Polyolefin/layered silicate nanocomposites via surface initiated ring opening metathesis polymerization

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Polyolefin/layered silicate nanocomposites via surface initiated ring opening metathesis polymerization

by

Sri Harsha Kalluru

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY

Major: Chemical Engineering

Program of Study Committee:
Eric W. Cochran, Major Professor
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Chris R. Williams

Iowa State University
Ames, Iowa
2016

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DEDICATION

I would like to dedicate this thesis to my family for always being there for me and supporting me through my studies and endeavors of my life.
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ABSTRACT

This thesis reports about the synthesis of thermoplastic elastomers via polyolefin/layered silicate nanocomposites and fabrication of porous membranes using a triblock Poly(styrene-b-isoprene-b-dimethylsiloxane) (SID) block copolymer. The first project work started as second phase of a NSF CAREER grant to study the properties of nanocomposites synthesized using polyolefins like norbornenes, alkyl substituted norbornenes and cyclopentene to engineer high performance nanocomposites. The polymers will be surface initiated from clay using ring opening metathesis polymerization and subsequent hydrogenation forms thermoplastic elastomeric nanocomposites with synergistic properties from mechanical reinforcement offered by layered silicates, enhanced thermal properties due to changed chain conformations and effects of block copolymers to combine different polymeric properties.

First published article on this work reported the successful synthesis of diblock copolymer/layered silicate nanocomposite via surface initiated ring opening metathesis polymerization (SI-ROMP) of norbornene and cyclopentene from montmorillonite clay (MMT) surface. The surface of MMT clay was organo modified using norbornene-terminated alkyl ammonium surfactant and block copolymer brushes were polymerized from the clay surface and disordering and dispersing the clay platelets in polymer matrix. Non-clay counterparts were obtained via reverse ion exchange methods and characterized in parallel with corresponding nanocomposite. Thermal, mechanical and morphological characterization showed the property enhancement due to addition of clay and showed good exfoliation of MMT.

After successful demonstration of exfoliated nanocomposites using surface initiated polymerization technique, we focused on development of nanocomposites with ethylidene norbornene as first block and cyclopentene as second block; subsequent hydrogenation of first block results in a soft and elastomeric poly(ethyl norbornene) block and second block results in a perfectly linear semi crystalline poly(ethylene) block. We followed the same experimental procedure used in the first article with necessary changes accommodating the needs of new monomer to synthesize exfoliated nanocomposites. We were successful in synthesizing surface initiated hydrogenated nanocomposites with clay exfoliation,
however subsequent property evaluation in conjunction with the non-clay analogs showed that addition of clay negatively effects the thermal properties of hydrogenated poly(ethylidene norbornene) block. This observation was contrary to our hypothesis that clay confines the polymer chain movement and results in enhancement of thermal properties.

The second project in my thesis work focused on the study of porous membranes fabricated from a class of triblock copolymers for carrying out separations. This project exploits the microstructures formed due to self-assembly of block copolymers to form percolating network of pores in membranes fabricated using block copolymer material. A Poly(styrene-b-isoprene-b-dimethylsiloxane) (SID) block copolymer was studied as a potential system. A SID triblock copolymer resulting in gyroid phase was synthesized, characterized and fabricated as a thin porous membrane after chemical etching of D block and forming a network of pores with I block as pore lining and S block as membrane backbone. This membrane was tested via flow through experiments to establish successful separation based on size.
CHAPTER 1. INTRODUCTION AND BACKGROUND

Part A: Nanocomposites

General introduction

A composite is a heterogeneous material synthesized from two or more distinct components resulting in a hybrid material with synergistic properties superior to its constituents. There are many important naturally occurring composites for example, wood - comprising cellulose in lignin matrix or bones - comprising collagen as flexible material. These examples have improved properties compared to their constituent materials. Ever-increasing demand for low cost materials with improved properties like high specific strength, improved processability, enhanced thermal properties and barrier properties has driven research in composites. Composite materials consist of a continuous bulk matrix, which can be polymer, metal or ceramic and a discontinuous dispersed reinforcement material like particles, filaments, platelets etc. In the world of polymers, addition of inorganic fillers to improve properties, mainly mechanical, is an age old practice. However, if there is no significant interaction between the filler and polymer, property enhancement would be very modest and sometimes constituent materials may even forego some of their inherent properties.  

Search for suitable fillers, optimal mixing compositions and efficient synthesis mechanisms to achieve maximum interaction between both the materials has always attracted researchers. The term “nanocomposite” refers to a composite in which at least one dimension of the filler is in nanometer range. Nanofillers characteristically have large particle densities, particle-particle correlations, and very high interfacial area per volume. These characteristics make nanocomposites distinct from conventional composites in that the fine dispersion of filler in the polymer matrix can lead to highly improved synergistic properties. Type of nanofiller employed (like nanotubes, nanoclay, nanosilicates etc) and mechanism of dispersion have greatly influenced the property enhancement as was observed by experimental research and computational studies. The dispersion of
nanofillers in polymer matrix has been a difficulty task because nanofillers would like to form aggregates because of strong particle-particle interactions and attractive forces. In late 1980s, researchers at Toyota synthesized a new group of nanocomposites called polymer/layered silicate nanocomposites (PLSNCs). These nanocomposites were synthesized by exfoliating layered silicate (clay) platelets into a polyamide matrix. They successfully synthesized nanocomposites comprising 1-5 wt% of organically modified montmorillonite (MMT) and nylon-6 by in situ polymerization. They reported substantial improvement in heat distortion temperature (HDT), tensile strength and tensile modulus. They studied the use of timing belt made from this material, successfully commercializing the product. This was the first commercially available nanocomposite which drove the exponential growth in research in this field of study.

Layered silicates

Clay has been studied widely because of its abundance in nature, good dispersion properties and established intercalation chemistry. Some of the commonly used clay minerals are montmorillonite (MMT), kaolinite, sepiolite, etc. Most of these clay minerals have strong dispersion and good cationic exchange capacities in most solvents, and are highly hydrophilic. Hence, the clay surface must be modified if they were to be used in nanocomposites with hydrophobic polymers. These surface modifiers will act as compatibilizers between the hydrophilic nano-clay and the hydrophobic polymer, resulting in good interaction. Nanofillers in which one dimension is in nanoscale range and other two dimensions in microscale range have assumed platelet structures; these are called 2:1 phyllosilicates. The phyllosilicate structure consists of a two dimensional layer formed by combining two tetrahedral metal/silicate layers with inter-gallery spacing to form an octahedral metal oxide lamina. MMT is the most commonly preferred layered silicate for synthesis of polymer nanocomposites. MMT is from pyrophyllite family with the general formula Al₄[Si₄O₁₀](OH)₂. MMT undergoes isomorphic substitution with other metal atoms like sodium and magnesium, and hence has charge on its layers, which helps MMT platelets hold together through weak electrostatic and Van der Waals forces, creating a gap called as inter gallery spacing. Water molecules can easily sweep into the gallery spacing, resulting in the hydration of the ions and causing considerable crystalline swelling. In particular, Na⁺-MMT has very good cation exchange capacity (CEC), making it an excellent candidate for organic modifica-
When the sodium ion is replaced with a suitable surfactant, the intergallery spacing can swell as much as three-folds. However, because of the size of these MMT platelets, they have very high internal surface area and hence greater tendency to form agglomerates rather than disperse independently. Depending on the extent of mixing that could be achieved between the layered silicates and polymers, three distinct scenarios have been observed: immiscibility, intercalation and exfoliation as shown in Fig.1.1. On the left side is the case of “immiscibility”, where in MMT clay is not wetted by the polymer and hence the clay particles form large tactoids or aggregates. In this case a XRD (x-ray diffraction) measurement of the polymer may show a strong peak corresponding to the original MMT $d$-spacing, indicating that clay platelets are not separated. The case in the center in Fig.1.1 illustrates the “intercalation” of clay; as suggested in the figure, the MMT $d$-spacing has increased because of the polymer entering the inter-gallery region. But, in this case a XRD measurement would just shift the peak to a slightly larger $d$-spacing, indicating that the crystal structure of the MMT clay is still intact. The case shown on the right in Fig.1.1 is the exfoliation, which would be a result of the delamination of the MMT clay crystal structure in the polymer matrix. A XRD measurement would not show any regular $d$-spacing peak in this case. Many methods have been employed to disperse the MMT clay in polymer matrix to achieve maximum exfoliation: more on this subject would be discussed in the synthesis of nanocomposites section.
**Organic modification of clay**

The organic modification of clay promotes thermodynamic compatibility between the clay and polymer. Surface modification of clay has been studied widely and a number of different synthesis procedures have been cited in the literature. The sodium ions in the inter-gallery space of the clay can be reversibly replaced via exchange process with surface modifiers and make it compatible with non-polar polymers. This material is a hybrid of organic/inorganic material and this principle is called an ion-dipole method. These compatibilizers can be molecules with hydroxyl, ester, ether, aldehyde or ketone functional groups. There are wide varieties of surface modifiers, but most popular are alkyl ammonium (quaternary ammonium cations). These surfactants have very long carbon chains, which, when attached to high energy Na⁺-MMT, will reduce its surface energy. Some examples of organic modifiers are octadecyltrimethylammonium or dioctadecyldimethylammonium etc. The negative charge on the modified clay associates with the cationic ammonium head group of the modifier while the tail radiates away from the surface. Many researchers have studied the effects of the surface modifiers to achieve maximum increase in inter-gallery spacing of the clay. This organic modification not only modifies the clay surface but will also increase the $d$-spacing, making it easier to synthesize nanocomposites. The amount of increase in the $d$-spacing because of the addition of the surface alkyl ammonium ions depends on the charge densities of the constituents and have been predicted using molecular modeling by Hackett et al. They have predicted models wherein monolayer, bilayer, and trilayer arrangements were possible, with highest amount of $d$-spacing increase observed for trilayer arrangement which nearly doubled the $d$-spacing compared to pristine MMT clay in one particular case study. Simons et al. have extensively studied the effects of alkyl ammonium surfactant architecture on the synthesis of nanocomposites. They concluded that for achieving exfoliation of MMT in polymer matrix by in-situ polymerization methods, the surface modifier should have the following structure: 1. Position of the ammonium ion on the surfactant (head/tail) 2. Presence of polymerizable group 3. Solubility of surfactant in the monomer 4. Very high exchange capacities and 5. Length of alkyl chain. This also adds to the observations that longer alkyl length on the surfactant and good compatibility of the surface modifier with the monomer being used for polymerization would increase the chances of achieving maximum exfoliation.
Controlled "living" polymerization

Precisely controlling the rate of polymerization becomes paramount to develop exfoliated nanocomposites. A living polymerization is a technique where instant chain initiation takes place, chain propagation is at a controlled rate for all the growing polymers chains and chain termination is insignificant. Such conditions would lead to polymer synthesis with target molecular weights and very low polydispersity indices (PDI) (PDI is a measure of molecular weight distribution). In a controlled living polymerization, once all the monomer is consumed, the end functionality of the polymer chain remains active hence propagation of a second monomer becomes viable leading to synthesis of block copolymers with precise control over block compositions. Many types of polymerizations like anionic polymerization, atom transfer radical polymerization, radical addition fragmentation chain transfer, ring opening metathesis polymerization among others are studied as living polymerization techniques. As discussed by Behling, most of the methods mentioned would be strong candidates to perform living polymerization with merits and demerits to each method. The method of polymerization depends on the choice of monomers being used, which in our case is Ring Opening Metathesis Polymerization (ROMP) because of the use of cyclic olefin based monomers.

Ring opening metathesis polymerization (ROMP)

Metathesis is a type of reaction in which two molecules interchange atoms. It can also be explained as a reaction where existing double bonds are broken and new ones are created, referring to metathesis. ROMP is a type of olefin metathesis involving a ring opening mechanism. ROMP is considered living polymerization reaction under conditions that it has instant initiation and chain propagation could be controlled. ROMP is a reversible reaction, and equilibrium is attained very fast, reaction rate is
as high as $10^4$, a truly remarkable reaction. Ease of performing ROMP depends on the ring strain in the monomer and is thermodynamically favorable for large membered rings. ROMP catalyst contains transition metal center (referred as [M]), and a ligand system (Ln) to enhance rate and good reaction control. In ROMP, initiation is started by forming a metal-carbon bond; then for propagation, monomer comes and attaches to the metal and previously polymerized group. The function of ligand system is explained in further sections. There are many ROMP catalysts with different metal centers and ligand systems, among them tungsten, molybdenum, titanium, ruthenium are very popular. The metal centers are limited by the use of different functional group monomers, polarity to different solvents and sensitivity to air and moisture. Two of the most commonly used modern day ROMP catalysts are: Schrock type catalyst with tungsten or molybdenum metal centers and Grubbs’ type catalyst with ruthenium metal center. The efficiency of ROMP catalysts was developed over a period of time to give better initiation and control over propagation aided by better use of ligand systems. Compared to ruthenium based metal center catalyst, Schrock type catalyst has lower functional group tolerance and poor sensitivity to air and protic solvents. Ruthenium (Ru) catalysts were developed with stable mechanisms for broad range of monomers, with electron rich ligand systems of high activity. Because of their flexibility, Ru type catalysts gained commercial importance and are widely used for living ROMP reactions and block copolymer synthesis.

Our choice of monomers for the current work are cyclic olefins like norbornene, ethylidene norbornene and cyclopentene. The factors leading to the use of these particular monomers are explained in further sections in detail. Herein, a brief knowledge about the monomers is given to better understand the ROMP mechanisms.

Norbornene is a canonical monomer for ROMP because of its ready commercial availability, high ring strain and ability to form living polymers. Polynorbornene (PNbn) is commercially available as Norsorex and is the first of olefin metathesis reactions to be commercialized. Schrock type catalysts were used for polymerization reactions with very high activity but the synthesized polymers have less syndiotacticity. On the other hand, despite having less activity Ru type catalysts give polymers with high trans and good isotactic bias, gives good functional group tolerance, does not require stringent inert conditions and polymerization rate could be controlled more effectively. There are different generations of Ru type catalysts available commercially for conducting ROMP, but norbornene is a pe-
Figure 1.3. Polymerization schematic of ROMP. This figure illustrates the polymerization process of ROMP, showing the initiation, propagation, and termination steps. The polymerization schematic involves a monomer (ligand L, metal M, and monomer R) reacting to form a polymer with good molecular weight distribution (MWD) and low polydispersity index (PDI).

Cyclopentene (CPE) is a five-membered ring with a low ring strain that makes the use of ROMP technique for polymerization a difficult process. It can be polymerized using a Schrock type ROMP catalyst with good control over molecular weight and PDI of the polymer. Trzaska et al. performed ROMP of CPE using a Mo-based Schrock type catalyst and demonstrated that living polymers with very low polydispersity indices could be synthesized. They also hydrogenated the polymer to get perfectly linear polyethylene. But, we would not want to deviate from using Grubbs’ catalyst because of norbornene and hence we will explore the use of Grubbs’ catalyst for ROMP of cyclopentene too. Performing ROMP of CPE using Grubbs’ catalyst gives acyclic diene metathesis (ADMET) reaction as a side reaction, which inhibits the preparation of high molecular weight polymers and increases the distribution of polymers by forming oligomers. Lee et al. discovered that ADMET effect in ROMP of
CPE can be reduced by adding excess of ligand and maintaining monomer concentration well over 3 M. They were able to synthesize block copolymers with CPE indicating the living nature. For this reason, the polymerization of CPE is terminated prematurely to suppress side reactions. Myers et al. prepared Poly(cyclopentene) (PCpe) at room temperature using Grubbs’ catalyst and a co-catalyst of tricyclohexylphosphine resulting in polymers with PDI of 1.15. Co-catalyst is a Grubbs’ catalyst ligand material which when added in excess to the ROMP reaction can control the amount of propagating active species effectively controlling the rate of polymerization. It also helps in keeping the oligomers concentration at minimum and shifts the equilibrium towards polymer as the monomer concentration gets depleted.

**Block copolymers (BCPs)**

Block copolymers contain two or more distinct polymers covalently attached to form one big polymer chain. BCPs combine properties of all the constituent polymers and possess superior properties compared to homopolymers. Usually, BCPs are synthesized using living polymerization techniques, by sequentially adding monomers after completely polymerizing the previous monomer. ROMP is especially an important polymerization route to form living polymers with cyclic olefins and opens a new arena for producing thermoplastic elastomers. Hatjopoulos et al. carried out polymerizations of block copolymers via ROMP and formed thermoplastic elastomers containing alkyl norbornenes by subsequent hydrogenation. Li et al. studied the synthesis of diblocks with PNbn and PCpe which on subsequent hydrogenation gives hydrogenated PNbn and linear polyethylene polymer. They have studied the effects of BCP composition and MWD on glass transition, crystallinity etc. Register et al. also studied diblock copolymers formed with PNbn and PCpe using a Schrock type catalyst, and adding a co-catalyst to control the MWD. This work cited in the literature was very helpful in modifying the ROMP to suit the needs of block copolymerization using layered silicates which is discussed in more detail in the next section.

**Synthesis of nanocomposites**

As explained in the figure 1.1, different synthesis procedures are being employed to fabricate polymer layered silicate nanocomposites (PLSNC). The synthesis procedures could be classified based on
the type of dispersion achieved in the nanocomposites like intercalated and delaminated hybrids. In intercalated hybrids, the preparation methods are: Solution dispersion, where preformed polymer is mixed with the clay in a solution; direct melt intercalation, where molten polymer and organically modified layered silicates are annealed above their glass transition temperatures and mixed under shear. The application of shear would break the clay aggregates and the molten polymer would enter the gallery spacing and further push the platelets apart. But the amount of dispersion is limited in these methods thus forming only intercalated structures is possible. However, this synthesis procedure is highly favored by industry because of its cost-effective nature and ease of processability. For delaminated/exfoliated hybrids the synthesis methods are: polymer adsorption process, where preformed polymer and modified clay is dissolved in solvent, and the solvent is carefully evaporated adsorbing the polymer onto the surface and efficiently sandwiching polymer and clay forming nanocomposites; in-situ polymerization technique where layered silicates are dissolved in monomer followed by polymerization, thus allowing the polymer to be formed in the confined molecule-sized inter gallery spacing. Polymerization can be carried out by diffusion of initiator or by exchanging catalyst onto the surface of clay. The later method is called Surface Initiated polymerization (SIP).\textsuperscript{5,58} Toyota researchers have used the former method in synthesizing their pioneering nylon-based nanocomposites. Because of the promise shown by in-situ polymerization technique many researchers have started working on using this technique to synthesize highly exfoliated nanocomposites.\textsuperscript{22,29,30,34,42} SIP method offers good diversity with the variety of polymerization types employed and monomers that could be used for in-situ polymerization, when having suitably modified clay platelets and good initiator. Because the clay platelets are already pushed apart because of addition of surfactant and initiator addition, polymerization of the monomer from the surface of the clay could efficiently delaminate the crystal structure of MMT, disordering it in different directions and potentially encapsulating each individual clay platelets in polymer matrix. However, because the SIP process is carried in the confined spaces of clay inter-gallery spacing, side reactions become more prevalent and polymerization control becomes more challenging compared to normal bulk polymerization. Over the past two decades, many surface initiated polymerization procedures were researched with fairly good success in achieving exfoliated structures. Weck et al. formed intercalated composites by attaching an anchor to the silica surface and performing surface polymerization. They have observed that due to confinement of the formed polymer in the small paces between
clay platelets and also due to steric factors, they tend to point towards the edge away from the contact point and wrap around the clay platelet.\textsuperscript{54} Kim et al. and Juang et al. performed surface polymerizations with silica-based anchoring molecules and they used norbornene as monomer and performed surface-initiated ROMP to successfully synthesize nanocomposites. They have covalently attached the polymer to the filler surface and effectively showed that the polymer thickness and growth could be controlled.\textsuperscript{25,28} Edmondson et al. reviewed all types of surface initiated polymerizations, and concluded that any living polymerization can give good exfoliated nanocomposites.\textsuperscript{12} Surface initiated polymerization is a very good way to control the growth of polymer brushes attached to surfaces and also impart some special physical properties by tailoring the polymer brushes. These synthesis methods provide evidence for use of ROMP surface initiated polymerization using many filler particles and we believe we can employ modified MMT as filler to develop exfoliated diblock copolymer nanocomposites.

**Part B: Block copolymers for porous membranes**

**General introduction**

We have discussed block copolymers (BCPs) and their applications in designing hybrid polymeric materials in the preceding sections. Numerous industry applications of BCPs take advantage of their synergistic bulk properties to develop like high strength materials, adhesives, additives and many others.\textsuperscript{24} In this section, an introduction to self assembly of BCPs and how that helps in understanding the structure-property-processing relationships is explained. Then, the mechanism in which the self assembly can influence the design of materials to suit applications related to fabricating porous membranes is discussed. BCPs consist of dissimilar polymers covalently attached to each other. Because the constituents are generally immiscible yet bound to one other, BCPs tend to microphase separate into numerous ordered microstructures. This phenomenon can be exploited to synthesize polymer derived membranes for applications like membrane separations, drug delivery, nanolithography among others.

**Block copolymer microstructures**

Block copolymers segregate into micro-phases with well-defined ordered microstructures (morphologies) because of thermodynamic balance between block-block contact energies and entropy driven
stretching. These ordered structures disappear if the system is heated above certain temperature called order-disorder transition. Depending on the type of polymer blocks, their volume fraction and how they are connected in the system, block copolymers can form microstructures like: lamellae, cylinders, spheres, gyroid (double gyroid, alternating gyroid) and many other structures. Based on the number of blocks in the system predicting the ordered structure may vary from being simple to very complex; diblock copolymer system may form very limited number of microstructures but as we move to triblock and higher identifying these structures becomes very complicated. As explained earlier, the phase separation due to enthalpic and entropic balance leads to ordered microstructures; Flory and Huggins have described the relation between thermodynamic properties to qualitatively asses the polymer-polymer interactions.\(^{20}\)

\[
\frac{F}{kT} = \frac{f_A}{N_A} \ln f_A + \frac{f_B}{N_B} + f_A f_B \chi_{AB}
\]

In last few decades, there has been great amount of research focused in determining how the network morphologies form by using both experiments and simulations.\(^{40}\) Development of living polymerization techniques made the possibility of synthesizing polymers with very well defined morphologies, compositions and also increased the number of monomers that could be used.\(^{21}\) Anionic living polymerization, a type of living polymerization resulting in precisely controlled block compositions enabled the synthesis of various commercially available block copolymers mainly styrenic block copolymers. This procedure is notoriously known to demand high purity precursors and highly sensitive air and moisture environments. However, the materials synthesized via this procedure showed highly promising applications. Hence, we used this procedure to synthesize the triblock copolymer system we studied in this work: poly(styrene)-b-poly(isoprene)-b-poly(dimethyl siloxane) (SID).

SID, being a triblock copolymer system, can form most of the structures showed in the figure 1.4. In particular, one triply continuous structure gyroid phase (third from left in 1.4) has found exciting applications because of its network continuity. One article by Shefelbine et al. talks about the formation of core-shell gyroid morphology\(^{46,50}\) using a certain triblock copolymer system. We chose a glassy first block, poly(styrene) and two rubbery blocks: poly(isoprene) and poly(dimethylsiloxane). The membrane should allow materials to enter one of the rubbery domains (e.g., D), and the S channel forms the membrane matrix and I channel gives the pore layer which having a double bond is convenient for
both crosslinking to increase strength and functional group attachment to facilitate transport.

Some disadvantages of currently available membranes are having random and wide pore network, tortuous pore path, high flow resistance, fouling and sub-par performance.\textsuperscript{53} One of the methods available to synthesize porous membrane structures from BCPs is etching of the desired polymer block using chemical methods. Changing the pore size in conventional membranes is a very laborious process while changing the pore diameter in block copolymer derived membranes presented in this work can be accomplished by just change in volume fraction of the etchable block. We have presented wider discussion on this topic in later chapters. The double-gyroid microstructure (space group $Ia\overline{3}d$) is a triply periodic network morphology, which has very high network continuity and known to form structures with very few crystal defects. The continuous network structure of double gyroid is believed to give a very good percolating pore structure, which could prove to be a very nice feature to develop porous membranes for separation applications. Identifying and synthesizing SID material with well defined microstructure, easy tunability of pore functionality and availability of wide pore size ranges can lead to exciting membranes with wide application range.

**Separations and membranes**

Fabrication of membranes using ordered network morphologies formed by block copolymers is one of the projects developed to meet the needs of separations industry for various applications like recovering green house gases, separation of toxic materials from feed systems, recovering high value products among many others. There is a demand for development of highly functional membranes to cater to the needs chemical, water treatment, food, dairy, pharmaceutical, textile and electronic industries among others.\textsuperscript{36,56} In current work, we aim to develop and investigate properties of a new class of innovative
nano structured membranes derived from block copolymer materials that can cater to broad range of separations needs of various industries. We believe biotechnology industry can be a key benefactor to porous membranes developed in the work reported here. The key to improvement of biotechnology field lays in development of large scale separation techniques which will suit to the needs of the materials being handled. Most of the bioseparations become very difficult as the products are labile and cannot be exposed to extreme thermal and mechanical stresses as observed in conventional separation processes like distillation, evaporation etc. Many researchers have studied the applied membrane separations for biotechnology needs like protein separation, hemodialysis, fermentation processes, antibiotics and recovery of bio-materials. We believe that polymeric membrane separations can be an advantageous technique that can be tailor made to variety of bioseparations and may also be able to scale-up for industrial production. Literature review has shown that many polymeric membranes have been employed for separation/extraction of different materials that met with different success rate.

