SANDIA REPORT

SAND2012-7479
Unlimited Release
September 2012

Triblock Polymers for Nanoporous Membranes

Joseph G. Cordaro, Nicolas R. Myllenbeck, Greg O'Bryan, Michael S. Kent, Amalie L. Frischknecht, Geoffrey L. Brennecka, and Matthew C. George)

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Approved for public release; further dissemination unlimited.

Sandia National Laboratories

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

NOTICE: This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, make any warranty, express or implied, or assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represent that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government, any agency thereof, or any of their contractors or subcontractors. The views and opinions expressed herein do not necessarily state or reflect those of the United States Government, any agency thereof, or any of their contractors.

Printed in the United States of America. This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

Telephone: (865) 576-8401
Facsimile: (865) 576-5728
E-Mail: reports@adonis.osti.gov
Online ordering: http://www.osti.gov/bridge

Available to the public from
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Rd.
Springfield, VA 22161

Telephone: (800) 553-6847
Facsimile: (703) 605-6900
E-Mail: orders@ntis.fedworld.gov
Online order: http://www.ntis.gov/help/ordermethods.asp?loc=7-4-0#online

SAND2012-7479
Unlimited Release
Printed September 2012

Triblock Polymers for Nanoporous Membranes

Joseph G. Cordaro, Nicolas R. Myllenbeck, Matthew C. George, Michael S. Kent, Amalie L. Frischknecht, Geoffrey Brennecka, Greg O'Bryan, Edward H. Feng
Materials Chemistry
Sandia National Laboratories
P.O. Box 969
Livermore, CA. 94551-0969

Abstract

The fabrication of nanoporous thin-film membranes from block polymers is proposed. A computational modeling effort is described, which optimizes the polymer block lengths in order to obtain thermodynamically favorable phase-separated morphologies. Synthetic routes to access poly(ethylene oxide) and poly (methyl methacrylate)-based block polymers are outlined. These materials were then prepared using controlled free radical polymerization. The relative advantages and disadvantages of numerous routes are discussed. Characterization of di- and triblock polymers using nuclear magnetic resonance spectroscopy and size-exclusion chromatograph revealed less than ideal re-initiation and chain growth of macroinitiators. Preliminary phase-behavior of these materials is reported from small-angle x-ray scattering and scanning electron microscopy.

ACKNOWLEDGMENTS

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

SANDIA REPORT
SAND2012-7479
Unlimited Release
Printed Month 2012

Contents

ACKNOWLEDGMENTS **4**
Contents **5**
Figures **6**
Tables **6**
Schemes **6**
1 Introduction **9**
2 LDRD Proposal **11**
2.1 White paper 11
2.1.1 Statement of Problem and Proposed Solution 11
2.1.2 Proposed R&D and Differentiating Technical Approach 11
2.1.3 Potential Benefit to SNL's Mission 12
2.1.4 Key Team Member 12
2.1.5 Proposed Total Funding 12
2.2 Full Proposal 13
2.2.1 Overview of the Problem and Idea 13
2.2.2 Proposed R&D 14
2.2.3 Key R&D Goals and Project Milestones 15
2.2.4 Technical Risk and Likelihood of Success 16
2.2.5 Relationship to Other Work 16
2.2.6 Resources 17
2.2.7 Strategic Alignment and Potential Benefit 18
2.2.8 Communication of Results 18
..... **20**
4 Project Outline **21**
4.1 Computational Modeling 21
4.2 Synthesis of Block Polymers 21
4.3 Isotopic Hydrogen Enrichment of Polymers 21
4.4 Characterization of Polymer Morphology 21
5 Polymer Synthesis **25**
5.1 Controlled Free Radical Polymerization 25
5.1.1 Nitroxide Mediate Polymerization for Triblock Polymer Synthesis 26
5.2 PMMA-Based Macroinitiators 26
5.2.1 Di and triblock syntheses of PMMA based polymers 26
5.3 PEO-Based Macroinitiators 30
5.3.1 Di and triblock syntheses of PEO based polymers 30
5.4 SEC and NMR Characterization of Polymers 34
5.4.1 Resolution and PDI from GPC 34

5.4.2 NMR Characterization of Di and Triblock Polymers 35
5.5 Polymer Functionalization 37
6 Isotopic Hydrogen Enrichment of Polymers 43
6.1 H/D Exchange Chemistry for Isotopic Enrichment of Polymers 43
6.1.1 Catalyst Selection and Preliminary Screening 43
6.1.2 Arene H/D Exchange 43
6.1.3 H/D Exchange on Polymers with Functional Groups 45
6.1.4 Aliphatic H/D Exchange 46
6.1.5 Copolymer H/D Exchange 46
7 Conclusions 49
8 Distribution 50
9 References 52

Figures

Figure 1. GPC Comparison of JGC-04-061 with two (red) versus three (black) PLgel columns. 34
Figure 2. ^{1}H NMR Spectrum of isolated triblock polymer PEO(20k)-b-PCMS(k)-b-PS(k). 38
Figure 3. 1H NMR spectrum of pyrene-functionalized triblock polymer. 39
Figure 4. 3-D UV-Vis absorption spectra collected using GPC/HPLC instrument. 40
Figure 5: ^{1}H NMR spectra of polystyrene before (bottom) and after (top) 48 hours of reaction time. 44

Tables

Table 1: PMMA-NMP macroinitiators. 28
Table 2: Triblock Polymer Mn* and PDI values. 29
Table 3: MePEO(20k)-based di and triblock polymers 32
Table 4: Deuteration of Polymer Substrates by Catalyst **1**. 45

Schemes

Scheme 1. Synthesis of triblock polymer using NMP techniques. 25
Scheme 2. Synthesis of bidirectional ATRP-NMP Initiator 1. 27
Scheme 4. Synthesis of PEO-ATRP macroinitiator with a photo-cleavable linker. 30
Scheme 3. Synthesis of triblock polymer beginning with ATRP-NMP initiator 1. 28
Scheme 5. Synthesis of ester-linked PEO macroinitiator. 31
Scheme 6. Synthesis of PEO macroinitiator using commercially available benzyl chloride NMP agent. 33
Scheme 8. Functionalization of triblock polymer using Huisgen cyclization reaction with **5**. 37

Scheme 7. Synthesis of alkyne-functionalized pyrene for Huisgen cyclization. 37

1 Introduction

The first report of using a triblock polymer for the preparation of a nanoporous membrane was in 1999.[1] The authors synthesized, via anionic polymerization, PI-*b*-PHEMA-*b*-P*t*BA (PI = polyisoprene, PHEMA = poly(2-hydroxyethyl methacrylate), P*t*BA = poly(*tert*-butylacrylate)), which was subsequently reacted with cinnamoyl chloride in pyridine to give PI-*b*-PCEMA-*b*-P*t*BA. Transmission electron microscopy (TEM) of OsO_4 stained thin-slices (50 nm) showed interconnected tortuous cylinders in the PI-*b*-PCEMA matrix. A gyroid morphology, well-known for diblock copolymers was proposed. Bulk films were crosslinked with UV irradiation followed by extraction of HP*t*BA to furnish a gas-permeable membrane.

Hillmyer and coworkers have carried out extensive work synthesizing and characterizing block copolymer membranes based on polylactide, poly(dimethylacrylamide) and polystyrene.[2-7] In their 2010 perspective on nanoporous membranes [6] they highlight the importance of high porosity, narrow pore size distribution, and tunable chemical and mechanical properties. Block copolymers, they propose, can meet these challenges through careful selection of monomers, synthetic strategies, and control of microphase separation.

The objective of this work was to accomplish many of the previously outlined challenges. An additional element was added to this proposal —optimization of the polymer morphology via a computational modeling effort carried out within DAKOTA. Sandia's ability to combine computational modeling with experimental research and characterization offered a unique strategy for tackling many of the barriers associated with utilizing block polymer membranes. Furthermore, another distinguishing element of this proposal was the concept of using a "functionalizable" middle segment. The advantages of such an approach are discussed in the original proposal. Briefly, such an approach would enable the morphology (a.k.a. porosity) to be established independent, and prior to, the chemical functionalization of the membrane. A polymer thin-film with well-defined morphology could first be fabricated from a block polymer with a cleavable linker.[8] UV-irradiation would release one polymer segment from the film to furnish the porous structure. Lastly, treatment of the membrane with a suitable chemical agent could functionalize the surface of the pores for specific applications without having to redevelop the arduous steps of polymer synthesis, film annealing conditions, and pore-etching.

In Section 2 the original LDRD proposal is reproduced. The basic principle of the project is outlined in addition to goals and milestone. Subsequent sections detail the computational and experimental work performed in pursuit of functionalizable nanoporous membranes. A side-project, investigating methods to incorporate deuterium into polymers for neutron scattering, is briefly covered. Lastly, a modeling program at UCSB sponsored through this LDRD is presented.

At the conclusion of the project, many of the goals/milestones had not been met. The single most challenging component of the project turned out to be synthesizing and properly characterizing triblock polymers. Optimization methods for predicting polymer morphology were also unable to describe triblock polymer systems.

2 LDRD Proposal

2.1 White paper

"A Flexible Approach to Nanoporous Thin-Film Membranes from Copolymer Matrices"
Energy, Resources & Nonproliferation (ERN) "Create" Proposal
PI: Joseph Cordaro

2.1.1 Statement of Problem and Proposed Solution

We propose to create novel nanoporous membranes with improved molecular transport and selectivity. The ability to fabricate inexpensive and robust nanoporous thin-film membranes for selective ion/molecule transportation is critical for developing efficient fuel cells, electrical storage systems, and water purification devices. While commercially available membranes are routinely tested and used at Sandia, they fail to perform efficiently for most applications. These membranes lack structural regularity, selectivity, and reliability because of ill-defined morphology and pore selectivity. A concerted effort to fabricate new membranes from a radically different approach is needed. We will combine the expertise at Sandia in modeling, synthesis, and device testing and fabrication to make new nanoporous membranes. We will use block-copolymers, which self-assemble into three-dimensional nanostructures, or crosslinked polymers patterned via imprint lithography, as flexible platforms for membranes. Modeling will be used to understand and predict self-assembly. Our general approach permits modification of both pore size and selectivity based upon block-copolymer length and post-polymerization treatment. Thin-films will be studied for selective ion/molecule permittivity. This work will significantly shift our efforts at SNL from testing commercial membranes to creating membranes critical to current needs and future projects.

2.1.2 Proposed R&D and Differentiating Technical Approach

Self-assembly of polymer thin-films into ordered nanodomains is an established process used in photolithography. We intend to exploit this phenomenon to fabricate nanoporous membranes from block-copolymers. State-of-the-art computational methods developed at Sandia will be used to predict and design the polymeric nanostructure based on the composition of the triblock-copolymers. Controlled polymerization techniques will be used to synthesize these polymers. Notably, a middle block will be included that can be chemically functionalized after the nanoporous architecture has been established. Advanced spectroscopy techniques will be employed to determine size and distribution of the nanoporous channels. These channels will then be chemically altered to customize the interior surface and ion/molecule selectivity. Alternatively, nanoporous films can be prepared by imprint lithography then grafted with functional groups and polymer chains. Ion transportation/selectivity will be modeled and measured at SNL. Better performance over commercial membranes is expected because

selectivity will be introduced during the final chemical treatment, not adversely affecting membrane integrity, and because of the innate control polymer self-assembly displays in establishing the nanostructure. This broad approach will give membranes that can be tailored for many applications without compromising the robustness of the polymer.

2.1.3 Potential Benefit to SNL's Mission

This work will combine sophisticated technologies and skills at Sandia to fabricate custom nanoporous membranes from a common platform. The proposed work is unique because most institutions lack the necessary resources to coordinate such a multidisciplinary program. If successful, Sandia will revolutionize thin-film membrane technologies and eliminate many obstacles to the fabrication and performance of fuel cells, water treatment systems, and batteries. The knowledge gained will be broadly applicable for numerous areas in the ERN Investment Area. Additionally, a strong collaborative program with UCSB will give Sandia new resources for both future research and recruiting efforts.

2.1.4 Key Team Member

Name	Org Num	Phone
HIBBS,MICHAEL	06338	(505)284-8790
FENG,EDWARD HUAN	08246	(925)294-3101
FUJIMOTO,CY H.	06338	(505)844-6432
FRISCHKNECHT,AMALIE L.	01814	(505)284-8585
BRENNECKA,GEOFFREY L.	01816	(505)845-0105
CORDARO,JOSEPH GABRIEL *	08223	(925)294-2351

2.1.5 Proposed Total Funding

	Funding Requested in $K
FY10	$400K
FY11	$430K
FY12	$460K

2.2 Full Proposal

The full proposal "Nanoporous Polymer Thin-Films from Tri-Block Copolymers: Proposal No. 10-0018" was submitted and accepted in FY09 with work to begin in FY10.

