Abstract

ROVIRA TRUITT, ROSIMAR. Synthesis and Characterization of Biopolymer Composites and their Inorganic Hosts. (Under the direction of Jeffery L. White.)

Biopolymers are biodegradable and biocompatible materials obtained from renewable sources. These polymers could have an increased impact in consumer or health applications, given a larger, more flexible range of physical properties. Targeting enhanced properties through the design of organic-inorganic hybrids requires novel synthesis routes. An in-situ polymer composite that differs from hybrids generated by simple mixing of the organic and inorganic phases has been demonstrated here. A known ring opening polymerization catalyst was supported within the channels of mesoporous hosts (e.g. MCM-41). A combination of elemental analysis, solid-state nuclear magnetic resonance, surface area, and microscopy experiments indicated that the stannous octoate catalyst was supported inside the host channels, and that a charged framework is not required for its incorporation. These Sn(Oct)$_2$ supported mesoporous catalysts were used to prepare poly(d,l-lactide) composites. Multiple experiments, including solid state NMR, BET nitrogen adsorption, and calorimetric analysis, gave evidence that the resulting polymer forms inside the host channels. In this way, a biopolymer which grows out of the crystallites is generated in-situ. Additionally, the acid catalyzed condensation polymerization of lactic acid with micro/mesoporous materials was investigated. Results indicate that Al-SBA-15 is a potential catalyst for improved composite synthesis, and are suggestive of higher molecular weights and no residual metal catalyst.
Synthesis and Characterization of Biopolymer Composites and their Inorganic Hosts

by
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Dedication

I dedicate this work to my mother, who always encouraged me to pursue a higher education and supported me through all my decisions; and to my husband for all his guidance, support, and love.
Biography

Rosimar Rovira Hernández was born on May 17th, 1981 to Rosa Hernández and Marcos Rovira in Río Piedras, Puerto Rico. She became a sister to Lysie Rovira Hernández born on December 1982 and Zorimar Rovira Hernández born on November 1984. She spent most of her childhood in Caguas, Puerto Rico, but in 1995, at 14 years old her family moved to Orlando, Florida, where she would spend the next two years.

Through her early years Rosimar had an interest for science and math. It was not until 1997 back in Puerto Rico while attending the Manuela Toro Morice High School, where she took her first chemistry course that she began her passion for chemistry. Her chemistry teacher inspired her to continue her studies in the field. She graduated with honors in 1999 and began her undergraduate studies that same year at the University of Puerto Rico at Cayey. In the spring of 2001, Rosimar began her first research experience with Dr. Jannett Gavillán. That following summer, Rosimar worked at the University of Illinois at Urbana-Champaign. Through the next year she kept working with Dr. Gavillán at UPR-Cayey and in summer of 2002 she worked at the State University of New York at Buffalo. After her last summer research experience with Dr. Jeffery White at North Carolina State University, Rosimar made the decision to return to NCSU and work for Dr. White for her Ph.D. While pursuing her doctorate degree, she met her husband Matthew Truitt from Burlington, NC, who was a fellow graduate student in Dr. White’s lab. In 2005, Dr. White moved his group to Oklahoma State University, speeding up the wedding ceremonies. Halfway to obtaining her degree, Rosimar remained a student at NCSU, and completed the remainder of her graduate research at OSU as a research associate.
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Chapter 1: Introduction to Polymers, Mesoporous Structures, Organic-Inorganic Hybrid Materials, and Experimental Methods

1.1 Polymer Concepts

Polymers can be found in almost everything; from our bodies, to commercial products like plastic bottles, plates, and bags, to glass windows, nylon fibers, paper and wood. Indeed, polymers play a vital role in today’s world. Polymers are large molecules or macromolecules of repeating structural units called monomers. They can be prepared by polymerization, meaning the linking of monomer molecules to form a macromolecule. The simplest form of a polymer is known as a homopolymer because it is comprised of only one type of monomer unit. When two different monomers are combined to form a copolymer there are four different classifications based on the arrangement of the monomeric units; random, alternating, block, and graft copolymers. These can be seen on Figure 1.1 (A and B depict the two different monomers).1-3 Random and alternating copolymers are, as their names suggest, random and alternating sequences of both monomer units in the polymer chain. Block copolymers are long blocks of one monomer (homopolymer subunit) joined to a block of the second or more monomers. If there are two distinct blocks, the polymer is called a diblock copolymer; three, triblock; four, tetrablock; and so on. For graft copolymers, side chains of a given monomer are attached to the main chain of a monomer or backbone. Similar to the homopolymer and copolymer terms, the combination of three different monomers to form a macromolecule is termed a terpolymer, and so on for combinations of more monomers. Polymers can be sub-divided based on their structural shape, meaning the
existence and / or arrangement of branches (Figure 1.2).\textsuperscript{1-4} Thus, a linear polymer consists of a single main chain, while a branched polymer consists of one or more polymeric side chains of the main “backbone” chain. \textbf{Figures 1.2 c and d} show some types of branched polymers based on the length and shape, star and comb-like. A crosslink or network polymer is an interconnected branched polymer. Polymers can be classified by many different ways and the main division is that they are natural (e.g. DNA) or synthetic (e.g. Nylon). Natural polymers such as amber (fossil tree resin) and cellulose (main constituent of wood) have been used for centuries. For example, cellulose has been used for the production of paper for several centuries. Other natural polymers called biopolymers (proteins (e.g. enzymes) and polysaccharides (e.g. starch)) are an essential part of living organisms and play crucial roles in biological processes. Synthetic polymers can be analogues of natural polymers or completely new materials not found in nature.

\textbf{Figure 1.1} Types of copolymers: (a) Random, (b) Alternating, (c) Block, and (d) Graft copolymers\textsuperscript{1-3}
Figure 1.2 Different structural polymer shapes: (a) Linear, (b) Branched, (c) Branched, star (d) Branched, comb, and (e) Crosslinked or network.