**Bibliography**


CHAPTER 2. THESIS OVERVIEW

Since late 1980s, after the first successful synthesis of polymer/layered silicate nanocomposites by researchers at Toyota, many scientists working in nanotechnology focused their research work on this area. However, synthesizing nanocomposites with highly exfoliated clay platelets dispersed in the polymer matrix is still a challenge. In this thesis work, we explored the surface initiated polymerization route for potentially synthesizing highly exfoliated clay structures in nanocomposites. In the method employed in this work, surface of clay platelets was organo modified with an alkyl ammonium surfactant which was initiated by a catalyst and subsequent addition of monomer starts polymerization from the surface of the clay thus disordering and homogeneously mixing clay in polymer matrix. This way the polymer was tethered to the clay surface, in theory encapsulating individual clay platelets in polymer, as represented in the figure 2.1. This procedure was used to synthesize diblock copolymers by sequential addition of monomers resulting in materials with synergistic properties. In the work presented here, we started working with Montmorillonite (MMT) clay and an in house made surfactant for clay surface modification. Then, surface initiated Ring opening metathesis polymerization was employed with monomers like norbornene, ethylidene norbornene and cyclopentene to form diblock copolymer nanocomposites. The mechanical reinforcement provided by MMT clay, polymer tethering to clay surface and block copolymer properties would enhance physical, thermal and mechanical properties compared to non-clay polymers. Literature review presented in the introduction section and the chapters 3 and 4, would present more detailed information on these methods and the results observed.

In another worked carried out relating to block copolymers, porous membranes fabricated from triblock copolymer materials were tested as potential candidates for carrying out in situ separations. Block copolymers are fascinating materials with synergistic properties from all its constituents polymer blocks. They are known to microphase separate into complex ordered microstructures because of incompatibility between individual polymer blocks covalently attached together. Researchers have
exploited the properties and microstructures of block copolymers for various engineering applications, for example employing them as membranes for separations.\textsuperscript{65,66} Need of energy sensitive separation methods in bioseparations and potential use of membranes as a viable methods is the main motivation of this work. Block copolymer based membranes are formed after selectively etching one of the polymer blocks resulting in a network of percolating pores. Few advantages of membranes fabricated via this route being, ability to change the pore size very easily and ability to functionalize the pore wall by careful selection of polymer blocks. One of the ordered block copolymer microstructure know as Core-shell gyroid morphology (\textit{Ia3d} symmetry) has very high continuity and least grain boundary defects making the materials possessing this microstructure a potential candidate for synthesizing membranes from block copolymers. In current work, we used poly(styrene-b-isoprene-b-dimethyl siloxane) (\textbf{SID}) triblock copolymer system to fabricate thin membranes and then selective chemical etching of \textbf{D} channel lead to formation of continuous network of percolating pores, with \textbf{I} channel as the pore lining (also slight cross linking of this block gives more strength to the membrane) and the \textbf{S} channel forming the membrane backbone, as can be seen in \ref{fig:2.2}. Successful synthesis of SID polymer with the required microstructure and its characterization; fabrication of porous membranes and their use for size separation is demonstrated in chapter 6 of this thesis report.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{reaction_scheme}
\caption{Reaction scheme for the synthesis of block copolymer nanocomposites via surface initiated polymerization route (reproduced from\textsuperscript{59})}
\end{figure}
Figure 2.2. Depiction of the double gyroid network morphology known to form in ABC triblock copolymers such as SID. Here the red region represents poly(styrene), the structural component of the membrane, while the green area is the poly(isoprene) that lines the pore walls. Pores are formed by first casting SID polymer into a membrane shaped disc, lightly crosslinking the poly(isoprene) with dicumyl peroxide (further enhancing mechanical integrity) and then applying TBAF to selectively etch the poly(dimethyl siloxane) (red color).

Bibliography


CHAPTER 3. EXPERIMENTAL AND ANALYTICAL METHODS

This Section contains comprehensive information about materials, synthesis procedures and characterization methods. The objective is to describe procedures carried out to synthesize materials in a detailed way and present background information about the characterization techniques used to analyze these materials. A brief description of methods section could be found in individual chapters with more emphasis on characterization part.

Nanocomposites project - Part A

Synthesis procedures

Materials

Chemicals used for synthesis of organic modifier were 5-norbornene-2,3- dicarbonyl chloride, 11-bromo-1-undecanol, diethyl ether, pyridine, magnesium sulfate, deionized water, hexanes, trimethyl amine, and ethanol. All chemicals were purchased from Sigma Aldrich and used as received. Montmorillonite(MMT) clay (Cloisite-Na+) was generously supplied by Southern clay products inc.

Equipment

Equipment like rotovap, alumina flash chromatography column and liquid liquid extraction were used in this method.

Surface modification of MMT

Synthesis of surfactant The synthesis procedure described here was adopted from literature after making necessary modifications to suit the needs of our research work. The surfactant synthesized via this procedure was used to modify the surface of MMT clay in nanocomposite materials prepared
in this work. The synthesis procedure started by mixing stoichiometric amounts of bromo undecanol and pyridine in diethyl ether stirring in an Erlenmeyer flask. A Second solution containing measured amounts of norbornene (di) carbonyl chloride in diethyl ether was prepared and poured into a graduated burette for a controlled drop-wise addition for over an hour into Erlenmeyer flask and stirred for at least 5 h. Care was taken to cover the flask mouth with aluminum foil to avoid vaporization of ether. The salt formed after the reaction was filtered, washed with diethyl ether for two times and the eluent was transferred into round bottom flask and roto-evacuated to get yellow oil, which was retained in the flask. Then, measured amount of diethyl ether was added to the recovered yellow oil and three liquid liquid extraction cycles were performed with deionized water. During each liquid liquid extraction cycle, the unwanted bromine salt gets separated into water phase and is discarded appropriately. The phase which is slightly yellow in color is retained for further steps. The final recovered solution was mixed with magnesium sulfate to remove any trace amounts of water and mixed with required amount of hexanes. This solution was passed through an activated alumina flash chromatography column with hexanes as eluent and the final solution was roto-evacuated to recover a highly viscous yellow oil. At this point, the surfactant needed is synthesized minus the ammonium ion head. The viscous yellow oil was dissolved in trimethyl amine and ethanol mixture and stirred at 40°C for 96 h. The resultant solution was roto-evacuated to recover a more viscous yellow oil which after vacuum drying resulted in a waxy solid. This waxy solid was analyzed for structure using NMR, the analysis procedure is discussed later in this section.

**Addition of surfactant to MMT clay** The organic modification of MMT clay was carried out by exchanging the sodium ions on the surface of MMT clay from the inter-gallery spacing with the in-house made alkyl ammonium surfactant in an aqueous solution. Measured amounts of this surfactant and water was mixed in deionized water at room temperature for at least 30 min. In another flask, required amount of MMT clay (usually 1:1.25 ratio for surfactant to MMT clay) was mixed in deionized water at 70°C and stirred for 1 h and then heating is stopped to cool the contents to room temperature. Both solutions were mixed and stirred for 4 h; then filtered out to recover ion exchanged clay. This functionalized clay was washed with excess of deionized water, filtered and vacuum dried to recover dry surfactant functionalized clay (f MMT). Functionalized MMT clay was analyzed with techniques
like XRD, to analyze the increase in \( d \)-spacing of the MMT due to surface modification; TGA, to analyze the amount of cation exchange.

### Synthesis of bulk polymers and surface initiated nanocomposites

### Materials

Precursors like norbornene, ethylidene norbornene, cyclopentene and dichloromethane were purchased from Sigma Aldrich. These chemicals were subjected to freeze-pump-thaw cycles to remove oxygen contamination. Norbornene being a solid material, was first dissolved in dichloromethane at required concentrations along with calcium hydride (purchased from Fisher) and distilled off as pure norbornene dissolved in dichloromethane to remove impurities and moisture. Ethylidene norbornene, cyclopentene and dichloromethane were purified by passed through an activated alumina column at least twice to remove inhibitors and moisture. All other chemicals used in this synthesis procedure were purchased from Sigma Aldrich and used as received. 1st generation Grubbs’ catalyst was used as an initiator for polymerization reactions, tricyclohexylphosphine was used as a co-catalyst, ethyl vinyl ether and propionaldehyde were used as terminating agents and methanol was used as a polymer precipitating agent.

### Ring opening metathesis polymerization (ROMP) of norbornene and ethylidene norbornene

ROMP procedure for these monomers was adopted from literature after making necessary modifications to suit this work.\(^{69,71}\) Polymerization procedure for norbornene and ethylidene norbornene is very similar with a small change in the amount of co-catalyst used. Experimental reaction conditions presented here were optimized to achieve targeted molecular weights and polydispersity index values less than 1.3. All materials were handled inside an argon pressurized MBraun glove box, while the ROMP polymerization reactions were performed outside of the glove box after sealing the reaction flasks in the glove box. A typical ROMP started by mixing measured amounts of catalyst, co-catalyst and dichloromethane in the main reaction flask and stoichiometric amounts of monomer and dichloromethane in a second vessel inside the glove box. Both flasks were tightly sealed with rubber septa, brought out of the glove box and the first reaction flask was submerged in a water bath equipped with a temperature controlled chiller set at 20 °C. Then using a syringe pump, the monomer solution
from second flask was pumped into the main reaction flask at a controlled rate and the reaction was allowed to continue for required amount of time. After the reaction time has elapsed, inert gas purged terminating agent was injected into the main reaction flask using a gas tight syringe and allowed stirred for further 15 min. Then, cold methanol was added to precipitate the polymer, decanted and vacuum dried overnight to get completely dried polymer. This polymer was analyzed using gel permeation chromatography (GPC) technique to ascertain molecular weight (MW) and polydispersity index (PDI).

For ROMP reaction with norbornene, the rate of addition of monomer was set at 0.03 g/min (solid norbornene was dissolved in dichloromethane) with the co-catalyst to catalyst ratio at 4 and terminated with ethyl vinyl ether. For polymerization reaction with ethylidene norbornene, the rate of addition of monomer solution was set at 1.4 mL/min with the co-catalyst to catalyst ratio at 6 and terminated with propionaldehyde.

**ROMP of cyclopentene**  Polymerization of cyclopentene was a difficult task compared to norbornene’s given the high susceptibility to undergo acyclic diene metathesis (ADMET), a side reaction which forms high concentration of oligomers and increases the polydispersity index of the material. To circumvent this problem, the reaction was conducted at a controlled temperature of 25 °C, with controlled monomer addition and terminated at 30% conversion accounting to 5 h of reaction time. The step-by-step procedure for synthesis of poly(cyclopentene) is same as the one used for ROMP of norbornene’s.

**ROMP of bulk diblock copolymer**  Bulk ROMP of diblock was carried out by starting with either norbornene or ethylidene norbornene as first block and then sequentially adding cyclopentene after the first block has polymerized. The reaction conditions used for synthesis of homopolymers were used correspondingly. Aliquot was taken before adding cyclopentene to analyze the molecular weight of norbornene homopolymer. The diblock was terminated with Ar purged ethyl vinyl ether and then analyzed using GPC to ascertain the MW, PDI and block compositions. SEC (Size Exclusion Chromatography) traces for synthesis of diblock copolymers are presented in subsequent chapters.

**Surface initiated ROMP of diblock copolymer (SI-ROMP)**  Surface initiated ROMP was carried out by attaching Grubbs’ catalyst to organo-modified MMT clay in order to synthesize diblock
nanocomposites. A typical synthesis started by mixing required amount of clay and dichloromethane in a reaction flask with vortex stirring and sonication for 3 h. The amount of clay to be added was calculated according to the filler loading required in the final nanocomposite. Then, a solution of catalyst and co-catalyst in dichloromethane was added to the reaction flask using a syringe pump and continued with stirring and sonication for another 2 h. This step dispersed the clay particles uniformly in the solution and the polymerizable group on the surfactant was initiated by Grubbs’ catalyst. Monomers were added to this flask according to the conditions described in the bulk polymerization sections with continued vortex stirring and sonication for the remaining of the reaction time. This procedure resulted in diblock copolymers that were tethered to MMT clay surface via surfactant; this process resulted in exfoliating the clay platelets very effectively. Nanocomposites were analyzed for thermal, mechanical and physical properties using different characterization techniques described below.

**Reverse ion exchange of polymers** Nanocomposite properties were subjected to reverse ion exchange to detether the diblock copolymers from the clay surface. Both nanocomposites and non-clay materials were analyzed in parallel to assess the role of MMT clay addition. Required amount of nanocomposite was dissolved in tetrahydrofuran solvent and stirred for 3 h, then a solution containing lithium chloride and tetrahydrofuran was added to this and stirred for 48 h. This mixture was centrifuged at 3000 rpm for 30 min. The solid pellet at the bottom was separated and the supernatant was used to recover the polymer by precipitating in cold methanol and vacuum drying overnight. The ion exchanged polymer was studied with the same characterization techniques as used for nanocomposite analogs.

**Characterization techniques**

This section gives a brief description of the methods used to characterize materials synthesized in this project. But, bear in mind that no results and discussion will be presented here.

**Nuclear Magnetic resonance (NMR)**

Nuclear Magnetic resonance spectroscopy is used to study chemical structures of chemicals. In this project, we used it to ascertain chemical structures of various compounds being synthesized in the lab. NMR was an important technique in analyzing the structure of the organic modifier for MMT to
determine that the required surfactant was synthesized with no impurities. We performed a 1H NMR spectra, the one dimensional proton technique to study the arrangement of H protons in the compounds. Analysis was performed by dissolving as little as 5 mg of surfactant in dueterated chloroform with 1 % TMS and getting the NMR spectra from -2 to 14 ppm with 8 scans and analyzed the spectra using MestReNova software. Chemical structure of the surfactant was drawn using a ChemBioDraw software and used the inbuilt 1H NMR prediction function to compare the NMR spectra obtained via the instrument.

**Gel permeation chromatography (GPC)**

Gel permeation chromatography or Size Exclusion chromatography is a type of Liquid chromatography with solid stationary phase and liquid mobile phase (also called as eluent) where in separation is based on the size of the molecules. The solid columns usually have pores of different sizes which could be used to elute different sized particles at different times and also these columns could be used with many types of solvents. The other end of these columns is equipped with detectors measuring properties like refractive index (RI), light scattering or Ultra violet (UV) radiation. The GPC system we used was a Waters Acquity APC GPC system equipped with Acquity APC XT 900 2.5 microns columns running with HPLC grade tetrahydrofuran as an eluent. This system was calibrated using polystyrene standards with a molecular weight range of 2 million Da to 400 Da. The polymer samples to be analyzed were dissolved in HPLC grade tetrahydrofuran at nearly 5 mg/mL concentration, filtered and sampled. All SEC traces analyzed here are acquired from RI channel and MWs reported against PS standards.

**X-ray diffraction (XRD)**

A powder X-ray Diffraction technique was used in this project to analyze the d-spacing of materials like MMT clay and functionalized MMT (f MMT). XRD is primarily a rapid analytical technique used to study crystal structures and unit cell dimensions. A finely ground sample was placed on a sample holder placed perpendicular to X-ray beam and radiated with a collimated beam. These X-rays are scattered upon incidence with the sample and could result in a constructive interference according to Bragg’s law ($n\lambda=2d \sin \theta$). This diffraction is plotted as intensity of X-ray beam against 2θ angle, where a peak at certain X-value could be converted to d-spacing. In this project, a Siemens D-500 powder
diffractometer using a copper $K_\alpha$ source ($\lambda_{avg} = 1.54$ Å) operating in variable slit mode measuring in 20 range from $2^\circ$ to $10^\circ$ was used. The samples measured were MMT clay, organo modified MMT ($f$ MMT) and catalyst activated $f$ MMT. The increase in d-spacing between these samples was analyzed to show that successful surface modification was achieved.

**Thermogravimetric analysis (TGA)**

Thermogravimetric analysis is a basic thermal technique wherein a sample is heated at a controlled rate in either air or inert atmosphere and weight loss/gain is studied as a function of temperature. Various second order thermal transitions like vaporization, degradation, oxidation could be identified using this analysis method. Analysis was carried on TA instruments thermal analysis system from room temperature to 900 °C or 1000 °C at 10 °C/min in nitrogen atmosphere with not more than 10 mg of sample weight. The samples used were MMT, organo modified MMT, bulk diblock copolymer or nanocomposites to study the loss of weight due to different compounds vaporizing at increasing temperatures. Step changes could be observed due to degradation of different materials at different temperatures. A difference in onset temperatures for degradation, final residue weight remaining were used to analyze the materials and characterized. TGA analysis of $f$ MMT allowed the calculation of the amount of surfactant exchanged onto clay based on the hydrolization of the surfactant from the surface of the MMT.

**Differential scanning calorimetry (DSC)**

Differential scanning calorimetry is a thermal technique used for polymers to study the effect of heat/temperature on polymers. DSC is usually used to measure first order transitions like melting and crystallization, second order transitions like glass transition temperature and oxidation/degradation. The mechanism in DSC equipment is very simple, a sample pan(containing very small amounts of material to be analyzed) and an empty pan are placed in a furnace and heated/cooled at a controlled rate and measure the differences in heat being supplied to both pans to maintain the same temperature. When a thermal transition occurs in the sample either more/less heat is supplied compared to empty pan, thus the difference in the heat flow is plotted against the temperature. A TA instruments DSC Q2000 system was used for temperature scanning from -60 °C to 150 °C at 10 °C/min in N$_2$ for three heating/cooling cycles.
for nanocomposites with ethylidene norbornene as first block. The temperature range was changed from 
-65 °C to 150 °C for nanocomposites with norbornene as first block. Analysis of nanocomposites and 
their non-clay analogs in DSC showed differences in glass transition temperatures which helped in 
assessing the role of clay addition. Since the addition of MMT changes how the polymer reacts to heat, 
changes were observed accordingly in the thermograms.

**Dynamic mechanical analysis (DMA)**

Dynamic mechanical analysis is a solid state rheology technique used to study the effects of tem-
perature, time or frequency on mechanical properties of polymers like stiffness and damping. In DMA 
equipment, a sinusoidal deformation is applied to the samples prepared in a certain geometry depend-
ing on the analysis being performed. The instrument measures the changes observed in sample as a 
function of temperature or frequency. Depending on the physical characteristics of the sample, different 
modes like tensile measurement, 3-point bending, 5-point bending or flexular bending could be used. 
Measured storage modulus, loss modulus and damping factor are plotted against temperature/frequency 
to identify thermal changes in the sample. This plot could be studied for various transitions showing 
polymer chain movement, bending/stretching, slippage, glass transition and melting. Tensile tests were 
conducted on rectangular blocks of nanocomposites and their non-clay counterparts. For nanocompos-
ite with ethylidene norbornene as first block, a TA Instruments ARES® G2, strain controlled rheome-
ter with necessary DMA modules was used with a rectangular block sample (usually L x W x T x of 
10mm,3mm,1mm) from -30 °C to 140 °C at 3 °C/min in nitrogen atmosphere. The test was run with 
amplitude of 0.02 % strain and a frequency of 1 rad/s. For nanocomposite with norbornene as first block, 
we used a TA Instruments DMA Q800 system for tensile testing from -50 °C to 100 °C at 3 °C/min 
in nitrogen atmosphere on a rectangular block samples of 1 mm thick with an amplitude of 7 and a 
frequency of 1 Hz.

**Transmission electron microscopy (TEM)**

Transmission electron microscopy is a technique where electrons are used in place of light in a con-
ventional microscope. An ultra thin sample is bombarded with a high voltage beam of electrons inter-
acting with the specimen material as it passes through. The sample could either absorb, refract/diffract
or make the electrons just pass through it. These electrons are detected by a camera and forms an image characteristic of the material. The typical range of voltages used in TEMs can range anywhere from 80 KeV for biological samples to 200 KeV for polymer or metallic samples. TEM can give very high resolution images typically in the order for tens of nano meters and they are usually in gray scale. Depending on the electron density, there could be shades ranging from white to black characteristic of the material in the sample. Ultra thin samples for polymeric materials could be made by using a Leica cryomicrotome, which could cut 70-90 nm thick sections at -100 °C. The temperature was chosen to get mechanically stable sections without changing the integrity if the material. The nanocomposite samples in this work are analyzed using a JEOL 2100 STEM or FEI-Tecnai 2 microscope operating at 200 keV at resolutions ranging from 10 nm to 1 µm. The presence of MMT platelets resulted in dark areas against the usual lighter gray background of polymer matrix. Depending on the concentration of the clay platelets in the nanocomposite, either the intercalation or exfoliation is determined.

**Bioseparations Project - Part B**

**Synthesis procedures**

**Materials** All chemicals used in this project were purchased from Sigma Aldrich. Monomers were cleaned extensively to remove inhibitors and impurities using in house cleaning methods. Styrene (99 %, 10-15 ppm of 4-tert-butylcatechol inhibitor) was purified by using di-tert-butyl magnesium (1.0 M in heptane). A freeze-pump-thaw cycle method removed oxygen and then distillation was used to separate purified styrene and inhibitors. Isoprene was purified by tert-butyl lithium (2.5 M in hexanes) using the same procedure as styrene but was repeated for two cycles. During the purification process, isoprene was kept at 0 °C in an ice bath because of its hazardous nature and possibility of run away reactions if exposed to air and high temperatures. Hexamethylcyclotrisiloxane (typically referred to as D3) was purified by mixing with calcium hydride and cyclohexane and stirring over night this helped in removing moisture from D3. This material was distilled to obtain pure D3 in cyclohexane solution. Monomers were cleaned as needed and not stored for more than a week to avoid auto polymerization. Cyclohexane (CHX) and tetrahydrofuran (THF) solvents were run through a series of activated alumina columns before being used. The initiator of polymerization sec-butyl lithium (1.3 M
in cyclohexane) was used as received. Dichloromethane, methanol and isopropanol were solvents and used with no further purification.

In later part of the project, we designed a patent pending standalone system for purification of styrene and isoprene monomers using activated alumina columns. This considerably reduced the time of purification, reduced hazard nature of the procedure and became efficient for purifying large volumes of monomers.

**Equipment** Glassware used in purification and synthesis of polymers were specially designed to handle the needs of this experimental procedure to keep the materials air and moisture free. Schlenk lines were constructed in the lab fume hoods for conducting purification of monomers and synthesizing triblock copolymers.

**Synthesis of triblock copolymers**

A typical synthesis procedure for poly(styrene)-b-poly(isoprene)-b-poly(dimethyl siloxane) (SID) through anionic polymerization route is described below. A 500 ml round bottom flask with two glass threaded connections was fitted with a special adapter having two teflon valve ports and one screw threaded end (one valve to connect to schlenk line and other to act as a securement to open/close the contents of the round bottom) and a needle port with teflon coated septa. A stir bar was placed in the flask to aid in stirring the reaction contents. All screw end connections were secured with a teflon bushings and plastic caps, new bushings and septa were used for each new reaction conducted. The reaction vessel was purged and vacuumed for three times to remove air/moisture using a schlenk line and connecting the flask with a cajon ultra torr fittings and corrugated stainless steel (SS) tubes. This reaction vessel setup was placed in a water bath placed on stir plate/heater. Required amount of purified cyclohexane was collected in the flask using air free collection methods (by use of schlenk line) and temperature was set to 40 °C. Stoichiometric amount of initiator was charged to the flask using a gas tight syringe via needle port on the flask and stirred for 10 min. Then, purified styrene was put in a graduated cylinder which could be attached to the reaction flask using the screw threaded end of the special adapter. Then, first monomer (styrene) was added drop wise to the reaction flask and allowed to react for 8 h. A slow change in color of the reaction contents to bright orange indicates the successful
initiation of styrene and formation of styrlithium ions. Absence of this color indicated presence of impurities and the reaction should be repeated from beginning. After the reaction time has elapsed, an aliquot of the PS (poly(styrene)) block was taken using a gas tight syringe and terminated with argon purged methanol. GPC was used to establish the MW and PDI of this first polymer block. Then, the empty styrene graduated cylinder is replaced with graduated cylinder containing purified isoprene and the liquid was added very slowly to the reaction. The polymerization of isoprene is exothermic and given that isoprene is very volatile, care should be taken to check the temperature/pressure of the reaction vessel. Addition of isoprene changes the color of the reaction to very light yellow; also increase in viscosity of the vessel contents was observed. The reaction was allowed to continue for 8 h and then PS-PI aliquot was taken for analysis using GPC. Then, D$_3$ and cyclohexane mixture was added at a controlled rate to the reaction using a graduated cylinder-screw thread end. Addition of D$_3$ made the vessel contents colorless. The temperature of the water bath was reduced to 25 °C and reaction was allowed to continue for 24 h. This allowed enough time for crossover over of all the polymer blocks to D segment. Purified tetrahydrofuran filled in a graduated cylinder was added to the reaction flask corresponding to 50% V/V of the CHX amount in the reaction and reaction was allowed to proceed for another 4 h, which accounted to 50 % conversion for the D$_3$ polymer. The triblock copolymer reaction was terminated with excess of chlorotrimethylsilane and stirred for 30 min. The reaction contents were roto-evacuated to reduce the liquid contents to nearly half; this evaporated cyclohexane and tetrahydrofuran making it easier to precipitate the polymer. Then the polymer was precipitated with 3:1 ratio of methanol/isopropanol and decanted. The decanted polymer was vacuum dried to obtain SID triblock copolymer. SEC traces and 1H NMR scans were obtained on the triblock to analyze the MW, PDI and block volume fractions.