2.2.1 Overview of the Problem and Idea

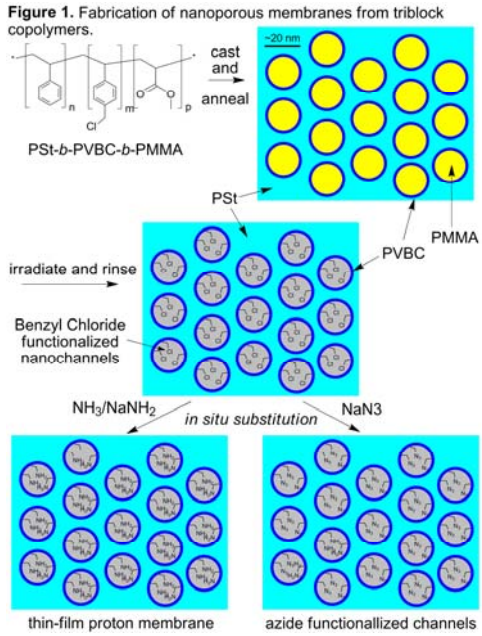


Figure 1. Fabrication of nanoporous membranes from triblock copolymers.

The efficient separation of one substance from another at the molecular level remains an unsolved problem. Membranes that perform this function are employed in a number of advanced electrochemical devices such as batteries, fuel cells, water purifiers, sensors, and MEMS packaging. Improved performance, including longer lifetimes, greater specificity, and altogether novel performance for these devices could be realized by developing better, more robust membranes with tunable properties. Some limitations to current membrane technologies include poor ion-selectivity, humidity sensitivity, difficult and expensive manufacturing techniques, ill-defined nanostructure, and weak mechanical properties. By controlling the morphology and pore selectivity on the nanoscale, many such limitations may be overcome. We propose a novel approach to create customized nano-structured membranes by the self-assembly of polymer thin-films using block-copolymers (BCPs). Our unique approach will be to integrate a middle block segment with chemically reactive groups that can be modified after the polymer architecture has been established. Our goal is to then develop new methods to selectively functionalize the nanoporous channels of this polymer thin-film and control permeability—an idea not described in the literature. While we will focus on a battery separator membrane and test its ion permeability, the approach is general because of the tunability of the membrane properties through chemical modification. Our aim is to develop new chemistries, combined with a "materials by design" philosophy, to address the technical challenges associated with using polymer membranes in various applications. This multi-disciplinary project involves researchers from six departments and combines computational design, polymer synthesis, chemical reactivity and measurement of transport properties to make a nanoporous membrane. If successful, the proposed research would give us the tools and platform from which better membranes could be built. The results of this work would impact our efforts at SNL to develop new energy storage devices and pave the way for expanding efforts into other EERE and DOE areas such as water purification systems and fuel cells.

2.2.2 Proposed R&D

2.2.2.1 Technical Approach and Leading Edge Nature of Work

The framework of this proposal will combine predictive computational methods and synthetic chemistry to make well-ordered polymer membranes containing functional groups within the pores. Our basic approach will take triblock copolymers synthesized via controlled free radical polymerization methods, and fabricate thin-films which can be annealed to give ordered nanostructures through self-assembled phase-separation (Figure 1). We will design a BCP so that ordered domains of cylinders surrounded by a middle-block shell within a bulk polymer matrix are formed upon phase-separation. A chemical or photochemical etching process will degrade the inner nanocylinders, rendering them soluble while cross-linking the bulk matrix polymer. The exposed nanochannels will then be chemically altered to modify the pores for specific membrane functionality or permeability. We will utilize our expertise in membrane characterization at SNL in order to determine whether post-modification of the nanochannels was successful. While a specific membrane prototype is not the thrust of this proposal, we envisage developing permeability experiments that measure cation (Li or H) and/or electrolyte mobilities. Our success will be determined by the ability to modulate the membrane permeability via *in situ* chemical functionalization of the nanoporous channel walls.

Numerous challenges are recognized: i) synthesizing a triblock copolymer with the desired block mole fractions and a low molecular weight distribution, ii) developing theoretical models to combine traditional self-consistent field theory (SCFT) with optimization for designing the best triblock copolymer, iii) obtaining the desired morphology as shown in Fig 1 after casting and annealing thin-films, iv) selectively etching the core polymer to yield the nanopores, v) functionalizing the channel walls by chemically modifying the middle block polymer, and vi) characterizing the surface and permeability of the nanoporous membranes.

<u>Synthesis and characterization:</u> Initially, we envision using polystyrene-*b*-poly(vinyl-benzyl-chloride)-*b*-poly(methylmethacrylate) or PSt-*b*-PVBC-*b*-PMMA, as the platform for our membrane. This material will be synthesized using free radical polymerization techniques to afford the desired block lengths and polydispersity. In this example, the monomers have been chosen because i) PSt has been shown to cross-link under irradiation, resulting in a material of high elastic modulus, ii) PVBC can be functionalized by nucleophilic displacement of chloride, and iii) PMMA degrades upon irradiation. The proposed ratio of PSt:PVBC:PMMA is estimated to be 60:10:30 but this value will be adjusted based upon the results of the calculations detailed below. Other methods for cleaving the PMMA block will also be explored[9] in addition to other monomers for the bulk matrix. Our ability to select monomers and use known physical properties in our theoretical model is essential for the materials design component of this project.

Spin-casting of the polymer from solution is a fast and reproducible method for making thin films on large areas (i.e. on 8” wafers). We will exploit this process to make films from our triblock copolymer and then investigate methods for achieving the thermodynamically stable phase-separated nanostructure as depicted in Figure 1. This type of architecture and cleavage of

the PMMA block has been demonstrated for PSt-*b*-PMMA-*b*-PEO (PEO = polyethylene oxide).[10] The differentiating aspect of our work is that we will re-order the polymer segments such that the inner cylinder of PMMA is cleaved, while retaining the middle block so that it can be chemically altered after cross-linking the PSt matrix. The morphology of our thin-films will be confirmed using a combination of electron microscopy and neutron and X-ray scattering/reflectivity measurements. To demonstrate that the middle PVBC segment is the major component of the shell and that chlorine atoms are available for substitution, *in situ* studies like XAFS and SAXS/SANS will be employed. Any nucleophile, such as amine or hydroxide, could be used to displace chloride from the outer channel wall to give functionalized pores. New reactivity at the surface interface will be required to chemically alter the nanoporous channels. Lastly, films will be removed from the wafer and characterized in our permeation labs. These labs include equipment for gas and water permeation measurements, proton conductivity determination, electrochemical characterization, and impedance spectroscopy. Collaborations with theorists and materials modeling experts will be exploited to understand our experimental data.

Computational modeling: We will develop state of the art computational methods to design triblock copolymers that self-assemble into a desired phase separated nanostructure. Self-consistent field theory (SCFT) is the standard method for understanding the self-assembly of a BCP into a phase separated morphology.[11, 12] SCFT is a statistical mechanical theory that treats the configurational entropy of the polymer as well as the enthalpic interactions between the different polymer blocks. In the theory, a triblock is parameterized by the lengths of each block and the interactions between them. Instead of laboriously calculating the phase diagrams in all these parameters, we will solve the inverse problem: for a target nanostructure, what polymer should be made? By combining traditional SCFT with optimization algorithms, we will determine the molecular parameters of a triblock copolymer that self-assembles into the desired cylindrical phase. For a given set of parameters, we first use SCFT to calculate the free energies of candidate phases. We then update the parameters with the intent of maximizing an objective function, such as the free energy difference between the target phases and all other candidate phases. Ultimately, this method converges on a set of parameters that is predicted to be most stable and can guide the synthesis of a desirable triblock copolymer. Throughout this process, discussions with the experimentalist are critical in order to assure synthetically reasonable outputs are obtained. We can also introduce other relevant criteria into the optimization procedure so we maximize the surface area of the PVBC/PMMA interface that contains the functional groups.

2.2.3 Key R&D Goals and Project Milestones

2.2.3.1 Goal/Milesone	**Completion Date**
Develop predictive modeling for materials design to optimize geometric parameters	04/14/2010 (ongoing)

Synthesize triblock copolymers with low polydispersity and functionalizable middle segment according to theoretic model	09/15/2010 (ongoing)
Spin-cast polymer thin-films, anneal, and obtain ordered, phase separated nanostructures	04/15/2011
Develop new chemistries to selectively functionalize membrane channel walls	02/15/2012
Characterize mechanical properties, permeability and diffusion coefficients of membranes	08/01/2012

Iterations between theory and experiments will be ongoing until the desired BCP material is synthesized and shown to undergo ordered phase-separation. Much of the work will be done sequentially, i.e. more synthesis and predictive modeling will be done at the onset with a gradual shift to thin-film preparation and functionalization towards the second half. Annual reports and a SAND report will be written as required by the LDRD office. Additional papers and presentations will be prepared as milestones are achieved.

2.2.4 Technical Risk and Likelihood of Success

Many of the technical challenges have been surmounted individually with the exception of functionalizing the channel walls, obtaining films with thicknesses larger than 500 nm and combining SCFT with an optimization algorithm. Our success relies on the ability to integrate experiment, theory, and modeling to understand polymer self-assembly and functionalization.

- Synthesis of complex block copolymers
  - Mitigated through alternative synthetic routes
- Combination of traditional SCFT and optimization never done before
  - Use well-established Sandia optimization software (Dakota); access local expertise as needed to couple codes
- Cylindrical structure not preserved through entire membrane
  - Investigate other annealing processes
- Chloride functional groups are not reactive to substitution
  - Switch chemistry of monomers or build in functionality
- Films too thin, not mechanically robust
  - Use porous supports for the functional membrane

2.2.5 Relationship to Other Work

2.2.5.1 Previous and Other Ongoing Work

The phase-separation and self-assembly of BCPs into ordered three-dimensional nanostructures has been well studied.[13] These materials have been used as templates for inorganic nanoporous films[14], directly as nanoporous membranes[15, 16], and as photolithography masks. At SNL,

polymer thin-films have been utilized as photolithography masks and templates for making inorganic structures. Also, through a collaboration between SNL and Paul Nealey's research group at the University of Wisconsin, the ability to self-assemble diblock copolymers on arbitrary substrate materials with widely varying surface chemistries has been developed and demonstrated. Typically, such films are used as a tool to achieve more complex structures. What is unique to this proposal is the development of chemistries that will allow for the porous films to be functionalized and tailored for specific ion permeability. Furthermore, no one in the polymer community is using optimization to design BCP's that self-assemble into a target structure.

2.2.5.2 Relationship to Other Work

Our approach for making nanoporous thin-film membranes has the advantage over conventional methods because we propose to establish the physical geometric requirements (pores size, distribution, etc.) before introducing the chemical functionality. Others routes to fabricate thin-film membranes rely upon the inherent properties of the bulk material, which compromises physical properties of the membrane. The tailored triblock copolymer building block will circumvent these issues by specifying physical and chemical properties for each segment of the polymer. This route will mitigate defects in the membrane, reduce mechanical failures, and allow us to develop a structure-property relationship for permeability.

2.2.6 Resources

2.2.6.1 Key Research Team Members

Name	Org	Role
Joseph G. Cordaro	08223	PI (Polymer synthesis)
Amalie L. Frischknecht	01814	SCFT Computational Modeling
Edward H. Feng	08246	Computational Modeling (post-doc)
Cy H. Fujimoto	06338	Membrane characterization
Michael S. Kent	08622	Thin-film characterization (AFM/SAXS/SEM)
Geoff L. Brennecka	01816	Patterning and etching of thin-films
Craig Hawker	UCSB	Synthetic polymer chemist- Professor/Director

2.2.6.2 Qualifications of the Team to Perform This Work

Joseph Cordaro is a synthetic polymer chemist and has had experience with interdisciplinary research efforts related to materials science projects. Amalie Frischknecht has over ten years' experience in modeling polymeric materials, using a variety of techniques including SCFT. Ed Feng has done statistical mechanics for almost a decade and has published SCFT calculations.[3] Cy Fujimoto is experienced in the area of membrane characterization, specifically in the area of fuel cells, electrolysis and water purification. Michael Kent has numerous years characterizing thin nanoscale membranes via scattering and reflectivity methods. Geoff Brennecka has experience in fabricating and characterizing solution derived thin-films. Prof. Craig Hawker is a

leader in polymer synthesis and materials science. He will function in an advisory role and we will possibly support a summer graduate student to work here at SNL.

2.2.7 Strategic Alignment and Potential Benefit

2.2.7.1 Relevance to Missions

The proposed synergy of synthetic polymer chemistry, materials characterization and self-consistent field theory calculations will lead to new and flexible methods for functionalizing ordered, nanostructured polymer membranes. Our work specifically addresses basic research efforts to understand materials properties across the "atomistic-to-micro-scales". This proposal is directly aligned with current efforts at CINT, programs for water and fuel systems, DHS projects, and the NTM call, which emphasizes the fundamentals of controlling and manipulating nanoscale properties so as to realize unique functions for novel devices. Success in this project will enhance Sandia's ability to respond to national needs in energy storage, water purification and management, and fuel cells.