Figure 1.3 Different types of polymer: (a) Phenol formaledehyde resin (Bakelite a thermoset polymer is based on this resin) and (b) Polyethylene, a thermoplastic polymer.
Based on their thermal behavior polymers are classified as either thermosetting or thermoplastic polymers. Thermoset polymers are heavily cross-linked materials that form a network, making them rigid. Their shape cannot be changed once it is set and degrade if heat is applied. In the early 1900’s a thermosetting-type polymer and the first synthetic polymer Bakelite based on a phenol formaldehyde resin (Figure 1.3a) was invented.\(^1\) Bakelite was used in radio and telephone casings, for billiard balls and pipe stems. Other examples of thermosetting polymers are epoxy resin and polyimides. Thermoplastics are linear or branched polymers that can melt (soften) when heated and turn to a brittle-glassy state (harden) when cooled. Thus, they can be molded and remolded when melted. Celluloid, the first thermoplastic, was discovered in the 1800’s. It is made of nitrocellulose and camphor (1,7,7-trimethylbicycloheptan-2-one). Polyethylene (Figure 1.3b) is a thermoplastic and was the first commercial synthetic polymer. It is now mostly used for the production of plastic bottles and sandwich/freezer bags. Other widely known examples of synthetic thermoplastics are nylon (polyamides), PVC (polyvinylchloride), Teflon (polytetrafluoroethylene), poly(methyl methacrylate) (PMMA), polypropylene, polystyrene (PS), and some biopolymers like poly(lactic acid) and poly(glycolic acid). According to their end use or application, polymers can be classified as plastics, fibers, or elastomers. Natural rubber, a soft and sticky material is found in the sap of some plants. The process known as vulcanization, which is the addition of sulfur with heat, turns this soft natural rubber into a stronger and elastic material known as vulcanized rubber by the addition of crosslinks. This material and synthetic rubbers are lightly crosslinked elastomers, which deform under stress, but then return to their original shape when the stress is released. Neoprene (polychloroprene,
Figure 1.4a), a synthetic rubber synthesized in the 1930’s, is resistant to heat and chemicals such as gasoline. Fibers are described as continuous filaments. Natural fibers include those produced by plants and animals, with examples like cellulose, spider silk, and wool. Synthetic fibers are generally derived from petrochemicals (e.g. nylon 6.10, Figure 1.4b), but some are based on natural products such as fiberglass made from quartz. Some polymers can be used as both fibers and plastics. Plastics have been around since the early 1900’s and have become a useful and vital part of our lives. These are malleable materials (mostly thermoplastics) which can be pressed or extruded, among other techniques, into a variety of shapes such as bottles, plates, films, and many others. Due to this versatility and relatively low cost, plastics are used in a large range of products. Some examples are Styrofoam cups and plates made out of polystyrene (Figure 1.4c); PVC or poly(vinyl chloride) used for plumbing and gutters; polyethylene used for packaging and containers; polyesters used for fabrics, films, and bottles; and nylon (polyamides) a fiber used for toothbrushes and stockings. The majority of plastics used today are petroleum-based polymers, meaning they are derived from petroleum, a non-renewable source. With the uncertain future of oil reserves and the ever growing concern of landfill impacts as these materials are not biodegradable and degrade very, very slowly, environmentally friendly materials such as biopolymers are being researched and in some cases implemented as alternates for petroleum-based plastics.
The polymer structure and chain size are important to the physical behavior of polymers. Thus, similar to micromolecular chemistry, configurational isomerism which is the spatial arrangement of bonds in the molecule can help us to further understand this. Geometrical isomers or polymers produced from double bonded molecules with different geometrical structures can be either cis (Z) or trans (E). 1,4-polyisoprene with cis configuration at each double bond is a natural rubber, which does not crystallize at room temperature, and is amorphous and elastomeric (Figure 1.5a). The trans version of this polymer is a more symmetrical, hard, non-elastic, and crystalline polymer (Figure 1.5b). We know from organic chemistry that stereoisomerism arises when an asymmetric center (chiral center or with four different substituents) is present. Analogous to this concept, stereoisomerism in polymers can happen, though the stereo center is termed pseudoasymmetric because the main chains of the polymer do not have the four different substituents needed for asymmetry. Thus, they are not optically active. For polymers synthesized from monomers with asymmetric centers the letters R and S, or D (d, dextrorotatory) and L (l, levorotatory), are added to the name. Isotactic, syndiotactic, and atactic are the three different types of spatial arrangements (tacticity) arising from the stereoisomerism. These are seen on Figure 1.6 using the general polymer -CH2═CXY-. 

**Figure 1.4** Classification of polymers based on common end uses: (a) Neoprene-synthetic rubber, (b) Nylon 6,10-Fiber, and (c) Polystyrene-Plastic.
An isotactic polymer is one where the same substituent is all above or all below the plane, designated as dddd… or llll…. The other stereoregular configuration, syndiotactic, refers to the alternate above and below plane arrangement of the substituents, dddl… or ldld…. An atactic polymer is not stereoregular, making its configuration more random. When a polymerization method yields a stereoregular (or tactic) polymer rather than an atactic one, it is said to be stereospecific. Stereoregular polymers can pack better and are more crystalline, thus, possessing higher melting points and greater rigidity. As seen for polypropylene, its isotactic configuration has a higher melting point and it is used as a fiber, while the atactic configuration is an amorphous soft material. The following terms describe the stereosequence of vinyl polymers, meso and racemic placements. Meso, meaning same, corresponds to the placement of the groups in the isotactic structure, while racemic corresponds to the syndiotactic structure. The letters m and r denoting meso and racemic, respectively, can be added to the nomenclature of polymers. These refer to the configuration of one chiral center to its neighbor (dyad). Thus, for an isotactic triad we would write “mm”, a syndiotactic triad “rr”, and for a mix or heterotactic “mr”. The same form is followed for the tetrad sequence, pentad, and so on. These configurational sequences are best determined by Nuclear Magnetic Resonance (NMR).

\[
\begin{align*}
(a) & \quad \text{H}_2\text{C} \quad \text{CH}_2 \quad \text{n} \\
& \quad \text{C} = \text{C} \quad \text{H} \\
\text{H} & \quad \text{H} \\
(b) & \quad \text{H}_2\text{C} \quad \text{C} = \text{C} \\
& \quad \text{H} \quad \text{H} \\
& \quad \text{CH}_2 \quad \text{n}
\end{align*}
\]

**Figure 1.5** Structures of 1,4-polyisoprene with (a) cis configuration (natural rubber) and (b) trans configuration (Balata)\(^1\,^3\)
1.1.1 Properties of Polymers

Unlike simpler organic compounds, individual polymer chains are not all composed of the same quantity of monomer units. Polymer molecular weights are given as average values. The two experimentally determined measurements are $M_n$, the number average molecular weight, and $M_w$, the weight average molecular weight. $M_n$ is determined by the mole fraction distribution of different sized molecules as seen in the following equation:

$$M_n = \sum n_i M_i \quad (1)$$

where $n_i$ is the mole fraction of species $i$ or molecules of the same size with molecular weight $M_i$. While $M_w$ is determined by the weight fraction:

$$M_w = \sum w_i M_i \quad (2)$$

where $w_i$ is the weight fraction of species $i$. The relation between $M_w$ and $M_n$ is known as polydispersity (D) or polydispersity index (PDI) and it is given by:

$$D = \frac{M_w}{M_n} \quad (3)$$
The number of repeating units that composes a polymer molecule is known as the degree of polymerization, \( \text{DP}_n \). The relationship between the degree of polymerization and the number average molecular weight is:

\[
\text{DP}_n = \sum n_x x
\]  

(4)

where \( n_x \) is the number fraction of molecules containing \( x \) number of repeating units. The DP relationship with the \( M_w \) is seen in the following equation:

\[
\text{DP} = \sum w_x x
\]  

(5)

where \( w_x \) is the weight fraction of molecules containing \( x \) number of repeating units. Many methods are employed for the determination of molecular weights. These methods can be primary (or absolute), which give estimated values of the molecular weight, or secondary, which give a comparison between the molecular weight of different polymers and are calibrated with a reference molecular weight that has been studied by an absolute method. Some primary methods are end group analysis by titration, light scattering, and colligative property measurements such as boiling point elevation and vapor phase osmometry, among others. Viscometry and gel permeation chromatography (GPC) are examples of secondary methods.

