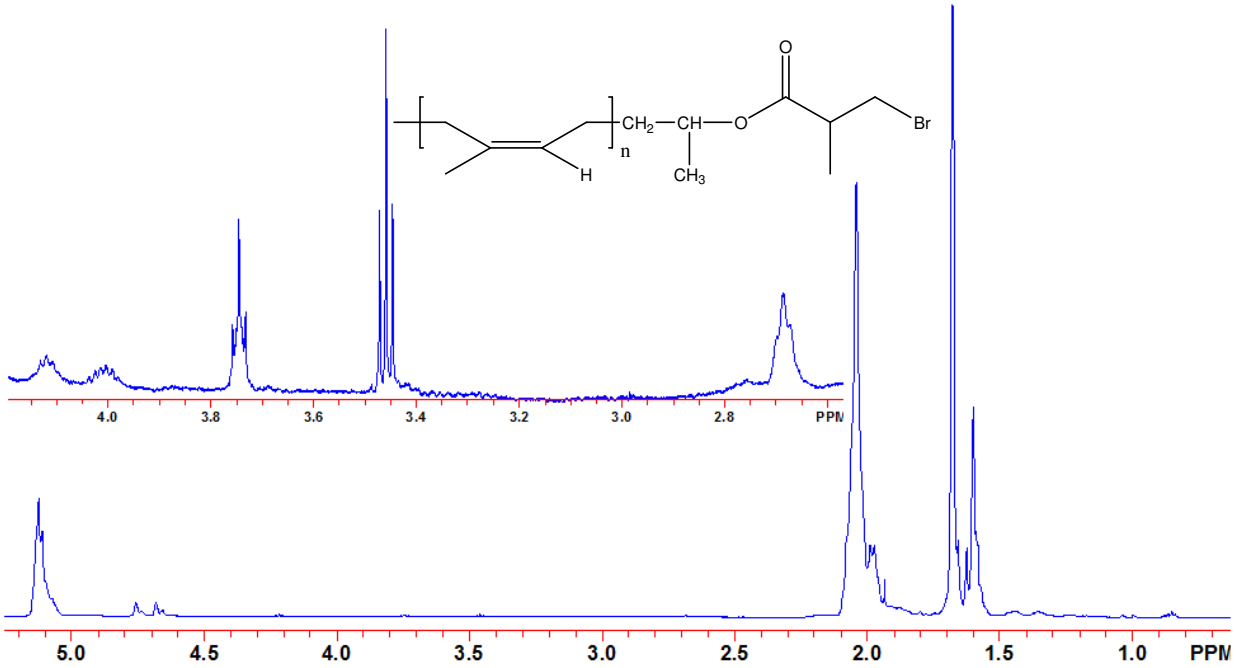


CNMR 10: 125 MHz ^{13}C NMR spectra of hydroxyl-terminated polyisoprene (13.9 kDa) in $CDCl_3$.

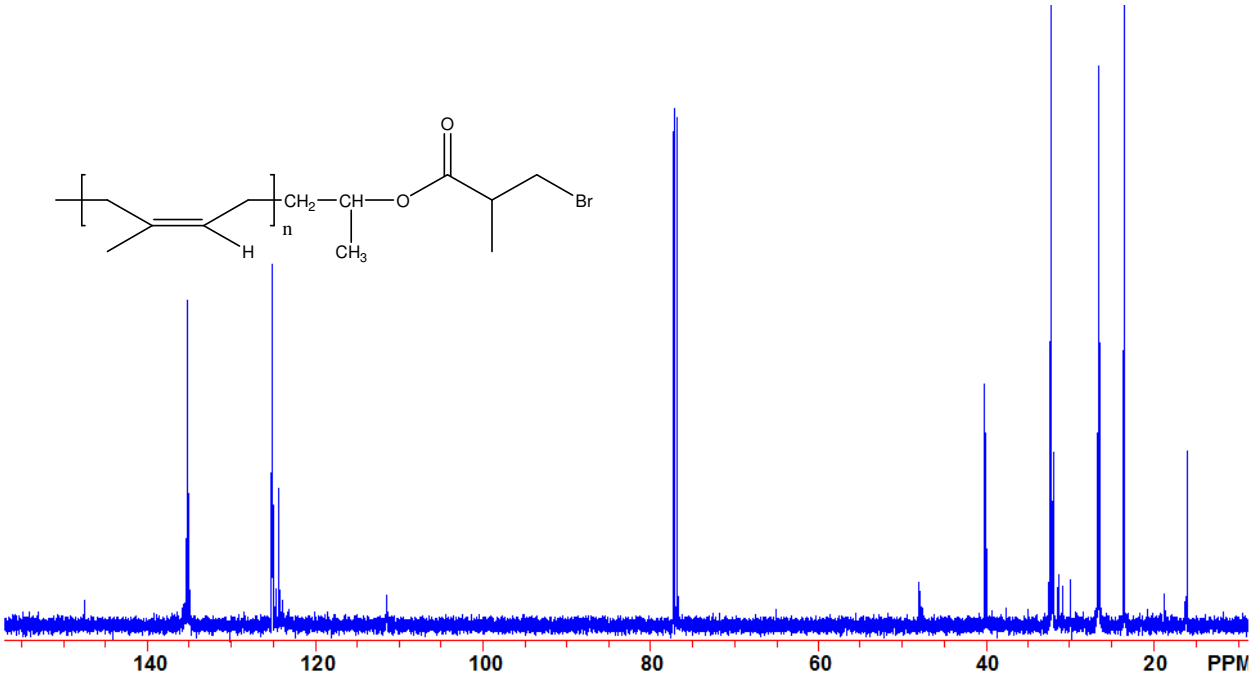


PNMR 11: 500 MHz ^{1}H NMR spectra of chloro-terminated polyisoprene (14.8 kDa) in $CDCl_3$.