Fabrication of membranes

Materials  SID triblock copolymer was synthesized in the lab. All chemicals were used as received and required no further purification. Dicumylperoxide was the chemical agent used to control the amount of cross linking of polyisoprene block. Tetrabutylammoniumfloride (TBAF) was the chemical etching agent to remove polydimethylsiloxane block.
Equipment  A carver press equipped with heat plates was used to melt press the membranes of required. Stainless steel mold with 150 micron thickness and 50 mm diameter was used to press thin film polymeric membranes. A Sterlitech HP 4750 flow cell equipped with a gas source was used to conduct flow experiments.

Cross-linking and etching of membranes  Required amount of SID triblock copolymer was mixed with measured amount of dicumyl peroxide in dichloromethane and stirred at room temperature for 24 h. After the time has elapsed, the polymer was precipitated and vacuum dried to remove solvent and cut into small pieces. The mold for melt pressing the polymer consists of five 6 inch square shaped plates sandwiched together with the two outer SS plates, two teflon plates (to prevent sticking of heated polymer) and one SS plate consisting circular shaped mold. Pieces of SID polymer was evenly spread in the mold plate and pressed in the carver press for up to a 10000 to 15000 psi force at nearly 160 °C. After five minutes of pressing, the heat was turned off and the polymer was annealed under constant force overnight. This helped in both pressing the uniform thickness membrane and cross linking the isoprene giving a mechanically robust membrane. Membranes with thickness as low as 150 microns were pressed using this method. For much thinner membranes, different methods like solvent casting could be used in future work. The melt pressed membrane was weighed and submerged in a petri dish filled with TBAF and THF solution for 24 h. This petri dish was covered tightly with aluminum foil to reduce the evaporation of the dish contents. After time has elapsed, the membrane was taken out from the petri dish, washed in a new petri dish filled with excess THF to wash off the TBAF stuck in the newly formed pores. Then the membrane was vacuum dried at 40 °C to constant weight. The difference in the final and initial weight of the membrane was compared to the amount of PDMS present in the SID polymer sample. This lead to successful fabrication of membranes with pores lined with PI (poly(isoprene)) block and PS as polymer matrix.

Conducting flow experiments  A stainless steel stirred flow cell operating in batch mode was used to perform various flow experiments. This reactor had a volume of 500 mL and a metallic porous support at the bottom. The
membrane was placed on the metallic support and assembled with the unit using teflon bushings and screws. Required amount of solution was slowly introduced into the cell and sealed with no pressure leaks. The top plate had arrangement for gas inlet to pressurize the flow cell. Required amount of pressure was applied and output flow was measured. A typical experiment varied pressure difference across the membrane measuring output flow rate for different types of solvents, poly(ethylene glycol)/water solutions. More discussion on this procedure can be found in the later chapters.

**Characterization techniques**

**Visco-elastic property measurement**

Melt phase rheology of polymeric materials is usually studied to find processability difficulties and deduce molecular structure correlations. This technique could be used to measure visco-elastic material properties like glass transition temperature, modulus and damping factor to study material performance at higher temperatures. Changes in modulus with change in temperature/frequency could be used to observe different thermal transitions, polymer chain movement, polymer branching among other things. A typical measurement is conducted by making a thin flat disc placed between two parallel plates, where in one of the plates is rotated with a particular frequency. A good rheological measurement depends on using suitable experimental conditions like temperature range, applied strain, frequency range and a perfectly flat surface. Any deviation from using optimum results could really skew the results. Strain sweep measurements were conducted to identify the plateau modulus for strain percentage at a particular temperature. Then, this strain percentage was used in the temperature frequency measurement test to construct a master curve. SID samples were subjected to this measurement in order to deduce the terminal nature of master curves. A TA ARES® G2 strain-controlled rheometer was used with 25 mm SS parallel plates configuration with a melt pressed disc, 25 mm diameter and 1 mm thick. The test was run from 120 °C to 240 °C at 20 °C interval from a frequency of 1 rad/s to 100 rad/s in inert atmosphere. The strain percentage for each temperature was selected in the newtonian region from a strain sweep test ran at that particular temperature. The individual frequency sweeps at different temperatures were shifted to form a smooth master curve and the slope of high temperature region (terminal region) on this curve gave information on the microstructure of SID material.
Small angle X-ray scattering (SAXS)

Small angle X-ray scattering, is an universal technique used to study structure of broad range of molecules. The sample may not be crystalline as needed in usual crystallography techniques. An appropriately prepared sample is illuminated by X-rays and the rays are scattered characteristic of the material and detected appropriately. The scattered intensities are plotted against 2θ angle and peaks correspond to the crystal structures. Published values of peaks angles could be studied to ascertain the appropriate microstructure. One of the main drawbacks of SAXS measurements is elimination of the high intensity main peak which just passes through the sample from the weak peaks scattered corresponding to the material. We used a point collimated beam to obtain a 2-dimensional scattering pattern. All samples were vacuum annealed at 180 °C prior to SAXS analysis. Samples were sliced into very thin sections (≤0.5 mm thick) to obtain a high resolution SAXS measurement. The incident beam with a wavelength of 1.54 Å was focused on the sample with the detector and sample at a distance of 4.3 m. The scattering vector, q was varied from 0.004 Å⁻¹ to 0.4 Å⁻¹.

Some SID samples were analyzed at Advanced photon source (APS) synchrotron in Argonne national lab, Chicago. A synchrotron is usually equipped with a particle accelerator to generate high intensity X-ray beams to radiate the samples. This gives a wide range of 2θ angles and high resolution of the SAXS measurement.

Transmission electron microscopy (TEM)

TEM analysis was performed after annealing samples at 180 °C in vacuum overnight before sectioning. The sectioning was carried out on the same instrument as mentioned above in TEM section. In addition, the ultra thin sections were exposed to 2 % osmium tetroxide vapors for a period of 1 h to stain the PI block. In the TEM images, the white regions corresponds to PS, the gray region is PDMS and the dark region is PI block. TEM images formed a major morphological analysis method to identify the microstructure of SIDs.
Bibliography


[69] Hiemenz, P. *Polymer chemistry / Paul C. Hiemenz, Timothy P. Lodge*.


CHAPTER 4. SYNTHESIS OF POLYOLEFIN/LAYERED SILICATE NANOCOMPOSITES VIA SURFACE INITIATED RING OPENING METATHESIS POLYMERIZATION

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Introduction

Since the 19th century, polymer composites have been widely investigated because of significant improvements in various properties (typically mechanical) of the composite material compared to its constituents. A polymer nanocomposite is distinct from traditional composites in that at least one characteristic dimension of the filler material is mesoscopic. Requirements like high surface area, good interaction with polymer matrix and method of dispersion being employed are considered for choosing nanofillers. Clays have been studied widely because of their abundance in nature, good dispersion properties, and established intercalation chemistry. Clays such as montmorillonite (MMT) are comprised of stacks of high-aspect ratio sheets of silicate material roughly 1 nm in thickness. Each sheet has a net negative charge, and so cationic species (in nature, aqueous Na\(^+\)) maintain charge neutrality within the 1–2 nm gap in between layers. The polar nature of MMT and the non-polar nature of common polymers makes the sorption of polymer onto naturally occurring clays difficult and this becomes increasingly difficult with increase in polarity of polymers which will be the case for olefinic polymers. In the late 1980s, Okada et al. of Toyota reported a series of polymer/layered silicate nanocomposites (PLSNCs) comprised of a dispersion of MMT into a polyamide matrix. Favorable filler/matrix interactions were achieved via ion-exchange of the native Na\(^+\) cations with long
chain alkyl-ammonium surfactants. These surfactants have very long carbon chains which reduce the clay surface energy and increase the d-spacing making it easier to form nanocomposites.

Kojima et al. demonstrated that key mechanical properties in completely exfoliated nylon-clay hybrids with 4.2 wt.% filler were elevated by as much as 50% with respect to the neat resin. Moreover, significant elevation in the service temperature, barrier properties, and resistance to oxidative degradation have been observed in PLSNCs. The degree of these improvements is strongly correlated to the degree of interfacial contact between the reinforcing filler and polymer matrix; this in turn is dictated by the quality of the filler dispersion. PLSNCs typically feature a mixture of three distinct filler morphologies: micron to sub-micron sized aggregates (minimal polymer/clay interaction); intercalated structures, tens of nanometers thick, where polymer has diffused into the interlayer gallery, but significant interactions remain between clay layers; and exfoliated structures where maximal contact is achieved by the complete encapsulation of isolated clay layers with polymer. Many researchers have demonstrated that complete exfoliation is especially desired because of the highest possible contact between filler and matrix and the attendant improvements in many of the properties. Nanocomposites can be formed by melt processing, in situ polymerization, and surface-initiated polymerization (SIP); each method produces a different degree of dispersion. For complete exfoliation of platelets in the polymer matrix, surface initiated polymerization is a desired route and is also expected to yield composites with superior properties.

The (SIP) route to polymer-modified surfaces is often preferred in the study of polymer brushes on macroscopic surfaces, e.g., polymer films or surface-modified glass/silicon. This is primarily due to the ease of achieving graft densities sufficient to force the polymer conformations into the “brush” regime, where crowding forces chains to extend far beyond their unperturbed dimensions. Analogously, SIP from clay platelets can potentially yield a graft density as high as \( \approx 1 \text{ chain/nm} \). Moreover, if chain growth is uniform throughout the clay surfaces, steric forces will quickly push neighboring particles apart from each other yielding highly exfoliated PLSNCs. In this way, SIP is distinct from melt processing and in situ polymerization in that the polymer/clay interface is guaranteed by molecular design, provided there is sufficient monomer diffusion compared to the polymerization rate. This important caveat can pose a hurdle to the successful SIP-based dispersion of nanoclays due to the tight confinement imposed by the closely placed layered silicates.
Behling et al illustrated using surface initiated atom transfer radical polymerization (SI-ATRP) that limiting the polymerization rate was crucial to the synthesis of fully exfoliated structures. When the kinetics were properly controlled, Behling showed essentially complete exfoliation in polystyrene/MMT PLSNCs. Extension of the synthesis to poly(styrene-block-t-butyl-acrylate) brushes produced an array of microphase-separated morphologies clearly influenced by the MMT substrate. Moreover, the glass transition temperature of the poly(t-butyl acrylate) block varied between its bulk value of $T_g \approx 43^\circ C$ and as high as $T_g \approx 68^\circ C$ depending upon the sample morphology, while the 100 °C polystyrene $T_g$ remained more-or-less constant across all of the specimens examined. While these studies were important to understand the nature of self-assembly in block copolymer/layered silicate nanocomposites, the model system employed is well-suited for morphological characterization but is far from ideal in understanding the influence of structure on mechanical properties.

In principle, any “living” polymerization scheme may be adapted to the SIP fabrication of PLSNCs. Ring Opening Metathesis Polymerization (ROMP), a type of catalyzed olefin metathesis reaction, is of particular interest to us for the access it provides to commercially relevant elastomers and plastics such as polyethylene. A ROMP catalyst is based on a transition metal center and a “cocatalyst” ligand system that has a pronounced effect on many of the kinetic steps that can ultimately produce polymers with living character. ROMP is especially an important polymerization route to form living polymers with cyclic olefins and opens a new arena for producing thermoplastic elastomers.

In this article we report the controlled surface-initiated ROMP (SI-ROMP) of norbornene (Nbn) and cyclopentene (CPE) from appropriately functionalized MMT clays based on the 1st-generation Grubbs’ catalyst (PCy$_3$)$_2$(Cl)$_2$Ru−CHPh. These monomers are interesting from a perspective of commercial relevance since hydrogenation of polycyclopentene gives perfectly linear polyethylene, a highly crystalline thermoplastic; hydrogenated substituted polynorbornenes yield low-$T_g$ rubbers; together these monomers offer an appealing route to thermoplastic elastomeric PLSNCs. Moreover, Nbn is a canonical monomer for ROMP, because of its commercial availability, high ring strain and ability to form living polymers. The successful synthesis of block copolymers employing norbornene and cyclopentene using Shrock’s catalyst has been reported in the literature. Due to low ring strain, the ROMP of
CPE is a more difficult process; a major hurdle is the competing acyclic diene metathesis (ADMET), a major side reaction which increases oligomer concentration. Sanford et al has shown that the addition of “cocatalyst” (excess ligand) to the polymerization is necessary to shift the equilibrium towards polymer propagation. On the other hand, with excellent moisture/air tolerance though with less activity, Ru-based Grubbs’ catalysts give high-trans polymers with good isotactic bias. Unfortunately, Ru-based ROMPs of norbornenes have not been as extensively studied as compared to Shrock’s catalyst. In the present article, we first explain how to conduct SI-ROMP to form PLSNCs with good exfoliation and reproducible molecular weight distribution using the first generation Grubbs’ catalyst, which is ideal for PLSNCs due to the intrinsic incompatibility with less tolerant systems. We then show PLSNCs characterization data exploring the thermal, mechanical, and morphological properties. In order to directly assess the influence of the filler particles in these materials, the polymer brushes were removed from the MMT surface via reverse ion exchange and characterized along with its counterparts.

**Experimental Details**

**Materials Synthesis**

**MMT surface modification.** Chemicals used for synthesis of organic surfactant modifier are 5-norbornene-2,3-dicarbonyl dichloride, 11-bromo-1-undecanol, diethyl ether, pyridine, magnesium sulfate, deionized water, hexanes, trimethyl amine, and ethanol. All chemicals were purchased from Sigma-Aldrich and used as received. Montmorillonite clay (Cloisite- Na+) was generously supplied by Southern Clay Products Inc. Based on the cation exchange capacity of 92 meq/100 g and specific surface area, MMT clay contains \( \approx 1 \) exchange site/nm\(^2\). The synthesis (Fig. 4.1) is closely related to that employed by Behling, and can be summarized as the addition of norbornene dicarbonyl chloride to bromoundecanol to form a norbornene ester; the addition of trimethylamine and extensive purification yields (1), 5,6-di(11-bromoundecoxy carbonyl)norbornene (NbnN\(^2\)). In a typical synthesis, 4 g of bromoundecanol in 2.6 ml of pyridine and 60 ml of diethyl ether is added dropwise to 2.58 ml (equimolar) of norbornene dicarbonyl chloride in 10 ml diethylether and stirred for 6 h. The mixture is concentrated with rotary evaporation prior to liquid-liquid extraction (LLE) with diethyl ether. The norbornene diester is then mixed with 15.3 ml of 30 vol % trimethyl amine in ethanol for 48 h under
Figure 4.1. Synthesis of 5,6-di(11-(N,N,N trimethylammonium) undecoxy carbonyl)norbornene (NbnN$_2^+$).

Ar, concentrated with rotary evaporation, purified using LLE with diethyl ether, and dried under dynamic vacuum for 4 d to yield the waxy surfactant material (2), 5,6-di(11-(N,N,N trimethylammonium) undecoxy carbonyl)norbornene (NbnN$_2^+$). $^1$H-NMR is available in the Supporting Information. 1 g (2) was then subsequently mixed with 1.25g MMT clay in 100 ml deionized (DI) water under reflux for 96 h to achieve maximal graft density.$^{75}$ NbnN$_2^+$-MMT (3) was recovered by filtration and dried under dynamic vacuum at room temperature for 24 h. According to the TGA data presented in Figure 4.2, the difference in mass loss due to water adsorbed (around 170 °C) and that due to dehydroxylation of MMT (around 700 °C) gives 25% of organic content in the clay; this corresponds to nearly 80% of the ion exchange capacity. x-ray diffraction spectra, Figure 4.3, show an increase of the inter gallery spacing of clay platelets from 11 Å to 21 Å after the ion exchange of Na$^+$-MMT with NbnN$_2^+$.

**Bulk Polymerization of norbornene and cyclopentene** Reagent grade norbornene and cyclopentene (Sigma Aldrich) were dried over calcium anhydride, subjected to three freeze/pump/thaw cycles, and vacuum distilled prior to use. Methylene chloride (MeCl, Sigma-Aldrich) was purified by three freeze pump thaw cycles. All chemicals were used within one week of purification in order to ensure there is no autopolymerization. Methanol, ethyl vinyl ether, first generation Grubbs catalyst ((PCy$_3$)$_2$(Cl)$_2$Ru=CHPh) and tricyclosubstitutedphosphine (PCy$_3$, Sigma-Aldrich) were used as received. All reactants were stored and handled in an Ar-filled glove box. The ROMP of norbornene is reported elsewhere in literature;$^{89,110,114}$ our procedure is similar with some modifications to be described in
more detail in the Results section. A typical ROMP of norbornene consists of the addition of the required amount of monomer in MeCl (1 g:7 ml) to a solution of first generation Grubbs’ catalyst in MeCl (1 mg:1 ml) at 20 °C; after 1 h the polymerization is terminated with ethyl vinyl ether and precipitated in methanol. In an exemplar with Monomer/Catalyst (M/C) ratio of 50, 0.45 g of norbornene in 7 ml MeCl were added at a rate of 0.03 g/min to a solution of 9 mg of Grubbs’ catalyst, 9 ml MeCl, and 36 mg of PCy₃ at 20 °C for 1 h. The number average molecular weight (\(M_n\)) was 46800 Da and the PDI was 1.067. ROMP of cyclopentene is performed as in literature and with same modifications as used for synthesis of norbornene. The reaction was terminated at 5 h, corresponding to 30% conversion, to
minimize unwanted side reactions. In bulk polymerizations, block copolymers were synthesized by sequential addition of the second monomer after the first monomer is polymerized. The molecular weight distribution of all polymers was determined with size exclusion chromatography (SEC).

**PLSNC Synthesis.** Surface modified clay platelets were used for synthesizing nanocomposites. Also, block copolymer nanocomposites were formed by sequential addition of monomers. All nanocomposites analyzed here in article are blockcopolymers nanocomposites with poly(norbornene) as first and poly(cyclopentene) as second block. ROMP-active NbnN$_2^+$ MMT substrates were prepared by the dispersion of 75 mg NbnN$_2^+$ MMT in 16 ml dichloromethane for 4 h with ultrasonication at 20 °C, followed by the addition of 50 mg Grubb’s catalyst and 103 mg PCy$_3$ (Fig. 4.4). The mixture was vigorously stirred with ultrasonication for 1 h to form (4). The first polymerizable group (Nbn) radiating outwards from clay surface gets initiated for polymerization and becomes active propagating species. The remainder of the SI-ROMP process is analogous to the bulk synthesis, with the polymers propagating from the active catalyst that is now attached to the surface of clay. A norbornene/MeCl solution (1 g:7 ml) was introduced to ultrasonicated mixture containing (4) at 0.03 g Nbn/min with a syringe pump. After 1 h neat cyclopentene was then added at a rate of 0.5 ml/min.

Neat polymer was recovered from PLSNCs for characterization and direct comparison with the PLSNC parent material via reverse ion exchange. In a typical reverse ion exchange procedure, 1 g PLSNC and 1 g LiCl are dissolved in 100 ml MeCl; the mixture is stirred under reflux for 24 h. The

![Figure 4.4](image-url)  
*Figure 4.4. Activation of NbnN$_2^+$-MMT (3) with Grubbs’ 1st generation catalyst to yield (4), ROMP-active MMT clay.*
mixture is then subjected to centrifugation after which the neat polymer solution is decanted, precipitated in methanol, and dried under dynamic vacuum.

Characterization Methods

Size Exclusion Chromatography (SEC)  Polynomial molecular weight distributions were measured with a Waters 515 HPLC system operating on HPLC chloroform at room temperature. Samples were dried overnight in vacuo oven prior to analysis. Then they were dissolved in HPLC chloroform, filtered and sampled. Molar masses are reported with respect to polystyrene standards.

Nuclear Magnetic Resonance (NMR)  Synthesized organic modifier was dissolved in CDCl$_3$ with 1% TMS. All experiments were conducted on Varian MR-400 MHz from 2–14 ppm in 1H NMR spectra and results were analyzed by using MestReNova software.

X-Ray Diffraction (XRD)  Increase in intergallery spacing of modified MMT and exfoliation of nanocomposites were analyzed with a Siemens D-500 powder diffractometer using a copper $K_{\alpha}$ source ($\lambda_{\text{avg}} = 1.54 \text{ Å}$) operating in variable slit mode. Scattering angles varied in the interval $2\theta \in [2^\circ, 10^\circ]$, or $q \in [0.14, 0.71] \text{ Å}^{-1}$, where $q \equiv \frac{4\pi}{d} \sin \theta$. Clay $d$-spacing is reported as $d = \frac{2\pi}{q^*}$, where $q^*$ corresponds to the peak in scattering intensity. $x$-ray diffraction patterns are available in Supporting Information.

Thermo Gravimetric Analysis (TGA)  TGA measurements were conducted on polymer nanocomposite and reverse ion exchanged polymer brushes. Analysis was done on TA instruments thermal analysis system from 50°C to 800°C at 15 °C/min in inert atmosphere. Data were analyzed with TA instruments data analysis software.

Differential Scanning calorimetry (DSC)  DSC was used to measure the glass transition temperature $T_g$ of the polymers and PLSNCs presented in this study. Prior to DSC measurements samples were dried above 150°C under vacuum for at least 24 h to eliminate the effects of small molecule plasticizing. All measurements were obtained using a TA instruments DSC Q2000 system scanning from -75 °C to 150 °C at 10 °C/min in $N_2$. Three complete heating/cooling cycles were collected for each specimen.
Data were analyzed by using TA instruments data analysis software and glass transition temperatures were reported.

**Dynamic Mechanical Analysis (DMA)** Solid state viscoelastic properties of PLSNCs and analogous neat polymers were measured using a TA Instruments DMA Q800 system from -50 °C to 100 °C at 3 °C/min in inert atmosphere. Rectangular samples of 1 mm thickness were prepared and tensile testing was done with amplitude of 7% strain and a frequency of 1 Hz.

**Transmission Electron Microscopy (TEM)** To image nanocomposites, polymer sections of 70-90 nm thick were cut by using a Leica cryo Ultramicrotome. Images were collected from multiple sections at various locations using a FEI-Tecnai 2-F20 STEM microscope operating at 200 keV. Images were analyzed by using Gatan Digital Micrograph.

**Rheological study** Crosslinking kinetics of block copolymer nanocomposite and its reverse ion exchanged counterpart were conducted on an ARES® strain-controlled rheometer. Isochronal temperature ramp tests at $\omega = 1$ rad/s and $\frac{dT}{dt} = 18.5$ °C/h in the parallel plate configuration were conducted on both samples. The samples were melt pressed into 25 mm diameter and 1 mm thick circular discs.

**Results and Discussion**

The characteristics of the materials that we discuss in this article are summarized in Table 4.1. In this section we first present results pertaining to the solution ROMP of polynorbornene (hereafter referred to as Nbn), cyclopentene (CPE), and poly(norbornene-b-cyclopentene) (NP) via Grubbs’ first generation ROMP catalyst, yielding optimized reaction conditions that allow the reproducible synthesis of block copolymers with narrow molecular weight distribution, and precisely targeted molecular weight and composition. We found that these optimized conditions can be applied directly to surface-initiated ROMPs from (4) to form MMT-graft-poly(norbornene-b-cyclopentene) (mNP); the polydispersity and block molecular weights are nearly identical to the analogous solution polymerizations. In the second part of this section we examine the extent of MMT dispersion within the mNP nanocomposite, and investigate the influence of the MMT substrate on the thermal and mechanical properties of the material.
Figure 4.5. Change in the molecular weight versus time in the ROMP of norbornene (Nbn1) at room temperature without cocatalyst.

Materials Synthesis

While the ROMP of norbornene via Schrock’s catalyst is a well-known reaction, conditions allowing for the controlled production of polynorbornene via Grubbs’ 1st generation catalyst are elusive. The high ring strain in norbornene ring makes it highly susceptible to ROMP polymerization; while Grubbs’ 3rd generation catalyst provides excellent control over the propagation rate, the more tolerant 1st generation system propagates so quickly that the typical outcome is highly polydisperse polymers that often gel in the reactor. Table 4.1 summarizes the results of norbornene polymerization in MeCl under a number of conditions. At room temperature, the reaction is rapid and uncontrolled; Figure 4.5 shows the evolution of the number-average molar mass $M_n$ for Nbn1 as a function of time for a ROMP of norbornene at room temperature ($\approx 23 ^\circ C$, no temperature control) with a 500:1 molar norbornene:Grubbs’ catalyst (M/C) ratio, corresponding to a target molecular weight of $\approx 50$ kDa.