Figure 1.7 Depiction of (a) semi-crystalline and (b) amorphous structures in polymers\(^{1,4} \)
Polymers can be crystalline (containing structural order) or amorphous (Figure 1.7). However, most crystalline polymers are not truly crystalline materials. Due to their large structure, they pack together in a non-uniform fashion with ordered or crystalline-like regions called crystallites mixed in with disordered or amorphous domains (termed the fringed-micelle theory). This semi-crystallinity arises from linear chains that are structurally oriented in a uniform three-dimensional matrix, hence, chain length and branching can affect the degree of crystallinity. We know that the more branched a polymer is, the harder it is for it to pack, and thus the less crystalline it is. This concept can be further understood by the properties of high density polyethylene (HDPE) and low density polyethylene (LDPE). High density PE has long unbranched chains which pack together easily making this polymer a crystalline, rigid, not easily stretched material. On the contrary, low density PE is a softer, easily stretched, less crystalline polymer due to its makeup of smaller highly branched chains, which do not form crystalline domains. Inter-molecular bonding can also affect crystallinity because it stabilizes the structure, making a polymer more crystalline. Given that an increase in degree of crystallinity tends to make a polymer more rigid and brittle, the opposite gives a more transparent glassy material. Several methods are employed for the determination of crystallinity, such as the density method and wide angle x-ray scattering (WAXS). The density method is based on the fact that crystalline regions in the polymer have a higher density than amorphous domains, as seen for HDPE and LDPE. The WAXS method takes advantage of the scattering from the crystalline areas which result in sharp peaks rather than humps obtained from non-crystalline regions.
Polymers can be characterized by many different properties as it has been shown with crystallinity and molecular weight. Other important properties which will be discussed in more detail are glass transition, melting point, tensile strength, and modulus, among others. Both the glass transition temperature \( T_g \) and the melting point \( T_m \) are thermal transitions, meaning a change of state occurs by changing the temperature. Melting and other known changes of state like freezing, condensation, vaporization (boiling point), etc. are first order phase transitions. The melting point is the transition of a solid to a liquid symbolized by the dotted line on Figure 1.8.\(^6\)\(^7\) At this melting point the system is at equilibrium, thus the Gibbs free energy is zero \( (\Delta G=0) \):

\[
0 = \Delta H - T \Delta S \quad (6)
\]

where \( \Delta H \) is the change in enthalpy, \( T \) the temperature of the system, and \( \Delta S \) is the change in entropy. For first order phase transitions the system either absorbs or releases energy, thus the change in enthalpy must not equal zero \( (\Delta H \neq 0) \). The following equation describes the change in enthalpy at constant pressure:

\[
dH_p = C_p \, dT_p \quad (7)
\]
where \( C \) is the heat capacity. The heat capacity can be defined by the following equation:

\[
C = \frac{\delta q_{\text{rev}}}{dT} \quad (8)
\]

Substituting the heat capacity definition (equation 8) into equation 7 gives:

\[
dH_p = q_p \quad (9)
\]

By determining the heat capacity at a range of temperatures (equation 7) or the heat (equation 9) the change in enthalpy of the transition can be obtained. If equation 7 is rearranged for the heat capacity, we would obtain:

\[
C_p = \frac{dH_p}{dT_p} \quad (10)
\]

which changes from one first order phase to another. However, the \( C_p \) is infinite at the transition temperature (dotted line for melting transition). As previously stated if the change in enthalpy is obtained then the change in entropy could also be obtained. Going back to equation 6, if \( \Delta G = 0 \) and \( T \) is the melting temperature, the rearrangement for \( \Delta S_m \) gives:

\[
\Delta S_m = \frac{\Delta H_m}{T_m} \quad (11)
\]

It can be observed from this equation that if the \( \Delta H_m \) (heat of the system) is high and/or the \( \Delta S_m \) (disorder or order of the system) is low, the \( T_m \) will be high corresponding to strongly bonded units in the polymer. Branching, molecular weight (length chain), symmetry, and tacticity, are all factors that affect crystallinity, and also affect melting point. For example, if a polymer’s chain is considerably branched, as previously stated the packing efficiency is reduced making the material less crystalline, and thus exhibiting a lower melting point. An amorphous polymer does not exhibit a true melting point as seen on Figure 1.9, rather they are characterized by the glass transition temperature.\(^1\) A semi-crystalline material exhibits both a melting point and a glass transition, whereas a truly crystalline material would only
exhibit the melting point ($T_m^0$) to become a viscous liquid. The melting point of a polymer can be determined by several instruments, such as a melting temperature apparatus and Differential Scanning Calorimetry (DSC). The former instrument analyses the material by placing it in a thin glass tube that is immersed in a heating block or oil bath. With a magnifier, the melting of the crystals can be observed. DSC will be discussed in more detail in a subsequent section.

**Figure 1.9** Volume versus temperature changes in polymers for (a) amorphous, (b) semi-crystalline, and (c) crystalline samples

**Figure 1.10** $C_p$ versus temperature diagram for a second order phase transition

1
The $T_g$ is a second order phase transition, where a glassy amorphous polymer becomes flexible or rubber-like and vice versa. This change is possible because of the onset (or start) of the motion of large segments due to available thermal energy. Opposite to first order phase transitions, second order phase transitions do not involve absorption or evolution of heat ($q_p=0$), as a result the change in enthalpy is zero ($\Delta H=0$). However, the first derivative of enthalpy i.e. the heat capacity at the transition temperature does change by a finite amount (see Figure 1.10). Figure 1.11 similar to Figure 1.9 illustrates the different phase transitions of a semi-crystalline polymer with respect to heat flow as the temperature is increased. An amorphous polymer when it is in the solid state and below the glass transition temperature exhibits glass-like characteristics, such as hardness and brittleness. As the temperature is increased, the polymer goes thru the glass transition temperature becoming rubber-like, resulting in a slight baseline shift rather than a sharp peak as it is for the melting point. With further increase of temperature the rubbery material may undergo crystallization, observed by the first peak. On the contrary, for a crystalline polymer no glass transition would be observed but rather a melting peak, as stated earlier. For semi-crystalline polymers all three transitions could be observed, glass transition, crystallization, and melting. Similar to the melting point the $T_g$ has several factors which affect it including chain flexibility, branching and crosslinking, molecular structure, and molecular weight. For example, if the chain of a polymer is highly flexible, the glass transition temperature will be low since less thermal energy is needed for the motion.
To this point, we have discussed the physical and thermal properties of a polymer, such as molecular weight, crystallization, melting point, and the glass transition temperature. In the following paragraph the mechanical properties of polymers will be discussed. Mechanical properties involve the polymer’s behavior under stress and allow us to determine possible end commercial uses for the polymer. Stress, $\sigma$ is defined by the following equation:
\[ \sigma = \frac{F}{A} \quad (12) \]

where \( F \) is the force exerted by the material and \( A \) is the cross-sectional area. The mechanical properties are better explained by the stress-strain curve seen on Figure 1.12.\(^2\)

The strain, or type of deformation, displayed on the x axis is the measure of the change in length of the polymer. Strain can be expressed in terms of elongation, \( \varepsilon \), a type of deformation as seen on the following equation:

\[ \varepsilon = \frac{(L - L_0)}{L_0} \quad (13) \]

where \( L \) is the length of the polymer after it is stretched, and \( L_0 \) is the initial length. In studying the stress-strain curve, we can distinguish the different mechanical properties. One of these properties is tensile strength; this is defined as the stress needed to break or permanently deform the material. Tensile strength is important for materials which are going to be stretched, such as fibers. Elongation, another mechanical property, as mentioned earlier is a type of deformation that the sample undergoes under stress. It is typically expressed in terms of percent elongation to break, or the strain on a material when it breaks as seen on the following equation:

\[ \% \text{ elongation} = \left( \frac{L}{L_0} \right) \times 100\% \quad (14) \]