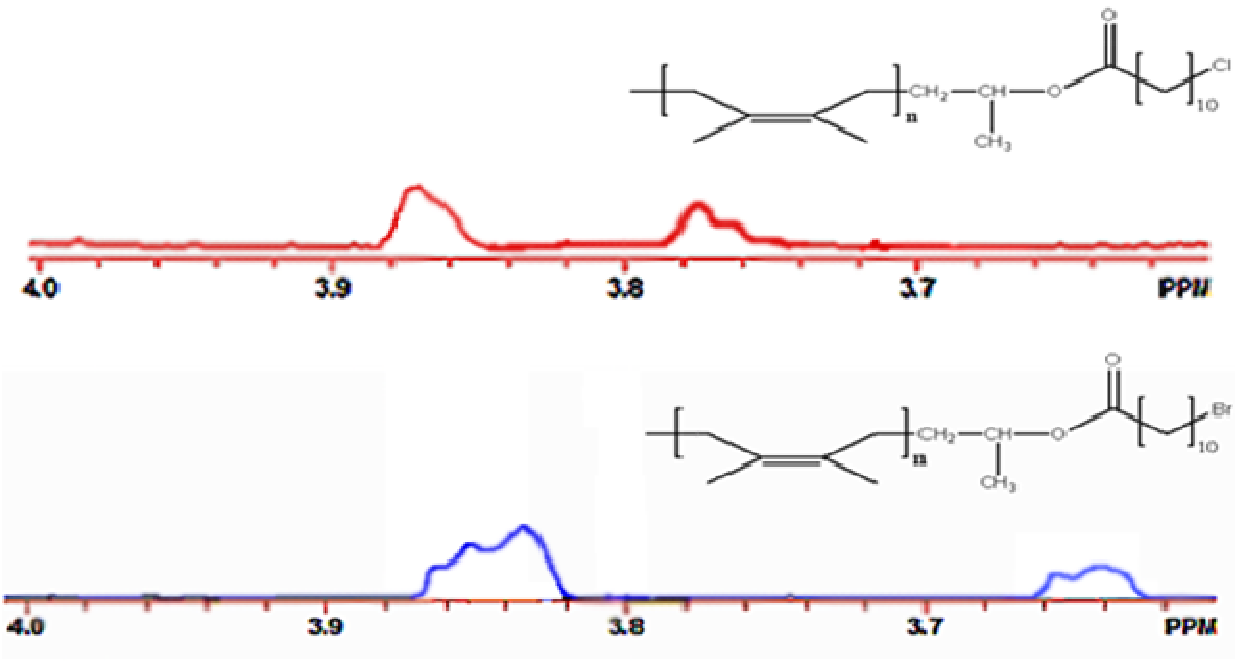
CNMR 12: 125 MHz ^{13}C NMR spectra of chloro-terminated polyisoprene (14.8 kDa) in $CDCl_3$.



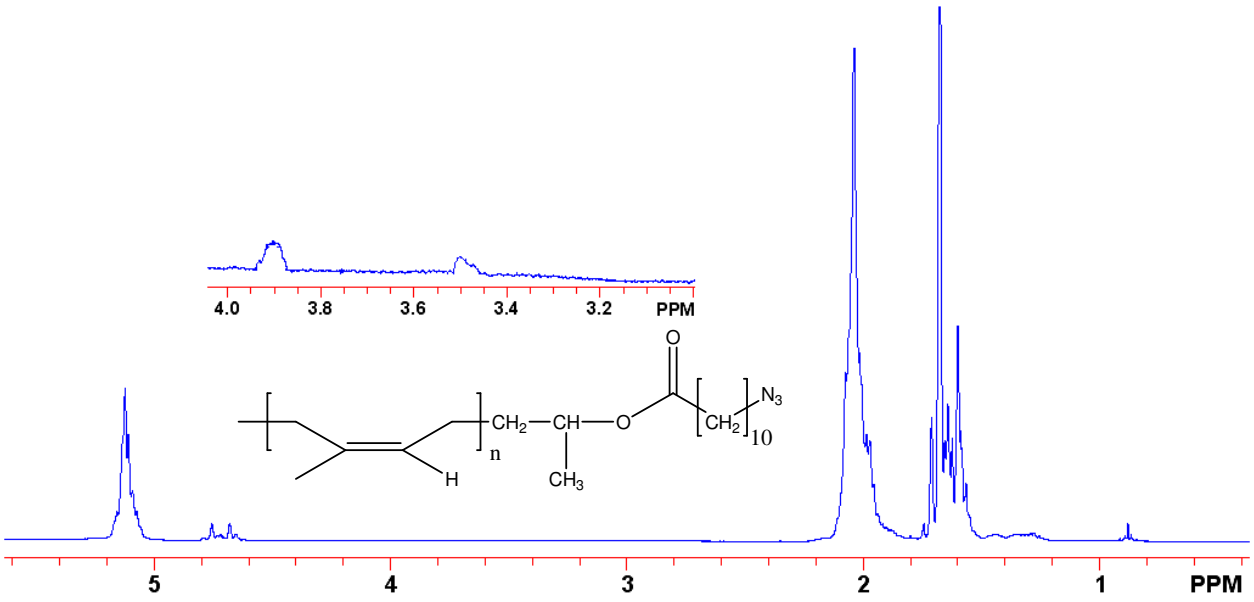
PNMR 13: 500 MHz ^{1}H NMR spectra of bromo-terminated polyisoprene (14.8 kDa) in $CDCl_3$.