The scatter in the $M_n$ vs. $t$ data of Figure 4.5 indicate that the polymerization is complete in less than 5 min; allowed to proceed for longer times, the reversible nature of the reaction is clearly problematic. To produce well-defined block copolymers, and also to encourage dispersion in the production of exfoliated PLSNCs, it is necessary to limit the kinetics of this polymerization. To achieve optimum conditions, we repeated ROMP reactions with a variety of combinations of reaction time, monomer/catalyst (M/C) ratio, cocatalyst/catalyst (Co/C) ratio, monomer addition rate, and temperature.
Table 4.1. Reaction conditions and molecular weight characteristics for poly(norbornene)s, poly(cyclopentene)s, block copolymers thereof, and PLSNCs thereof produced via ROMP.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T, °C</th>
<th>Process&lt;sup&gt;a&lt;/sup&gt;</th>
<th>M/C&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Co/C&lt;sup&gt;c&lt;/sup&gt;</th>
<th>t, h</th>
<th>$M_n$,&lt;sup&gt;d&lt;/sup&gt; kDa</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nbn1</td>
<td>RT</td>
<td>batch</td>
<td>500</td>
<td>0</td>
<td>2</td>
<td>65.9</td>
<td>2.46</td>
</tr>
<tr>
<td>Nbn2a</td>
<td>15</td>
<td>batch</td>
<td>500</td>
<td>0</td>
<td>1</td>
<td>33.9</td>
<td>4.47</td>
</tr>
<tr>
<td>Nbn2b</td>
<td>15</td>
<td>batch</td>
<td>500</td>
<td>0</td>
<td>2</td>
<td>34.8</td>
<td>2.97</td>
</tr>
<tr>
<td>Nbn2c</td>
<td>15</td>
<td>batch</td>
<td>500</td>
<td>0</td>
<td>9</td>
<td>40.3</td>
<td>2.35</td>
</tr>
<tr>
<td>Nbn2d</td>
<td>15</td>
<td>batch</td>
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<td>16</td>
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<td>500</td>
<td>0</td>
<td>24</td>
<td>82.9</td>
<td>1.79</td>
</tr>
<tr>
<td>Nbn3a</td>
<td>20</td>
<td>batch</td>
<td>500</td>
<td>0</td>
<td>1</td>
<td>64.3</td>
<td>1.97</td>
</tr>
<tr>
<td>Nbn3b</td>
<td>20</td>
<td>batch</td>
<td>500</td>
<td>0</td>
<td>2</td>
<td>77.9</td>
<td>1.99</td>
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<tr>
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<td>20</td>
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<td>500</td>
<td>0</td>
<td>9</td>
<td>79.0</td>
<td>1.71</td>
</tr>
<tr>
<td>Nbn3d</td>
<td>20</td>
<td>batch</td>
<td>500</td>
<td>0</td>
<td>16</td>
<td>85.3</td>
<td>2.02</td>
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<tr>
<td>Nbn3e</td>
<td>20</td>
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<td>500</td>
<td>0</td>
<td>24</td>
<td>88.7</td>
<td>1.53</td>
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<tr>
<td>Nbn4a</td>
<td>20</td>
<td>semibatch</td>
<td>300</td>
<td>0</td>
<td>0.5</td>
<td>91.1</td>
<td>2.45</td>
</tr>
<tr>
<td>Nbn4b</td>
<td>20</td>
<td>semibatch</td>
<td>200</td>
<td>0</td>
<td>0.5</td>
<td>118</td>
<td>2.79</td>
</tr>
<tr>
<td>Nbn4c</td>
<td>20</td>
<td>semibatch</td>
<td>150</td>
<td>0</td>
<td>0.5</td>
<td>94.6</td>
<td>1.71</td>
</tr>
<tr>
<td>Nbn5a</td>
<td>20</td>
<td>semibatch</td>
<td>150</td>
<td>0</td>
<td>0.5</td>
<td>58.7</td>
<td>2.74</td>
</tr>
<tr>
<td>Nbn5b</td>
<td>20</td>
<td>semibatch</td>
<td>150</td>
<td>4</td>
<td>0.5</td>
<td>46.8</td>
<td>1.07</td>
</tr>
<tr>
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<td>20</td>
<td>semibatch</td>
<td>150</td>
<td>4</td>
<td>1</td>
<td>146</td>
<td>1.13</td>
</tr>
<tr>
<td>Nbn5d</td>
<td>20</td>
<td>semibatch</td>
<td>150</td>
<td>4</td>
<td>2</td>
<td>149</td>
<td>1.12</td>
</tr>
<tr>
<td>CPE1</td>
<td>25</td>
<td>semibatch</td>
<td>150</td>
<td>0</td>
<td>5</td>
<td>33.2</td>
<td>1.94</td>
</tr>
<tr>
<td>CPE2</td>
<td>25</td>
<td>semibatch</td>
<td>150</td>
<td>4</td>
<td>5</td>
<td>50.4</td>
<td>1.07</td>
</tr>
<tr>
<td>NP1&lt;sup&gt;e&lt;/sup&gt;</td>
<td>20, 25</td>
<td>semibatch</td>
<td>150, 150</td>
<td>4, 4</td>
<td>1, 5</td>
<td>134, 195</td>
<td>1.09, 1.11</td>
</tr>
<tr>
<td>mNP1&lt;sup&gt;e&lt;/sup&gt;</td>
<td>20</td>
<td>batch</td>
<td>30</td>
<td>0</td>
<td>0.5</td>
<td>62.6</td>
<td>1.39</td>
</tr>
<tr>
<td>mNP1&lt;sup&gt;e&lt;/sup&gt;</td>
<td>20, 25</td>
<td>semibatch</td>
<td>150, 150</td>
<td>4, 4</td>
<td>1, 5</td>
<td>133, 189</td>
<td>1.09, 1.07</td>
</tr>
<tr>
<td>mNP2&lt;sup&gt;e&lt;/sup&gt;</td>
<td>20, 25</td>
<td>semibatch</td>
<td>62.5, 150</td>
<td>4, 4</td>
<td>1, 5</td>
<td>61.3, 118</td>
<td>1.24, 1.27</td>
</tr>
</tbody>
</table>

<sup>a</sup>In semi-batch experiments norbornene solution was added at a rate of 0.03 g Nbn/min to the catalyst solution. The cyclopentene addition rate was 0.5 ml/min.
<sup>b</sup>Molar monomer to catalyst ratio
<sup>c</sup>Molar cocatalyst to catalyst ratio
<sup>d</sup>With respect to polystyrene calibration standards in chloroform at 23 °C.
<sup>e</sup>Comma-separated values indicate poly(norbornene) block, poly(norbornene-b-cyclopentene) diblock copolymer.
<sup>f</sup>MMT surface-initiated ROMP.
To decrease the reaction rate, we first repeated the polymerization with at 0 °C, 15 °C (Nbn2a–e), and 20 °C (Nbn3a–e). We observed that the ROMP of norbornene at 0 °C did not yield any polymer, evidently because the initiation rate is negligible at this temperature. Table 4.1 shows that the Nbn3 series at 20 °C produces more consistent $M_n$ and PDI values than the other temperatures that we attempted, although the polymerization is essentially complete within 5 min. To limit the polymerization rate through the monomer concentration, we then produced Nbn4a by adding monomer at a rate of 0.03 g/min with a syringe pump; this semibatch process significantly reduced the polymerization rate although the polydispersity index (PDI) of the product remained $\gg 2$. The Nbn4a–c series explores the role of the M/C ratio, and suggests that better control over polydispersity is realized at higher catalyst concentration.

A final reaction parameter that we investigated was the use of PCy$_3$, corresponding to the ligand system in the Grubbs’ catalyst, as a cocatalyst. PCy$_3$ reversibly binds to the catalyst system on the chain ends, which renders them temporarily dormant. The Nbn5a–d series demonstrates that PCy$_3$ significantly reduces the polymerization rate, and yields polymers with very narrow molecular weight distributions, e.g. Nbn5b at 46.8 kDa and PDI = 1.067 after 30 min as shown in Figure 4.6. Under these conditions the polymerization appears to be complete at 1 h; the molecular weight distribution remained stable for up to 2 h. SEC traces that show the influence of PCy$_3$ are available in the Supporting Information.
We also produced several bulk poly(cyclopentene)s via ROMP; again, semibatch monomer addition along with the use of PCy$_3$ as a cocatalyst appear to be crucial to produce well-defined polymers. As stated earlier, acyclic diene metathesis (ADMET) is a problematic side reaction that inhibits the preparation of high molecular weight polymers and broadens the molecular weight distribution. Figure 4.7 illustrates the influence of PCy$_3$ in the synthesis of CPE1 and CPE2 over time. Clearly, as the reaction proceeds the cocatalyzed polymerization features monotonic chain growth over the course of 5 h and the PDI is characteristic of a “living” polymerization. After 5 h, the monomer is nearly depleted and depolymerizations reactions severely broaden the molecular weight distribution.

Based on our observations of controlling ROMP reactions for individual monomers, synthesis of block copolymers using norbornene as first block and cyclopentene as second block was carried out accordingly. An SEC trace for NP1 is shown in Figure 4.8, where we can see increase in molecular weight of the polymer after subsequent addition of second monomer yielding an overall PDI of 1.11. We applied identical conditions to the surface-initiated polymerization of norbornene and cyclopentene to produce mNP1 from NbnN$_2^+$-MMT, a 189 kDa poly(norbornene-$b$-cyclopentene) diblock copolymer PLSNC. A portion of mNP1 was subjected to the reverse ion exchange process as described in the Experimental section to yield mNP1*, i.e., mNP1 with the MMT substrates removed. An SEC trace of mNP1* appears in Figure 4.8, and illustrates that the surface initiated polymerization proceeds with
Figure 4.8. SEC traces of NP1-pre (poly(norbornene) precursor, gray dashed), NP1 (gray), and mNP1*.

kinetics identical to the solution polymerization under otherwise analogous conditions.

Nanocomposite Characterization

XRD patterns of mNP1 (Figure 4.3) show only background scattering, which indicate that the material is free of MMT aggregates sufficiently large to contribute to measurable Bragg scattering. Figure 4.9 shows representative TEM images that further support the nearly full exfoliation of MMT within the block copolymer matrix. Figure 4.9a shows at high magnification a typical region in which a dispersion of hairlike particles 1 nm in thickness is visible, corresponding to fully exfoliated MMT particles. In some sections, however, we found regions such as that depicted in Figure 4.9b, which shows a \(1 \mu m^2\) area containing a number of intercalated structures \(\approx 10-50 \text{ nm in thickness}\).

Fully exfoliated nanocomposites via SIP are only produced when the monomer mass transport rate from the bulk solution to the clay interlayer gallery is sufficiently large compared to the polymerization rate. When the polymerization rate is comparatively large, the polymers on the exterior of clay aggregates will grow more quickly than those on the interior of aggregates. In this situation monomer access to the aggregate interior may be precluded altogether. Under the conditions that we employed, our SI-ROMP PLSNCs polymerized at roughly 150 kDa/h; according to our x-ray diffraction and microscopy data, the resultant nanocomposites have excellent yet incomplete exfoliation. For comparison, the fully exfoliated PLSNCs produced by Behling via SI-ATRP were synthesized at a polymerization rate more
Figure 4.9. TEM micrographs showing the morphology of MMT clay in unstained mNP1. (a) High-magnification image in which \( \approx 1 \text{ nm} \times 10-100\text{nm} \) hairlike features corresponding to exfoliated MMT platelets are visible. (b) Lower magnification image showing a region that contains intercalated structures up to \( \approx 50 \text{ nm} \) thick.

Table 4.2. Thermal properties of mNP1 and mNP1*

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_{10}, ^\circ\text{C} ) (^a)</th>
<th>( T_{50}, ^\circ\text{C} ) (^b)</th>
<th>( T_{max}, ^\circ\text{C} ) (^c)</th>
<th>residual mass, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>mNP1</td>
<td>407</td>
<td>452</td>
<td>491</td>
<td>14.5</td>
</tr>
<tr>
<td>mNP1*</td>
<td>314</td>
<td>434</td>
<td>490</td>
<td>6.2</td>
</tr>
</tbody>
</table>

\(^a\)Temperature at 10% weight loss  
\(^b\)Temperature at 50% weight loss  
\(^c\)Temperature at maximal weight loss

than an order of magnitude less at 12.9 kDa/h. Based on this observation, in future work we will report on the further optimization of the SI-ROMP polymerization conditions to further reduce the polymerization rate. We speculate that these efforts will eliminate the small fraction of intercalated structures that we report in mNP1.

The high degree of dispersion in clay particles throughout mNP1 corresponds to a large polymer/clay interphase region. Substantial differences between mNP1 and mNP1* in thermal and mechanical behavior indicate strong interactions between the MMT substrate and block copolymer brushes. The thermal degradation characteristics of mNP1 and mNP1* were compared with TGA; the data in Figure 4.10, summarized in Table 4.2, show that higher temperatures are required to achieve the same level of mass loss in mNP1 compared to mNP1*. For example, 10% mass loss occurs at 314 °C
in mNP1*, whereas for the parent nanocomposite the mass loss remains less than 10% until 407 °C. The difference in final residual mass for these two samples corresponds to the mass composition of clay in mNP1, ≈ 9%. The enhanced thermal stability of mNP1 is consistent with that of other highly exfoliated nanocomposite systems reported in the literature, where the stability enhancement is believed to be a direct consequence of the barrier properties imparted by the high-aspect ratio filler.

MMT also appears to strongly influence the properties of the block copolymer brushes. Differential scanning calorimetry, Figure 4.11, shows a glass transition of 15.6 °C in mNP1*, corresponding to polynorbornene domains; this transition increases by nearly 20 °C, to 34.6 °C, in mNP1. This substantial elevation in the glass transition temperature is similar in magnitude to that reported by Behling et al. in poly(styrene-\textit{b}-t-butylacrylate) PLSNCs formed by surface initiated atom transfer radical polymerization. Strongly stretched polymer brushes have been shown in the past, through both simulation and experiments, to dramatically retard the chain relaxation dynamics. This may be understood qualitatively through the steric restriction of the cooperative motions that are believe to underpin the nature of the glass transition. These factors suggest that the \( T_g \) elevation that we observe supports that mNP1 is comprised of highly exfoliated polymer brushes.

The solid-state viscoelastic properties further support the altered dynamic behavior of mNP1 compared to its MMT-free analog. Figures 4.12 and 4.13 show isochronal DMA temperature scan data collected in the linear viscoelastic regime (< 10% strain) at 1 °C/min and 1 Hz for mNP1 and
mNP1*. At temperatures below their softening points, the loss moduli of both materials are within 10% of each other and show no dependence on temperature; that is, they represent a plateau modulus $G'_0$ characteristic of an elastic solid. The softening point, defined here as the temperature at which the loss modulus decreases to 0.8$G'_0$, is -9 °C for mNP1* and 30 °C for mNP1. The temperature-span of the softening transition in mNP1 is much narrower than that of mNP1*, 36°C wide for the former and 89°C
Figure 4.13. Dynamical mechanical analysis (isochronal temperature ramp) of mNP1 (solid) and mNP1* (dashed) at a frequency of 1 Hz. Open symbols denote the inflection of $G''(T)$ as another indication of the onset of the glass transition.

for the latter. The peak in $\tan \delta$, often reported as a measure of $T_g$, is 17 °C for mNP1* in quantitative agreement with the $T_g$ value from DSC. $T_{g, DMA}$ for mNP1, on the other hand is significantly greater than the DSC-value at 52°C. The loss moduli, $G''(T)$, of these two materials closely mirror the behavior of $\tan \delta(T)$; interestingly though, $G''(T)$ for mNP1 has a slight upward inflection at -18°C, in the vicinity of the softening onset temperature for mNP1*. This similarity suggests that the confinement induced by the MMT particles are suppressing the onset of a relaxation process that precedes the glass transition.

Due to the high level of unsaturation in ROMP-based polymers, they are highly susceptible to crosslinking on exposure to ultraviolet radiation or elevated temperature. To assess the role of the clay substrate in this process, we conducted an isochronal temperature ramp at $\omega = 1 \text{ rad/s}$ and $\frac{dT}{dt} = 18.5 \text{ °C/h}$ in the parallel plate configuration of an ARES® strain-controlled rheometer. Figure 4.14 shows the complex dynamic modulus $G^*$ vs. temperature and time. Remarkably, we note that the melt-phase modulus of mNP1 is 3–6 times lower than that of its analogous clay-free counterpart, mNP1* throughout the 12 h experiment. This contrasts the solid state DMA data of Figure 4.12 where the nanocomposite is of similar modulus far below the glass transition temperature and nearly an order of magnitude larger than mNP1* at room temperature. Thus, in the melt, polymer/clay brushes have substantially lower viscosities which is desirable from a processing perspective. The modulus of mNP1 and mNP1* both increase by $\approx 2000\%$ over the course of the 12 h experiment. $G^*_{mNP1*}$ increases monotonically throughout the experiment; $G^*_{mNP1}$ increases monotonically until 150°C, where it plateaus through
Figure 4.14. Dynamic complex modulus at $\omega = 1$ rad/s for mNP1 and mNP1* in the linear viscoelastic regime, heating at $\frac{dT}{dt} = 18.5$ °C/h. Both materials show evidence of crosslinking; however, the modulus of the neat copolymer mNP1* (dashed line) grows monotonically, while the nanocomposite (solid line) features a plateau ranging from $\approx 150$°C to $\approx 190$°C. This suggests that mNP1 crosslinks in two regimes: an “intraparticle” regime where crosslinking is limited due to chain ends remaining tethered to the clay surface, and a high-temperature “interparticle” regime where chain ends gain sufficient mobility to leave their host particle.

$\approx 190$°C. This behavior is consistent with crosslinking which proceeds at essentially a constant rate until 150°C. Over the plateau region, mNP1 exhibits behavior characteristic of an elastic solid. At 190°C, $G_m^{*}$ increases monotonically once again, suggesting that a new process has been thermally activated allowing the material to crosslink further. We speculate that this two-phase crosslinking behavior is related to the relative immobility of chains tethered to the clay surface at low temperature, which are then liberated at high temperature. In the low temperature regime, chains may only crosslink with their neighbors, limiting the extent of crosslinking. At high temperature, the ionically bound chain ends become liberated from their substrate and crosslinking again continues unabated. Classical elasticity theory lends plausibility to this interpretation: The plateau modulus of mNP1 at 400 K is roughly 50 kPa; assuming a mass density of mNP1 of $\rho \approx 0.9$ g/cm$^3$ yields an average molecular weight between crosslinks of $M_c = \frac{\rho RT}{G_m^{*}} = 75$ kDa, or approximately 1–2 crosslinks per chain given $M_n = 189$ kDa.
Conclusion

In this work we have demonstrated that well-defined homopolymers and block copolymers of norbornene and cyclopentene can be synthesized via surface-initiated ring opening metathesis polymerization from montmorillonite functionalized with 1st-generation Grubbs’ catalyst. Polydispersity indices less than 1.2 and reproducible molecular weights were achieved by the semibatch addition of monomer and the use of cocatalyst to suppress the polymerization rate. Under the polymerization conditions that we employed, 150 kDa polymers were produced over the course of 1 h. These conditions for solution polymerizations produced identical results as surface-initiated polymerizations NbnN₂⁺-MMT. The resultant nanocomposites were free of aggregates as determined by x-ray diffraction and electron microscopy. Electron microscopy showed that the materials are highly exfoliated, although we found some regions where intercalated structures were present. This indicates that further reduction of the polymerization rate is necessary to achieve full exfoliation. We found substantial differences in the thermal, dynamic, and viscoelastic behavior of the nanocomposites compared to the neat polymer recovered by reverse ion exchange, most remarkably a 20–35 °C elevation in the polynorbornene glass transition temperature. These results show that SI-ROMP may be an attractive route to a new family of high performance polyolefin thermoplastics and thermoplastic elastomers.

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Supplementary Data

Molecular Weight Distributions

Figure 4.15. $M_n(t)$ data from family Nbn1 for ROMP of norbornene.

Figure 4.16. SEC traces that illustrate the influence of PCy$_3$ as a cocatalyst in the ROMP of norbornene. The solid curve corresponds to Nbn5b, polymerized with 4 mol PCy$_3$ per mol Grubbs’ catalyst. The dashed trace is Nbn5a, prepared without PCy$_3$ under otherwise identical conditions.
Characterization of Surfactant

Figure 4.17. Structure confirmation of organic modifier used to modify MMT clay surface.
Bibliography


CHAPTER 5. ROMP BASED THERMOPLASTIC ELASTOMERS VIA BLOCK COPOLYMER/LAYERED SILICATE NANOCOMPOSITES

A paper to be submitted to Macromolecules journal

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Introduction

Polymer composites are hybrid materials, wherein polymers are mixed with a filler material to result in combined properties superior to the individual constituent material properties. If at least one dimension of the filler is in nanometer range, then they are called nanocomposites.\textsuperscript{136,140} Nanocomposites is one of the bright fields of nanotechnology being researched; current applications include but are not limited to high strength materials, flame retardant materials, high barrier materials and various engineering materials with good electric and optical properties. Nanocomposites can show remarkable improvements in their properties when compared to normal composites making the study of their structure property relationships a highly valuable research topic.\textsuperscript{139} Current research in nanocomposites widely uses filler materials like graphene, spherical nanoscopic particles like silica, tubes, clay, fibers among other fillers in nanoscale range.\textsuperscript{140} In our current work reported here, we are interested in looking at hybrid organic-inorganic nanocomposites consisting of exfoliated clay in polymer matrix. Based on the amount of dispersion achieved for the nanofiller in a polymer matrix, the enhancement in final properties of the composite could vary considerably. Hence, methods to develop materials with very high degree of dispersion of filler have been extensively researched. Figure 5.1 shows the various types of mixing that could be observed in nanocomposites; more discussion will be provided later in the article. Clay type fillers are usually considered ideal candidates for synthesizing exfoliated nanocomposites because of their high aspect ratio, natural occurrence, established intercalation chemistry, and abundance.
However, their uniform dispersion (exfoliation) becomes more challenging because of strong attractive forces between clay platelets and their hydrophilic nature conflicting with traditional hydrophobic nature of most polymers. In pioneering work done at Toyota in 1985, researchers demonstrated the successful dispersion of MMT clay into polyamide matrix. The main mechanism was a surface modification of the hydrophilic clay to make it compatible with highly hydrophobic polymers predominantly using organo modified clay technology. Toyota researchers have demonstrated that MMT clay-nylon 6 nanocomposite achieved enhanced barrier and flame retardant properties. They showed that a clay loading of 4.2 wt % has increased modulus two times with no compromise in stiffness and heat distortion temperature by 80 °C. The enhancement of modulus/strength of nanocomposites could be realized because of the high surface area contact between polymer matrix and clay, which depends on the amount of dispersion of clay in the polymer matrix. If there are aggregates of clay tactoids dispersed in clay (intercalation) they could lead to brittleness of material though they may show high strength. This demonstrated that enhancement in physical, mechanical, chemical properties could be achieved with very low filler loading but designing methods that could synthesize nanocomposites with high exfoliation of filler material in polymer matrix is the key in obtaining highest property enhancement. Synthesis of layered silicate nanocomposites can be accomplished with different processing techniques like solution polymerization, rubber latex method, melt processing and in-situ polymerization. In solution polymerization, pre-formed polymer and clay are mixed in a suitable solvent followed by slow and careful evaporation of solvent resulting in the formation of a hybrid nanocomposite. This method has been successfully employed for resin type nanocomposites but its usage is not universal as it poses prob-
lems when selecting suitable solvents and difficulty in controlling solvent evaporation. When it comes to the rubber latex method, it is very limited to few types of polymer and layered silicate systems; but it was found to be very effective in forming nanocomposites with high barrier properties. Melt processing technique is the one method that has received a lot of research attention because of its simplicity and has been studied for synthesizing highly intercalated structures and to certain extent even exfoliated nanocomposites. In this method, clay filler is mechanically blended with melted polymer and then allowed to cool down which sandwiches the clay platelets in polymer matrix. Many researchers developed methods to perfect the mixing process and is employed in the industry because of its simplistic, cost effective nature and feasibility of large scale synthesis. However, limitations with respect to achieving high exfoliation of the filler and high temperature operation have dwarfed the application of this technique. In-situ polymerization process is where the clay is wetted with monomer and then the polymerization is initiated via a suitable initiator or by application of heat. This process was commercially used by researchers at Toyota for nylon-clay based nanocomposites and found to result in highly exfoliated structures and overwhelming enhancement in properties. A recently developed technique, but still in its very nascent stages of development, is surface-initiated polymerization, also a type of in-situ polymerization. In this method, clay platelets are organically modified with suitable surfactants, where initiator is attached to the surfactant end. Polymerization of the monomer is subsequently initiated directly from the clay surface. Recently our group has observed that surface-initiated polymerization (SIP) could result in high graft densities to form brush regime and the resultant steric forces could also result in highly exfoliated nanocomposites. Based on the type of processing technique being used, different degrees of mixing for polymer and clay could be achieved resulting in mainly three types of structures: phase separated, intercalated or exfoliated structures as visualized in figure 5.1. Depending on the type of polymer, layered silicate, polymerization chemistry and degree of dispersion of clay expected, different approaches for SIP could be employed. In the work reported here, we extend our understanding of the use of SIP method to synthesize polymers with polyolefins like poly(ethyldene norbornene) and poly(cyclopentene) to form thermoplastic elastomeric nanocomposites. The first step is the synthesis of a suitable alkyl ammonium surfactant to modify the clay platelet surface. The difficulty level of this compatibilization increases because of the polyolefin based monomers we intend to use. Researchers have studied factors that influence the synthesis of a
suitable surfactant and proposed some guidelines like having long enough alkyl chain, polymerizable end group and amount of exchange capacity needed.  