Elastomers, as one would imagine, possess high elongation-to-break ratios. The slope of the stress-strain curve, or the ratio of stress to strain, is known as Young’s modulus. Young’s modulus, \( E \), is a measure of the stiffness of an elastic sample and is expressed using the known definitions of stress and strain stated earlier in equations 12 and 13, respectively:

\[ E = \frac{\sigma}{\varepsilon} = \frac{(F / A_0)}{((L - L_0) / L_0)} = \frac{(F \times L_0)}{(A_0 \times (L - L_0))} \quad (15) \]
It should be noted that not all of the material’s stress-strain curves are linear, thus the Young’s modulus applies to the range of stress in which Hooke’s Law holds, usually the initial linear slope. Rigid materials such as metals and fibers have high moduli, elastomers have low values and plastics lie in between. The last mechanical property seen on the stress-strain curve is toughness. Toughness is mathematically expressed as the integral from the initial strain, 0 to the strain upon breaking, $\varepsilon_f$ of the strength derivative of strain:

$$ \text{Area} = \int \sigma \, d\varepsilon \quad (16) $$

This equation shows that toughness is a measure of the energy a sample can absorb before it breaks. If a sample is strong (high strength or stress) it does not necessarily mean that it is tough. These mechanical properties define the different types of polymers as seen on Figure 1.13. For example, fibers (e.g. Nylon, Figure 4b) have high initial moduli, and possess high percent elongation and low or high strength. Plastics have in-between moduli, and a varied percent elongation. For rigid plastics (e.g. polystyrene) the strain is low, and for tough plastics (e.g. semicrystalline polyethylene) it is high. Elastomers such as vulcanized rubber have initial low moduli, and then get stiffer as stress and strain increase. Elastomers, as mentioned before, have high percent elongation.
Materials that exhibit both elastic and viscous characteristics when undergoing deformation are said to be viscoelastic. For amorphous and semi-crystalline polymers, five regions of viscoelastic behavior are observed near the glass transition temperature (Figure 1.14).\textsuperscript{1} Region I, or the glassy region, is where the polymer is brittle, thus it exhibits a high Young’s modulus. The glass transition temperature (region II) is where the Young’s
modulus is lowered by a great amount making the material tougher. In region III, the rubbery plateau, the polymers display rubber-like characteristics. If the polymer is semi-crystalline, the dotted line is followed; if it is a crosslinked amorphous polymer, the dashed lined is followed knowing that it won’t exhibit the next two regions; and if it is a linear amorphous polymer, it follows the solid line. The rubbery-flow region (region IV) is only observed for linear polymers. In this region polymers show rubber elasticity and flow characteristics with more visible flow seen for materials under longer stress at higher temperatures. The last region (V), or the liquid flow region, is the melting point temperature.

### 1.1.2 Polymerization Methods

Monomers can undergo different types of polymerizations to produce synthetic polymers. The two main types of polymerization mechanisms are step and chain, or condensation and addition based on the polymer’s structure. Most step polymerizations and chain polymerizations produce condensation and addition polymers, respectively. When the synthesis involves the elimination of small molecules, the polymer chain contains functional groups, or some atoms observed in the monomer are missing from the repeating chain, the polymer is considered a condensation polymer. When none of these specifications are met the polymer is an addition polymer. For example, polyesters, polyamides, polyurethanes, and polysiloxanes are condensation polymers (Figure 1.15) and polystyrene, polyethylene, poly(vinyl chloride), and polyacrylonitrile are addition polymers (Figure 1.16).
Step growth polymerization occurs by a stepwise reaction between the functional groups of reactants. It proceeds from monomer to dimer, to trimer, and so on, until molecular weights $>10,000 \text{ g/mol}$ are obtained, as observed in the following scheme:

Monomer + Monomer $\rightarrow$ Dimer
Monomer + Dimer $\rightarrow$ Trimer
Dimer + Dimer $\rightarrow$ Tetramer
Monomer + Trimer $\rightarrow$ Tetramer
Dimer + Trimer $\rightarrow$ Pentamer
Etc.

Thus, the average molecular weight of the polymer molecules gradually increases. It can be observed from the above scheme that the reactions occur between any size species present. At any point, molecules of different sizes are observed, giving a large range of
molecular weights. High molecular weight polymer is only obtained at very high conversions (Figure 1.17a). Esterification, amidation, formation of urethanes, aromatic substitution, among others, are examples of reactions that can produce polymers by step polymerization. Some of the polymers obtained by these reactions are seen in Figure 1.15.

Chain polymerization involves molecules with double or triple bonds that when reacted break and link with other monomers to form the repeating polymer chain. It involves three steps, initiation, propagation, and termination. In the initiation step, an initiator is used to create a species with a reactive center such as a free radical, anion, or cation. As the name suggests, propagation occurs as the reactive center propagates by the successive addition of monomer regenerating the reactive center. This process continues until the reactive center is destroyed by combination or disproportionation termination. Opposite to step-growth, chain polymerization only takes place by monomer reacting with the reactive center rather than with monomer or other sized molecules (e.g. dimer, trimer, etc.). Thus, it will produce high molecular weight polymer at all levels of conversion (Figure 1.17b). Atom transfer radical polymerization (ATRP), radical addition-fragmentation transfer (RAFT), cationic polymerizations, and anionic polymerization are some examples of chain polymerizations. The last graph in Figure 1.17 labeled as non-terminating or living polymerization depicts a polymerization where a linear increase of molecular weight occurs with percent conversion. In this type of polymerization with the absence of something that would react to terminate the ionic structure, we can theoretically have a “living polymer-ionic structure”. Thus, living polymerizations are useful for preparing block copolymers. This type of behavior is observed in biological syntheses of proteins and in certain chain polymerizations. For
example, the ring opening polymerization (ROP) of cyclic monomers usually proceeds by the chain-mechanism. However, its molecular weight dependency on percent conversion usually follows the linear behavior observed in Figure 1.17c. Thus, ROP is studied as a separate category of polymerization. Ring opening polymerization can be initiated by both anions and cations. Anionic ROP involves the formation and propagation of the anionic reactive species, which in turn attack the monomer. On the contrary, cationic ring opening polymerizations involve the nucleophilic attack of the monomer on the cation species. In recent years another type of initiator has been of much interest, namely enzymes such as lipases. Enzymatic polymerization or activated monomer polymerization (AM) involves cations and anions derived from the monomer.
Figure 1.17 Molecular weights vs. % conversion for (a) chain, (b) step-growth, and (c) non-terminating polymerizations.

The graphs show the relationship between molecular weight and % conversion for different types of polymerizations.
Figure 1.18 Examples of lactones and their corresponding polymers (a) lactide to poly(lactic acid), (b) glycolide to poly(glycolic acid), (c) 3-butyrolactone to poly(3-hydroxybutyrate), (d) 3-valerolactone to poly(3-hydroxyvalerate), and (e) ε-caprolactone to poly(ε-caprolactide)
The monomers under study in this research are lactones (cyclic esters) such as the ones seen on Figure 1.18, specifically the dilactone lactide (Figure 1.18a). Lactide typically undergoes anionic ring opening polymerization, although cationic ROP has been used but not as extensively.\textsuperscript{4,8} The anionic polymerization involves both ionic-anionic initiators\textsuperscript{9} (e.g. potassium methoxide, potassium tert-butoxide, and butyl lithium) and covalent-anionic (coordination) initiators. Focus has been shifted in recent years towards coordination initiators. For example, metal alkoxides (e.g. tin (II) butoxide\textsuperscript{10} and iron (III) butoxide\textsuperscript{11}) and metal carboxylates (e.g. tin (II) 2-ethylhexanoate\textsuperscript{12,13} and zinc (II) lactate\textsuperscript{14}), among others, are coordination initiators. For most lactones, anionic polymerization initiates by the nucleophilic attack of the reactive specie on the carbon of the carbonyl followed by the cleavage of the acyl-oxygen bond (see Figure 1.19).\textsuperscript{15} In the case of coordination initiators or coordination-insertion ROP, the metal coordinates with the carbonyl oxygen first as it is seen in Figure 1.20.\textsuperscript{8,15} As mentioned above, enzymes as initiators for ROP are a novel research field, and lactones have been polymerized with their use.\textsuperscript{16-19} The enzymes act as nucleophilic catalysts requiring the presence of a protic agent as initiator. The precise mechanism is not known, but a reasonable pathway described by Dechy-Cabaret, O. and co-workers is depicted in Figure 1.21.\textsuperscript{8} It is similar to the anionic polymerization but with the protic initiator ROH reacting with the lactide-nucleophile to form the polymer-chain and release the nucleophile.
Figure 1.19 Anionic ring opening polymerization of lactones\textsuperscript{15}