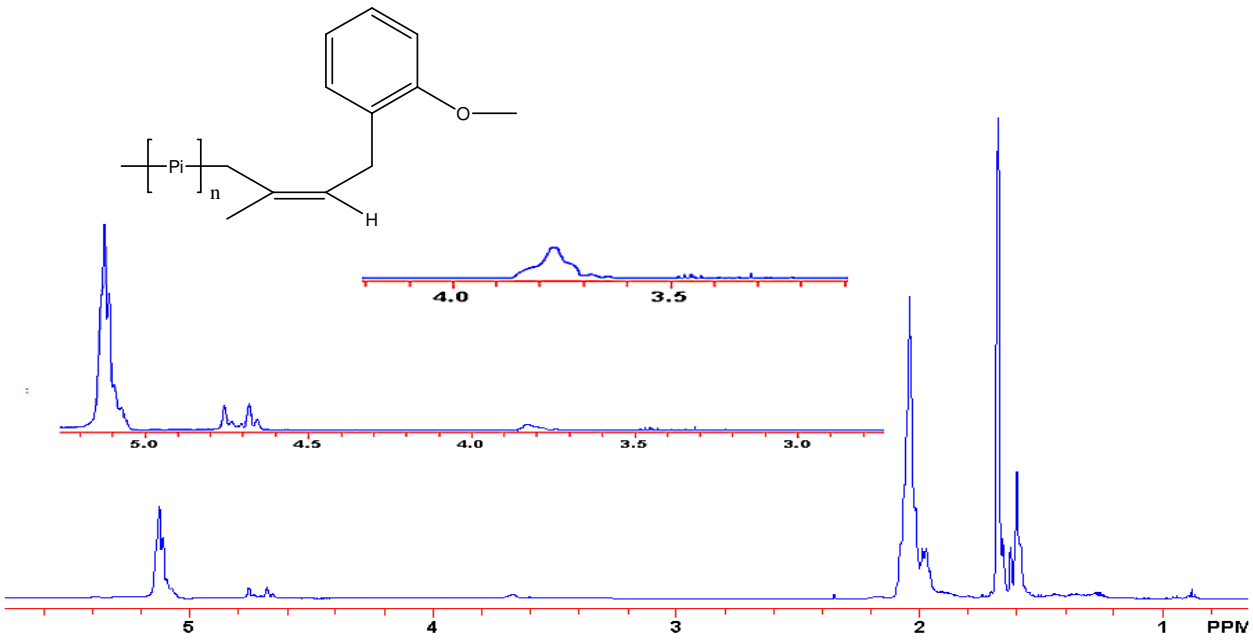
CNMR 14: 125 MHz ^{13}C NMR spectra of bromo-terminated polyisoprene (14.8 kDa) in $CDCl_3$.



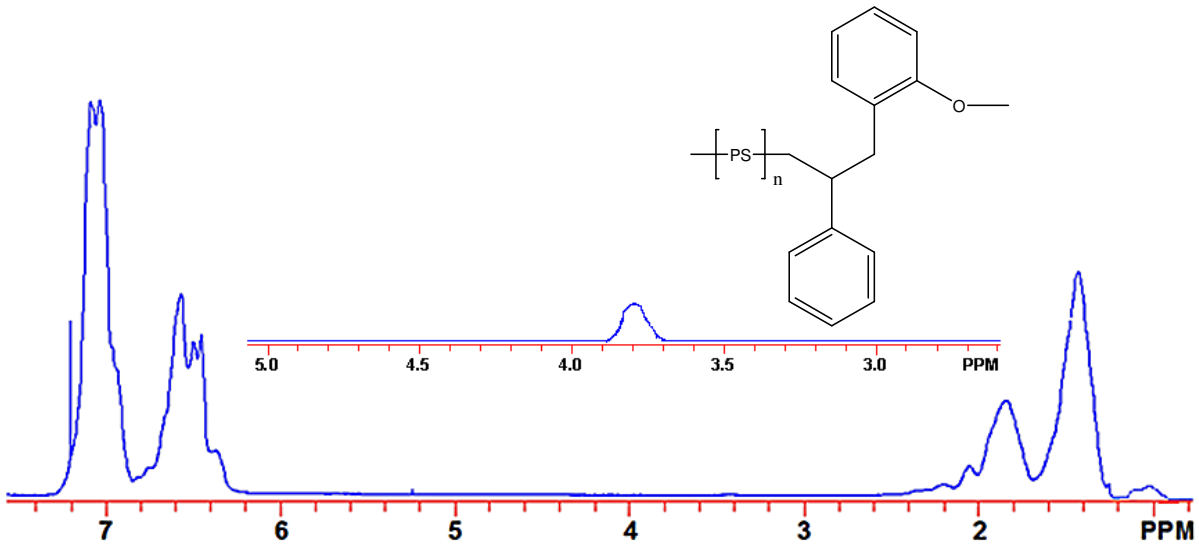
PNMR 15: Zoomed 500 MHz ^{1}H NMR spectra of chloro and bromo-terminated polyisoprene (14.8 kDa) from 11-haloundecanoyl chloride in $CDCl_3$