2.2.7.2 Programmatic Benefit to Investment Area, if Successful

The knowledge gained from this proposal will give us an expanded toolbox available in designing and fabricating new devices that are currently limited by inadequate materials properties. Proof that the channel walls are indeed coated with the functionalizable middle block will confirm our theoretical models and help elucidate the mechanism by which polymers phase-separate. Through the successful development of a flexible membrane platform that can be functionalized for tailored applications, new membranes suitable for fuel cells, water and gas filtration devices, and novel biological applications and pattern-transfer will be accessible. If the NTM IAT and Sandia's ambitious plans to develop new programs related to energy, water, and security are to be successful, an increased support for predictive computational polymer modeling and synthetic methods to access new materials is critical. Potential future support for this project will come from BES, DOD, and EERE for projects related to energy storage, vehicle electrification, water purification and management, and security.

2.2.8 Communication of Results

Over the course of three years, team members will have more or less critical roles within the project. The PI will coordinate efforts to communicate with the team members regularly, tracking progress and ensuring resources are allocated to the appropriate member for each task. We anticipate communicating our results via publications and presentations as milestones are achieved. All required reports will be submitted to the LDRD office including a final SAND report at the end of FY12.

4 Project Outline

This project was divided into three tasks. 1) Predictive computational modeling to guide the synthesis of block polymers. 2) Synthetic chemistry to make block polymers with the appropriate molecular weights to obtain thermodynamically favorable microphases. 3) Characterization of polymer morphology and membrane properties. All three steps were designed to be iterative but relied on the initial success of the synthetic chemistry to provide materials for characterization and model validation. Two additional side-projects evolved during the course of this project; a) deuterium enrichment of polymers using H/D exchange catalyzed by an iridium complex and b) kinetic modeling of solvent annealing conditions using a course-grain approach.

4.1 Computational Modeling

Computation modeling, specifically self-consistent field theory (SCFT) calculations were developed to aid in the design of block polymers. The goal of this modeling effort was to determine the optimal polymer segment lengths such that a bicontinuous, gyroid morphology would be the lowest energy structure relative to lamellar or cylinder morphologies. A related effort conducted at UCSB was aimed at modeling the kinetic effects of solvent annealing of block polymer films. This work is described in a separate SAND report.

4.2 Synthesis of Block Polymers

Block polymers were synthesized using controlled free-radical polymerization (CFRP) techniques. The di and triblock polymers were designed to include cleavable linker for pore formation and 4-chloromethyl styrene (CMS) repeat units for functionalization. Characterization via nuclear magnetic resonance (NMR) spectroscopy and size-exclusion chromatography (SEC or GPC) are outlined in Section 4

4.3 Isotopic Hydrogen Enrichment of Polymers

Enrichment of polymers and block polymers with deuterium was the focus of Section 5. This experimental work explored using an iridium catalysts for isotopically scrambling hydrogen and deuterium atoms between an inexpensive deuterium source (acetone-d_6 or benzene-d_6) and polymer. The goal of this work was to develop an economical method for enriching polymers with deuterium so that better neutron scattering measurements could be made.

4.4 Characterization of Polymer Morphology

Various techniques were used to characterize the morphology of polymers including small angle X-ray scattering (SAXS), grazing-incidence small-angle X-ray scattering (GISAXS), scanning

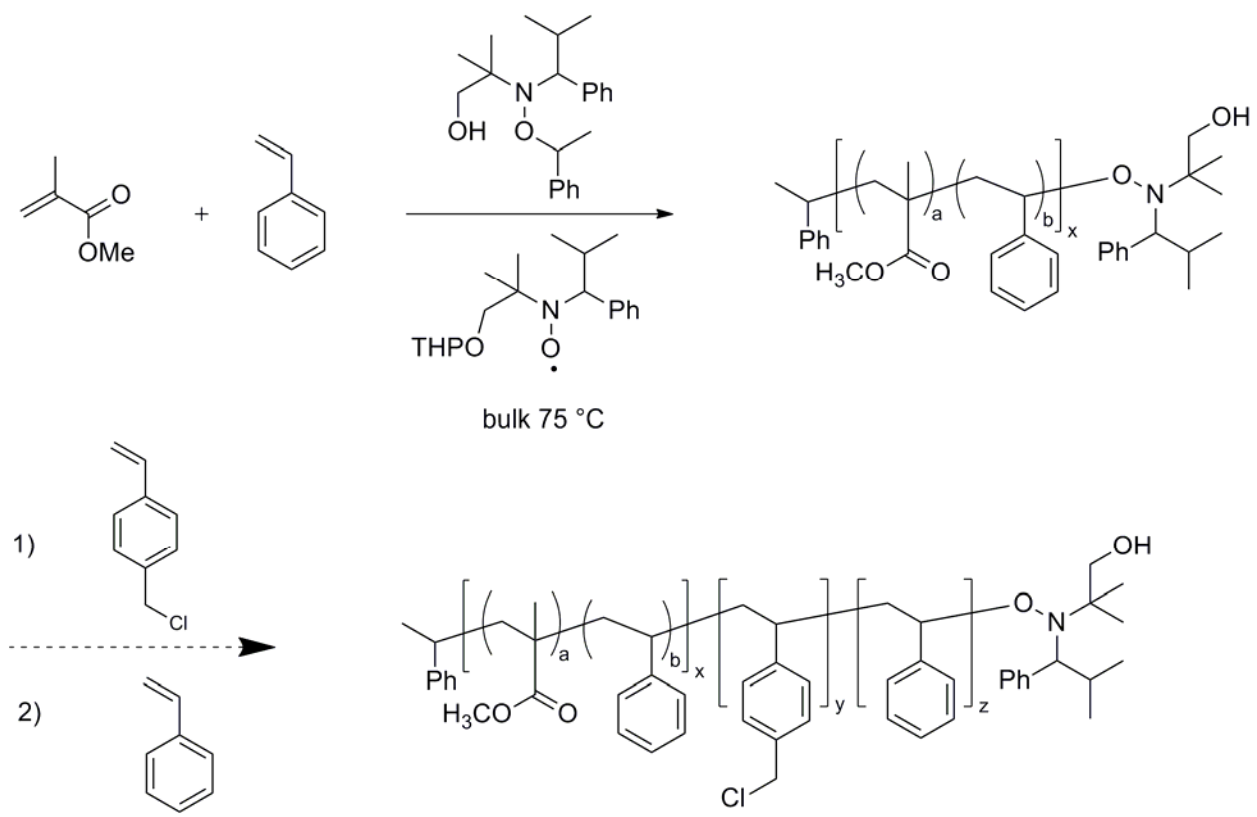
electron microscopy (SEM) and neutron diffraction. This work is summarized in a subsequent SAND report.

5 Polymer Synthesis

5.1 Controlled Free Radical Polymerization

Over the past two decades, new techniques for the controlled polymerization of various monomers have been developed based on free-radical initiators and mediators.[17-20] Theoretically, these processes allow for the synthesis of block polymers in a much more accessible procedure compared to anionic polymerization methods. Furthermore, free-radical polymerization techniques are more functional-group tolerant than cationic or anionic routes. Controlled-free radical (CFR) polymerization is not without its drawbacks. The polydispersity index (PDI) of materials is typically higher than comparable polymers synthesized using anionic methods. Furthermore, termination of free-radicals via polymer-polymer coupling must be avoided, which means conversions have to be kept low. Despite some limitations, controlled-free radical polymerization methods can be very useful for synthesizing block polymers due to the ability to re-initiate dormant polymer chains after isolation and purification—something inherently difficult for polymers made via anionic polymerization.

Prior work had shown that the triblock polymer PS-*b*-PMMA-*b*-PEO (PS = polystyrene; PMMA = poly(methyl methacrylate); PEO = poly(ethylene oxide) could self-assemble into well-ordered



Scheme 1. Synthesis of triblock polymer using NMP techniques.

core-shell cylindrical domains in a polystyrene matrix. Upon UV-irradiation of this polymer in thin-films the major PS component was crosslinked while the PMMA shell segment degraded, liberating the PEO from the matrix. Nanoporous polystyrene thin films were the result of this process.[10] Alternatives to the UV-etching process quickly emerged, including the introduction of a photocleavable linker.[8] This early work inspired two approaches for generating nanoporous polymer thin-films; a) photo-degradation of PMMA or b) utilizing a cleavable linker to liberate the core polymer from the matrix. Therefore, triblock polymers containing polystyrene for crosslinking, poly(methyl methacrylate) or poly(ethylene oxide) for pore formation, and a functionalizable middle block of 4-chloromethyl styrene (CMS) were targeted.

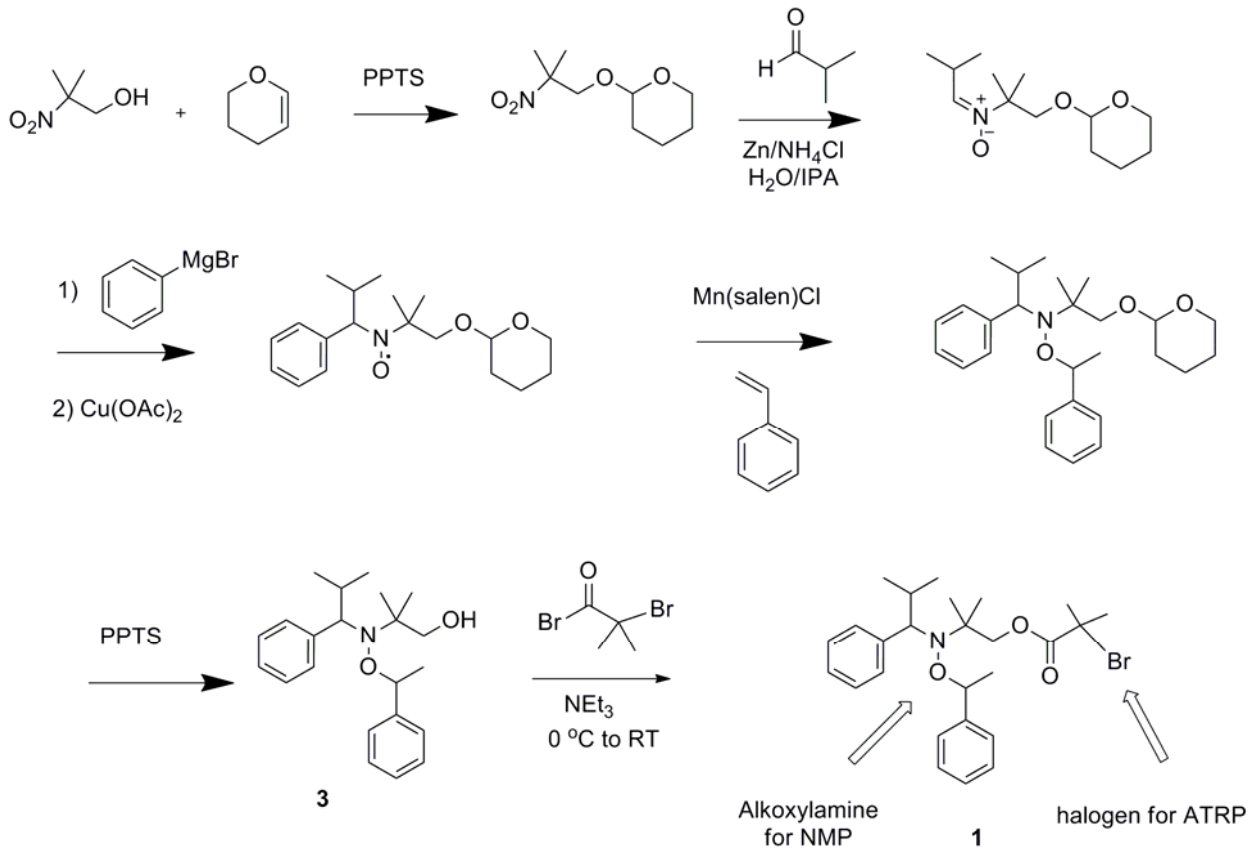
5.1.1 Nitroxide Mediate Polymerization for Triblock Polymer Synthesis

A simple route for accessing a triblock polymer is depicted in Scheme 1. Initially this approach was anticipated to be the quickest method for synthesizing the desired material, however, some shortcomings were evident. First, the NMP mediator had to be synthesized or acquired though a NDA with a commercial supplier. Second, re-initiation with alkoxyamine-based PMMA-NMP mediators does not proceed with high efficiency, which could mean the final polymer would contain homopolymer. Third, the oxidative cleavage of the alkoxyamine N-O bond described in section 5.1 would not be applicable in this architecture for releasing one of the polymer segments. Four, since oxidative cleavage to remove one segment is not possible with this architecture, a photo-degradation of the PMMA would have to be developed, which could also degrade the Cl-C bond of the PCMS segment. Due to these reasons, routes using macroinitiators were developed.

5.2 PMMA-Based Macroinitiators

PMMA-based macroinitiators were investigated because of their susceptibility to UV-degradation as discussed above.