A surfactant for clay modification was developed in our previous work which nearly doubled the d-spacing for modified clay compared to pristine one.  

The monomers used in the current work are similar to those used in our previous work, so we decided to use the same surfactant modifier for the clay. Ring opening metathesis polymerization (ROMP) is usually employed for the polymerization of cyclic olefins. It exploits the high ring strain of these cyclic materials, which makes their polymerization a nearly uncontrolled reaction. By modifying the rate of propagation of ROMP reaction through the use of very controlled reaction conditions, ROMP can be made to act as a living polymerization and can be used to synthesize block copolymers. There are two main types of ROMP catalysts available, Shrock type and Grubbs’ type, the main difference being the transition metal center and ligand system. Our group has previously established the effects of these catalysts, co-catalyst system and effects of experimental conditions on the successful synthesis of diblock copolymers involving norbornene and cyclopentene as monomers. We will employ similar environmental conditions in the synthesis of nanocomposites in our current work by making necessary changes to accommodate the use of new monomers. In the present article, use of this method is relevant for SIP of diblock comprising of poly(ethylidene norbornene) (PEnbn) as the first block and poly(cyclopentene) (PCpe) as an outer block segment. We wish to hydrogenate this diblock copolymer nanocomposite to synthesize thermoplastic elastomeric nanocomposites wherein hydrogenated PEnbn acts as a rubbery soft block and hydrogenated PCpe renders highly linear poly(ethylene) semi crystalline block. Synthesis of perfectly linear poly(ethylene) (PE) has been accomplished by using various polymerization mechanisms but are plagued with difficulties like slow kinetics, very low PE molecular weights, and low melting points. ROMP has arguably been the most successful route in this endeavor; ROMP of cyclobutene using a Grubbs’ catalyst and subsequent hydrogenation resulted in narrow distribution linear PE blocks. Because cyclobutene is a gas, researchers have tried to use cyclopentene to synthesize linear PE targeting many applications. ROMP of cyclopentene is a difficult task because of its low ring strain, and high possibility of forming oligomers but the successful synthesis of narrowly distributed PCpe has been accomplished in the literature. Properties of PE block depend mainly on its linearity which in turn translates to melting point and crystallinity. Because of its semi-crystalline nature, PE is an ideal candidate for many applications in plastics industry, mainly
Figure 5.2. MMT clay (gray rectangles) was modified with in-house made alkyl ammonium surfactant (black dots) to form functionalized clay (fMMT). This fMMT was used to conduct surface initiated ROMP (SI-ROMP) of ethylidene norbornene and cyclopentene in that polymer blocks order. Resultant diblock nanocomposite was hydrogenated to convert poly(ethylidene norbornene) (gray) into rubbery, soft poly(ethyl norbornene) block and poly(cyclopentene) (black) into glassy, semi-crystalline perfectly linear poly(ethylene) block.

in packaging. Block copolymers with PE block as hard segment attached to a soft rubbery polymer block for example, in our work, hydrogenated P(Enbn) can lead to TPEs (Thermoplastic elastomers) with interesting properties. In addition to the advantages of synthesizing a linear PE block, because of the advantage of using a highly dispersed nano filler these materials can find applications specifically in developing high barrier materials, flame retardant materials and high strength materials. In the work reported here, synthesis of nanocomposite TPEs (NC-TPEs) can have syngergistic effects of using highly exfoliated nanoclay to increase the mechanical, thermal and barrier properties. We believe that NC-TPEs derived from this work will have superior properties compared to their non-clay analogs. Here, we present the synthesis of thermoplastic elastomeric nanocomposite employing surface initiated ROMP on an organically modified clay (MMT) to synthesize poly(ethylidene norbornene-b-cyclopentene) and subsequently hydrogenate resulting in poly(ethyl norbornene-b-ethylene). Then, we will conduct reverse ion exchange to cleave the diblock polymer chains from clay to compare them to their clay analogs. We will study these materials based on thermal, mechanical and morphological properties to investigate the affects of clay addition.
**Experimental Details**

**Surface modification of MMT**

This process starts with the synthesis of alkyl ammonium surfactant and then functionalizing the clay with it. The surfactant used in this work was synthesized in the same way as described previously. As shown below in the schematic 5.3, the end that attaches to the clay surface has two anchor points and the end that radiates out from surface of clay contains a polymerizable group. NMR measurements conducted on this sample as shown in figure 5.4 shows the successful synthesis of targeted surfactant and XRD measurements 5.5 conducted show modification of MMT and that the surfactant addition has pushed the clay platelets sufficiently apart. Also evident from the figure 5.5, addition of Grubbs’ catalyst to the organically modified MMT has further pushed the plates apart indicating that catalyst is also entering the intergallery spacing thus creating an surface adhered effective initiator ready for surface polymerization. A thermogravimetric analysis of the functionalized MMT has showed that hydroxylation of the organic surfactant is completed by 700 °C, which leaves nearly 26.3% of organic content in modified clay. This corresponds to nearly 81% of ion exchange capacity of MMT clay.

**ROMP of diblock**

Monomers for the diblock copolymer synthesis, ethylidene norbornene and cyclopentene were purchased from Sigma Aldrich. Monomers were passed through an activated alumina column three times.
to eliminate moisture, inhibitors and any impurities and then subjected to three freeze/pump/thaw cycles to take out oxygen. 1st generation Grubbs’ catalyst was purchased from Sigma Aldrich and used without any further purification. Co-catalyst, tricyclohexylphosphine was purchased from Fisher and used as received. Solvent for the polymerization reaction, dichloromethane was purchased from Sigma Aldrich and subjected to three freeze/pump/thaw cycles before use. Methanol, precipitating agent was purchased from fisher and used as received. We used two different terminating agents viz propionaldehyde and ethyl vinyl ether; both purchased from Sigma Aldrich. These were argon purged for 15 min before injecting into reaction vessel for the termination of polymerization reactions. All chemicals were stored and handled inside an argon pressurized MBraun glove box. A typical ROMP of ethyldiene norbornene started with a mixture of ethyldiene norbornene and dichloromethane (2 mL:8mL) being added at a controlled flow rate of 1.4 mL/min at 20 °C to a round bottom flask containing a mixture of catalyst, co-catalyst (co-catalyst to catalyst ratio was 6) and dichloromethane; the contents were allowed to polymerize for 80 min and then terminated with argon purged propionaldehyde, precipitated in cold
methanol and decanted. This was vacuum dried overnight and final polymer material was analyzed using Gel permeation chromatography (GPC) to estimate the molecular weight (MW) and polydispersity index. Study on the effects of the ratio of co-catalyst to catalyst, reaction time and terminating agent is discussed in the results section of this article. For the synthesis of diblock, second monomer, cyclopentene is sequentially added to the reactor after 80 min of reaction time for the first polymer block. This reaction was terminated after 5 h, which is at 30 % conversion. The reason for terminating the cyclopentene polymerization at 30 % conversion was discussed in detail previously; briefly, the influence of the uncontrolled ADMET (acyclic diene metathesis) side reaction is minimal at this conversion level. The diblock was terminated with argon purged ethyl vinyl ether, precipitated in methanol, decanted and

![XRD spectra for neat MMT, Organo functionalized-MMT, and catalyst activated organo functionalized-MMT.](image)

**Figure 5.5.** XRD spectra for neat MMT, Organo functionalized-MMT, and catalyst activated organo functionalized-MMT.
dried in vacuum overnight.

**Synthesis of nanocomposite**

Synthesis of nanocomposite started with the preparation of functionalized clay as described in the section above. First, the organo modified clay was dispersed in dichloromethane with high vortex stirring and sonication at 20 °C for 3 h. In this step, the clay platelets were given enough time to sufficiently wet with the solvent and uniformly disperse in the solution. Then, this solution was mixed in high vortex with measured amounts of catalyst and co-catalyst in dichloromethane while continuing sonication for 2 h at 20 °C. This allowed for the catalyst to enter into intergallery spacing of the clay and initiate the norbornene polymerizable end group on the surfactant, which is radiating out from the surface of the clay. Then, the procedure as used for the bulk polymerization of diblock is followed to synthesize the diblock copolymer nanocomposite. In this step, the monomer is polymerized via the catalyst that is attached to the clay surface and thus surface initiated polymerization proceeds. Figure 6.3 shows the successful synthesis of diblock copolymer containing clay.

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**Figure 5.6.** SEC traces for synthesis of diblock copolymer nanocomposite through SI-ROMP: Surface initiated poly(ethylidene norbornene) (thin), surface initiated poly(ethylidene norbornene)-b-poly(cyclopentene) (thick). The first block MW was 56 kDa with a PDI of 1.25 and diblock MW was 138 kDa with PDI of 1.4 (MWs and PDIs were measured against polystyrene standards).
**Hydrogenation of nanocomposite**

Hydrogenation of nanocomposite materials was carried out using a stoichiometric method via reduction mechanism using a diimide chemical. This reaction, also known as transfer hydrogenation, can be carried out at low temperature and low pressure without the need of a Parr reactor. Reaction procedure for nanocomposite hydrogenation has been borrowed from literature and was modified to achieve optimum results. The diimide chemical, (the hydrogen source in the reaction) p-toluenesulfonylhydrazide (TSH), xylene (solvent) and 2,6-di-tert-butyl-4-methylphenol (commonly referred as BHT) were bought from Sigma Aldrich and used as received. Hydrogenation reaction was carried out in a three neck flask equipped with a reflux condenser, a stir bar and an oil bubbler. Measured amount of nanocomposite and trace amount of BHT was dissolved in xylene at 2 (w/w) % for an hour. Stoichiometric amount of TSH was added to the xylene solution and stirred for another 30 min under constant inert gas purge. The amount of TSH corresponded to 8 equiv. moles relative to double bonds in the nanocomposite material. The solution was heated to 135 °C and nitrogen gas started to evolve. The reaction was continued for another 3 to 4 h depending on when the nitrogen gas stops evolving as evident from the oil bubbler. Then, the reaction is cooled to room temperature and the reaction mixture was poured into 5 fold excess cold methanol. The material is decanted, redissolved in tetrahydrofuran and re-precipitated using cold methanol. This process is aimed at removing the p-toluene sulfonic acid that forms as by product and remove any excess TSH left out unreacted. The polymer is dried in vacuum oven overnight until it reaches constant dry weight. A GPC and 1H NMR analysis were conducted on this sample to ascertain the effectiveness of the hydrogenation process.

**Reverse ion exchange**

Detethering of the diblock copolymer from the surface of clay was carried out by using lithium chloride (LiCl) salt as an ionic agent to reversibly exchange alkyl ammonium headed polymer chains with lithium ions. A typical experiment started by mixing two solutions in a big round bottomed flask; one containing measured amounts of nanocomposite sample dissolved in 5 (w/v) % amount of THF solvent and other with LiCl and THF for nearly 48 h with vortex stirring. Then, this mixture was centrifuged at 3000 rpm for 30 min, the supernatant is decanted, precipitated with methanol and vacuum dried to
obtain neat polymer.\textsuperscript{120,137} TGA analysis performed on the sample was used to show that MMT clay was separated from the neat polymer.

**Characterization**

**Gel permeation chromatography (GPC)**

Size exclusion chromatography was carried out in Waters Acquity APC GPC equipped with Acquity APC XT 900 2.5 microns columns to measure Molecular weights and polydispersity index (PDI). The system was operating on HPLC tetrahydrofuran (THF) at room temperature fitted with an Refractive Index detector. Dried samples were dissolved in HPLC THF, filtered and sampled. All reported MWs in this article are calibrated against polystyrene standards.

**Nuclear magnetic resonance (NMR)**

The structure of the organic modifier was ascertained by analyzing the 1H NMR spectra with the sample was dissolved in CDCl$_3$ with 1% TMS on a Varian MR-400 MHz from 2-14 ppm.

**X-Ray diffraction (XRD)**

A Siemens D-500 powder diffractometer using a copper $K_{\alpha}$ source ($\lambda_{\text{avg}} = 1.54 \ \AA$) operating in variable slit mode was used to measure the increase in d spacing for the organo modified MMT and catalyst activated functionalized MMT compared to pristine MMT. The scattering was measured in the $2\theta$ range from 2$^\circ$ to 10$^\circ$.

**Thermogravimetric analysis (TGA)**

Thermal analysis was carried on TA instruments thermal analysis system from room temperature to 900 $^\circ$C at a heating rate of 10 $^\circ$C/min in nitrogen atmosphere. The analysis looked for difference in the onset temperatures and amount of residue remaining between polymers with and without clay to see the effect of the addition of the MMT in polymer matrix.
Differential scanning calorimetry (DSC)

Measurements for glass transition temperature $T_g$ and melting peaks $T_m$ of both the clay and non-clay hydrogenated samples were obtained using a TA instruments DSC Q2000 system scanning from -60 °C to 140 °C at 10 °C/min in N$_2$ atmosphere for three heating/cooling cycles. Because there were subtle differences in heat capacities for thermal transitions, all thermograms showed in this article will be zoomed in to show the step change of glass transition and crystallization peaks clearly and they are exothermic upward graphs.

Dynamic mechanical analysis (DMA)

Visco-elastic properties of hydrogenated diblock copolymer nanocomposite and its reverse ion exchanged analog were conducted on a TA ARES® G2 strain-controlled rheometer with a rectangular tension geometry using a melt pressed rectangular bar (usually L×W×T of 10 mm, 8 mm, 1 mm). The isochronal temperature ramp tests in tension mode were run from -50 °C to 140 °C for hydrogenated nanocomposite sample and -50 °C to 120 °C for its non-clay analog at a rate of 3 °C/min heating rate and $\omega = 1$ rad/s with amplitude of 0.1 % strain in inert atmosphere. The strain percentage was selected in the newtonian region from a strain sweep test ran in that particular temperature ranges.

Microscopic imaging

Nanocomposite and its non clay analog polymer samples were cut by using a Leica cryo-ultramicrotome at -100 °C into 70-90 nm thick sections. Imaging was done using a JEOL 2100 STEM microscope operating at 200 keV at resolutions ranging from 10 nm to 1 µm. Images were taken from different parts of the sections to ensure homogeneity and images were analyzed on a Gatan Digital micrograph suite.

Results and discussion

Synthesis of nanocomposites via SI-ROMP is discussed in this section, followed by characterization of the extent of exfoliation in the nanocomposite using TEM micrographs, and then we will evaluate the role of MMT addition in thermal and mechanical properties. Surface initiated polymerization is very closely related to bulk polymerization with one basic difference: The monomer has to diffuse into the
intergallery spacing of the functionalized clay where it will be polymerized from the surface of the clay. The rate of polymerization of monomer has to be slower than or equal to rate of diffusion of monomer into the intergallery spacing to achieve good exfoliation. In our last article, we studied the kinetics of ROMP of norbornene which was very helpful in extending the experimental method to ROMP of ethylidene norbornene in this work.

**Ring opening metathesis polymerization (ROMP) of ethylidene norbornene**

Bulk polymerization of homopolymer ethylidene norbornene with 1st generation Grubbs’ catalyst is studied in this work. We know that ROMP at room temperature gives poor control over reaction rate, so we first adopted the same conditions as was used for ROMP of norbornene in our previous work. However, the co-catalyst to catalyst ratio of 4 did not result in a good control over the polymerization as it would for norbornene. This could be attributed to the presence of substituted alkyl group on the norbornene which could have caused steric effects. A SEC trace for poly(ethylidene norbornene) after 60 min of reaction time yielded a polymer with polydispersity index of 2.5. Further increasing the ratio to 6 gave good control over the reaction for up to 90 min, as evident from the kinetics as shown in Fig 5.7. But, an aliquot at 120 min increased the polydispersity index and the doubling of the MW of the polymer at this time shows that chain backbiting would have started. The kinetics of the ROMP
with ratio 6 put the reaction time at 90 min, after which back biting of the polymer chains may start increasing the PDI. As seen from 5.7, it is evident that the polymerization of PEnbn was completed in first one hour of reaction time and the back biting does not start until another 30 min into reaction. It has been observed that the choice of terminating agent affects the time required to precipitate the polymer. Three different terminating agents viz., ethyl vinyl ether, benzaldehyde and propionaldehyde were studied to observe the effects. Though, ethyl vinyl ether and benzaldehyde gave polymers with good PDI, there was a tail on the SEC trace to the right side of the peak indicating small amount of low MW oligomers. Terminating the ROMP reaction with propionaldehyde did not have this tail and the PDI observed was good. The reaction kinetics of termination of the poly(ethylidene norbornene) block could be different for each of these terminating agents. Below shown are the SEC traces for ROMP of poly(ethylidene norbornene) terminated with each of these terminating agents for a reaction time of 60 min 5.8. The reaction was stopped at 60 min after which back biting side reactions would start 5.9.

**Synthesis of surface initiated nanocomposites**

Same experimental conditions were employed for surface initiated polymerization as used for bulk polymerization, as explained in the methods section of this article. SEC traces in figure 6.3 show
narrowly distributed polymers were synthesized via SI-ROMP route. SEC traces for surface initiated poly(ethylidene norbornene) (thin), surface initiated poly(ethylidene norbornene)-b-poly(cyclopentene)(thick) shown in the figure 6.3 have narrow dispersity index. The first block MW was 56 kDa with a PDI of 1.25 and diblock MW was 138 kDa with PDI of 1.4 (MWs and PDIs were measured against polystyrene standards). It is evident from the increase in MW from first block to diblock that successful synthesis of diblock copolymer was carried out using ROMP polymerization technique. TEM micrographs shown in 6.6 (left side) show that surface initiated polymerization resulted in exfoliation of MMT clay platelets in diblock copolymer matrix. As seen from image 6.6 (right side), there are some areas in the polymer matrix where intercalation was observed, however the size of tactoids is not be more than 10-20 nm.

**Investigation of thermal properties**

**Thermogravimetric analysis of samples to assess role of Clay particles**

The thermograms for hydrogenated SI-BCP and its non-clay analog shown in the figure 5.11 has residual weight percentages of 13.5 % and 7.4 % respectively. The difference between these two numbers (6.1 wt%) corresponds to the 6.5 wt% of clay loading in the nanocomposite. The thermograms show no or very little weight loss up to temperatures as high as 400 °C. In temperature range from 400 °C to 475 °C, thermograms show no major differences in thermal degradation profile for both
Figure 5.10. TEM micrographs showing exfoliation of MMT in diblock copolymer matrix synthesized via SI-ROMP mechanism

Figure 5.11. TGA thermogram showing the weight loss of hydrogenated nanocomposite (very thick) and its non-clay analog (thick)
samples. This may mean that addition of clay does not have any effect on the high temperature degradation of the nanocomposite sample. But, at temperature 475 °C, the nanocomposite sample is at 31 wt % where as it’s non-clay analog is at 18 wt %. This shows that addition of clay does play role in the final degradation of polymer. Increasing the temperature from this point forward shows that the nanocomposite sample degrades at slower rate compared to non-clay sample.

**Differential scanning calorimetry analysis**

Figure 5.12 shows glass transition temperature, $T_g$, for homopolymer ethylidene norbornene with MW of 59 kDa, which is 70.7 °C, increasing the MW to 89 kDa increases the $T_g$ to 93.2 °C and further increase in MW to 120 kDa puts $T_g$ at 103.5 °C. We speculate that high MW of poly(ethylidene nor-
Figure 5.13. DSC heating plot at 10 °C/min showing ethylidene norbornene block glass transition; with clay-top, without clay-bottom

bornene) may increase the entanglement of the polymer, resulting in substantially higher $T_g$ values. The homopolymer sample with MW 120 kDa has a sharp glass transition which has a range of nearly 10 °C while the one with 89 kDa has a much wider transition but in the range of 10 °C. The homopolymer with 59 kDa has a glass transition in the window of nearly 30 °C. This may suggest that PEnbn glass transition is a subtle thermal transition which gets attenuated at high MWs.

Figure 5.13 shows that $T_g$ for poly(ethylidene norbornene) clay sample is 109.6 °C and $T_g$ for its non-clay counterpart is 96.7 °C showing an increase of nearly 13 °C. In the past, nanocomposites synthesized by surface initiated route have showed substantial increase in $T_g$ for nanocomposite compared to non-clay analogs. We believe the polymer brush being attached to the surface of clay restricts the chain motion compared to that of the bulk polymer. This makes the polymer confined in the inter-gallery spacing of the clay thus requiring much higher temperatures to cause unrestricted chain motion.

Figure 5.14 shows DSC heating plots for block copolymer nanocomposite with poly(ethylidene norbornene) as inner block and poly(cyclopentene) as outer block with $T_g$ close to 39.5 °C which is much lower value compared to the $T_g$ of poly(ethylidene norbornene) nanocomposite shown in figure 5.13.
There is only one observable glass transition contrary to expectation of two different glass transitions for diblock copolymer. This is the case of block copolymers where the two homopolymers are miscible with each other to form a single phase rather than phase separate. We speculate that very good mixing between the two polymers could also be undermining the glass transition elevation usually caused by addition of clay. We believe that this miscibility of polymers would change after hydrogenation, because of the thermoplastic-elastomeric nature of the hydrogenated material.

Figure 5.14 shows the thermogram for non-clay hydrogenated sample which has a glass transition temperature at 10.85 °C corresponding to the soft and rubbery poly(ethyl norbornene)(hPEnbn) block and a melting peak with peak melting temperature at around 98 °C corresponding to the hard and semi-crystalline poly(ethylene) (PE) block. Figure 5.16 shows the thermogram for hydrogenated nanocomposite where in the melting peak corresponding to poly(ethylene) block is at 100.3 °C and the glass transition temperature is at -2.4 °C corresponding to the soft and rubbery poly(ethyl norbornene) block. Though there is a very modest increase of 2 °C in the melting temperature observed for PE block, the glass transition temperature change between nanocomposite and its non-clay analog is in contrast to our understanding of the effects of clay on thermal properties of polymers. It appears that
Figure 5.15. DSC heating plot at 10 °C/min showing glass transition for poly(ethyl norbornene) block and melting peak for poly(ethylene) in a non-clay hydrogenated nanocomposite.

Figure 5.16. DSC heating plot at 10 °C/min showing glass transition for poly(ethyl norbornene) block and melting peak for poly(ethylene) in a hydrogenated nanocomposite.
the addition of clay negatively effects the transition for SI-hPENbn decreasing the \( T_g \) by nearly 13 °C compared to non-clay one and shows no effect on the melting peak for PE block. Two separate thermal transitions for hPENbn and PE block suggests that the two blocks are phase separated. However, as pointed out by rangarajan et al., it is not clear whether this phase separation is because of polymer blocks incompatibility or the crystallization of one of the blocks (PE). In order to find more information about the effects of clay on hPENbn and PE, surface initiated homopolymer PENbn and bulk homopolymer PENbn were synthesized with same MWs and then hydrogenated both samples. Figure 5.18 shows the DSC heating plots for SI-hPENbn and hPENbn samples with \( T_g \)'s at -8 °C and -16 °C respectively. Also surface initiated homopolymer PCpe and bulk homopolymer PCpe were synthesized with same MWs and then hydrogenated both samples. DSC cooling plots for SI-PE and PE samples show that the peak melting temperature has increased by at least 5 °C because of addition of clay. This observation is in agreement with the hypothesis that addition of clay increases the thermal transitions of polymers. Based on this observation, a surface initiated diblock copolymer consisting of hPENbn and PE should have inflated thermal properties compared to its non-clay polymer. So, we speculate that in a surface initiated diblock with hPENbn and PE, the crystallization of PE block in the presence of MMT clay and amorphous hPENbn may have been the reasons behind imparting negative effects on glass transition temperature. The reason could be a mixed effect, one being an increase in the free volume of the hPENbn block caused by the addition of clay compounded by the other one which could be the phase separation caused by PE crystallization in the presence of clay platelets resulting in the increase in amorphous hPENbn chain mobility. Thus, the chain confinement caused because of addition of nano filler may actually be counteracted because of increased free chain movement. This may cause the glass transition of hPENbn to occur at temperatures lower than that corresponding to non-clay analog.

**Investigation of mechanical properties**

**Through Dynamic mechanical analysis**

Dynamic mechanical analysis DMA is also referred to as solid state rheological measurement usually giving information about phase behavior of polymeric materials. Figure 5.19 shows storage mod-
Figure 5.17. DSC heating plot at 10 °C/min showing melting peak for poly(ethylene) for with clay and without clay hydrogenated nanocomposites

Figure 5.18. DSC heating plot at 10 °C/min showing glass transition for poly(ethyl norbornene) block for with clay and without clay hydrogenated nanocomposites
ulus changes in a temperature scan in the linear strain regime for hydrogenated nanocomposite sample and its non-clay analog. For clay hybrid, there is an inflection point in the modulus around -10 °C suggesting the transition from glassy to rubbery state. There is a rubbery plateau from 20 °C to 95 °C and then another inflection occurs after 100 °C indicating the melting of the material. Increasing the temperature much higher than this point shows that there is a plateau up to temperatures as high as 140 °C. For non-clay analog, the first transition in modulus occurs at around 8 °C and then there is a very sharp decrease in the modulus approaching the temperature 22 °C. Compared to clay hybrid, this transition has high step change showing the effect of clay. Increasing the temperature causes gradual decrease in modulus up until around 90 °C in contrast to the rubbery plateau observed for the clay hybrid. With further increase in temperature the modulus decreases monotonically until the material melts and no further measurement was possible above 125 °C. The non-clay analog has much lower modulus at any given temperature with the exception of the first transition point. The low temperature behavior of clay hybrid is in agreement with the glass transition anomalies observed using DSC technique. As expected, the clay hybrid starts its transition much before the non-clay counterpart and at one point both the clay and non-clay analogs have same modulus values. The difference in behavior of clay and non-clay materials at high temperatures is attributed to the presence of clay. Clay imparts immobility to the free movement of polymer chains making it more resistant to the heat. Also, the high temperature (above 90 °C) behavior suggests that the structural stability imparted by clay provides resilience even after the material started melting.