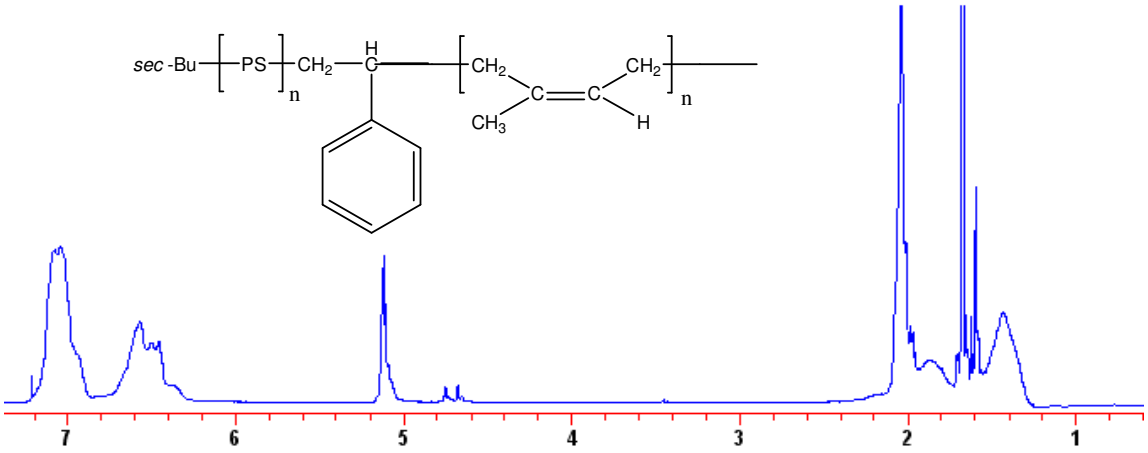
PNMR 16: 500 MHz ^{1}H NMR spectra of azido-terminated polyisoprene (8.1 kDa) in $CDCl_3$.



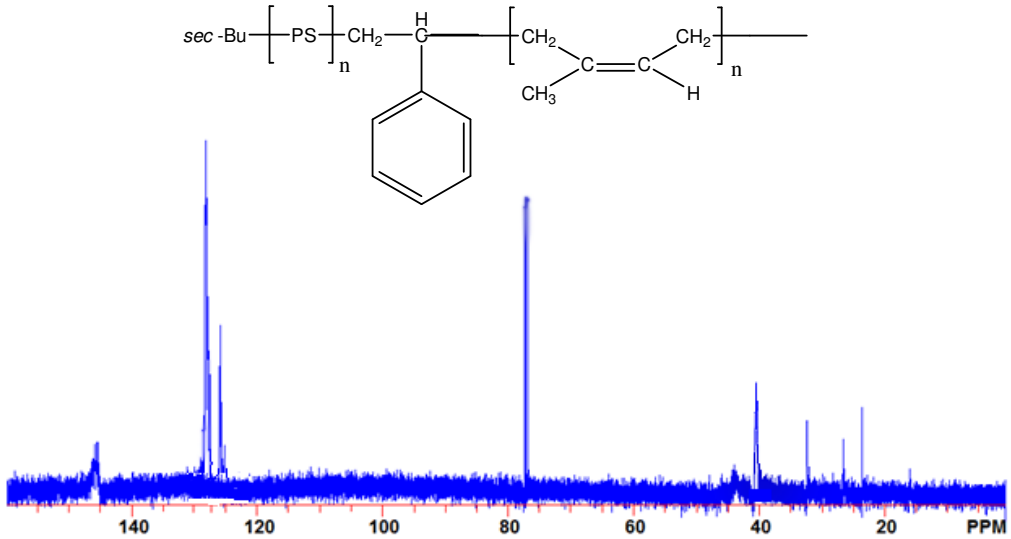
PNMR 17: 500 MHz ^{1}H NMR spectra of *o*-methyl anisole-terminated polyisoprene (3.1 kDa) in $CDCl_3$.