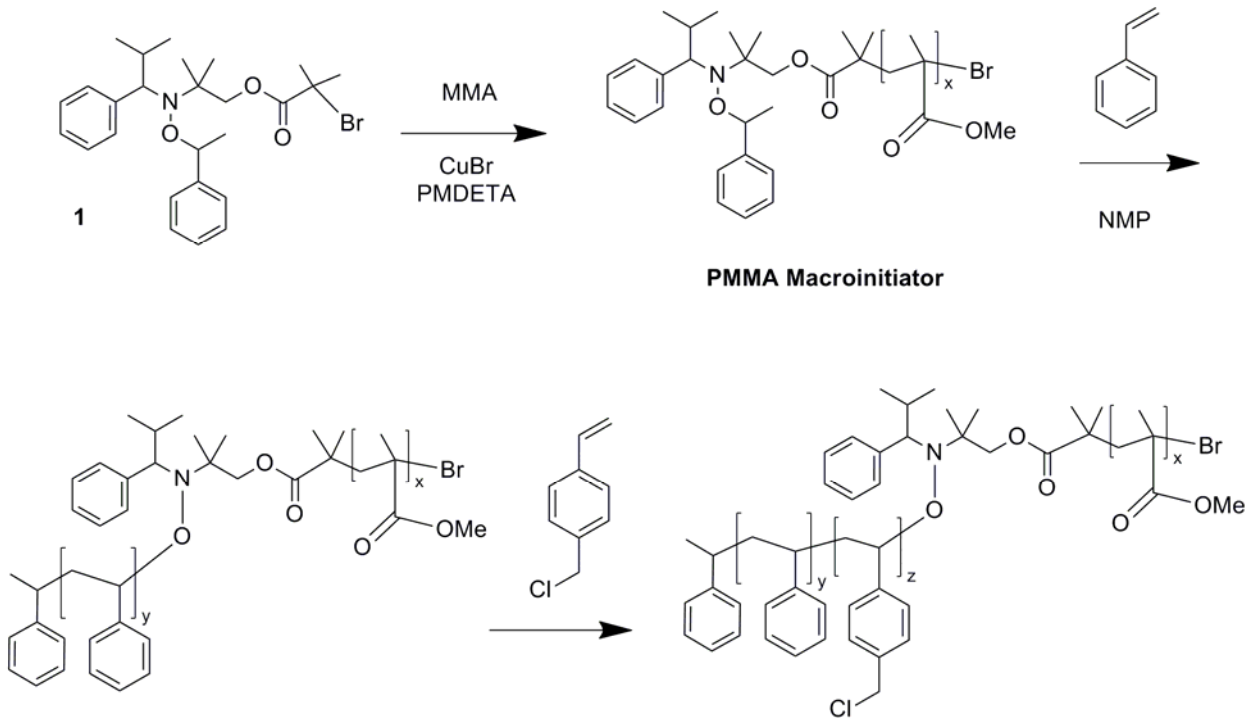
5.2.1 Di and triblock syntheses of PMMA based polymers



Scheme 2. Synthesis of bidirectional ATRP-NMP Initiator **1**.

Multiple routes were explored for the synthesis of a triblock polymer with a functionalizable middle segment and a cleavable linker or photodegradable PMMA segment. Initially, efforts were focused on the synthesis of bidirectional initiator **1**, which could be used for atom-transfer radical polymerization (ATRP) followed by nitroxide mediate polymerization (NMP) (Scheme 1).[21] This N-alkoxyamine was chosen for the versatility it offers in polymerizing methacrylate and vinyl monomers. Additionally, prior work had shown that the N-O bond could be cleaved using mild oxidation chemistry, which provides a route for pore-formation.[22] Photodegradation of the PMMA is also possible. The drawbacks to using **1** include a multi-step synthesis required to make it and three polymerization are required to obtain a triblock polymer. Despite these hurdles, multiple grams of initiator **1** were synthesized in six steps as outlined in Scheme 2.

For two reasons described next, methyl methacrylate was polymerized using standard ATRP conditions (Scheme 3). First, re-initiation from PMMA macroinitiators is difficult, which can lead to broad molecular weight distributions. Second, the polymerization of 4-chloromethyl styrene is not possible using ATRP conditions because of the competing chlorine abstraction from the monomer. Therefore, MMA was polymerized to give a series of PMMA-NMP macroinitiators with molecule weights ranging between 19 – 30 kg/mol. The molecular weights



Scheme 3. Synthesis of triblock polymer beginning with ATRP-NMP initiator **1**.

and PDI values of the polymers were determined by light-scattering analyses and RI measurements (*dn*/*dc* for PMMA = 0.083 in THF). The value Mn determined for the PMMA macroinitiators was used for reference in calculating the Mn of the di and triblock polymers via NMR spectroscopy. Table 1 lists the PMMA-NMP macroinitiators synthesized via ATRP. The polymer codes are generated based on the electronic notebook page where a record of the synthesis is kept.

Table 1: PMMA-NMP macroinitiators.

Code	Mn (kg/mol)	PDI
NRM-03X-057P[a]	24.5	1.04
NRM-03X-058P[a]	30.1	1.03
NRM-03X-071P[a]	22.9	1.04
NRM-03X-072P[a]	27.6	1.04
NRM-03X-073P[b]	25.7	1.06
NRM-03X-083P[b]	26.6	1.07

a) Measured using three SEC columns b) measured using two SEC columns

Styrene was polymerized using the PMMA-NMP macroinitiators with the goal of obtaining an Mn of 25 – 50 kg/mol for the PS block. After isolation and characterization, 4-chloromethyl styrene was polymerized using the diblock macroinitiators to furnish the desired triblock polymers. Table 2 lists the triblocks synthesized via NMP and the Mn values obtained by NMR spectroscopy. Because only a short, 5 – 10 kg/mol segment was desired, reaction times were kept short (15 – 20 min versus six hours for the polymerization of styrene). Changes in the GPC trace upon inserting the PCMS block were minimal. However, by NMR the growth of PCMS could be observed and the Mn of the segment could be calculated. Shoulders at low retention time in the GPC traces are evidence of polymer-polymer coupling or uncontrolled polymerization leading to high molecular weight polymers.

Of the six triblock polymers, three were selected for analysis by SAXS. The criteria for selecting which polymers where annealed included low PDI values and Mn values within a range that may be suitable for forming a cylindrical morphology upon annealing. The characterization is discussed in Section 6.

Table 2: Triblock Polymer Mn* and PDI values.

Code	PMMA Mn[a]	PCMS Mn[b]	PS Mn[b]	PDI
JGC-04-060	24.5	6.8	32.8	1.317
JGC-04-061	30.1	7.2	40.2	1.505
JGC-04-062[c]	22.9	8.7	28.7	1.279
JGC-04-063[c]	27.6	8.1	33.1	1.396
JGC-04-064[c]	25.7	7.5	29	1.336
JGC-04-059	26.6	8.3	29.7	1.398

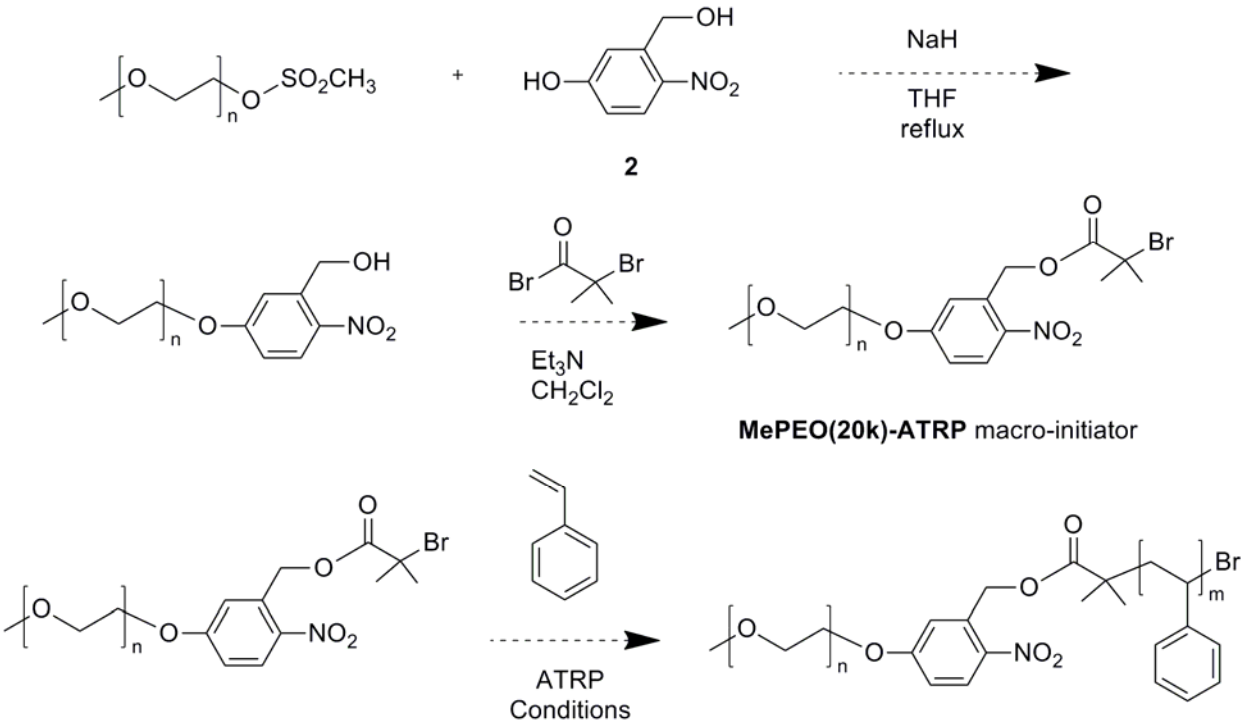
*All Mn values given in kg/mol. a) Mn values calculated from GPC data.
b) Mn values calculated from NMR spectroscopy relative to PMMA Mn.
c) Selected for characterization via SAXS.

5.3 PEO-Based Macroinitiators

End-group functionalization of commercially available, hydroxyl terminated poly(ethylene oxide) was used as an alternative route to PMMA-based macroinitiators. The advantages of using PEO-based macroinitiators are twofold. 1) Utilizing a commercial macroinitiator means one less polymerization step is required, reducing the likelihood of low re-initiator yields. 2) The segregation energy of PEO/PS is higher than PMMA/PEO, which means phase-separation will be more thermodynamically driven compared to PMMA/PS polymer thin-films. Multiple routes to making PEO-based macroinitiators were proposed and attempted.

5.3.1 Di and triblock syntheses of PEO based polymers

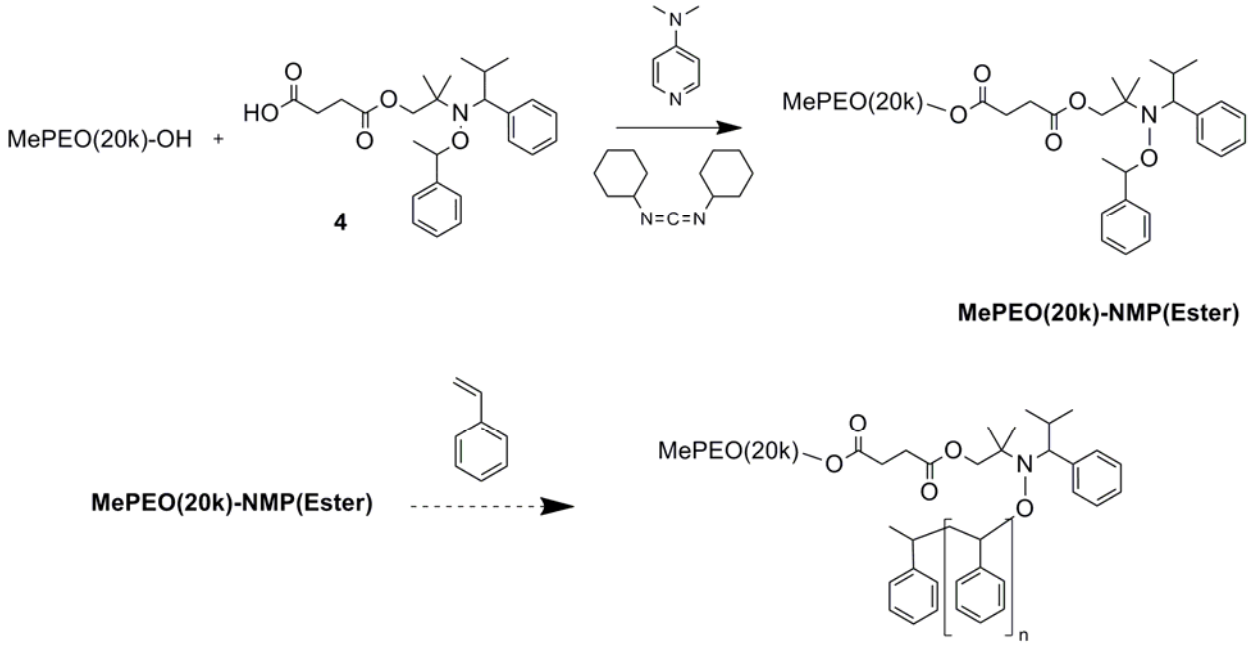
Introduction of a photo-cleavable linker between the PEO and PS block was the goal of reacting mesyl-terminated PEO or MePEO(20k)-Ms (Ms = -OSO_2CH_3) with benzoyl nitroarene **2** (Scheme 4).[23] Nitroarene **2** is made in one step via the reduction of 5-hydroxy-2-nitrobenzaldehyde with sodium borohydride.[8] Due to the higher acidity of the phenol proton compared to the benzoyl proton, selective substi tution should occur at this spot. The resulting nitro-benzyl alcohol is treated with base and 2-brom o-2-methylpropanoyl bromide to give the desired MePEO(20k)-ATRP macroinitiator. Subsequent polymerizations using ATRP conditions



Scheme 4. Synthesis of PEO-ATRP macroinitiator with a photo-cleavable linker.

will yield block polymers. While this sequence of reactions was reported to work with a 5,000 g/mol PEO-based macroinitiator, broad polydispersity indices were observed for polymers made using the 20k PEO macroinitiator. It is suspected that end group functionalization of MePEO(20k)-OH was incomplete. Regardless, as noted above 4-chloromethyl styrene cannot be polymerized using ATRP conditions due to the abstraction of the chlorine atom. Should this route be re-visited, it would only be suitable for making PEO-*b*-PS or PEO-*b*-PMMA materials.