Figure 5.20 shows the loss modulus temperature scan plots for clay and non-clay materials. The loss modulus curves show that the materials relax in the same fashion at low temperatures. At high temperatures, the non-clay analogs relax at much faster rate compared to its clay hybrids. The plateau region for non-clay analog is observed until around 75 °C but the clay hybrid has plateau region extending until 100 °C. This could be because of suppression of chain mobility by the presence of clay causing a delayed relaxation. The peak of tan δ in DMA plot 5.21 gives the glass transition temperature measured by mechanical methods which is at 10 °C for hydrogenated nanocomposite which is different from the DSC measurements but the difference could be attributed to the change in the method of measurement. For non-clay analog, peak of tan δ is around 16 °C which is higher compared to clay hybrid, an anomaly observed in DSC measurements. Other trends observed in tan δ plot are similar to
Figure 5.19. Dynamic mechanical scan showing storage modulus (Log E') for diblock copolymer nanocomposite and its non-clay analog. nanocomposite-thick, non-clay analog-very thick

Figure 5.20. Dynamic mechanical scan showing loss modulus (Log E") for diblock copolymer nanocomposite and its non-clay analog. nanocomposite-thick, non-clay analog-very thick
Figure 5.21. Dynamic mechanical scan showing damping coefficient (\(\tan \delta\)) for diblock copolymer nanocomposite and its non-clay analog. nanocomposite-thick, non-clay analog-very thick

the trends observed in storage modulus plots.

**Conclusion**

In this article we have demonstrated the successful synthesis of clay grafted poly(ethyldene norbornene-b-cyclopentene) diblock copolymer via SIP route. Subsequent hydrogenation of the diblock copolymer led to poly(ethyl norbornen-b-ethylene) forming TPE-NC. TEM micrographs show that the MMT clay is delaminated in the block copolymer matrix, though there were small amounts of intercalated structures. We have observed that glass transition temperature for clay hPENbn was at lower temperature than its non clay analog. This is in contrast with the conventional nanocomposite behavior which usually says that addition of clay confines the polymer chain mobility thus increasing the thermal transitions to occur at high temperatures. We believe this is an anomaly caused because of the crystallization of PE block attached to the rubbery hPENbn block in the presence of MMT clay. We have found evidence in the mechanical tests that clay enhances the modulus behavior of nanocomposite material compared to detethered polymer, showing proof that good interfacial contact has been established between polymer and MMT clay platelets.
Bibliography


CHAPTER 6. POROUS MEMBRANES DERIVED FROM POLY(STYRENE-\textit{b}-ISOPRENE-\textit{b}-DIMETHYLSILOXANE) TRIBLOCK COPOLYMER SYSTEM VIA ETCHING OF POLY(DIMETHYLSILOXANE)

A paper to be submitted to Journal of membrane science journal

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Introduction

Block copolymers are self-assembling materials, where two or more distinct polymers are covalently attached to form hybrid macromolecules with synergistic properties of constituent materials. Block copolymers separate into microphases with well-defined ordered structures because of thermodynamic balance between block-block contact energies and entropy driven stretching. This allows for tunability of desired microstructure into block copolymers to form: lamellae, cylinders, spheres, and gyroid (double gyroid, alternating gyroid) among others. Advanced applications for nanolithography, drug delivery, membrane separations and energy applications have come to be realized thanks to the development of synthesis procedures such as anionic polymerization and other living radical polymerizations that enabled control of architecture, molecular weight, composition and functionality of block copolymers.

Membrane separation technology has been employed for wide range of applications for use in chemical, petrochemical, water treatment, food, dairy, pharmaceutical, paper, textile and electronic industries. There is a demand for developing highly functional membranes to cater to the needs of applications in capture of greenhouse gases, desalination of water, drug delivery and many other technologies. Membranes can be synthesized either by organic or inorganic materials. But, membranes synthesized from polymers (organic materials) are gaining more attention due to their ability
to be engineered to suit for wide spectrum of applications. However, there are some disadvantages like high hydrophobicity of polymeric materials, fouling and low mechanical strength which should be overcome warranting novel research in this field.\textsuperscript{166} It is well-known that block copolymers with their self-assembly are able to form mesoscale morphologies, including a family of continuously percolating three dimensional network structures which could be exploited to develop porous thin film membranes. These ordered block copolymers can form mesopores (according to IUPAC mesoporous films or membranes refer to materials with pore diameters in the 2–50 nm ranges).\textsuperscript{158} Block copolymers, because of their ability to form homogeneous nano structures, can achieve uniform pore size distribution in membranes. Also, the wide pore wall functionalization ability of block copolymer membranes could be a solution to various applications in membrane separation field. Block copolymers also offer exceptional control over their physical, mechanical and thermal properties to fine tune the resulting membranes for much wider applications otherwise hard to realize.\textsuperscript{160}

One of the first applications of block copolymer derived membranes were synthesized from poly(styrene-butadiene-styrene) system for gas permeation by Odani et al.\textsuperscript{168} Then there are porous membranes, ion-exchange membranes, and other types of separation mechanisms employed in membranes.\textsuperscript{175} In present work, we are interested in porous membranes, mainly focusing in mesoporous range that could be synthesized with block copolymer systems. Here, we present literature on use of block copolymeric materials for membrane fabrication targeting different applications. Epps et al. have studied the use of block copolymer materials as an effective electrolyte in fuel cell systems.\textsuperscript{153,154} Sander et al. have studied the use of block copolymer membranes with different blends to improve selectivity while extracting carbon dioxide.\textsuperscript{170} Crawford et al. have studied sulfonated PS-PIB-PS triblock copolymer films for water transport properties and reported that they could achieve membranes that could be used as military grade protective clothing.\textsuperscript{152} Yeo et al. have studied the properties of sulfonated block copolymer membranes for water purification applications where-in they controlled the chain architecture to induce the relevant properties.\textsuperscript{178} Galletti et al. have shown usage of membrane bioseparations in hemodialysis by using it to cure end stage kidney disease.\textsuperscript{157} Aharon et al. have demonstrated separation of carboxylic acids in industrial scale using membrane separations and they have stated that this process may be an economical option without compromising on product purity.\textsuperscript{156}
Block copolymer membranes could be fabricated using different techniques like phase inversion, sol-gel process, microfabrication, and etching among others. Phase inversion process has been employed widely in academia, also finding its way into some commercial scale processes. Mathias et al. have discussed in detail about various research works, wherein membranes were developed using this procedure. We are interested in the chemical etching process by selectively removing one of the polymer blocks to form porous structures. Lee et al. in one of their pioneering works in this type of fabrication process, developed membranes from poly(4-vinyl phenyl) dimethyl-2-propoxy silane-b-isoprene system by crosslinking silane block and then cleaving of isoprene block by using chemical methods. They have showed that porous thin film membranes could be fabricated using this method. By changing the size of the etchable block, this process enables design of membranes with a wide range of pore sizes. In the work reported here, We exploit the process of selective etching to remove a single block copolymer mesophase by using chemical methods. Apart from different pore sizes, tuning the pore wall of the membrane with different functionality leads to application of one particular material to different separation procedures. Rzayev et al. have reported the fabrication of hydrophilicity in pores of membranes derived from polystyrene-block-poly(dimethyl acrylamide)-block-polylactide system after etching of polydimethyl acrylamide block. Because of endless possibilities that could be achieved with pore wall functionality, this process has gained much more importance in recent times. But, it remains that these materials full potential has not been exploited. Our work in this field could lead to materials made from block copolymers with percolating pore networks, where the pore diameter can be tuned on demand and pore geometry can be tuned by manipulation of the copolymer formulation.

Some disadvantages of currently available membranes are having random and wide pore network, tortuous pore path, high flow resistance, fouling and sub par performance. Some of these obstacles could be solved by fabricating membranes derived from block copolymers with very well defined ordered structure for example gyroid morphology. In this article we talk about building a membrane from poly(styrene-b-isoprene-b-dimethyl siloxane) triblock copolymer system (SID, ABC triblock copolymer system in our work) and investigate how the gyroid ordered structure will help in fabricating a continuous porous structure. One article reported by Shefelbine et al. talks about formation of core-shell gyroid morphology (Ia3d symmetry) which is known to form bi-continuous cubic structures in ABC triblock copolymer system, similar to one depicted in left side of figure 6.1. This structure exhibits
high connectivity making it an ideal porous membrane backbone. Researchers postulate about the potential of these structures in membrane applications due to their apparent resiliency in maintaining their connectivity even at grain boundaries. For this reason, we want to tap into the gyroid (double gyroid or alternating gyroid) ordered structure and selectively etch out one of the blocks forming percolating networks of pores in block copolymer matrix. The main idea behind use of SID triblock copolymer system to study as a candidate for membrane separation comes from the characteristics offered by individual block segments. We will show in this article that these membranes can elute or retain via molecular size. To do this, we chose a glassy first block, poly(styrene) and two rubbery blocks; a poly(isoprene), poly(dimethyl siloxane). The membrane should allow materials to enter one of the rubbery domains (e.g., D), and the S channel forms the membrane matrix and I channel gives the pore layer which having a double bond is convenient for both crosslinking to increase strength and functional group attachment to facilitate transport like preferential separation of toxic gases, recovery of target products to alleviate product toxicity, removal of fermentation side products that slow or prevent downstream processing to name a few. 150,151,155,159

The proposed materials poly(styrene-b-isoprene-b-dimethyl siloxane) (SID) copolymers, where the D domains may be quantitatively removed via exposure to tetrabutylammonium fluoride (TBAF) are

dicumyl peroxide

SID unit cell as cast

Mesoporous SI monolith after TBAF

Figure 6.1. Depiction of the double gyroid network morphology known to form in ABC triblock copolymers such as SID. Here the red region represents poly(styrene), the structural component of the membrane, while the green area is the poly(isoprene) that lines the pore walls. Pores are formed by first casting SID into a membrane-shaped disc, lightly crosslinking the poly(isoprene) with dicumyl peroxide (further enhancing mechanical integrity) and then applying TBAF to selectively etch the poly(dimethyl siloxane).
used to fabricate thin porous membranes. The strength of the embedded S domains aids the process-
ability of the materials while offering access to a variety of network phases in the SID system. Thus,
this system offers access to network phases while simultaneously allowing for control over the mech-
nical properties, pore diameter, and pore connectivity. We report in the remaining section of this article
that SID materials have been synthesized and characterized to be in the gyroid region. After successful
synthesis of SID polymers, they are characterized to show that they are indeed phase separating into
gyroid microstructure. Then thin film membranes successfully fabricated, chemically etched to form
porous structures and tested out in a stirred cell to show separation of components.

Experimental section

Anionic polymerization has been used to synthesize polymeric blocks with precise segment com-
position, block volume fractions, and get nearly monodisperse polymer block. However, this polymer-
ization technique comes with its own difficulties as it demands air and moisture free environment and
high purity of the precursors. Monomers were reacted with pyrophoric organometallic compounds to
remove inhibitors and then distilled to collect purified materials to be used in the polymerization reac-
tions. A process called freeze-pump-thaw method was used to achieve air and moisture free materials to
be used in the polymerization reactions. This section gives a detailed synthesis procedure to make a SID
triblock copolymer material that will be characterized and will be used to fabricate a porous membrane
to be tested for flow through.

Materials

Styrene, isoprene and hexamethylcyclotrisiloxane (typically referred to as D₃) are the monomers.
All monomers were cleaned extensively to remove inhibitors and impurities using in house cleaning
methods. Cleaning agents used are: di-n-butyl magnesium, n-butyl lithium and calcium hydride. The
initiator of anionic polymerization was sec-butyl lithium. Cyclohexane, tetrahydrofuran, dichloromethane,
methanol and isopropanol are solvents, used after in house cleaning to remove impurities, air and mois-
ture. Dicumyl peroxide is the chemical agent used to control the amount of cross linking of polyisoprene
block. Tetrabutylammoniumfluoride (TBAF) is the chemical etching agent to remove the poly(dimethyl
Figure 6.2. Reaction schematic for synthesis of SID block copolymers. All monomers are sequentially polymerized in the sequence shown above where in polystyrene and polyisoprene reactions go to near completion but because of reversible nature of D block addition, reaction will be stopped at 50% conversion.

Synthesis procedure

Synthesis of the SID triblock copolymer material started with purification of monomers by using specialized glassware attached with vacuum pump and inert gas source to achieve air and moisture free atmosphere. Styrene was purified with di-\textit{n}-butyl magnesium to remove inhibitors by a series of mixing and distillation techniques. Purified styrene was stored in clean and dry place with minimum light exposure before being used. Isoprene was purified using \textit{n}-butyl lithium using the same purification technique as styrene. D$_3$ was dissolved in cyclohexane and purified by distilling from calcium hydride. Cyclohexane and tetrahydrofuran were purified by passing through columns containing activated alumina and Q$_5$. The reaction starts with addition of 220 mL of cyclohexane solvent to 0.528 mL of sec-butyl lithium at 40 °C in a air and moisture free round bottom flask equipped with stir bar. Then, 5.5 mL of styrene is added to this reactor at a slow drop-wise rate; after few minutes of mixing, the contents of the reactor showed a bright orange color signifying that styrlithium ions formed, this was taken
as indication for a successful initiation reaction. If the color was not observed, that may be because of presence of air or impurities in the reaction. The reaction was allowed to proceed for 8 h, which was enough time to achieve nearly 99% conversion. Then, 18 mL of purified isoprene was sequentially added to the reaction flask, changing the bright orange color to very light yellow. After 8 hrs time has elapsed, there should be styrene and isoprene diblock copolymer. Then, a solution of D₃ and cyclohexane at 0.5 gm/mL concentration was added at 25°C and then reacted for 24 hrs to allow for crossover to D block. The, 100 mL of tetrahydrofuran was added to the reaction and reacted for 4 h at 25°C. The addition of tetrahydrofuran aids in changing the polarity of the contents, propagating the D block and the reaction was terminated at 50% conversion with excess amount of chlorotrimethylsilane. After few minutes of stirring, polymer is precipitated with methanol and isopropanol and decanted. The decanted polymer is dried in vacuo, added with 0.1 g of BHT inhibitor and stored in a cool and dry place. A combination of NMR and size exclusion chromatography was run to determine the block molecular weights and volume fractions.

**Membrane fabrication**

SID triblock copolymer synthesized using the above procedure was used to fabricate a thin film membrane. 2.8 g of bulk polymer and 0.49 g of dicumyl peroxide were mixed in 50 mL of dichloromethane and stirred for 24 h at room temperature. The amount of polymer and dicumyl peroxide used in the reaction corresponds to 8:1 for number of double bonds to peroxide molecules. The polymer was precipitated in methanol, decanted and dried overnight. This polymer was pressed in a Carver press at a temperature of 160°C and 15000 psi force to form a thin membrane of nearly 150 microns thickness and 50 mm in diameter. This membrane was left in the Carver press under a constant force of 15000 psi but allowed to cool to room temperature aiding in annealing the polymer and partial cross-linking of polyisoprene (PI) block. Later on, the cross-linked membrane was dissolved in TBAF solution in a petri dish for 48 hrs to chemically etch the D block. The etched membrane was dried in vacuum oven and weighed to make sure that D block has been etched out in its entirety. This membrane was used to perform flow experiments.
Flow experiments

The SID membrane measuring 150 microns thick fabricated using the above method was used in a Sterlitech HP4750 stirred cell to study the flow rate and pressure combinations for various solvents. A PEG/water solution, wherein PEG molecular weights were varied from 1500 Da to 8000 Da was used for size separation experiments. The membrane was placed on a porous metal plate for mechanical support, then measured amounts of solvent/solution was poured carefully into the stirred cell and the set-up was sealed. This stirred cell was pressurized with argon to create a pressure difference across the membrane, where the input pressure is read against the output flow rate of the solvent/solution being collected on the eluent side of the membrane. Analysis and results of this are presented in results section.

Characterization methods

**Size Exclusion Chromatography (SEC)**  Polymer block molecular weights and molecular weight distributions were measured with a Waters APC Acuity system with HPLC grade tetrahydrofuran as eluent at room temperature and molecular weight calibration was done using polystyrene standards. All samples were dried in a vacuum oven prior to analysis run. Then they were dissolved in HPLC grade tetrahydrofuran at no more than 5 mg/mL concentration, filtered, and sampled.

**Nuclear Magnetic Resonance (NMR)**  Synthesized SID polymer was dissolved in deuterated chloroform (CDCl$_3$) with no more than 5 mg/ml concentration in a NMR tube. All experiments were conducted on Varian MR-400 MHz from 2 to 14 ppm in 1H NMR spectra, and peaks were analyzed by using MestReNova software.

**Small Angle X-ray Scattering (SAXS)**  Samples were sliced into very thin sections (< 0.5 mm thick) to obtain a high resolution SAXS measurement. The incident beam with a wavelength of 1.54 Å was focused on the sample on a 6 meter SAXS line. The scattering vector \( q \) was varied from 0.004 Å$^{-1}$ to 0.4 Å$^{-1}$. 
Transmission Electron Microscopy (TEM)  Triblock copolymer sections of 70 nm thick were cut by using a Leica cryo Ultramicrotome at -100 °C. All sections were stained using OsO₄ vapors at 4 % concentration for about an hour resulting in selective staining of domains. This staining produced necessary contrast between I and D block for clear distinction. Sections were imaged using a FEI-Tecnai 2-F20 STEM microscope operating at 120 keV at multiple locations to test for homogeneity and then high resolution images collected to observe the microstructures.

Rheological Study  Master curves for the polymer samples were studied on a strain controlled ARES®G2 strain controlled dynamic shear rheometer from TA instruments. Frequency sweep tests from 0.1 rad/s to 100 rad/s were performed from 120 °C to 240 °C with a step change of 20 °C with a 3 % strain. Master curve was constructed by combining all the frequency scans to study the slope of the curve at high temperatures. Circular discs with 25 mm diameter and 1 mm thick were melt pressed using a carver press.

Results and Discussion

This section starts with discussion on the synthesis and characterization of the microstructure for SID triblock copolymer. We move on to discussing fabrication of membrane and flow studies using stirred cell. Anionic polymerization, the polymerization technique used for the synthesis of SID triblock copolymer is a very difficult process to conduct and the procedure demands air and moisture free environment, high purity of materials and a lengthy synthesis time. As mentioned in the introduction section of this article, a triblock copolymer system can microphase separate into numerous microstructures; identifying a particular microstructure and synthesizing the triblock copolymers with precise block compositions is an ardent task.

Materials synthesis

SEC traces for polystyrene(PS) block and SID block shown in figure 6.3 have very narrow peaks showing a polydispersity index very close to 1, this shows that there were no side reactions during the experiment. The small coupling peak to the left of PS peak is attributed to oxygen contamination while taking an aliquot. As measured against the PS standards run on the same Gel Permeation chromatogra-
Figure 6.3. SEC traces for the first block which is polystyrene (PS) and the SID triblock (thick) obtained by sequential addition of I and D monomers.

Microstructure characterization

Rheology analysis

The terminal response region in a master curve of storage modulus is known to be influenced by the morphology of that particular block copolymer. Kossuth et al., have researched the effects of the same in cubic structures by conducting oscillatory shear experiments in both diblock and triblock copolymers. They have observed a plateau modulus at very low frequency response in gyroid (for example, triply periodic structure) microstructures. They have derived a power law relation between frequency and elastic modulus for observing the dependence of plateau modulus and morphology. The power law relation which goes as relation between \(\log G' \propto \omega^\delta\), where \(\delta\) can range from 0 for a perfectly elastic
Figure 6.4. 1H NMR plot showing a SID architecture in the inset figure. The peak at around 3.4 ppm refers to methanol in the sample which was the precipitating agent and probably the sample needs more drying before analysis. The peak at 4.8 corresponds to the 3,4 polyisoprene which is less than 2% of the total polyisoprene formed via anionic polymerization route solid to 2 for Rouse like dynamics for un-entangled system. It is speculated that this observation is because of presence of distribution of domain orientations. For SID triblock copolymer in focus, we constructed a master curve in a frequency range of 0.1 to 100 rad/s and a temperature range of 140 to 240 °C to show curves plotted as logarithm of elastic modulus (log $G'$) against log ($\omega aT$). When we derive the slope ‘a’ for this curve and it falls in the range of $0 \leq a \leq 1$, and depending on how close it is to 0, we can speculate that the microstructure could be a triply periodic cubic structure. In the figure 6.5, the calculated slope ‘a’ for terminal region is 0.14, which is not zero but very close to it, based on which we can speculate the microstructure as a triply periodic cubic structure, possibly double gyroid ($Q^{230}$), but further support is needed from a different characterization technique. Bergman et al. have recently observed that slopes far below 1/3 but not equal to zero for a gyroid kind of structure could be because of slippage around grain boundaries, they had very strong indication from SAXS measurement pointing
Figure 6.5. A log-log graph of master curve for SID polymer plotted for elastic modulus, Pa against \( \omega aT \) at a reference temperature of 180 C.

towards \( Q^{230} \) microstructure. It can be observed that the terminal response is horizontal indicating a solid like behavior.

**TEM analysis**

We observed the 70 nm thin sections of the SID triblock copolymer under TEM to aid in evaluating the morphology. The sections were stained for long enough to help distinguish between I and D blocks, giving darker color to I and leaving the D in gray color, and as we know S block is observed as white. All this is possible because of the differences in the electron density of the material being observed. The poor resolution of the TEM image could be attributed to difficulties faced obtaining a uniform thick and mechanically perfect sections. The high amount of I and D blocks which are rubbery blocks could be the reason for this difficulty. From the picture 6.6 we speculate that this TEM image corresponds to the plane perpendicular to \( <111> \) and also the wagon wheel highlighted in the figure 6.6 shows a six fold symmetry which could be pointing to \( Q^{230} \) morphology. We also constructed a TEM projection of this Ia3d space group which is shown in the figure 6.7 below. As we can see, the TEM micrograph very closely corresponds to the TEM projection for the gyroid microstructure.
Figure 6.6. TEM micrograph of the SID triblock copolymer showing a triply continuous gyroid microstructure. All measurements are shown in nanometers.

Figure 6.7. TEM projection showing Ia3d space group symmetry for a [111] projection plane. All measurements are shown in nanometers.
The high resolution SAXS measurement performed on a thin film section of SID triblock is shown below in the figure 6.8. Masaki et al have observed similar distribution of peaks in their SAXS measurement while studying different homopolymer blends with SID triblocks. Further to their measurement while resolving a 2D SAXS, they saw that the these peaks were actually 6 different peaks and they speculated that the structure for this could be core shell gyroid. They supported this prediction using TEM images\textsuperscript{174}[25]. In our scenario, we were not able to conduct another 2D SAXS measurement to support our speculation but this SAXS measurement if viewed in conjunction with the analysis of TEM and rheology measurements presented above, we strongly believe that the SID triblock copolymer could be a triply continuous gyroid microstructure.

**Flow experiments**

Figure 6.9 shows images of thin membranes derived from SID triblock copolymer believed to be having gyroid network morphology. (A) shows a 50 mm diameter and 150 microns thick membrane melt pressed in Carver press and slightly crosslinked with dicumylperoxide. (B) shows the same membrane after selective chemical etching process to remove D domain. (C) is an image showing the cross section of the membrane. This membrane was used in the batch mode stainless steel stirred cell for flow
Tests were carried out with common solvents like water, acetone and ethanol and mixture of PEG of different MW and water at uniform concentrations.

Below are a series of graphs which show various tests that were performed on this membrane; the tests are detailed as follows: a flow test with a fixed volume of water and varying the pressure difference across the membrane (this was also used to construct the graph showing the pressure difference versus flow rate), a flow test with acetone, ethanol and water for a fixed volume of solvent at a constant pressure and a flow test with different Molecular weights of poly(ethylene glycol) dissolved in 120 ml of water at a concentration of nearly 0.02 g/ml at 10 bar constant pressure difference across the membrane. The flow experiment with water at different pressures indicates that higher the pressure applied the faster the flow rate will be. Figure 6.10 shows that the curve is exponential correlation for the pressure difference versus flow rate, which is expected for mesoporous membranes. Figure 6.11 is a representation of the same experiment showing total time it takes to elute certain volume of liquid at different pressure differences. In the graph 6.12 showing data for different solvents, water shows a steady exponential increase with high elution rate while ethanol falls in moderate elution rate and acetone has lowest. The
membrane pore wall poly(isoprene) being hydrophobic could lead to larger swelling of pores resulting in higher flow rates for water. The difference in flow rates for water, acetone and ethanol could be because of polarity differences between solvents and the membrane materials. Water being the most polar material in the lot has high flow rate and acetone being the least polar of the lot has the least flow rate. One potential application for this observation could be fractionation of materials from a mixture of solvents based on polarity difference. These results could help us understand more about the medium that could be best suited for filtration but needs more analysis and study.