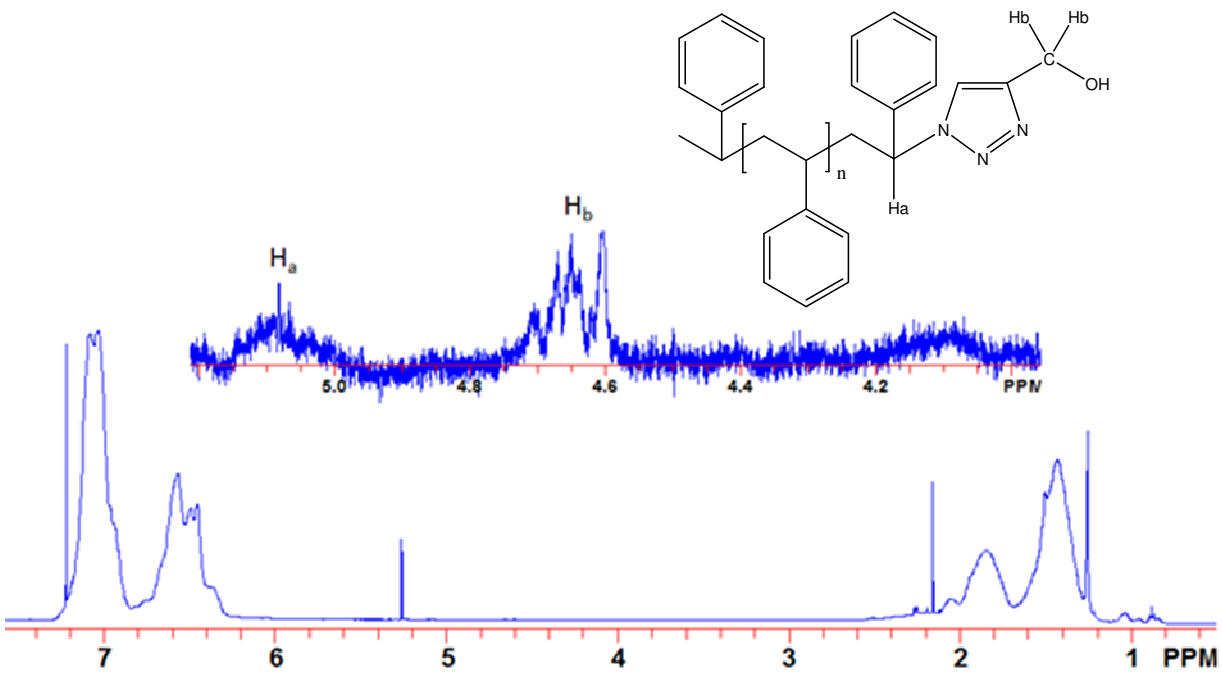
PNMR 18: 500 MHz ^{1}H NMR spectra of anisole-terminated polystyrene (4.9 kDa) in $CDCl_3$.



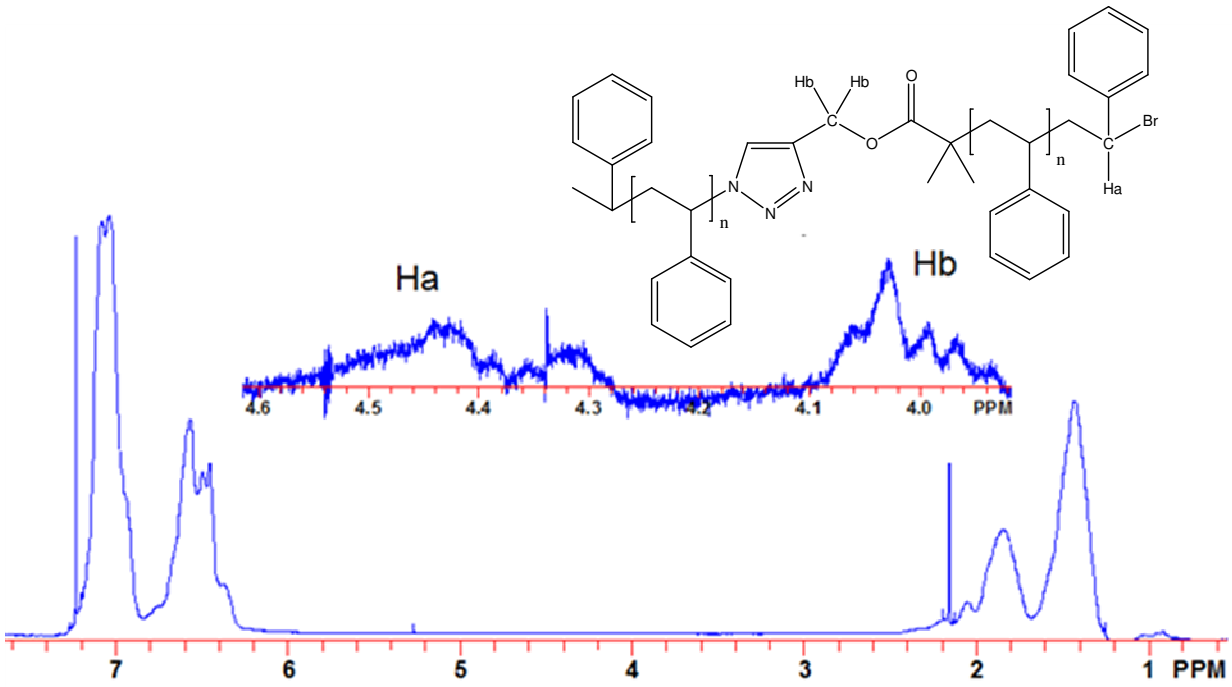
PNMR 19: 500 MHz ^{1}H NMR spectra of polyisoprene-polystyrene block copolymer (102.1 kDa) in $CDCl_3$.