Figure 1.20 Coordination-insertion ring opening polymerization of lactide\textsuperscript{8,15}

Figure 1.21 Enzymatic ring opening polymerization of lactide\textsuperscript{8}
Coordination-insertion polymerization (as seen on Figure 1.20) is by far the most used synthesis for producing lactones, mainly due to the fact that they produce stereoregular polymers with narrow molecular weight distributions (MWD). The most common coordination catalyst is tin (II) 2-ethylhexanoate, also known as stannous octoate or Sn(Oct)$_2$ (Figure 1.22). Stannous octoate has been approved by the FDA as a food additive.$^{15,20}$ Carboxylates like this one are weak nucleophiles and are considered to behave more as catalysts than initiators (similar to enzymes). Thus, they are used together with co-initiators containing active hydrogens (e.g. alcohols).$^{15}$ In Figure 1.20 the alcohol ROH is shown forming the active species by attaching to the stannous octoate.
The ring opening polymerization of lactide explained above produces the polymer Polylactide (PLA) seen on Figure 1.20. The polycondensation (step-growth) of lactic acid also produces PLA or Poly(lactic acid). As seen on Figure 1.23, two lactic acid molecules condense releasing water to form the polymer chain. Typically the polycondensation method produces low molecular weight polymer which is not useful for many applications. This is mainly due to the presence of water impurities and the equilibrium reaction that produces the cyclic ester, lactide. On the contrary, the ROP of lactide produces high molecular weight polymer (Figure 1.20). Hence, it is the most widely used method for synthesizing PLA.

1.2 Biodegradable Polymers

Biopolymers are polymers derived from renewable sources. These can be natural (e.g. polysaccharides and proteins) or synthetic (e.g. biopolyesters). In the past decade,
biopolymers have been under increasing levels of study for materials applications due to their properties. They are inherently biodegradable, meaning they biodegrade or are broken down into smaller molecules (i.e. carbon dioxide and water) by enzymes in living organisms. In the case of the polyester poly(lactic acid), biodegradation starts by abiotic degradation; simply the hydrolysis of ester bonds without the presence of enzymes. This breaks down the high molecular weight polymer to lower molecular weight oligomers.\textsuperscript{21,23,24} The material then continues to degrade into carbon dioxide, water, and humus by microorganism action (degraded organic materials). Petroleum-based polymers also degrade (by photodegradation, exposure to sunlight) but are not considered biodegradable because they could take up to hundreds of years more than biopolymers to degrade. It should be noted that without the presence of oxygen or water, as in landfills, everything degrades slower. Even paper made from natural the biopolymer cellulose takes approximately twenty years or more to degrade in landfills. Also, the majority of commodity polymers (i.e. plastics) used today are petroleum-based polymers which are derived from a non-renewable source. Biopolymers provide a solution to the world’s decreasing oil resources and to our dependence on foreign oil. Another important property in some biopolymers is their biocompatibility, meaning their ability to integrate with living tissue.
Figure 1.24 Applications of biopolymesters

The focus of this research is towards biopolymesters such as PLA, poly(glycolic acid) (PGA) and polyhydroxyalkanoates (PHA’s) like poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxyvalerate) (PHV). PHA’s are microbial intracellular storage products and are hence naturally occurring polymers. In contrast, PLA and PGA are not naturally occurring polymers but are considered biopolymers because their monomers lactic acid and glycolic acid respectively can be obtained from renewable resources. These materials have been accepted by the U.S. Food and Drug Administration for internal use. The many applications of these biopolymesters can be divided into environmental, due to their biodegradability, and medical, due to their biocompatibility (Figure 1.24). Since the 1960’s, biopolymers have been used in medical devices. Some of these include orthopedic fixations (e.g. scaffolds, screws, and pins), tissue engineering, dental devices, sutures or wound closures, and drug delivery devices, among others. Biopolymesters are readily used for
orthopedic fixations because they eliminate the need for rigid metal parts and subsequent operations for implant removal due to their flexibility/strength and controlled biodegradation.\textsuperscript{27-30} Organic-inorganic composites and copolymers of PHA’s and composites of PLA and PGA with natural polymers like collagen have been used as materials for tissue engineering or reconstruction.\textsuperscript{31-34} Dental devices (e.g. void fillers and guided tissue regeneration membranes) is another interesting emerging application for biopolymers.\textsuperscript{35-37} Absorbable sutures based on biopolymesters have been commercially used since the 1970’s.\textsuperscript{38-40} Dexon® and Medifit® based on a multifilament of PGA, Vicryl® based on a copolymer of PGA and PLA, and Biosyn® based on a tri-copolymer containing both PGA and PLA are some examples. In addition, biopolymesters have been implemented in controlled drug delivery devices, which are used in medicine,\textsuperscript{41-45} veterinary medicine (e.g. release of medicine in animals),\textsuperscript{46} and for agrochemical purposes (e.g. timed release of fertilizers and pesticides).\textsuperscript{47} Controlled drug delivery devices consist of the release of an active ingredient/drug from a polymeric matrix that should biodegrade in a controlled manner.

For a long time, biopolymers did not emerge in environmental applications because they could not compete with the cost-effective petroleum-based polymers mostly used for commodity products like plastics. By the 1990’s the dependence on petroleum and waste disposal of these petrochemicals had become a genuine problem, making the way for the use of biopolymers as solutions. These environmentally friendly materials are being implemented today but their higher cost compared to petroleum-polymers still plays a big role in their further use. Nonetheless, many studies have been and are being dedicated to this matter. It should be mentioned that for most of the desired materials applications, the
physical properties of these biopolyesters need tailoring. For example, the separation of stereoisomers, control of molecular weight distribution, and other molecular parameters that affect properties like crystallinity are ways of tailoring biopolymers.\textsuperscript{21} In addition to plastics (e.g. bottles, containers, shopping bags, sandwich wraps), other applications are paper coating, fibers, and films (e.g. agricultural mulch films).\textsuperscript{21,48-51}