Next set of graphs 6.13 show relation between elution volume and elution time for different molecular weights of solute(PEG). This graph shows that higher the molecular weight of the solute the longer it takes for the solution to elute, suggesting that bigger molecules could be blocking the membrane pores making it harder and longer times for elution. Concentration difference between the solution before and after filtration was measured to see the difference in retention coefficients for different MWs of PEG. We have observed that it takes longer time for the PEG with high MW to elute and the total time taken to elute decreases gradually with decrease in MWs. One observation from the retention coefficient of 0.45 for 8000 Da PEG in water shows that close to half of solute is retained back on the retentant side probably because the membrane pore size blocks most of the big molecules but the retention coefficient of zero for 2000 DA PEG solution indicates that pore size range is big enough to allow all of the solute
Figure 6.12. Graph showing the elution of different solvents through the membrane at constant pressure of 5 bar. (Water-thin, acetone-tick, ethanol-very thick)

Figure 6.13. Graph showing PEG solution in water for different MW and the total time taken to elute a fixed volume of solution at 10 bar. 1500 Da-thin, 2000 Da-thick, 6000 Da-very thick, 8000 da-dashed)

molecules to pass through. We observed that for 6000 Da PEG solution the retention coefficient is 0.036 which is very close to zero, indicating that the size of these PEG molecules is where the size of maximum of the pores in the membrane fall within. With further analysis into the filtration of different molecules and size ranges could help analyze what type of materials could be filtered through these SID membranes.
We have shown in this article that a SID triblock synthesized in a triply continuous cubic structure (possibly double gyroid) could be pressed into a thin film membrane, slightly cross-linked I block to give mechanical integrity and then chemically etch out one of the blocks (D block in this case) to form a continuous network of percolating pores to result in a membrane that could be successfully used to do separation of molecules based on size. In future, we would like to study more into this membranes to ascertain the use for different bioseparations, for facilitated transport after functionlization of the double bond on I block and scale up and optimization for in situ operations.

**Conclusions**

In this article we report the successful synthesis of poly(styrene-b-isoprene-b-dimethyl siloxane) triblock copolymer and have shown by characterization methods that it is phase separated and forms a gyroid microstructure. GPC and NMR results have helped in determining the volume fraction of each block in SID; a combination of SAXS, TEM and rheological measurements helped in confirmation of the microstructure of the polymer. Order-disorder transition for this particular polymer has been noticed between 225 °C and 235 °C, which could possibly provide high service temperatures. This polymer was melt pressed into a 150 microns thick thin film membrane, which was then chemically etched to successfully remove the D block forming a continuous network percolating mesopores. The resultant
mesoporous membrane was tested for flow through and the test results indicate that the membrane can withstand pressures up to 10 bar, which was comparable to pressures seen in a typical ultra filtration technique. Experiments with different molecular weights of PEG dissolved in water showed that, there was higher retention of high molecular weight PEG compared against low molecular weight PEG indicating that the membrane was could be applied to separate molecules based on size. We strongly hope that these results will enable the future prospects of this project to modify the membranes for various separations and scale up.

Bibliography


CHAPTER 7. GELS DERIVED FROM POLY(ETHYLIDENE NORBOR NENE-b-CY CLO-PENTENE) BLOCK COPOLYMER NANOCOMPOSITES

A paper to be submitted to Macromolecular Rapid Communications

Sri Harsha Kalluru and Eric W. Cochran

Introduction

High viscosity polymer gels have been studied widely for their applications in fields like oilfield development, biomaterials, superabsorbents, drug delivery and many others. Most of the aforementioned applications are realized via synthesis of hydrogels.\textsuperscript{182} Polymeric hydrogels are formed when a polymeric material forms a highly swollen three dimensional network when mixed with water. A number of synthetic and naturally occurring polymeric materials form hydrogels through a variety of physical and chemical mechanisms. Guar seed based material is a widely known hydrogel with many applications in hydraulic fracturing and viscosity modifiers field. Synthetic polymeric materials based on poly(ethylene oxide), poly(acryl amide), or poly(vinyl alcohol) are highly studied hydrogels.\textsuperscript{184,185} To further improve the properties of these hydrogels, researchers have turned to hydrogel formed via composites, wherein hydrogels are mixed with another inorganic material in small quantities to achieve synergistic properties. Polymer nanocomposites are hybrid materials wherein a nanometer-scale inorganic filler is dispersed in an organic polymer matrix. Appropriately designed polymer nanocomposites have advantages of improved thermal, mechanical and barrier properties compared to non-filled polymers. Clay-based inorganic fillers have found wide usage because of their established intercalation chemistry, good cation exchange capacity, and natural availability.\textsuperscript{180} Nanocomposite hydrogels based on clay are mechanically stable materials, usually formed via crosslinking mechanism where the polymer is crosslinked in order to form a networking structure.\textsuperscript{185} Haraguchi et al. have introduced
a different type of hydrogels where in the hydrogel was not formed via crosslinking mechanism. They have developed a nanocomposite hydrogel by performing in situ polymerization of water soluble polymers on the surface of clay. In this material, polymer chains tethered to adjacent clay particles are terminated via recombination and disproportionation reaction and other polymer chains are not. Thus, the material has less chains attached to each other than in a cross-linked gel overcoming shortcomings in structural inhomogeneity and mechanical properties. In present work, we have developed a polymeric nanocomposite material that can form high viscosity gels in tetrahydrofuran (THF) solvent. We have observed that the mechanism of gel formation is entirely different from the already known clay-based gel systems. First, the gel formation is not a result of chemical crosslinking, which is the usual case of nanocomposite hydrogel formation to date. Second, the gel formation does not occur in situ during the polymerization, for example as reported by Haraguchi et al. In this work, the nanocomposite polymeric material was synthesized as a thermoplastic and then gel is reversibly formed by mixing it in THF in presence of an ionic salt. The presumptive mechanism for gel formation would be the formation of a network structure between clay, ionic salt and polymer chains. More detailed explanation on this will be given in results and discussion section of this article. We believe the type of synthesis route used for making these nanocomposite materials, which gives exfoliated clay structures, forms the prerequisite needed form a mechanically stable gel structure. Polymer nanocomposites are usually synthesized via melt blending, solution blending and in situ polymerization techniques. Depending on the type of synthesis route being used, different degrees of inorganic filler dispersion in the polymer matrix is observed. In situ polymerization is the most favored route to achieve highly dispersed (exfoliated) state for nano filler in polymer matrix. We have successfully employed surface initiated ring opening metathesis polymerization (SI-ROMP) technique for growing a diblock copolymer from the surface of montmorillonite (MMT) clay. In this work, the same synthesis procedure was adopted for poly(ethylidene norbornene-b-cyclopentene) and this material was used to form the high viscosity gels. High viscosity gels were formed with very low solids loading of the clay grafted poly(ethylidene norbornene-b-cyclopentene) (SI-BCP).

The polymeric materials synthesized in this current work are highly hydrophobic. Though hydrophobic materials showing the above mentioned characteristics have applications as viscosity modifiers in oils, we think hydrophilic gels have broader impact and wide application range. We believe
that by developing water soluble polymers via surface initiated polymerization route will enable us to synthesize high viscosity gels formed via the mechanism as explained above. These water soluble nanocomposite materials would have applications as thickening materials in hydraulic fracking, and viscosity modifiers at very low polymer loading compared to present alternative materials.

**Experimental section**

**Synthesis procedure**

The nanocomposite material used to form NC gels was synthesized via surface initiated ring opening metathesis polymerization (SI-ROMP) of poly(ethyldene norbornene)[P(Enbn)], as the inner block and poly(cyclopentene)[P(Cpe)], as the outer block. The synthesis started by modifying the surface of MMT clay by using an in-house synthesized alkyl ammonium surfactant to make the clay compatible with the polymer. MMT clay (Na\(^+\)-Cloisite) when mixed with alkyl ammonium surfactant, the surfactant ion exchanges onto the clay surface thus modifying its hydrophilic nature. The organo-modified clay or functionalized clay (fMMT) was initiated with Grubbs’ 1st generation catalyst to start the polymerization process. Sequential addition of ethyldene norbornene and cyclopentene monomers to this mixture synthesized the desired nanocomposite block copolymer. The synthesis procedure used for poly(ethyldene norbornene-\(b\)-poly(cyclopentene) block copolymer nanocomposite is similar to one described in detail in our previous publication.\(^{180}\) The targeted SI-BCP materials for forming NC gels had clay loading of 3 wt%, block copolymer molecular weight (MW) of 119 kDa, and block composition of 0.63 for P(Enbn) and 0.37 for P(Cpe). The synthesized nanocomposite block copolymer material was dissolved in tetrahydrofuran (THF) at different polymer weight percentages with different salt loadings as shown in table 7.1.

**Characterization methods**

**Transmission electron microscopy (TEM)** NC gel sample was cut by using a Leica cryo ultramicrotome at -140 \(^\circ\)C into 60 nm thin sections. After obtaining thin sections, they were placed on a carbon grid and left inside a fume hood for at least 30 min for the THF solvent to evaporate and then loaded into TEM. Imaging was done using a JEOL 2100 STEM microscope operating at 200 keV at a
Table 7.1. NC gels derived by mixing different amounts of NC (w/v %) in 35 mL of THF along with different sodium chloride salt loading (wt%). The salt loading is calculated based on the NC loading.

<table>
<thead>
<tr>
<th>W/V %</th>
<th>Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75</td>
<td>15</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>1</td>
<td>15</td>
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</tr>
<tr>
<td>1.5</td>
<td>15</td>
</tr>
</tbody>
</table>

resolution of 200 nm. Images were taken from different parts of the section to ensure homogeneity and images were analyzed in a Gatan Digital micrograph suite.

**Rheological Study**  Rheological properties of NC gels were measured by using a TA ARES® G2 strain-controlled rheometer with 8 mm SS parallel plates configuration for obtaining the temperature ramp measurements. Temperature ramp test was carried out from -100 to -20 °C at a rate of 3 °C/min heating rate and ω = 1 rad/s in nitrogen atmosphere. For obtaining viscosity data, APS (Advanced Peltier System) attachment on TA ARES® G2 instrument with a cup and recessed bob geometry was used. The temperature control on the APS was achieved by using a water cooled chiller. The geometry was equipped with a solvent trap cover keeping the solvent evaporation minimal. Nearly 7 ml of NC gel was used in the geometry at room temperature and shear rate was varied from 0.01 1/s to 10 1/s.

**Results and Discussion**

**Materials synthesis**

The NC gels were formed with SI-BCP material with sodium chloride salt and THF. Experiments with mixing nanocomposite material and THF solvent without salt did not result in any gel formation. Diblock copolymers synthesized without MMT clay but with the surfactant (organo-modifier used to functionalize clay) also did not result in gel formation. These observations helped us in hypothesizing the mechanism for gel formation. When a nanocomposite is dissolved in THF solvent, polymer chains get solvated and dissolve in the solvent but the clay can not dissolve in the solvent. However, when a salt (e.g., NaCl, MgCl₂, or LiCl) is added to this solution, the cations (from ionic salt) will exchange
onto the surface of clay replacing the polymer chain which were attached to clay surface via an alkyl ammonium surfactant. Thus, the polymeric chains are much more liberated and free to move in the THF solution. We speculate that for a certain block composition and MW of the diblock in a nanocomposite, the presence of clay, addition of ionic salt, and the polymer chain with alkyl ammonium surfactant head all are held together via interaction forces resulting in a high viscosity nanocomposite gel. A pictorial representation of this mechanism is presented in the figure 7.1. This representation is just a presumption, we are awaiting more information to ascertain the exact mechanism. In order to further understand the effects of polymer and salt loading on NC gel formation, we have prepared few NC gel samples by varying solids loading and conducted rheological measurements as reported in the results section below.

Figure 7.1. A presumptive cartoon showing the mechanism of gel formation. The MMT clay (thin gray rectangles) are exchanged with cations (in this case sodium ions) which are ionically bonded to anions (in this case chloride ions) which in turn are attracted to the cationic alkyl ammonium head of the diblock copolymer (Poly(ethylidene norbornene)-b-poly(cyclopentene)). Please note that the block lengths are not to scale.
Characterization

We used morphological and rheological characterization techniques to understand the mechanism leading to the formation of NC gels and ascertain the gel properties. It was observed that the gel was very cohesive in nature and maintains physical stability until upon acted by an external force.

**Transmission Electron Microscope (TEM) imaging**

TEM micrograph 7.2 shows the NC gel structure after all the solvent has evaporated. It was observed that the material did not degrade after exposing it to TEM electron beam for an hour. The nanocomposite material seems to have created an inter-penetrating network in the solvent and retained its structure after solvent evaporation.

**Rheology measurement**

Figure 7.3, a temperature scan of NC gel shows that the viscosity of the gel remains constant until -50 °C. Given that the THF freezing point is at -108 °C, we do not expect the gel to have the structural stability shown in the plot though the material being measured contains nearly 90 % of THF.
Figure 7.3. Temperature ramp measurement of nanocomposite gel formed with 1 wt% polymer and 15 wt% salt (polymer weight basis) showing viscosity (dotted line) and stress (solid line)

This suggests that the nanocomposite material has absorbed all of the THF and essentially trapped it from evaporating. Increasing the temperature above -50 °C causes very big increase in the viscosity, which takes the value to nearly 400 Pa.s at -30 °C. This abnormal increase could have been the result of tetrahydrofuran evaporating from the sample. Though the boiling point of THF is above ambient temperature, we believe that the measurement is exaggerated because of the type of temperature control being used in the instrument, which is a forced convection oven.

Next set of graphs show the effects of changing the polymer and salt loading (table 7.1) on viscosity of NC gels. Figure 7.4 shows that NC gel formed with 0.75 wt% of gel is substantially less viscous compared to 1 wt% and 1.5 wt%. However, the later two does not show any viscosity differences. In a conventional crosslinked gel, increasing the solids loading usually leads to increased viscosity which is contrary in NC gels. This observation is in contrast when compared to a typical crosslinked gel wherein increasing the solids loading typically results in increased viscosity profile. We believe that in NC gels this is not happening because the mechanism of formation of gel is more dependent on the amount of ionic salt present in the gel corresponding to the amount of polymer present. The stress curves for all solid loadings show a finite amount of stress even at low shear rates. This is especially desired in oil field applications where nanocomposite polymer gels are used.
Figure 7.5 shows the viscosity profile of 1 wt% and 1.5 wt% polymer gels with two different salt concentrations. For NC gel with 1 wt% solids loading (black colored plots), increasing the salt concentration from 5 wt% to 15 wt% increases the viscosity profile by at least 2 times. The NC gel formed with 1.5 wt% also exhibits similar increase in viscosity profiles between salt concentrations 5 wt% and 15 wt%. Interestingly, viscosity profile for 5 wt% salt loading and 1 wt% polymer loading has lower viscosity profile compared to that of same salt loading for 1.5 wt% polymer loading. This is in contrast to what has been observed for both polymer loadings at 15 wt% salt loading. This suggests that, when certain polymer loading NC gel is prepared with certain salt concentration, increasing the polymer loading may need comparable increase in salt concentration to form a gel with similar viscosity profile. Based on this, increasing the polymer concentration may have higher effect on viscosity compared to salt concentration. However, increasing the salt concentration to 15 wt% for 1 wt% polymer substantially increases the viscosity profile, comparable to 1.5 wt% polymer loading with same salt concentration. More experiments on NC gels with different polymer and salt loading need to be conducted in order understand the trends; this will be subject to future work.
Figure 7.5. Cup and bob measurement of nanocomposite gel formed with 1 wt% (black) and 1.5 wt% (gray) of polymer and 5 wt%(dotted) and 15 wt% salt (dashed) (polymer weight basis) showing viscosity profile

Conclusions

Block copolymer nanocomposites of Poly(ethylened norbornene-b-cyclopentene) synthesized via surface initiated ROMP when dissolved in tetrahydrofuran solvent along with an ionic salt (for example NaCl) results in formation of very high viscosity gels. NC gels formed with polymer loading as low as 0.75 wt% and salt loading as low as 5 wt% (polymer weight basis) showed measured viscosities in the range of 100 Pa.s at room temperature. We have observed that there is a minimum 5 wt% of salt requirement for the NC gel to form and absence of ionic salt or MMT clay did not result in any gel. TEM micrographs have shown that nanocomposite forms a three dimensional network in the gel. More discussion on the effects of polymer and salt loading and mechanism of gel formation will be subject of subsequent research articles.

Bibliography


CHAPTER 8. FUTURE WORK

The current research work focused on learning the effects of (Montmorillonite) MMT clay addition in a nanocomposite. It was hypothesized that the addition of nano clay to polymer matrix will result in synergistic effects and result in materials with enhanced thermal and mechanical properties. We have observed that for a diblock copolymer system comprising of poly(norbornene-b-cyclopentene) addition of clay has pronounced effects on thermal and mechanical properties. However, for a diblock copolymer system comprising of poly(ethyl norbornene-b-ethylene) addition of clay didn’t result in increase of thermal properties although there was increase in mechanical properties at high temperatures. Moreover, clay addition showed negative effect by decreasing the glass transition temperature of poly(ethyl norbornene). We did not ascertain the mechanism as to why a clay grafted poly(ethyl norbornene-b-ethylene) material results in subdued thermal properties. One of the reasons discussed in this thesis was the effect of crystallization of poly(ethylene) block in the diblock copolymer and the presence of clay. We believe that ascertaining the reason behind this anomaly could lead to an in depth understanding of the effects of filler addition in nanocomposites involving crystalline polymers. This could be accomplished by synthesizing clay grafted poly(ethyl norbornene-b-ethylene) nanocomposite materials with different levels of poly(ethylene) crystallinity and studying the effects by thermal and mechanical characterization. These experiments may shed light on how the glass transition temperature of the soft block is being affected as the crystalline nature of the poly(ethylene) block changes. Based on morphology studies reported in this work evident from the TEM micrographs presented in chapters 4 and 5, we believe that MMT addition to polymer matrix via surface initiated polymerization technique has accomplished a brilliant job in exfoliating the clay into individual platelets although we observed some degree of intercalation in these nanocomposites. Though we have not carried out any barrier property measurements on these exfoliated nanocomposites, our morphological study suggests that these materials would be ideal candidates in restricting the motion of air or moisture. If it
is successful in achieving superior barrier properties compared to non-clay analogs, they can find very 
good applications in packaging industry. The properties of poly(ethyl norbornene) being rubbery and 
poly(ethylene) being semi-crystalline forms a perfect combination providing toughness and elasticity. 
One of the interesting properties that were discovered towards the end of this research work is that 
the clay grafted poly(ethylidene norbornene-b-cyclopentene) when dissolved in tetrahydrofuran solvent 
along with an ionic salt (like lithium chloride or sodium chloride) results in formation of really high 
viscosity gels at very low solids loading. It was observed that this happens only for nanocomposite 
material with certain block volume fractions and certain MWs. Though we were not able to ascertain 
about the mechanism leading to the formation of high viscosity gels, we believe the salt, clay and poly-
mer may have been forming a three dimensional network leading to structural stability. Preliminary 
rheological results suggest that these gels are shear-thinning and can be formed with solids loading as 
small as 0.75 W/V\% and salt loading as low as 5 wt\% (polymer weight basis). Future work can be 
conducted to ascertain the mechanism of gel formation. These nanocomposite gels if synthesized in 
large scale can have interesting applications in oil exploration field as viscosity modifiers.

One of the other works carried out in this thesis work was evaluating the suitability of mesoporous 
membranes fabricated by using poly(styrene-b-isoprene-b-dimethyl siloxane) (SID) triblock copoly-
mer material for various in-situ separations. We successfully synthesized SID materials, fabricated 
porous membranes and tested them for flow through. It was observed that these membranes were able 
to carry out size based separations. Although we have not functionalized the poly(isoprene) block, liter-
ature suggests that unsaturation of the isoprene block can be used to functionalize it to aid in facilitated 
transport which could speed up the separation process. We believe this material holds properties needed 
to be a potential candidate for broad separations applications in bioseparations industry. It is easy to 
make these membrane materials suitable to different size based and affinity based bioseparations by just 
changing the pore size range and by changing the functionalization of the isoprene block. Large scale 
synthesis of the triblock copolymer material needed to fabricate these membranes could be practical as 
the anionic polymerization route for these materials is being practiced by the industry.
Introduction

Block copolymer (BCP) self-assembly has intrigued polymer scientists for nearly five decades with a variety of fascinating morphologies and tunable material properties. Most polymer pairs are immiscible and thus tend to phase separate, but the covalent linkage between different monomer sequences in BCPs limits this segregation causing microphase separation into well-defined ordered structures.\textsuperscript{219} Linear diblock BCPs are most frequently studied due to the relative simplicity of their phase diagrams; the complexity increases with multi-blocks, star blocks and branched arm BCPs.\textsuperscript{187,195,216} Hierarchical control of complex block polymer (BCP) morphology has been progressively advancing for the past decade. Recently work has focused on confinement effects of BCP assemblies in lithographic patterned channels,\textsuperscript{191,211,212,214,215} oil-in-water emulsions,\textsuperscript{201,220} and surface grafted nanoparticles.\textsuperscript{198,207,213} Each of these phenomena can be viewed independently as specialized applications for self-assembled BCPs or they can be viewed collectively as the tools for hierarchically engineered materials.\textsuperscript{204} Of primary concern to this work is the application of BCP self-assembly to nanoparticle alignment and study of BCP phase diagrams, resultant morphological and mechanical behaviors. Study of property enhancement by addition of fillers like MMT began in the late 1980s when researchers at Toyota discovered that addition of as little as 5 wt % of filler to bulk polymer led to incredible increase in mechanical and thermal properties.\textsuperscript{205}
We have introduced BCP self-assembly to layered silicate nanocomposites (NCs) in a previous communication. NCs are polymers with small amount of filler with at least one dimension of filler in nanoscale. NCs formed with dispersed nano-clay (platelet like montmorillonite clay, MMT) and homopolymer have been very widely studied because of their improved mechanical, thermal and barrier properties compared to non-composite analogs. Factors like extent of dispersion, morphology and orientation of dispersed fillers, and polymer-filler interactions dominate in determining the degree of elevation of material properties. A substantial body of research has focused on methods to increase the dispersion of MMT in polymer matrix, namely solution intercalation, high shear melt intercalation, in situ polymerization, and graft-from surface-initiated polymerization techniques. The latter technique is of particular interest to us in that it affords a mechanism to achieve excellent particle dispersion (exfoliation), maximizing the particle/polymer interfacial volume, while incorporating secondary structure through BCP self-assembly.

Bockstaller et al have noted that BCP NC structure formations have applications beyond just mechanical property enhancements. They also state that composites formed with nanoclay have received far less attention from researchers, particularly in regards to the study of ordered structures and relation of morphology to property enhancements. Indeed, the exploration of MBB phase diagrams may yield exciting structures that enable new application driven by unanticipated emergent properties. Explaining the importance of nanocomposites, Vaia et al report that unlike in classic composites, inherent properties of the polymer matrix are not compromised in nanocomposites. They also explain how the interfacial region between filler and polymer matrix is realized in nanocomposites vs classic composites. This further reckons on the point that study of the various morphologies, and knowing the microscopic interactions between polymer and filler can lead to deeper understanding of NCs to help engineer novel materials. Ha et al have studied ordered NCs synthesized by mixing MMT grafted with PS with varying molecular weights and SBS polymer. They reported evidence that the orientation and exfoliation of clay effects the global orientation of the BCP and hence greatly influences the mechanical behavior of the composite. For a particular lamellar domain, they reported that in-plane modulus decreased compared to that of neat BCP because of misorientation of BCP and clay layers. Mitchell et al. have studied rheological behavior of various MBBs to elucidate the relation of clay loading and structure formations. They observed that viscoelastic characteristics of MBBs show how the mesoscale
structures control the dynamics of the systems. Silva, Hasegawa and Groenewold et al. have tried to study the self-assembly of NCs by various characterization methods and they observed that inclusion of MMT clay has affected development of different microstructures in a different way. Length scales of the filler have to be sufficiently larger compared to the length scales of the microstructure being developed otherwise filler would have negative impact on the properties of NCs.

The inclusion of nanoparticles into BCP domains by grafted homopolymers has become commonplace in nanotechnology research however there are relatively few examples of BCP grafted directly to the nanoparticle surface. There is a paucity of literature that presents a detailed discussion about phase diagrams of MBBs and thus our attempt to synthesize NCs in different microstructure regions and study their mechanical properties. Li et al. produced silica particles with a difunctional initiator-terminated monolayer to produce spherical brushes. These “hairy” nanoparticles were produced by a combination of atom transfer radical polymerization (ATRP) and nitroxide mediated radical polymerization (NMRP). The resulting environmentally responsive nanoparticles formed colloidal suspensions in solvents such as chloroform and methanol. Similar to Li et al., the present research utilizes surface initiated ATRP, but instead of T-junction initiators we use end-tethered BCPs. The resulting MMT block copolymer brushes (MBBs) exhibit remarkable morphology phenomena not seen with bulk BCPs. In this article we systematically investigate two model systems of MBBs: MMT-\textit{graft}-poly(styrene-\textit{block}-n-butyl acrylate) (PS/PnBA) and MMT-\textit{graft}-poly(styrene-\textit{block}-tert-butyl acrylate) (PS/PtBA). By evaluating a total of 33 materials with varied block sequence, brush molecular weight, and composition, we are able to construct a thorough description of the morphological, rheological, and mechanical behavior of MBBs.