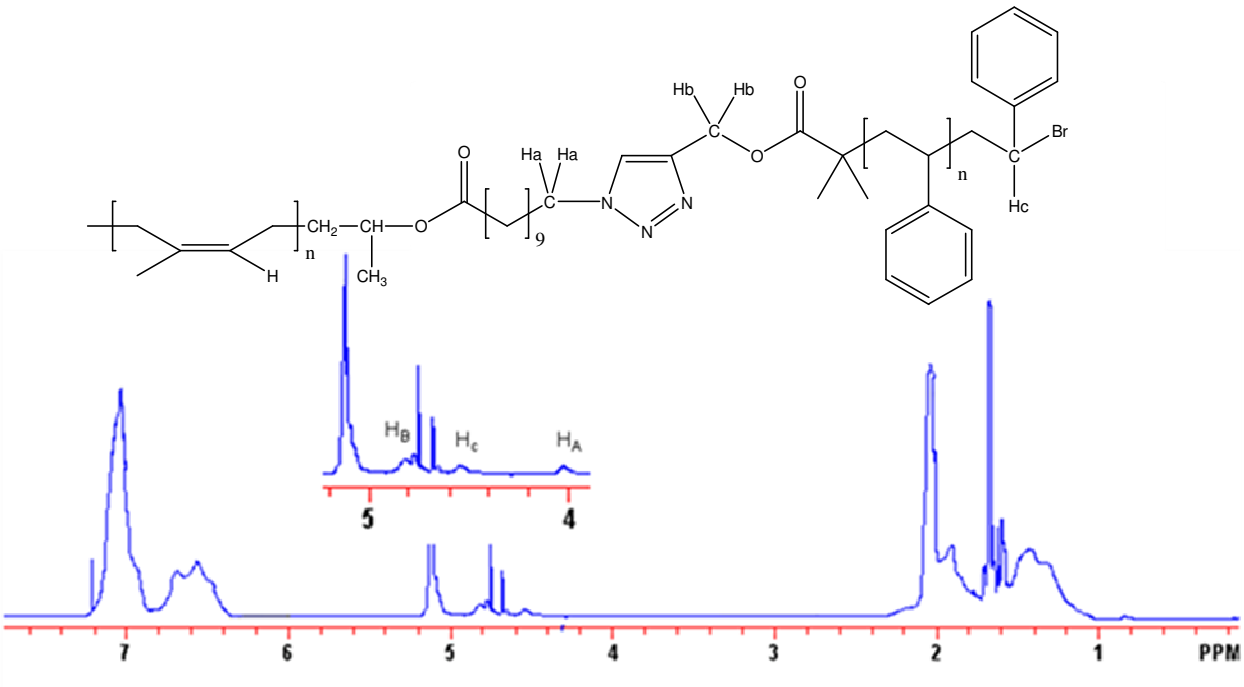
CNMR 20: 125 MHz ^{13}C NMR spectra of polyisoprene-polystyrene block copolymer (102.1 kDa) in $CDCl_3$.



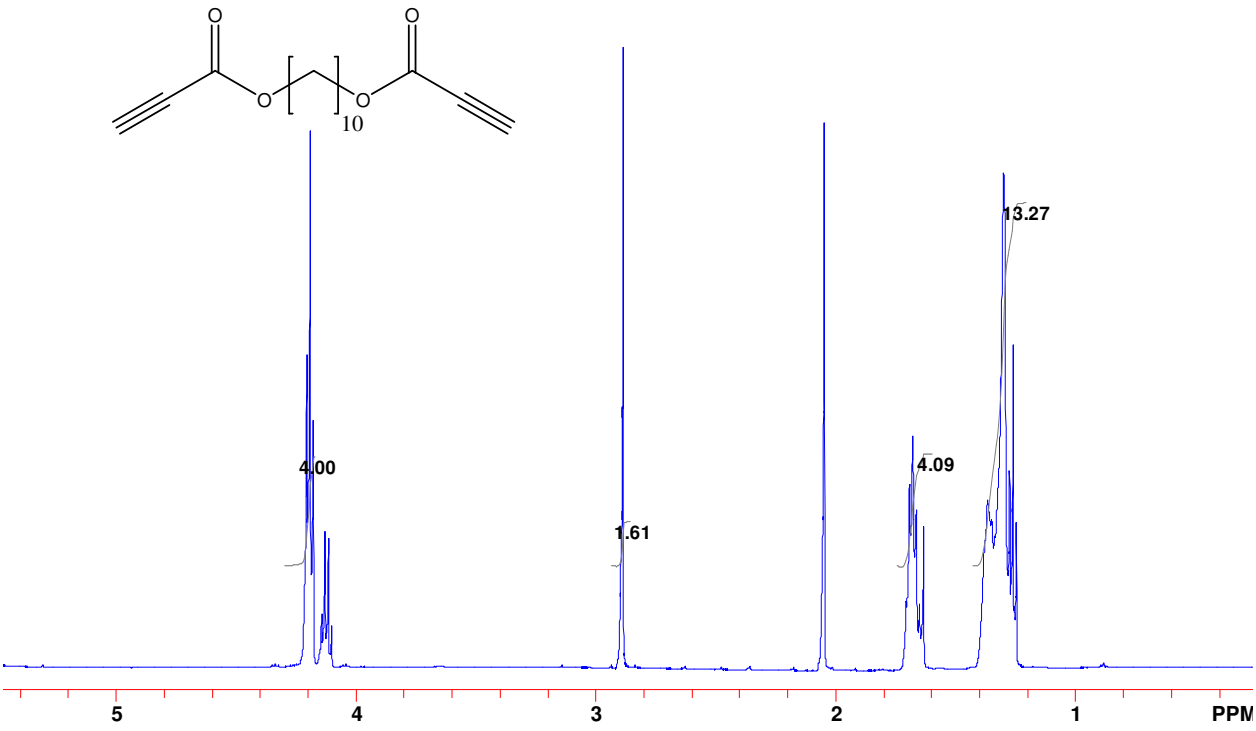
PNMR 21: 500 MHz ^{1}H NMR spectrum of practice click (3.0 kDa). Zoomed region corresponds to end group.