\textbf{Figure 1.25} Production of poly(lactic acid) starting from a renewable resource\textsuperscript{21-23}
Our main interest is in poly(lactic acid), which is derived from the condensation polymerization of lactic acid or ROP of lactide. Lactic acid (2-hydroxypropanoic acid) can lose a proton from the acidic group and produce lactate \((\text{CH}_3\text{CH(OH)}\text{COO}^-)\). In humans, lactate can be removed by oxidation in well-oxygenated muscle cells to pyruvate \((\text{CH}_3\text{COCOO}^-)\) or by conversion to glucose by gluconeogenesis, which is a metabolic pathway to generate glucose from non-carbohydrate carbon substrates. In addition, lactic acid can be found in sour milk products, such as yogurt and cottage cheese. Lactic acid is the simplest hydroxyl acid with an asymmetric carbon atom that exists as two enantiomers, D (+) and L (-) with L-lactic acid being the naturally occurring isomer. It can be obtained by the carbohydrate fermentation of starches in corn, sugar beet, and rice, which are converted to dextrose and then fermented to form lactic acid. As mentioned earlier and seen on Figure 1.25, lactic acid can produce low molecular weight polymer, but also may form the cyclic ester lactide by dimerization. The lactide can be obtained in the form of L-lactide, D-lactide, rac-lactide (DL-lactide), or the synthetic blend of D-lactic and L-lactic acid, known as meso-lactide (see Figure 1.26). D-Lactide is not discussed frequently in the literature as its usefulness is somewhat limited. L-lactide and DL-lactide are readily used to produce polylactide by ROP (seen on Figure 1.26). Poly(L-lactic acid) (PLLA) is a semicrystalline material exhibiting high tensile strength and low elongation, and consequently, has a high modulus that makes it more suitable for load-bearing applications such as in orthopedic fixation and sutures. It exhibits a melting point of 173-178°C, a \(T_g\) of 60-65°C, 37% crystallinity, and a degradation time of more than 24 months. Poly(DL-lactic acid)
(PDLLA) is an amorphous polymer with lower tensile strength, higher elongation, low modulus, much more rapid degradation time (12 to 16 months), and a $T_g$ of 55-60$^\circ$C.$^{9,21,22,26}$

![Schemes of L-lactide (A), D-lactide (B), and rac/meso-lactide (C)](image)

**Figure 1.26** Schemes of L-lactide (A), D-lactide (B), and rac/meso-lactide (C)

### 1.3 Micro/Mesoporous Structures

Mesoporous compounds can have regular and uniform framework structures containing pores, or an unordered worm-like pore system. They can vary by pore size and shape, channel dimensionality and direction, and composition of the channels or framework. In the 1700’s the first microporous materials were discovered, natural zeolites. Zeolites are microporous aluminosilicate structures, meaning their pore sizes are below 20Å (<2nm). As the aluminosilicate name suggests they are composed of tetrahedrally coordinated silicon (Si) and oxygen (O) atoms (or silica, SiO$_2$) with aluminum (Al) atoms replacing some of the Si atoms, as seen on **Figure 1.27a**. The amount of aluminum atoms substituted for silicon atoms defines the silicon to aluminum ratio (Si/Al). For example, a material with low Si/Al ratio of 4.0 means it contains 1 aluminum atom per every 4 silicon atoms, making it a high aluminum content zeolite. Increasing aluminum content or lowering the silicon to aluminum ratio leads to higher acid density in zeolites. Aluminum has 3 valence electrons and in this
tetrahedral-type framework it acquires four bonds, making it obtain a formal charge of -1. To balance this charge a neighboring oxygen donates a lone pair to a hydrogen to obtain a formal charge of +1. This hydrogen is considered a Brønsted acid (proton donor) and the Al, O, and H are called the Brønsted acid site. It is also possible for zeolites to contain Lewis acid sites (acceptor of electrons), like trivalent aluminum (seen on Figure 1.27b), which is typically considered extraframework though the depiction illustrates a possible framework Lewis acid. These Lewis acids usually arise during thermal treatment by removing framework aluminum. Synthetic analogues to natural zeolites and new zeolites came about a century later than natural ones, with some examples like ZSM-5 (framework MFI), Beta (*BEA), zeolite Y (FAU), and mordenite (MOR) (Figure 1.28). These zeolites differ in their framework type specified with the parenthesis (channel size and dimensionality). For example, ZSM-5 is a three dimensional structure possessing 10-T-atom (T-atoms are Al or Si) channels of ~5Å in size. Beta also has a three dimensional structure, but has channels containing 12-membered rings, making them larger than ZSM-5. Some synthetic zeolites are prepared with ionic-forms of atoms within the aluminosilicate framework rather than H⁺; these are known as impregnated-zeolites (e.g. zeolite Y with Na, Ca, or NH₄). There are other microporous structures besides zeolites (aluminosilicates) that incorporate other atoms into the framework of the basic zeolite structure known as zeno-type materials. Aluminophosphates are well known zeno-type materials with their framework mainly composed of tetrahedrally coordinated Al and phosphorous. For example, SAPO-40 (AFR) is an aluminophosphate-type material composed of Si, Al, and P. Due to the open-type structure (channels) and high surface areas, zeolites and these other microporous structures
are used extensively as catalysts, catalysts supports, absorption or separation materials, and for many other applications.

![Diagram](image1)

**Figure 1.27** Depiction of zeolite framework: (a) Brønsted acid site and (b) possible Lewis acid site

![Diagram](image2)

**Figure 1.28** Structure of zeolites (a) ZSM-5 and (b) Beta (Reproduced from the IZA structure database web site at http://www.iza-structure.org/databases/)

In 1992 Beck, J.S, et al. at Mobil laboratories first discovered the M41S family of mesoporous compounds. Since this discovery, mesoporous molecular sieves with pore sizes ranging from 20Å – 500Å (2-50nm) have attracted much attention due to their excellent properties. Mesoporous molecular sieves are ordered porous materials with readily
accessible, well defined, and highly ordered pores or channels beyond the sizes obtainable with zeolites or other microporous structures. They exhibit large surface areas and pore volumes and their frameworks can be based on silicon oxides (SiO$_2$) with different channel sizes, shapes and networks. The may also be composed of SiO$_2$ with other metals (e.g. aluminum) and organic compounds, or many other oxides, such as titanium oxide (TiO$_2$) and antimony oxide (SbO$_2$).\textsuperscript{53,56-59} Initially, these materials were less thermally and hydrothermally stable when compared to microporous materials because their channels are surrounded by amorphous walls (not ordered at atomic level). However, recent syntheses of many materials with thicker walls have reported stability enhancements in different mesoporous materials.\textsuperscript{60} Similar to zeolites, mesoporous structures are also extensively used as catalysts, catalysts supports, or hosts, which can in turn be used for optical devices, electronics, drug delivery devices, among others.\textsuperscript{61} Besides microporous and mesoporous structures another class of molecular sieves exists, that is macroporous materials. Macroporous materials are a relatively new class of molecular sieves with pores larger than 500Å (>50nm).

Figure 1.29 Scheme depicting mesoporous silicate MCM-41
Two mesoporous materials of interest to this investigation are MCM-41 and SBA-15 and their aluminum-containing analogues. MCM-41 (Mobil composite of matter) was the first mesoporous M41S family member to be synthesized in 1992.\textsuperscript{54,55} It consists of a honeycomb-like array containing a Si\textsubscript{2}O\textsubscript{2} tetrahedrally coordinated framework with in some cases aluminum (known as Al-MCM-41) or other atoms replacing some of the silicon atoms (see Figure 1.29). MCM-41 is synthesized in a basic medium with a silicon source and a template or surfactant obtaining pore sizes between 15Å and 100Å. It has been proposed that the surfactant forms what it is known as a surfactant micelle, which then aggregates to form a rod-like structure (see Figure 1.30).\textsuperscript{54,55,62} The inorganic silicate species then interact with this rod-micelle surrounding them to form a silicate tube. Then through condensation these silicate rods pack in a hexagonal arrangement forming the known long-range structure with a wall thickness of \textasciitilde10Å. Subsequent removal of the template through calcination reveals the channels or pores of MCM-41. It should be noted that the size of the pores are dependent upon the dimensions of the surfactant micelle which is in turn are determined by the carbon content.