Functionalization of MePEO(20k)-OH via *N,N'*-dicyclohexylcarbodiimide (DCC) coupling was also attempted (Scheme 5). In this sequence of reactions, an acid-functionalized NMP mediator **4** was synthesized from hydroxyl-NMP **3** and succinic anhydride. Using DCC coupling conditions, the mediator **4** was reacted with MePEO(20k)-OH. NMR spectroscopy was used to analyze the isolated polymer, which confirmed the presence of the NMP end group. However, quantitative analysis is not possible with a polymer of this high molecular weight. Macroinitiator **MePEO(20k)-NMP(Ester)** was then used for polymerization of styrene under standard NMP conditions. Three advantages of using this route include 1) starting from a macroinitiator so only one re-initiation is required, 2) mild cleavage of the N-O bond with Ce^{2+} is possible to generate pores, and 3) both CMS and vinyl pyridines can be polymerized using NMP techniques. Analysis of the resulting polymer revealed a broad polydispersity, suggesting that polymer functionalization via DCC coupling was incomplete. With more time to optimize the synthesis of the macroinitiator, this route for making triblock polymers may yield better results. Alternatively, MePEO(20k)-OH could be reacted with succinic anhydride to make the acid. Coupling of this macromolecule to **3** could give the desired macroinitiator **MePEO(20k)-**



Scheme 5. Synthesis of ester-linked PEO macroinitiator.

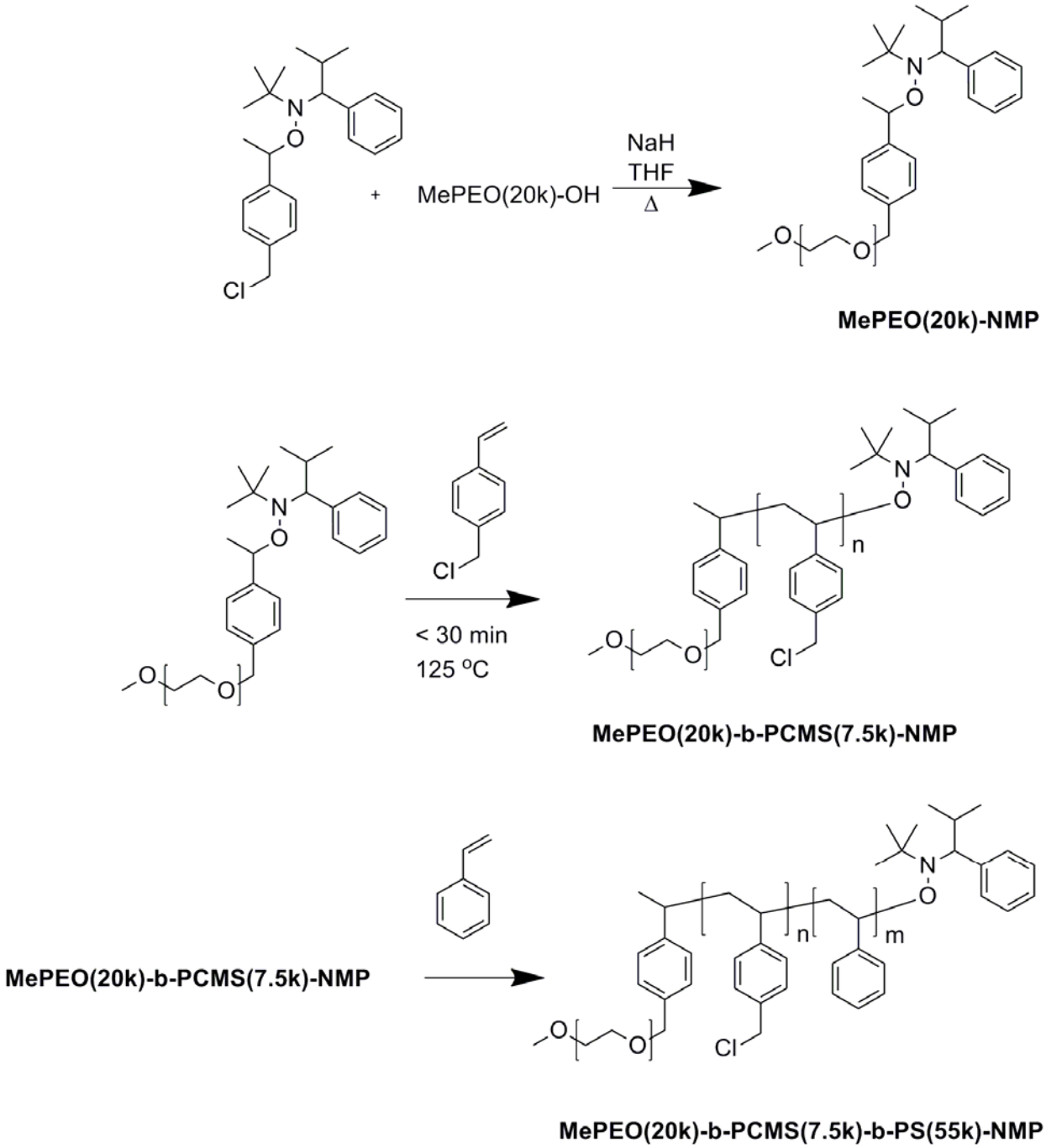
NMP(Ester). However, multiple end group functionalizations of a large polymer usually proceed with less than ideal efficiency

Lastly, a PEO-NMP macroinitiator was synthesized in one step using commercially available MePEO(20k)-OH and 4-chloromethyl styrene functionalized NMP **2**.[24] This reaction was performed in refluxing dry THF with the addition of sodium hydride to deprotonate the hydroxyl group of MePEO(20k)-OH. The macroinitiator **MePEO(20k)-NMP** product was isolated by precipitating the polymer into cold diethyl ether. A series of diblock polymers were made using macroinitiator **MePEO(20k)-NMP** and 4-chloromethyl styrene. Reaction times were less than 30 minutes at 125 °C in order to add only a short PCMS segment (<10 kg/mol) and minimize polymer-polymer coupling. The diblock polymers were next used to mediate the polymerization of styrene. A PS segment of > 30 kg/mol was achieved by heating the reaction to 125 °C for four to nine hours. The % conversion for the polymerization of CMS and styrene, and the final Mn of the second and third polymer segments were determined by NMR spectroscopy. The assumption was made that the molecular weight of the PEO was 20 kg/mol, which gave an internal reference for the Mn of the two adjoined segments. Table 3 lists the molecular weights of triblock polymers synthesized following Scheme 6.

Table 3: MePEO(20k)-based di and triblock polymers

Code	PEO Mn	PCMS Mn	PS Mn	PDI	Macroinitiator Source
JGC-04-083	20	7.94	NA	1.17	JGC-04-075.1
JGC-04-086	20	8.7	NA	1.35	JGC-04-075.1
JGC-04-092	20	7.5	NA	1.28	JGC-04-091
JGC-04-084	20	7.94	47.3	1.67	JGC-04-083
JGC-04-085	20	7.94	66.2	2.03	JGC-04-083
JGC-04-093	20	7.5	56.3	2.561	JGC-04-092

At the end of the LDRD project, the route d epicted in Scheme 6 proved to be the most reliable for obtaining triblock polym ers. However, th ere is no obvious m ethod to m ake a nanoporous membrane by cleaving the PEO segm ent from the polymer. Despite this limitation, triblock polymers synthesized using this m ethod provided interesting material for functionalization and morphological studies. The m acroinitiator **MePEO(20k)-NMP** is also useful for polym erizing



Scheme 6. Synthesis of PEO macroinitiator using commercially available benzyl chloride NMP agent.

other monomers such as vinyl pyridines or acrylates and methacylates.

5.4 SEC and NMR Characterization of Polymers

A brief discussion of polymer characterization is presented below. Gel-permeation chromatography (GPC) and size-exclusion chromatograph (SEC) are used interchangeably. Also, a formula for calculating the molecular weight (Mn) of a triblock polymer using NMR spectroscopy is given.

5.4.1 Resolution and PDI from GPC

Preliminary GPC data was acquired using two PLgel 5 µm Mixed-C columns purchased by Agilent Technologies. Towards the end of the project, three columns were used in series with improved resolution: PLgel 5 µm Mixed-D columns, also from Agilent. With these three columns, shoulders previously unseen using the two columns became evident. Contamination with homo and diblock polymers in isolated triblock polymers was also more obvious. For example, a comparison between triblock JGC-04-061 run with two versus three columns is show in Figure 1. (Different retention times are due to the different column lengths. The signals between 25 and 30 min are attributed to solvent.) For the trace shown in red between 10 and 15 min, two columns were used in series, which appeared to give a monodispersed peak with slight

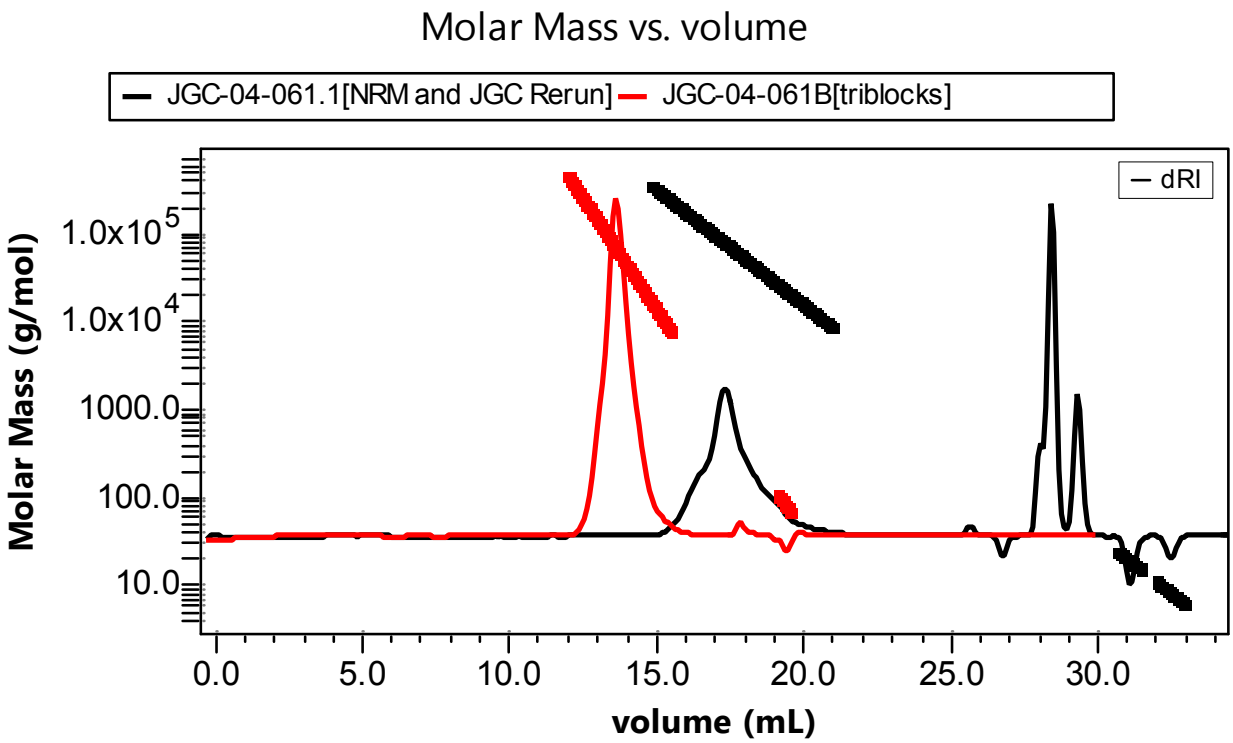


Figure 1. GPC Comparison of JGC-04-061 with two (red) versus three (black) PLgel columns.

shoulders on both sides. Conversely, using three columns the trace shown in black between 15 and 20 min was obtained, which shows a much broader signal containing sizable low and high molecular weight shoulders. Clearly, it is important to have the capabilities to resolve polymers in order to properly characterize their composition. Had three columns not been utilized, the improper conclusion that a nearly monodispersed polymer was synthesize, samples like JGC-04-061 would be incorrectly characterized.