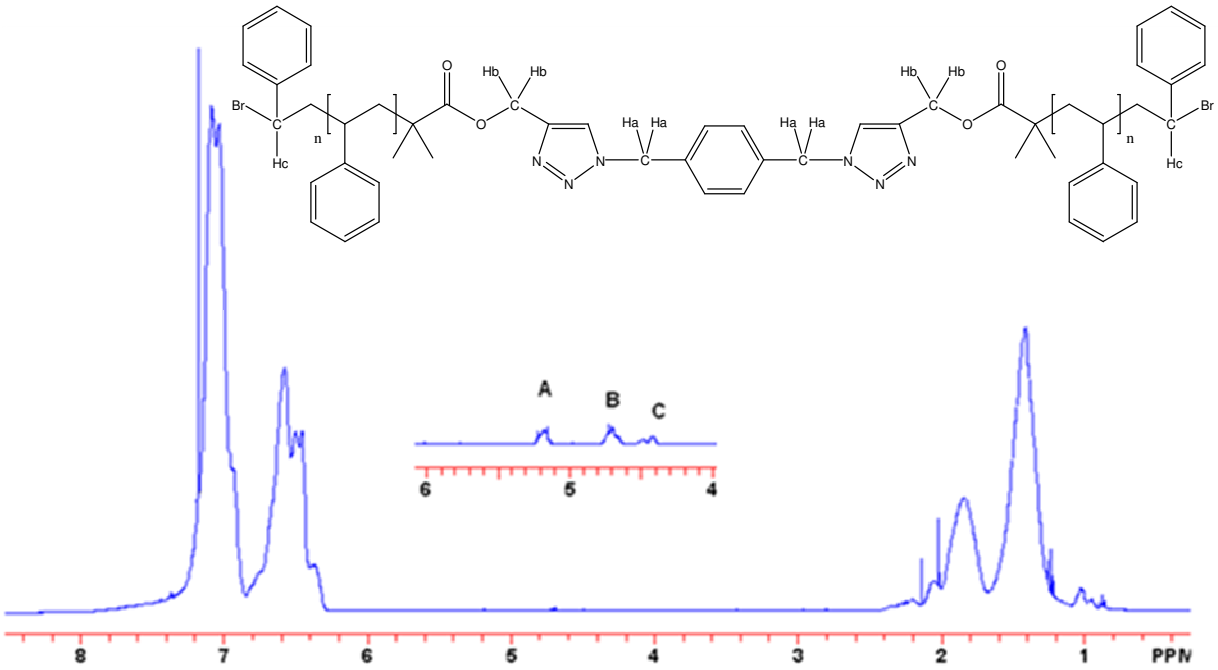
PNMR 22: 500 MHz ^{1}H NMR spectrum of PS-PS click reaction (24.2 kDa). Zoomed region corresponds to end group protons.