**Experimental Section**

**ATRP-initiator functionalized montmorillonite.** Montmorillonite clay (MMT) was generously supplied by Southern Clay Products Inc. Based on the ion exchange capacity, 92 mequiv/100g and measurements of the specific surface area, MMT clay contains $\approx 1 \text{site/nm}^2$. Functionalized MMT clay (fMMT) was prepared via ion exchange of pristine MMT clay with an in-house synthesized bromine terminated alkylammonium surfactant (11’-(N,N,N-trimethylammonium bromide)-undecyl-2-bromo-
2-methyl propionate, 11-MUBMP), prepared as described previously. Typically, the fMMT clay was synthesized by mixing required ratio of MMT and surfactant in a suitable solvent and then drying in oven.

Briefly, 2-bromoisobutyryl bromide (98%), benzyl bromide, copper(II) bromide (Cu(II)Br), N,N,-N',N'-pentamethyldiethylenetriamine (PMDETA), ethyl-2-bromopropionate, and Dowex®Marathon@MSC hydrogen-form exchange resin (20-50 mesh) were purchased from the Aldrich Chemical Co. and used as received. Tert-butyl acrylate (98%, Aldrich), n-butyl acrylate (98%, Aldrich), and styrene (99%, Fisher Scientific Co.) were purchased from the Aldrich Chemical Co. and purified by passing over basic alumina and degassing with argon prior to use. Copper powder (99.7%) was purchased from the Aldrich Chemical Co. and heated to 200 °C under 5% H2/nitrogen gas for 6 hours prior to use. 11-bromo-1-undecanol (98%) was purchased from the Aldrich Chemical Co. and recrystallized from 75 vol % methanol / 25 vol % deionized water prior to use. Methanol, isopropanol, acetone, toluene, pyridine (99%), and trimethylamine (33 wt % in ethanol) were purchased from the Fisher Scientific Co. and used without further purification. Montmorillonite clay (MMT) was generously supplied by Southern Clay Products Inc. (92 meq per 100 g).

The production of 11-MUBMP is a simple two step synthesis combining 11-bromo-1-undecanol with 2-bromoisobutyryl bromide (2,2-dimethyl acetyl chloride) and subsequently adding trimethyl amine to produce a charged alkyl chain with a terminal halide. The surfactants are then used to displace the native Na+ cations through ion exchange. Initiator and MMT clay were continuously stirred in 50 mL of acetone in an erlenmeyer flask at a mass ratio of 2:2.5 respectively for 96 hours. Functionalized MMT (fMMT) was then filtered, washed alternately with 25 mL water and acetone, then dried in vacuum at 80 °C for 24 h, and ground into a fine powder, and then stored under nitrogen. Complete ion exchange was confirmed via XRD and TGA.

Copper(I) Bromide Purification. Copper(I) bromide (99.999%) was purchased from the Aldrich Chemical Co. and purified with glacial acetic acid, rinsed with absolute alcohol and ethyl ether, dried under vacuum, and stored under nitrogen prior to use. While the cleaning of copper(I) bromide with glacial acetic acid works well, it requires a costly pure starting material. In an alternate and more economical preparation, 10g copper(I) bromide (98%) was stirred for 24 hours with 50mL sulfuric acid (95-98%) then rinsed extensively with absolute alcohol and ethyl ether on a filter frit. It was then
transferred to a preheated vacuum oven (80 °C), dried for 20-25 minutes and moved into the glovebox for storage.

**MMT grafted homopolymer synthesis.** The surface-initiated ATRP (SI-ATRP) of homopolymers from MMT can be summarized as the addition of fMMT, styrene (S), CuIBr, Cu(II)Br$_2$, and PMDETA to a 50 mL round bottom flask equipped with a 24/40 rubber septum and magnetic stir-bar under an $N_2$ atmosphere. Chemicals were added in molar ratios relative to the amount of initiator used; 1 : 1000 : 1 : 0.06 : 1.06 respectively. A sonication probe was placed within one inch of the exterior of the reaction vessel for the duration of the experiment to maximize exfoliation without compromising the closed atmosphere. $t$-Butyl acrylate (tB) and $n$-butyl acrylate (nB) were also synthesized as homopolymers from the fMMT surface at 75 °C and 65 °C respectively. nB samples initially showed poor polydispersity (PDI), so they were allowed to sonicate for 6 h at 30 °C before reacting at 65 °C. To test for untethered polymer, samples were subjected to ultrafiltration using a 100 kDa cutoff membrane (Millipore), evaporation of the supernatant, followed by measurement of the mass of the residue. In every case the residual mass was < 0.1% of that of the original sample.

**Diblock synthesis from MMT homopolymer brushes.** The subsequent polymerization of nB from MMT-polystyrene brushes was conducted by the addition of dry PS macroinitiators, nB, Cu(I)Br, Cu(0), and PMDETA to a 100 mL round bottom flask equipped with a 24/40 rubber septum and magnetic stir-bar. Chemicals were added in molar ratios relative to amount of macroinitiator used; 1: 4000: 2: 0.1: 2.1 respectively. The reaction flask was placed in an oil bath at 65 °C with continuous stirring, and reaction time was varied to produce blocks of differing lengths. In the reverse block sequence where PS was synthesized from nB macroinitiators, a second equivalent amount of Cu(I)Br, Cu0, and PMDETA were cannula transferred into the reaction vessel after 12 h using additional styrene monomer as a solvent. MBBs are named based on MMT content (M), core block, corona block, and then number-average molecular weight ($M_n$) in kDa of each block respectively. Thus MnBS-60-63 (from Figure A.5) is a MMT grafted (60-b-63 kDa) poly($n$-butyl acrylate-b-styrene) brush. Bulk BCPs of identical $M_n$ and composition were produced by reverse ion exchange of polymer from the clay surfaces via basic alumina flash chromatography.

**Experimental Techniques.** MBBs were annealed at 150 °C in vacuo for over 96 hours prior to being steady shear processed at 0.5 s$^{-1}$ and 160 °C for 20 minutes on a TA Instruments ARES-LS1
Table A.1. Results of tB containing MBB polymerizations.

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<tr>
<th>Name-M_{n_1}-M_{n_2}</th>
<th>N</th>
<th>f_S</th>
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<th>Wt. Clay</th>
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<td>1.5%</td>
</tr>
<tr>
<td>MtBS-59-145</td>
<td>204.3</td>
<td>0.71</td>
<td>1.39</td>
<td>0.9%</td>
</tr>
<tr>
<td>MtBS-60-172</td>
<td>231.7</td>
<td>0.74</td>
<td>1.45</td>
<td>0.8%</td>
</tr>
</tbody>
</table>

strain controlled rheometer in the parallel plate geometry under N₂. Ultrathin (≈100 nm) sections for electron microscopy were obtained at -100 °C using a Leica Ultramicrotome Ultracut 125UCT with a Leica EM FCS cryo-stage. RuO₄-stained sections were examined on a Tecnai G² F20 scanning / transmission electron microscope at a high tension voltage of 200 kV.

Results and Discussion

A library of samples containing styrene and either n- or tert-butyl acrylate MBBs has been synthesized to span a wide region of composition-space for both tB (nB) core and tB (nB) corona MBBs. A complete list of examined tB-MBBs and nB-MBBs can be found in Tables A.1 and A.2 respectively. A great many more nB-MBBs were prepared than tB-MBBs owing to an increase in MBB synthesis expertise and the need to study MBB mechanical properties independent of tert-butyl cleavage. A detailed discussion on the molecular assembly leading to MBBs’ morphology has previously been published by this group; for this work it is sufficient to know that MBBs can be viewed as large pseudo-particles where intraparticle versus interparticle assembly is a critical parameter.¹⁸⁹

Looking first at the tB-MBBs, there appears to be five distinct morphologies: worm-like cylinders (W), interpenetrating networks (IPN), oblate spheres (OS), isolated discoids (ID), and toroids (T). Figure A.1 displays a “phase portrait” of all the tB-MBBs examined with representative micrographs to demonstrate each phase; it is important to note that the phase lines are only approximations intended
Table A.2. Results of nB containing MBB polymerizations.

<table>
<thead>
<tr>
<th>Name-M_{n_{1}}-M_{n_{2}}</th>
<th>N</th>
<th>f_{S}</th>
<th>PDI</th>
<th>Wt. Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSnB-68-187</td>
<td>210.7</td>
<td>0.27</td>
<td>1.21</td>
<td>0.7%</td>
</tr>
<tr>
<td>MSnB-68-151</td>
<td>183.0</td>
<td>0.31</td>
<td>1.19</td>
<td>0.8%</td>
</tr>
<tr>
<td>MSnB-62-85</td>
<td>126.4</td>
<td>0.42</td>
<td>1.10</td>
<td>1.2%</td>
</tr>
<tr>
<td>MSnB-68-84</td>
<td>130.5</td>
<td>0.45</td>
<td>1.35</td>
<td>1.1%</td>
</tr>
<tr>
<td>MSnB-62-76</td>
<td>119.9</td>
<td>0.45</td>
<td>1.10</td>
<td>1.2%</td>
</tr>
<tr>
<td>MSnB-68-78</td>
<td>125.8</td>
<td>0.46</td>
<td>1.43</td>
<td>1.2%</td>
</tr>
<tr>
<td>MSnB-66-44</td>
<td>98.1</td>
<td>0.60</td>
<td>1.25</td>
<td>1.6%</td>
</tr>
<tr>
<td>MSnB-66-36</td>
<td>91.4</td>
<td>0.65</td>
<td>1.20</td>
<td>1.7%</td>
</tr>
<tr>
<td>MSnB-66-32</td>
<td>88.5</td>
<td>0.67</td>
<td>1.15</td>
<td>1.8%</td>
</tr>
<tr>
<td>MSnB-66-30</td>
<td>86.6</td>
<td>0.69</td>
<td>1.19</td>
<td>1.8%</td>
</tr>
<tr>
<td>MSnB-67-27</td>
<td>84.6</td>
<td>0.72</td>
<td>1.20</td>
<td>1.9%</td>
</tr>
<tr>
<td>MSnB-59-22</td>
<td>73.9</td>
<td>0.73</td>
<td>1.19</td>
<td>2.1%</td>
</tr>
<tr>
<td>MSnB-68-22</td>
<td>82.2</td>
<td>0.75</td>
<td>1.23</td>
<td>1.9%</td>
</tr>
<tr>
<td>MSnB-80-26</td>
<td>97.6</td>
<td>0.75</td>
<td>1.16</td>
<td>1.6%</td>
</tr>
<tr>
<td>MSnB-80-14</td>
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<td>0.85</td>
<td>1.16</td>
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</tr>
<tr>
<td>MnBS-60-35</td>
<td>80.4</td>
<td>0.36</td>
<td>1.18</td>
<td>1.8%</td>
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<tr>
<td>MnBS-60-40</td>
<td>85.9</td>
<td>0.40</td>
<td>1.16</td>
<td>1.7%</td>
</tr>
<tr>
<td>MnBS-60-63</td>
<td>107.2</td>
<td>0.51</td>
<td>1.14</td>
<td>1.4%</td>
</tr>
<tr>
<td>MnBS-60-66</td>
<td>110.1</td>
<td>0.52</td>
<td>1.16</td>
<td>1.4%</td>
</tr>
<tr>
<td>MnBS-40-76</td>
<td>104.6</td>
<td>0.66</td>
<td>1.15</td>
<td>1.5%</td>
</tr>
<tr>
<td>MnBS-41-98</td>
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<td>0.71</td>
<td>1.17</td>
<td>1.3%</td>
</tr>
<tr>
<td>MnBS-41-103</td>
<td>130.6</td>
<td>0.72</td>
<td>1.15</td>
<td>1.2%</td>
</tr>
<tr>
<td>MnBS-41-144</td>
<td>169.8</td>
<td>0.78</td>
<td>1.23</td>
<td>1.0%</td>
</tr>
</tbody>
</table>

To guide the eye. The complex morphologies seen in this figure appear to follow more of a continuum rather than the rigid boundaries observed in traditional bulk BCPs morphologies. As can be observed in the series of micrographs A.1g → A.1h → A.1f → A.1c, a barely ordered ID morphology (A.1g) transitions to a more regular ID pattern (A.1h) that fills the entire void space. Then there is a more dramatic transition to OS (A.1f), but there still remains similarities to the previous ID morphology. Finally, a fully developed OS morphology forms (A.1c) that is clearly distinct from the ID morphology. This series of micrograph also demonstrates that the order of synthesis (tB-PS versus PS-tB) has little to no impact on the MBB morphology formed. Sequence independence is corroborated by the nB-MBBs (Figure A.2) where the lamellar (A.2c–d, A.2f–g) and disordered lamellar (A.2b, A.2e) phases are represented by both interior and exterior nB-MBBs.
It was hypothesized that the large BCP polydispersities (PDI > 1.2) observed in tB-MBBs could be contributing to the indistinct morphologies developed, therefore a literature survey was conducted to evaluate this possibility. In a very methodical study of PDI effects in BCP morphology formation, Lynd and Hillmyer investigated the selective increase of PDI of the DL-lactide block of a poly(ethylene-alt-propylene)-b-poly(DL-lactide) diblock copolymer. Lynd and Hillmyer observed a linear increase in lamellar domain spacing with increasing PDI resulting from large chains filling the void space between domains more easily, thus eliminating the need for unfavorable stretching. When non-lamellar samples were examined the asymmetric increase in PDI of the minority block induced phase transitions towards increased mean interfacial curvature (i.e., lamellar became gyroid etc.), conversely increasing PDI in the majority block decreased mean interfacial curvature. The change in interfacial curvature was attributed to the movement of the interface towards the block that previously had the larger stretching penalty. Thus it seems unlikely that PDI had any significant impact on the indistinct morphologies observed in tB-MBBs but it may contribute to the large domains spacings observed.

The larger nBA-MBB sample set displays a great deal more symmetry than the tB-MMBs and follows a progression more reminiscent of traditional BCP morphologies: perforated lamellae (PL), disordered lamellae ($L_D$), and lamellae ($L$). Figure A.2 is an nB-MBB phase diagram with select micrographs to illustrate each phase; again, phase lines are only approximations intended to guide the eye. Unlike tB-MBBs where complex microstructures were observed, these materials seem to resist the formation of curved interfaces and only lamellae-like structures appear. Given the underlying planar nature of the supporting clay particles, this absence of curvature implies that the forces generated by the PS/PnBA interfaces are insufficient to overcome the stiffness of the clay. This is consistent with a weaker PS/PnBA interaction strength compared to PS/PtBA. Again, the phases we observe appear to be independent of block sequence, which suggests that conformational asymmetry effects are not responsible for a shift of the lamellar region towards one particular side of the composition space. Of particular interest is Figure A.2c which shows a remarkably low defect density. We discuss more about this particular sample in detail below. Samples that fall outside of the approximate phase boundaries typically demonstrated incomplete phase separation as shown in Figure A.2f. This inability to fully phase separate is attributed to the constraint imposed on mean interfacial curvature by the large flat clay platelets.
Figure A.1. Representative TEM micrographs of different observed morphologies in PS/PtBA MBBs: worm-like cylinders (W), interpenetrating networks (IPN), oblate spheres (OS), isolated discoids (ID), and toroid (T). Phase lines are approximations intended to guide the eye. Triangles (△) refer to PS core MBBs and squares (□) refer to PtBA core MBBs. Scale bar for (e) is 100nm otherwise scale bar is 50nm.
Figure A.2. Representative TEM micrographs of different observed morphologies in PS/PnBA MBBs: perforated lamellae (PL), disordered lamellae (LD), and lamellae (L). Phase lines are approximations intended to guide the eye. Diamonds (⋄) refer to PS core MBBs and circles (○) refer to PnBA core MBBs. Scale bar is 50nm.
Understanding MBB phase behavior is important for designing materials with desirable anisotropic properties, equally important is the melt state behavior as measured by rheology. Figure A.3 presents four time-temperature superposition (TTS) master curves for both grafted and liberated homopolymers/BCPs. The MMT grafted samples are the shaded in symbols while the bulk BCP samples are the open symbols. Terminal relaxation dynamics of BCPs has been used in the past as a facile method for screening BCP phase behavior. However, before extracting any inferences about MBB structure from rheological data it is important to establish baseline behavior of disordered materials. The easiest way to ensure a disordered material is to examine free homopolymer as shown in Figure A.3a, its terminal behavior, $G' \propto \omega^{-1.82}$, is in close agreement with the liquid-like behavior of previously reported disordered homopolymers ($G' \propto \omega^2$). The MMT grafted homopolymer on the other hand displays a terminal regime that reflects the influence of chain tethering, $G' \propto \omega^{0.56}$. Figure A.3b–d are comparisons of MBBs to their bulk BCP counterparts. The behavior of grafted and free samples of the same composition are remarkably similar with nearly identical terminal behavior. Looking at the series based on composition it becomes apparent that the MBB sample shifts from having a higher modulus than the bulk (A.3b), to nearly equal (A.3c), to significantly lower (A.3d). Given how close MSnB-66-36 and MSnB-66-30 are in total molecular weight and composition it is evident that an entirely different mechanism is responsible for this shift in modulus intensity. Based on the rheology results of additional samples (including nB interior MBBs), it appears that morphology is the governing factor for relative intensities of MBB modulus versus bulk BCP modulus. In the case of the lamellar morphology MBBs and bulk BCPs appear to have nearly identical moduli (A.3c), while lower $f_S$ morphologies result in superior MBB moduli (A.3b), and higher $f_S$ morphologies result in superior bulk BCP moduli (A.3d). MBB samples (3c) and (3d) may particularly be interesting in processing perspective that addition of MMT does not significantly change the rheological characteristics. This is also observed by our work in synthesizing MBBs via ROMP (Ring Opening Metathesis polymerization) mechanism but an entirely different system. Although these results show promise for designing a stronger or tougher MBB, more research is needed before any conclusive statements can be made.

In addition to the melt state rheological behavior of MBBs we have also studied the solid state tensile behavior. Table A.3 displays a comparison of MBB ultimate stress, $\sigma$, and Young’s modulus, $E$, for MBBs and their corresponding bulk BCPs. Three factors have been observed to noticeably impact $\sigma$.
Figure A.3. Time-temperature superposition master curves for both grafted and liberated (a) homopolymer and (b–d) block copolymers. MMT grafted samples are the shaded in symbols and bulk BCP samples are the open symbols, where diamonds (⋄) represent $G'$ and circles (◦) represent $G''$. The sample $M_n$'s and styrene fraction are as follows (a) MS-35; (b) MSnB-68-78, $f = 0.46$; (c) MSnB-66-36, $f = 0.65$; (d) MSnB-66-30, $f = 0.69$. 

\[ \text{Log Modulus (Pa)} \]
Table A.3. MBB/bulk BCP tensile testing comparison

<table>
<thead>
<tr>
<th>Name</th>
<th>$M_{n1}$</th>
<th>$M_{n2}$</th>
<th>$f_S$</th>
<th>$\sigma_{MBB}$</th>
<th>$\sigma_{bulk}$</th>
<th>$E_{MBB}$</th>
<th>$E_{bulk}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSnB-67-84</td>
<td>0.45</td>
<td>3.2</td>
<td>2.3</td>
<td>109</td>
<td>102</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MSnB-62-77</td>
<td>0.45</td>
<td>3.7</td>
<td>1.1</td>
<td>104</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MSnB-66-44</td>
<td>0.60</td>
<td>4.6</td>
<td>—</td>
<td>131</td>
<td>—</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MSnB-66-32</td>
<td>0.67</td>
<td>—</td>
<td>10.7</td>
<td>—</td>
<td>91</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MSnB-66-26</td>
<td>0.72</td>
<td>10.8</td>
<td>16.1</td>
<td>514</td>
<td>376</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MSnB-59-22</td>
<td>0.73</td>
<td>24.9</td>
<td>20.0</td>
<td>843</td>
<td>829</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnBS-60-40</td>
<td>0.40</td>
<td>—</td>
<td>1.9</td>
<td>—</td>
<td>83</td>
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<td></td>
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<tr>
<td>MnBS-60-65</td>
<td>0.52</td>
<td>1.7</td>
<td>5.1</td>
<td>187</td>
<td>280</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnBS-41-98</td>
<td>0.71</td>
<td>12.0</td>
<td>17.1</td>
<td>626</td>
<td>692</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnBS-41-144</td>
<td>0.78</td>
<td>15.4</td>
<td>16.3</td>
<td>854</td>
<td>788</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

and $E$: MBB core block chemistry, styrene content, and morphology. We know that the amount of MMT loading also contributes to mechanical behavior, but that is not the focus part of this particular work. MBBs with an $S$ core demonstrate moderate elevations in $\sigma$ and $E$ relative to bulk while the $nB$ core MBBs demonstrate moderate reductions. Also when comparing $S$ core MBBs versus $nB$ core MBBs, where MSnB-59-22 clearly has superior tensile properties relative to MnBS-41-144 even though its $S$ block is almost 100kDa smaller, the presence of $S$ block attached to MMT clay becomes predominant. After MBB core block chemistry, the fraction $S$, $f_S$, in MBBs and bulk BCPs is another principle factor contributing to overall $\sigma$ and $E$, however it is surprising that total $M_{ns}$ has a much larger impact than $f_S$.

Location on the phase diagram also plays a strong role in MBB tensile properties, specifically looking at the center of the phase diagram. Sample MSnB-62-77 displays nearly an order of magnitude increase in $E$ and a 3 fold increase in $\sigma$ relative to its bulk analog, while sample MnBS-60-65 presents nearly the exact opposite behavior where $E_{bulk} > E_{MBB}$ by 100 MPa and $\sigma_{bulk} > 3^* \sigma_{MBB}$. Beyond the quantitative tensile properties of MBBs, is the qualitative shape of the material deformation. Figure A.4 presents two stress strain curves which exemplify the two-stage yield behavior observed for many MBB samples. The exact mechanism for the MBB two-stage yielding is not yet known but we believe that the first yield point is related to chain disentanglement which could be expressed as intra-particle movements while the second yield point arises from the difficulty of large MBB pseudo-particles to translate past one another which could be inter-particle movements.
Figure A.4. Tensile testing stress strain curves for MSnB-62-77 ($f = 0.45$) and MSnB-66-44 ($f = 0.60$) demonstrating a two-stage yield behavior which was observed for many of the MBB samples.

Given the incredibly complex nature of examining silicate nanocomposites it is important to re-examine MBBs in respect to orientational control of the MMT filler. A complex succession of morphologies are forming than can be accounted for by simply shifting along a typical BCP phase diagram in the MStB system. These samples have overcome the clay curvature limitation by strongly stretching the tethered brushes to increase domain sizes. Many of the samples display elliptical structures measuring tens to hundreds of nanometers across, which is commensurate with the dimensions of a highly bent MMT platelet. Conversely, the MSnB system was found to form only lamellar structures with a strong resistance to any other morphologies. The incorporation of clay particles in the lamellar morphology promotes the formation of defect-free areas by creating a high free energy penalty for misaligning the large MMT sheets away from lamellar domains. Figure A.5 is a micrograph of MnBS-60-63 demonstrating a $4 \times 4\mu m$ square of defect free lamellae. Also contributing to defect-free lamellae is an effect similar to the open-ended channels of Ruiz et al., where MBBs offer a terminal zone of increased polymer mobility such that defects can migrate to the edge of the MMT platelets. Even though MMT introduces a free energy of bending which encourages an enthalpic trend towards lamellar formation, it is surprising that the observed lamellar window of $0.45 < f_\text{St} < 0.7$ is comparable in size to that observed by Bates and Fredrickson when studying polystyrene-$b$-polyisoprene BCPs.
In the case where BCP composition is too asymmetric to form lamellae the MMT bending energy becomes more apparent. The relatively large MMT platelets appears to inhibit the formation of morphologies that requires high mean curvature. The semi-rigid platelet resists the deformation necessary to accommodate the non-lamellar BCP morphologies. The best example of this phenomenon is the partially segregated cylindrical morphology in Figure A.2f. It is possible that a fully developed cylindrical morphology is still forming and has not yet reached equilibrium as asymmetric BCPs microphase segregate more slowly than their symmetric counterparts.
Conclusions

The synthesis of a library of tB-MBBs and nB-MBBs was accomplished and allowed for the comparison of phase diagrams for two nearly identical materials. Some remarkable morphologies were realized in terms of domain period, complex structure, and long-range order. Also mechanical property evaluation on both MBBs have shed some light on interesting effects of MBB core block chemistry and $f_S$. The nB-MBBs were then further studied for mechanical properties of MBBs in the melt and solid state. A comparison to bulk BCPs of identical molecular weight and composition was provided, however no dramatic improvements in mechanical properties were observed. This area certainly merits further research to optimize MBB mechanical properties.

Acknowledgements

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Bibliography