\textbf{Figure 1.30} Proposed mechanism for the synthesis of MCM-41 where (a) is the surfactant micelle, (b) is the surfactant micelle-rod, (c) is the silicate rod, (d) is the hexagonal arrangement of the silicate rods, and (e) is calcined MCM-41\textsuperscript{54,55,62}
chain length of the surfactant used. Al-MCM-41 is MCM-41 containing aluminum atoms in place for some silicon atoms. This aluminum adopts a similar structure to that found in aluminosilicates illustrated in Figure 29-a, forming Brönsted acid sites and also Lewis acid sites. Many authors have published studies based on NMR, IR, and catalytic conversions where the acidity or concentration of Brönsted acid sites is lower than in zeolites.\textsuperscript{63-67} They attribute this mainly to the amorphous pore walls of mesoporous materials in general. Al-MCM-41 has been synthesized directly and by post-synthetic grafting (post-alumination) of MCM-41. The direct synthesis method incorporates the aluminum source together with the original batch for MCM-41. However, this method has proved to be challenging because it produces Al-MCM-41 with low thermal stability and low Brönsted acidity.\textsuperscript{68-70} The need for improved stabilities and higher Brönsted acidity led to the development of post-synthesis grafting. Post-alumination consists of reacting silanol groups in siliceous MCM-41 with the aluminum source (e.g. aluminum alkoxides) in an organic solvent. Results show that grafted Al-MCM-41 has improved hydrothermal stability and higher surface acidity than the counterpart-materials synthesized through the direct method.\textsuperscript{71-74}

SBA-15 was first discovered in 1998 by Zhao at the University of California, Santa Barbara giving it its name.\textsuperscript{75,76} Similar to MCM-41, SBA-15 consists of a honeycomb-like array and a silicate tetrahedral-type framework. Its pore size varies between 40Å - 300Å based on the synthesis composition and conditions (e.g. different ratios of ethylene oxide and propylene oxide). Its walls are much thicker than MCM-41, with sizes between 20Å to 60Å, leading to a higher thermal and hydrothermal stability. An interesting feature of SBA-15 is that it contains micropores within the framework or walls when it is synthesized at low
temperatures (~30-40 °C). This mesoporous structure is typically synthesized using the template triblock-copolymer poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) in an acidic medium. A proposed mechanism for this synthesis is shown in Figure 1.31. The reaction begins with the formation of the PEO-PPO-PEO micelles. These micelles change into a flexible thread-like form by the addition of silicate oligomers within the micelle. Then, these thread-like micelles (TLM) with silicate become straighter with the additional condensation of silicates within the micelle. Further formation of the TLM’s leads to bundles of similar dimensions to the final material and finally the hexagonal structure is observed. The aluminum form of SBA-15, Al-SBA-15 has been successfully prepared by post-synthetic methods. Opposite to the results encountered with directly synthesized Al-MCM-41 materials, the direct synthesis of Al-SBA-15 is carried out by adjusting the pH. The pH needed for the incorporation of aluminum has to be slightly higher than for the formation of silicious SBA-15 since the Al-O-Si bond is easily dissociated under highly acidic conditions. However, the pH is still acidic enough to form the SiO₂ framework.
As mentioned earlier, mesoporous materials can be used as catalyst supports mostly for the design of organic-inorganic hybrids. These catalyst supports can be achieved by (1) the adsorption of a material onto pores of the support; (2) direct incorporation; (3) grafting of a material onto the surface of the mesostructure by covalent bonds. Physical adsorption, which is possible depending on the size of the pores and the adsorbed molecule, could take place through a weak interaction of the introduced molecules and the surface of the host. When the desired material is added to the synthesis mixture of the mesostructure, a direct inclusion can occur. This type of hybrid is sometimes preferred because of the facile “one-pot” method and also the added molecule is bonded through the silicon on the surface and not the external silicon (-Si<sub>surf</sub>-material or -Si<sub>surf</sub>-O-Si<sub>ext</sub>-material). Depending on the conditions of the reaction the supported catalyst’s oxygen-silicon bond to where the catalyst is

Figure 1.31 Proposed mechanism for the synthesis of SBA-15 where (a) are the surfactant micelles, (b) are flexible thread-like micelles (TLM) after addition of silicate oligomers, (c) are straighter silicate TLM’s, (d) are bundles of straighter silicate TLM’s, and (e) is the final hexagonal structure.
supported to (-O-Si<sub>ext</sub>-material) could cleave. Nevertheless, many hybrid materials have been prepared by post-grafting or through functionalization of the mesoporous molecular sieve. These functionalized materials have been obtained through direct bonding (covalently) with the external silicon (-Si<sub>surf</sub>-O-Si<sub>ext</sub>) or the oxygen of the surface hydroxyl group (-Si<sub>surf</sub>-O-H). Numerous functionalized mesoporous solids by “post-grafting” or “direct-synthesis” utilized as catalysts, for controlled drug delivery systems, etc. have been reported in the literature.

Zhao reported the distribution of free or single, geminal, and H-bonded silanol groups throughout the surface of MCM-41 as determined by $^{29}$Si CP/MAS NMR, FTIR, and pyridine adsorption (see Figure 1.32). The single and geminal silanol groups are said to be responsible for MCM-41’s modification. The hydrogen-bonded silanol groups are not included because of the hydrophilic network formed among them (meaning they are stable).

Jana presented the addition of a copper (II) complex in organically modified MCM-41. The MCM-41 was functionalized by mixing it with an amino-ethoxysilane ligand in a solvent under nitrogen atmosphere at room temperature. The ligand covalently bonded through the silane to the surface oxygen, releases ethanol. The functionalization of SBA-15 with an atom transfer radical polymerization initiator was reported by Moreno. The authors first mixed in a solvent SBA-15 and an amino-ethoxysilane under reflux where in a similar manner to Jana the silane attached to the surface hydroxyl released ethanol. Later the desired functionality was added through the attached amino group. Directly synthesized MCM-41 containing disulfide-linkers or other modifications throughout the surface were used for controlled-release delivery systems. The capture of a drug of interest into the channels of the mesoporous material and the capping of the pores with cadmium sulfide (CdS) or other
nanoparticles was investigated. The CdS nanoparticles covalently bonded to the disulfide-linkages blocking the pores however, these nanoparticles are easily cleaved with the use of disulfide reducing agents. Thus, with the use of a stimuli (release triggers) the drugs inside the pores could be easily released. Liu\textsuperscript{136} and Casasus\textsuperscript{137} in a similar way to the previous authors studied capping mechanisms for mesoporous silica-like structures. The capped or contained “guests” were released by redox- or pH–responsive stimuli.