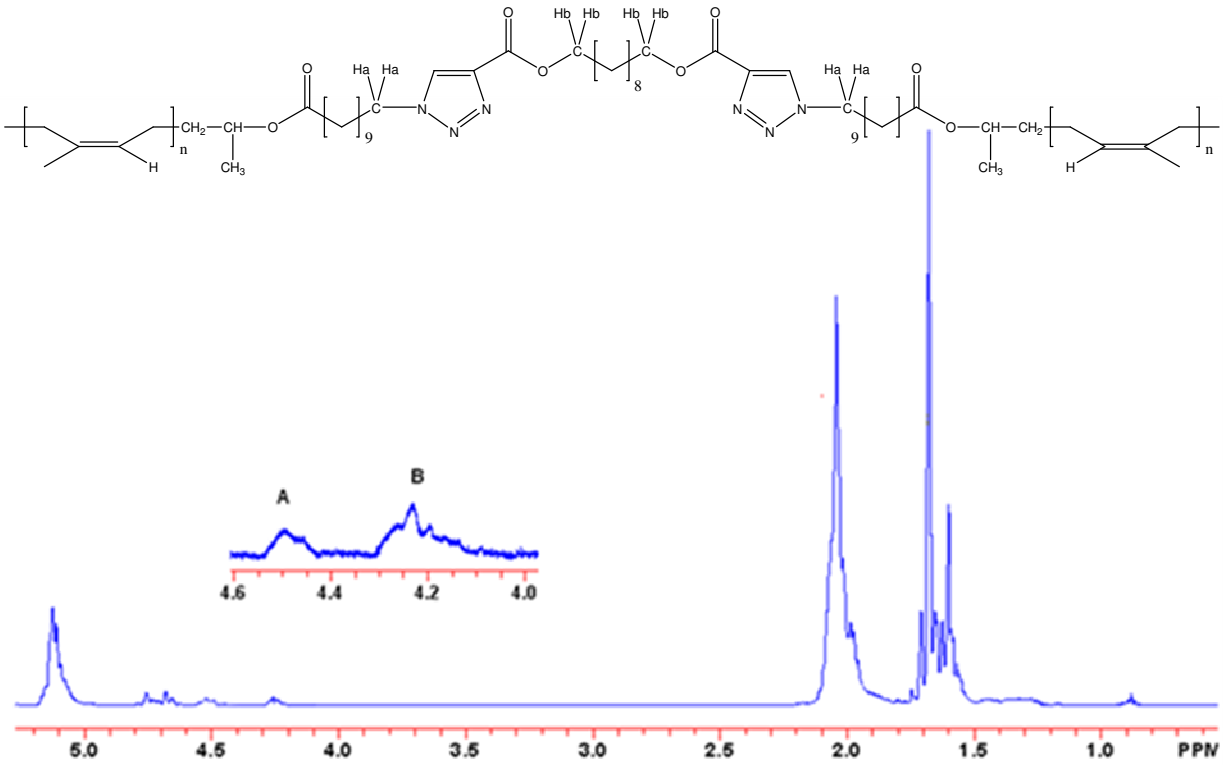
PNMR 23: 500 MHz ^{1}H NMR spectra of "clicked" polyisoprene-polystyrene block copolymers (10.6 kDA) in $CDCl_3$.



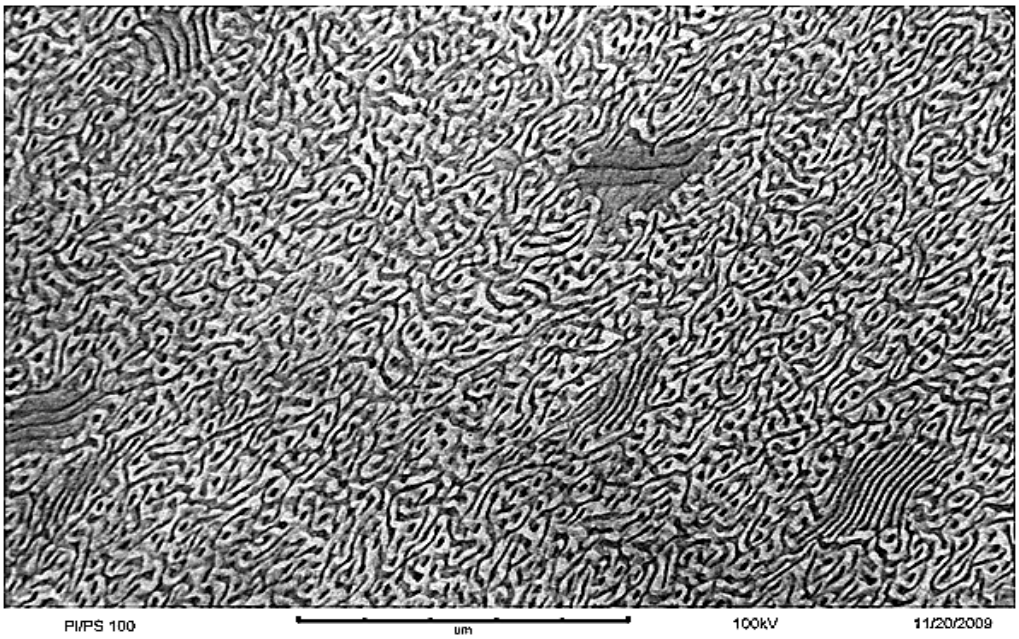
PNMR 24: 500 MHz ^{1}H NMR spectra of decane-1,10-diyl dipropiolate "click" linker in $CDCl_3$.



PNMR 25: 500 MHz ^{1}H NMR spectra of "clicked" chain extended polystyrene (9.8 kDa) in $CDCl_3$.



PNMR 26: 500 MHz ^{1}H NMR spectra of "clicked" chain extended polyisoprene (8.4 kDa) in $CDCl_3$.



PTEM 1: TEM image of polyisoprene-polystyrene (102.1 kDa) block film.