5.4.2 NMR Characterization of Di and Triblock Polymers

The molecular weight (Mn) of di and triblock polymer segments can be calculated using ^{1}H NMR spectroscopy integration. A preliminary assumption has to be first made—that the Mn of the macroinitiator was accurate (20 k for commercial PEO or as determined by light-scattering analysis for PMMA). An example for PEO-*b*-PCMS-*b*-PS is given below based on the ^{1}H NMR spectrum shown in Figure 2.

In this example, the signal at 3.66 ppm represents the PEO backbone, with a Mn of 20,000 g/mol. Since the repeat unit in PEO has a MW of 44 g/mol with 4 H atoms, the integration for this signal represents approximately 1,818 protons. Let the number of protons for this signal at 3.66 ppm divided by the integration area be equal to A, *Eq. 1*.

$$\frac{\#\ of\ protons}{integration\ value\ of\ PEO} = A \qquad \textbf{Eq. 1}$$

The broad signal at 4.3 – 4.65 ppm represents the two protons of the methylene unit of PCMS [-Ar-CH2-Cl]. The number of CMS repeat units can be calculated via *Eq. 2*.

$$\frac{\mathbf{A} \times \mathbf{integration\ value\ of\ PCMS}}{\mathbf{2}} = \mathbf{\#\ CMS\ repeat\ units} \qquad \textbf{Eq. 2}$$

The total number of PS and PCMS alkyl protons can be determined from the integration at 1.0 – 2.4 ppm using *Eq. 3*.

$$(\mathbf{alkyl\ integration}) \times \mathbf{A} = \mathbf{\#\ alkyl\ protons} = \mathbf{B} \qquad \textbf{Eq. 3}$$

Knowing the number of CMS repeat units determined in equation 2 and B, the number of styrene repeat units can now be calculated via *Eq. 4* and *Eq. 5*.

$$\mathbf{B - 3} \times (\mathbf{\#\ CMS\ repeat\ units}) = \mathbf{\#\ PS\ protons} \qquad \textbf{Eq. 4}$$

And

$$\frac{\textbf{\# PS protons}}{\textbf{3}} = \textbf{\# styrene repeat units} \qquad \textit{Eq. 5}$$

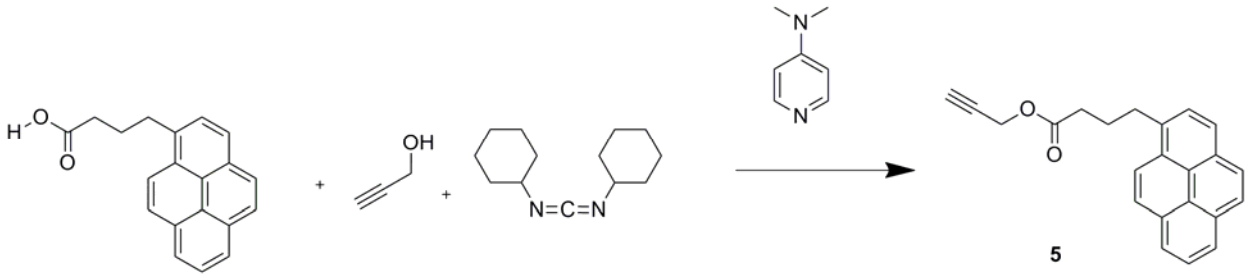
If the integration of the two protons of the methylene unit of PCMS [–Ar-CH_2-Cl] is set to two, then the following *Eq. 6* and *Eq. 7*.

$$\frac{\textbf{\# of protons in PEO backbone (1818)}}{\textbf{PEO integration}} = \textbf{\# CMS units} \qquad \textit{Eq. 6}$$

And

$$\frac{(\textbf{alkyl integration} - \textbf{3})}{\textbf{3}} \times (\textbf{\# CMS repeat units}) = \textbf{\# of styrene repeat units} \qquad \textit{Eq. 7}$$

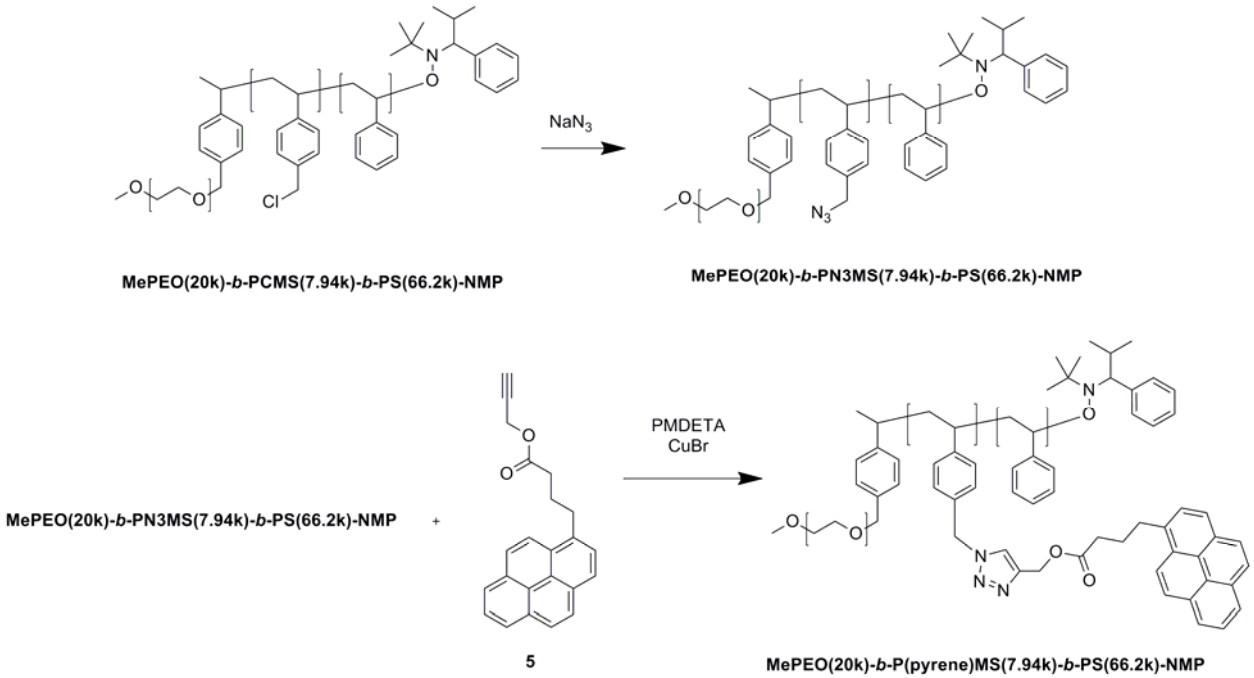
A similar approach can be taken for PMMA-based polymers. However, for these block polymers MMA has a contribution to the alkyl region at 0.8 – 2.2 ppm in addition to a signal at 3.60 ppm for the -OCH_3.



Scheme 7. Synthesis of alkyne-functionalized pyrene for Huisgen cyclization.

5.5 Polymer Functionalization

Functionalization of the middle polymer segment poly(chloromethyl styrene) was explored using a nucleophilic substitution reaction with sodium azide followed by Huisgen cycliza tion with an alkyne. Alkyne-functionalized pyrene **5** was synthesized in one step from 4-(pyren-1-yl)butanoic acid and propargyl alcohol via DCC coupling (Scheme 7).The product was isolated after passing the crude material through a pad of basic alumina followed by crystallization from hot hexanes.



Scheme 8. Functionalization of triblock polymer using Huisgen cyclization reaction with **5**.

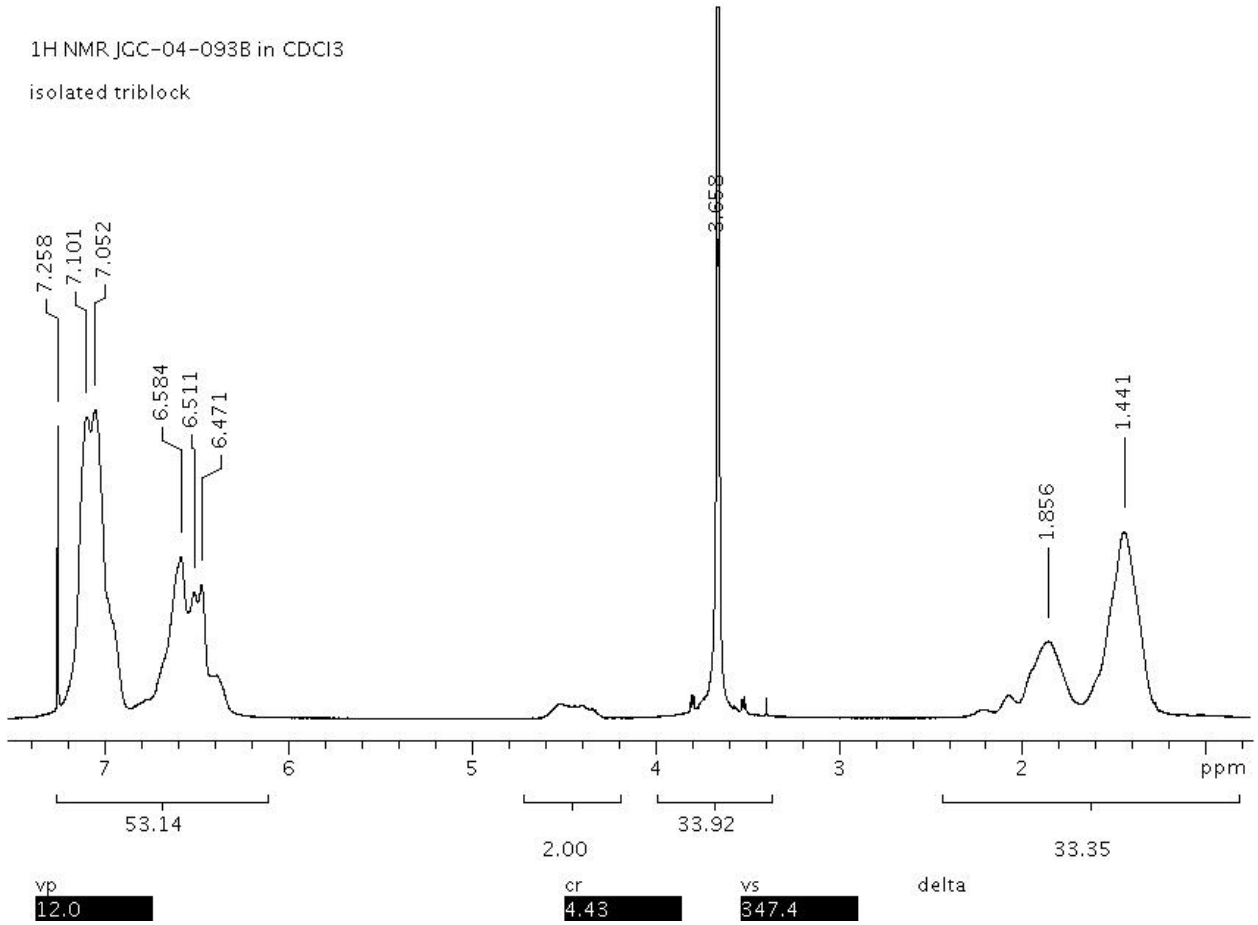


Figure 2. ^{1}H NMR Spectrum of isolated triblock polymer PEO(20k)-b-PCMS-b-PS.

The triblock polymer MePEO(20k)-*b*-PCMS(7.94k)-*b*-PS(66.2k)-NMP was reacted with 104 equivalents of NaN_3 (two equiv relative to each chloromethyl styrene) in DMF (). After 24h of mixing, the polymer was precipitated into water and isolated. A downfield shift in the -CH_2- methylene signal was observed in the ^{1}H NMR spectrum, indicative of the chloride substitution for an azide. No change in the GPC was observed for the isolated polymer MePEO(20k)-*b*-PN3MS(7.94k)-*b*-PS(66.2k)-NMP. Conversion of the azide to a triazole via cyclization with an alkyne using Huisgen conditions was successful to give the pyrene decorated triblock polymer (Scheme 8). A ^{1}H NMR spectrum of the isolated triblock polymer functionalized with pyrene is shown in Figure 3. Most notable is the shift in the methylene signal at 5.1 ppm and the new broad aryl signals at 7.8 – 8.1 ppm. Based on the integration of these two signals the cyclization reaction proceeded in > 98% yield.

Pyrene was chosen to functionalizing the triblock polymer because it has a UV-Vis absorption extending out to 360 nm (λ_{max} = 330 nm) where the triblock does not absorb. Using a UV-Vis detector in line with an RI detector on a GPC system it should be possible to measure the extent of functionalization by measuring the absorption spectra of the eluent with time. By knowing the

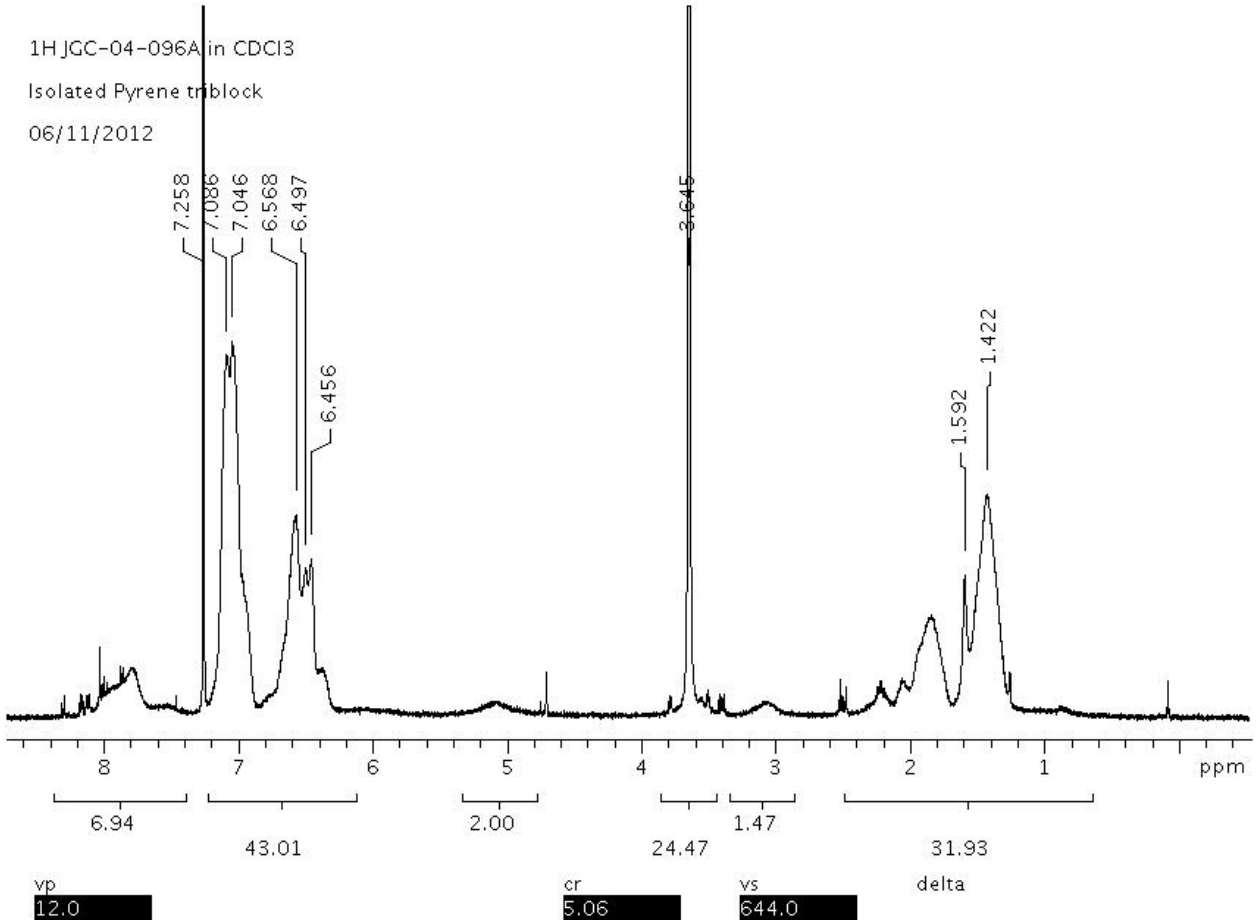


Figure 3. 1H NMR spectrum of pyrene-functionalized triblock polymer.

extinction coefficient (ε) for the pyrene moiety the concentration can be determined from the UV-Vis spectrum. Quantitative analysis of the functionalized polymer should be possible. Three 3-D plots showing the UV-Vis spectra versus time for alkyne-pyrene **5**, azide-triblock, and pyrene-functionalized triblock are displayed in Figure 4. A strong UV-Vis absorption signal is seen for both **5** and pyrene-functionalized triblock extending to 360 nm. Conversely, the UV-Vis spectrum for azide-triblock extends only to 280 nm. The retention time for the three different samples can be seen

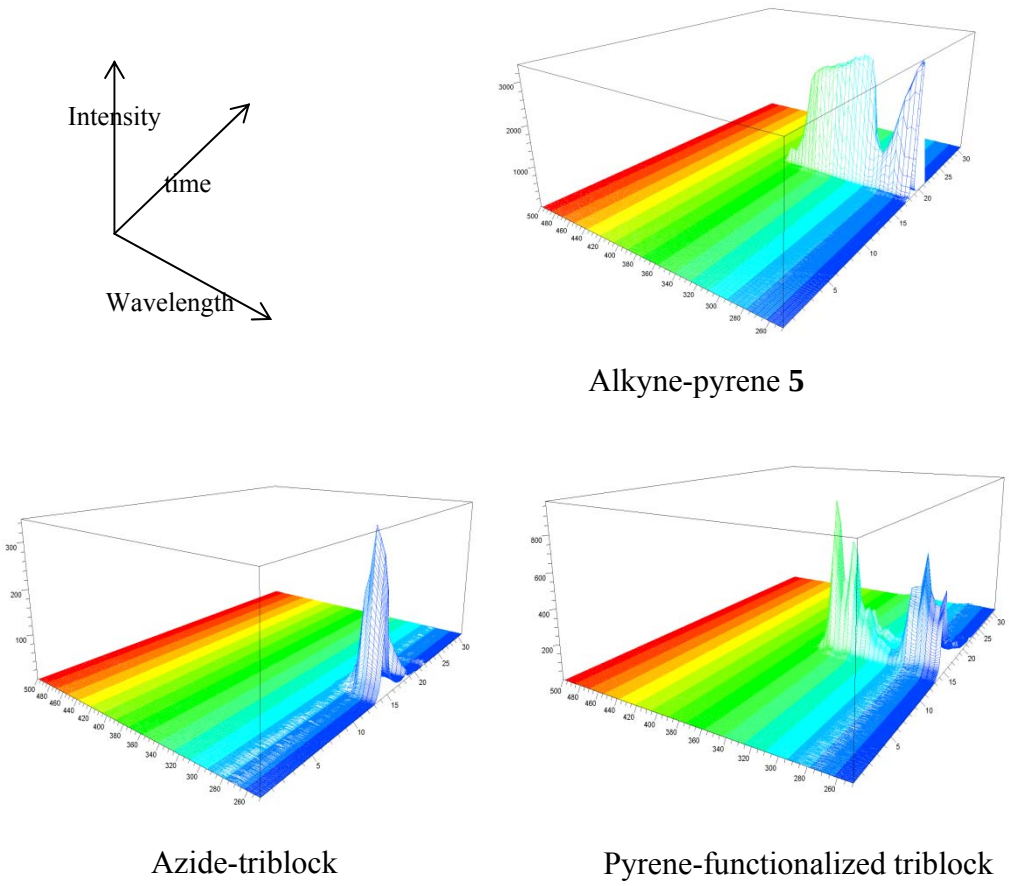


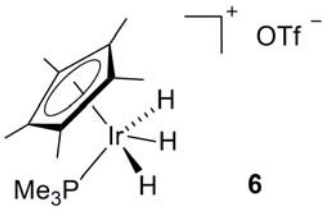
Figure 4. 3-D UV-Vis absorption spectra collected using GPC/HPLC instrument.

6 Isotopic Hydrogen Enrichment of Polymers

6.1 H/D Exchange Chemistry for Isotopic Enrichment of Polymers

Morphological studies on block polymers or other phase-separated materials can be conducted using neutron scattering techniques. The resolution of small-angle neutron scattering measurements, which can identify microphase-separated domains, can be enhanced if hydrogen atoms are replaced with deuterium. Typically, polymers are made with isotopically enriched monomers, which must be synthesized from the appropriate starting materials. Because polymerization methods frequently use an excess of monomer, a large amount of expensive reagents can be wasted following this approach. An attractive alternative would be to develop a method for isotopically enriching a polymer with deuterium atoms after polymerization. The main caveat to this approach is selectively incorporating deuterium into only one block so that enhanced contrast is achieved. This goal, of developing a low cost and facile method for incorporating deuterium into a specific block, was demonstrated for a series of block polymers using an iridium-based catalyst and deuterated acetone.

6.1.1 Catalyst Selection and Preliminary Screening



Based on previous literature precedent [25-30]the cationic iridium trihydride complex **6** was selected as a catalysts for hydrogen/deuterium exchange of various types of aliphatic and aromatic C-H bonds in polymeric substrates. Initially, a substrate scope was conducted among commercially available polymers and block copolymers (Table 4) with a range of steric and functional group diversity. Reactions were carried out in a J. Young-style or flame-sealed NMR tube complete with a sealed glass capillary tube containing 1,3,5-trimethoxybenzene and the same deuterated solvent chosen for the experiment (acetone-d_6 or benzene-d_6). The amount of catalyst used varied for each reaction but generally was less than 10 mol% relative to monomer repeat unit. The extent of H/D exchange was monitored over the duration of the experiment by ^{1}H NMR spectroscopy.

6.1.2 Arene H/D Exchange

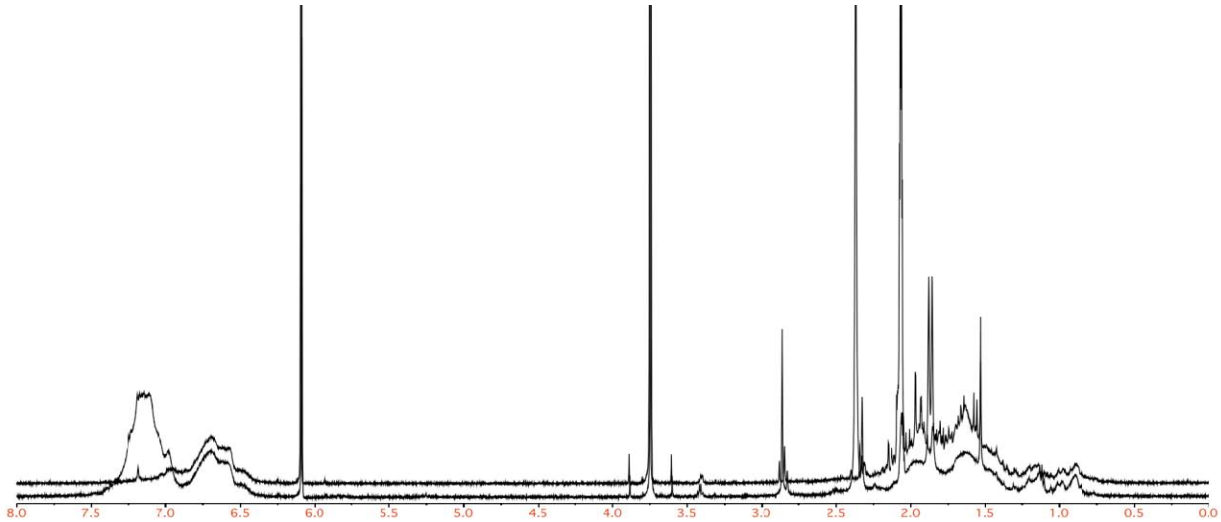


Figure 5: ^{1}H NMR spectra of polystyrene before (bottom) and after (top) 48 hours of reaction time.

Polystyrene showed the largest incorporation of deuterium of any of the pure single polymers, averaging 60% incorporation into the aryl C-H bonds in both acetone-d_6 and benzene-d_6. This amount of conversion could be reached in 10 minutes at 135 °C. The distribution and percentage of incorporation reflects the steric shielding of the ortho-position of the phenyl ring by the polymer backbone. No appreciable exchange was seen in the backbone over the course of 12 hours, which is consistent with literature precedent (Figure 5). The phenyl group of poly(benzyl methacrylate) also showed a similar amount of conversion of the aryl C-H bonds with no other H/D exchange noted elsewhere on the polymer chain. Other arene-containing polymers such as poly-4-vinylpyridine, poly(bisphenol A carbonate), poly(9-vinylcarbazole) were insoluble in the solvents necessary for catalyst activity, and polyaniline decomposed under the reaction conditions. Using D_2O might serve as an alternative solvent for these more-polar polymers.

6.1.3 H/D Exchange on Polymers with Functional Groups

Table 4: Deuteration of Polymer Substrates by Catalyst **1**.

Polymer	Deuteration in Acetone-d_6	Deuteration in Benzene-d_6
Polystyrene	60% (arene)	60% (arene)
Poly(ethylene oxide)	decomposition	decomposition
Poly(4-vinylpyridine)	insoluble	insoluble
Poly(2-hydroxypropyl methacrylate)		
Poly(methyl methacrylate)	0%	0%
Cellulose (Avicel)	insoluble	insoluble
Cellulose (trimethylsilylated)	decomposition	decomposition
Polyaniline	decomposition	decomposition
Poly(bisphenol A carbonate)	insoluble	insoluble
Polybutadiene	decomposition	decomposition
Poly(benzyl methacrylate)	60% (arene)	60% (arene)
Poly(9-vinylcarbazole)	insoluble	insoluble
Polycaprolactone	decomposition	decomposition
Poly(*N*-vinylpyrrolidone)	decomposition	decomposition
Poly(dimethylsiloxane)	decomposition	decomposition
Polystyrene-Poly(ethylene oxide)	60% (arene)	60% (arene)
Poly(ethylene oxide)- Poly(butylene oxide)	0%	0%
Polystyrene-Poly(methyl methacrylate)	60% (arene)	60% (arene)
Polystyrene-Poly(2-hydroxypropyl methacrylate)	60% (arene)	60% (arene)
Polystyrene-Poly(2-vinylpyridine)	50% (arene)	-

Polymers with functional groups such as ethers, esters, amides, and alcohols were tested and gave mixed results. Polyethylene oxide (PEO) and poly(2-hydroxypropyl methacrylate) were successfully deuterated in acetone-d_6 at 135 °C. Poly(2-hydroxypropyl methacrylate) has several different types of C-H bonds which are difficult to discern via NMR spectroscopy. The exchange gave indeterminate but measurable deuterium incorporation into the polymer after 48 hours. It is likely that the H/D exchange occurred on the propyl portion based on literature precedent.

Further spectroscopic studies are needed to confirm the exact location of the exchanged positions. Poly(methyl methacrylate) (PMMA) did not show any deuteration over 48 hours of reaction time, and cellulose (Avicel), trimethylsilyl-cellulose (silylated on every alcoholic position), poly(ethylene oxide), polycaprolactone, and polyvinylpyrrolidone all decomposed under the reaction conditions. The observation that PMMA and PEO are left unchanged while PS rapidly undergoes H/D exchange gives a promising route for making deuterium-enriched arene-containing block polymers.

6.1.4 Aliphatic H/D Exchange

Polybutadiene and poly(dimethylsiloxane) were subjected to the H/D exchange reaction conditions. By ^{1}H NMR spectroscopy polybutadiene (both the phenyl and hydroxyl-terminated variants) gave complete exchange of the alkenyl and allylic C-H bonds in benzene-d_6 but no conversion in acetone-d_6. Further analytical methods, including SEC are required to ensure that the polymer was not decomposing in addition to undergoing H/D exchange. Poly(dimethylsiloxane) decomposed under the reaction conditions. Polyethylene was not investigated because it of its poor solubility in the deuterated solvents used in this investigation.

6.1.5 Copolymer H/D Exchange

With preliminary screening of individual polymers completed, various block and co-polymers were subjected to isotopic scrambling experiments. Polystyrene was paired with poly(2-vinylpyridine), poly(2-hydroxylpropyl methacrylate), and poly(ethylene oxide). In all cases, polymer signals in the ^{1}H NMR decreased in intensity according to the results above. Poly[styrene-*b*-(2-vinylpyridine)] showed deuterium incorporation in both the phenyl and pyridyl signals (50% total conversion of aryl C-H bonds). Deactivation of the catalyst via coordination to nitrogen was not a barrier preventing H/D exchange for this block copolymer. The related poly(4-vinylpyridine) is expected to show H/D exchange chemistry due to the more accessible nitrogen atom, however, the control experiment was not performed. These results confirm that selective deuterium labeling of a single monomer or block-type can be achieved using iridium catalyst **6**.

7 Conclusions

The synthesis of various block polymers was attempted using controlled free radical polymerization. The best results for synthesizing a triblock polymer began from a commercially available hydroxyl-terminated PEO (MePEO(20k)-OH), which was converted into an NMP-containing macroinitiator. Polymerization of styrene and 4-(chloromethyl styrene) was successful but re-initiation did not always proceed with high efficiency. A difunctional initiator was synthesized for more diverse monomer selection. Materials synthesized via two orthogonal polymerization methods followed by a re-initiation of a diblock macroinitiator gave broadly dispersed triblock polymers. These polymers were characterized using NMR spectroscopy, size-exclusion chromatography, and small-angle x-ray scattering (forthcoming SAND report). No triblock polymers were synthesized containing a photo- or chemically cleavable block. A functionalizable polymer was synthesized via nucleophilic substitution of PCMS with sodium azide. This polymer was treated with the pyrene-alkyne moiety to give a pyrene containing PEO-b-PS material. Lastly, H/D exchange reactions were shown to isotopically enrich arene-containing polymers with deuterium over alkyl polymers. This selectivity leads to the possibility of making deuterium-enriched block polymers for neutron scattering.

8 Distribution

2	9018	Central Technical Files	8944
1	0899	Technical Library	4536

9 References

[1] Liu, G. J., Ding, J. F., and Stewart, S., 1999, "*Preparation and Properties of Nanoporous Triblock Copolymer Membranes*," Angew. Chem., Int. Ed. , 38 (6), pp. 835-838.
[2] Phillip, W. A., Rzayev, J., Hillmyer, M. A., and Cussler, E. L., 2006, "*Gas and Water Liquid Transport through Nanoporous Block Copolymer Membranes*," J. Membrane Sci., 286 (1-2), pp. 144-152.
[3] Chen, L., Phillip, W. A., Cussler, E. L., and Hillmyer, M. A., 2007, "*Robust Nanoporous Membranes Templated by a Doubly Reactive Block Copolymer*," J. Am. Chem. Soc., 129 (45), pp. 13786-13787.
[4] Chen, L., Hallinan, D. T., Elabd, Y. A., and Hillmyer, M. A., 2009, "*Highly Selective Polymer Electrolyte Membranes from Reactive Block Polymers*," Macromolecules, 42 (16), pp. 6075-6085.
[5] Phillip, W. A., Martono, E., Chen, L., Hillmyer, M. A., and Cussler, E. L., 2009, "*Seeking an Ammonia Selective Membrane Based on Nanostructured Sulfonated Block Copolymers*," J. Membrane Sci., 337 (1-2), pp. 39-46.
[6] Jackson, E. A., and Hillmyer, M. A., 2010, "*Nanoporous Membranes Derived from Block Copolymers: From Drug Delivery to Water Filtration*," ACS Nano, 4 (7), pp. 3548-3553.
[7] Phillip, W. A., O'neill, B., Rodwogin, M., Hillmyer, M. A., and Cussler, E. L., 2010, "*Self-Assembled Block Copolymer Thin Films as Water Filtration Membranes*," Acs Applied Materials & Interfaces, 2 (3), pp. 847-853.
[8] Kang, M., and Moon, B., 2008, "*Synthesis of Photocleavable Poly(Styrene-Block-Ethylene Oxide) and Its Self-Assembly into Nanoporous Thin Films*," Macromolecules, 42 (1), pp. 455-458.
[9] Zhang, M. F., Yang, L., Yurt, S., Misner, M. J., Chen, J. T., Coughlin, E. B., Venkataraman, D., and Russell, T. P., 2007, "*Highly Ordered Nanoporous Thin Films from Cleavable Polystyrene-Block-Poly(Ethylene Oxide)*," Adv. Mater., 19 (12), pp. 1571-+.
[10] Bang, J., Kim, S. H., Drockenmuller, E., Misner, M. J., Russell, T. P., and Hawker, C. J., 2006, "*Defect-Free Nanoporous Thin Films from Abc Triblock Copolymers*," J. Am. Chem. Soc., 128 (23), pp. 7622-7629.
[11] Feng, E. H., Lee, W. B., and Fredrickson, G. H., 2007, "*Supramolecular Diblock Copolymers: A Field-Theoretic Model and Mean-Field Solution*," Macromolecules, 40 (3), pp. 693-702.
[12] Fredrickson, G. H., Ganesan, V., and Drolet, F., 2002, "*Field-Theoretic Computer Simulation Methods for Polymers and Complex Fluids*," Macromolecules, 35 (1), pp. 16-39.
[13] Bates, F. S., and Fredrickson, G. H., 1999, "*Block Copolymers - Designer Soft Materials*," Physics Today, 52 (2), pp. 32-38.
[14] Gong, Y. M., Joo, W., Kim, Y., and Kim, J. K., 2008, "*Inorganic Nanoporous Films from Block Copolymer Thin Film*," Chem. Mater., 20 pp. 1203-1205.
[15] Yang, S. Y., Ryu, I., Kim, H. Y., Kim, J. K., Jang, S. K., and Russell, T. P., 2006, "*Nanoporous Membranes with Ultrahigh Selectivity and Flux for the Filtration of Viruses*," Adv. Mater., 18 (6), pp. 709-+.
[16] Olson, D. A., Chen, L., and Hillmyer, M. A., 2008, "*Templating Nanoporous Polymers with Ordered Block Copolymers*," Chem. Mater., 20 (3), pp. 869-890.

[17] Matyjaszewski, K., and Xia, J. H., 2001, "*Atom Transfer Radical Polymerization*," Chem. Rev., 101 (9), pp. 2921-2990.
[18] Moad, G., Rizzardo, E., and Thang, S. H., 2008, "*Toward Living Radical Polymerization*," Acc. Chem. Res., 41 (9), pp. 1133-1142.
[19] Lowe, A. B., and Mccormick, C. L., 2007, "*Reversible Addition-Fragmentation Chain Transfer (Raft) Radical Polymerization and the Synthesis of Water-Soluble (Co)Polymers under Homogeneous Conditions in Organic and Aqueous Media*," Prog. Polym. Sci., 32 pp. 283-351.
[20] Moad, G., Rizzardo, E., and Thang, S. H., 2006, "*Living Radical Polymerization by the Raft Process—a First Update*," Australian Journal of Chemistry, 59 (10), pp. 669-692.
[21] Ruehl, J., and Braslau, R., 2007, "*A Bidirectional Atrp-Nmrp Initiator: The Effect of Nitroxide Size on the Rate of Nitroxide-Mediated Polymerization*," J. Polym. Sci., Part A: Polym. Chem., 45 (10), pp. 2015-2025.
[22] O'brya, G., and Braslau, R., 2006, "*Terminal Functionalization of Polymers Via Single Electron Oxidation of N-Alkoxyamines*," Macromolecules, 39 (26), pp. 9010-9017.
[23] Zhao, H., Sterner, E. S., Coughlin, E. B., and Theato, P., 2012, "*O-Nitrobenzyl Alcohol Derivatives: Opportunities in Polymer and Materials Science*," Macromolecules, 45 (4), pp. 1723-1736.
[24] Cordaro, 2012,
[25] Klei, S. R., Golden, J. T., Tilley, T. D., and Bergman, R. G., 2002, "*Iridium-Catalyzed H/D Exchange into Organic Compounds in Water*," J. Am. Chem. Soc., 124 (10), pp. 2092-2093.
[26] Klei, S. R., Tilley, T. D., and Bergman, R. G., 2002, "*Iridium(Iii) and Rhodium(Iii) Complexes Bearing Chelating Cyclopentadienyl-Phosphine Ligands as C-H Activation Catalysts for the Deuteration of Hydrocarbons in D2o*," Organometallics, 21 (23), pp. 4905-4911.
[27] Chappelle, M. R., Harding, J. R., Kent, B. B., Jones, J. R., Lu, S. Y., and Morgan, A. D., 2003, "*Combining Microwave-Enhanced Deuteriation Reactions with Parallel Synthesis Procedures*," J. Labelled Compd. Radiopharm., 46 (6), pp. 567-574.
[28] Skaddan, M. B., Yung, C. M., and Bergman, R. G., 2004, "*Stoichiometric and Catalytic Deuterium and Tritium Labeling of "Unactivated" Organic Substrates with Cationic Ir(Iii) Complexes*," Org. Lett., 6 (1), pp. 11-13.
[29] Yung, C. M., Skaddan, M. B., and Bergman, R. G., 2004, "*Stoichiometric and Catalytic H/D Incorporation by Cationic Iridium Complexes: A Common Monohydrido-Iridium Intermediate*," J. Am. Chem. Soc., 126 (40), pp. 13033-13043.
[30] Golden, J. T., Andersen, R. A., and Bergman, R. G., 2001, "*Exceptionally Low-Temperature Carbon-Hydrogen/Carbon-Deuterium Exchange Reactions of Organic and Organometallic Compounds Catalyzed by the Cp*(Pme3)Irh(Clch2cl)(+) Cation*," J. Am. Chem. Soc., 123 (24), pp. 5837-5838.