![Figure 1.32 Depiction of (a) free, (b) geminal, and (c) H-bonded silanol groups at the surface of MCM-41\textsuperscript{124,125}](){}

1.4 Organic-Inorganic Composite Materials

Poly(lactic acid) and other related biopolymers are commercially used in areas like plastics, agriculture, medical devices, etc. However, they are a long way from substituting traditional non-biodegradable polymers (i.e. petroleum-based polymers) due to their deficient properties and higher cost. Preparation of copolymers, blends, and composites of biopolymers has been shown to improve the properties of these polymers, as compared to their pure analogues. Since the 1960’s, copolymers and blends of biopolyesters have been commercially used for medical applications. For example, a glycolide and l-lactide copolymer known as Vicryl® produced by Ethicon was developed for absorbable sutures with slightly larger strength than the homopolymers;\textsuperscript{26} a terpolymer of PGA, trimethylene
carbonate (TMC), and p-dioxanone known as Biosyn® developed by US Surgical Corp. is an available suture with a reduced stiffness when compared to pure PGA;\textsuperscript{26} and a blend of BioGlass® (glass particles composed of SiO\textsubscript{2}, Na\textsubscript{2}O, CaO, and P\textsubscript{2}O\textsubscript{5}) and PDLLA for coating surgical sutures was developed with greater microstructure homogeneity.\textsuperscript{38} However, it was not until the 1990’s that biopolymer-based materials started emerging in areas not related to medicine, such as plastics. Some commercial examples of these are Metabolix® a copolymer of hydroxybutyrate and hydroxyvalerate (PHBV) with toughness comparable to polycarbonate and nylon 6 used for adhesives and coatings;\textsuperscript{48} and PLA resins known as NatureWorks® developed by NatureWorks, LLC (formerly Cargill, Inc.) used for drinking cups, food containers and packaging, apparel, and pillow fibers.\textsuperscript{50} Even with these stated commercial applications biopolymer-based materials’ properties need further tailoring given that they are still competing with the more cost-effective petroleum-based polymers. Thus, studies with either blends\textsuperscript{85,86-91} or copolymers\textsuperscript{92-96} are still being performed to better understand their properties.

Organic-inorganic composites have been prepared with the use of layered crystals, carbon nano-particles, natural fibers, bioactive glass, micro/mesoporous structures, and other materials through melt or solution intercalation or by in-situ polymerizations. A recent approach to composites is the design of nanocomposites, which either introduce nanoscale particles to the polymer matrix or fabricate polymers on the nanoscale. The latter approach, a relatively new technique which has received much recent attention, is based on the hierarchical self-assembly of biopolymers. This is typically observed in natural polymers like DNA, polypeptides, and polysaccharides which can spontaneously, by stimuli-response,
etc. fold to monodispersed three dimensional forms that assemble into defined structural nanocomposites.\textsuperscript{97-100} This type of self-assembly has been put to the test with synthetic polymers to prepare ordered organic-inorganic nanocomposites.\textsuperscript{101,102} In comparison to the self-assembly approach the design of polymer nanocomposites or traditional composites have been more extensively studied.

![Figure 1.33 Different types of polymer-layered crystals: (a) phase separated, (b) intercalated, and (c) exfoliated\textsuperscript{104,105}](image)

Layered crystals have been extensively investigated for the design of biopolymer composites.\textsuperscript{103} These minerals with a layer thickness of \(\sim 1\) nm can be divided into many different groups with examples like phyllosilicates (e.g., montmorillonite, MMT \([M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4]\) and hectorite \([M_x(Mg_{6-x}Li_x)Si_8O_{20}(OH)_4]\)), apatite (e.g., hydroxyapatite, HA \(Ca_5(PO_4)_3(OH)\)), and inosilicates (e.g., wollastonite \(CaSiO_3\)). Their layers organize into stacks forming gaps in between (the interlayer) and relatively weak van der Walls forces hold them together. Three different types of composites can be obtained when a polymer is linked to layered crystals, namely phase separated, intercalated, and exfoliated as seen on Figure
When the polymer is unable to intercalate within the layers a phase separated composite is obtained. The intercalated layered crystal composite is observed when one or a few polymer chains are intercalated between the sheets. The latter type of composite seen on Figure 1.34 is obtained when the layers are completely and uniformly dispersed within the polymeric matrix. Most of these natural layered crystal bio-composites are used for bone regenerations or tissue engineering since some of the nano-fillers like HA are found within the human body (in teeth and bones). Reported literature has established the enhancement of biopolymer properties by the preparation of composites with layered crystals.\textsuperscript{106-111}

Bioactive glass (BG) or glass ceramics are surface reactive glass-ceramics which have been extensively investigated for tissue engineering-type applications due to their biocompatibility and biodegradability.\textsuperscript{112} Hydroxyapatite is considered to be a bioactive glass-filler with some other examples like BioGlass®, calcium silicates, etc.. It has been found that when BG is in a physiological environment, it forms HA-like substances on its surface which mimic the natural mineral phases in bones.\textsuperscript{113} Organic-inorganic composites using bioactive glass-type materials have been generally investigated for medical-type applications (bioactivity, tissue-guiding properties, etc.)\textsuperscript{112,114} Natural nanofibers such as cellulose fibers are novel nano-fillers in composites, owing its growth to environmental concerns.\textsuperscript{118-120} The advantage of these natural fibers in a similar manner to biopolymers is their biodegradability and renewable nature.

Interest for carbon nanoparticles mostly seen as carbon nanotubes (CNT), nanowires, and nanofibers began in the 1990’s, but it was not until recent that they have been investigated for the design of polymer nanocomposites. Nonetheless, reports have been
published about the improved properties of prepared biodegradable polymer composites, for example, with the use of CNT’s\textsuperscript{115,116} and nanofibers\textsuperscript{117}. Carbon nanoparticles as the nano-fillers in nanocomposites have applications in medicine, electronics, and plastics.

### 1.4.1 Use of Micro/Mesoporous Materials in Hybrids

Biopolymer nanocomposites have been extensively investigated since the 1990’s, mostly with the use of layered crystals or clays as the nano-scale fillers. Microporous and mesoporous solids offer advantageous properties, like their ordered pore structure and large surface areas for mesoporous materials, to the design of organic-inorganic composites. Numerous investigations based on micro/mesoporous materials as the nano-fillers for nanocomposites have been reported, however, the majority has been directed towards the improvement of petroleum-based polymers. Alvaro described the in-situ polymerization of ethyne within the channels of metal-exchanged zeolites.\textsuperscript{126} It was claimed that polymer could be found strictly within the channels of the zeolite, as confirmed by the reduced surface areas, when compared to the host, and microscopy images, which revealed no polymer on the particle’s surface. In addition, void volume calculations provided percentage fillings of the channels from 54\% to ~100\% depending on the zeolite. Wang also studied in-situ prepared polymer composites (based on polystyrene and polymethylmethacrylate), but within the channels of mesostructure MCM-41.\textsuperscript{127} The authors claim to have restricted the growth of polymer to be within the pores by using supercritical CO\textsubscript{2}. They detected the improvement of the Young’s modulus and yield strength, reduction of the elongation at break, and SEM images illustrated a smooth surface for the pure polymer while fibrils were featured for the
nanocomposite. Another investigation distinguished between the polymer (polypropylene) synthesized inside and outside the channels of MCM-41 by extracting or dissolving the outside polymer with a solvent. Thermogravimetric analysis of the “rinsed” composite revealed weight loss assigned to the polymer. From this, it was concluded that the polymer must be within the channels, since the wash/rinses should have removed the outside polymer. β-Cyclodextrin, which is larger than the channels of the MCM-41 presented in the publication, was used to further investigate the confinement effects of the mesostructure. The authors stated that β-Cyclodextrin could destroy the MCM-41’s incorporated catalyst through reaction with its OH’s groups. The resulting polymer composite exhibited a melting temperature (observed by DSC) different than the “rinsed” composite without cyclodextrin, attributed to the polymer chains growing out of the channels forming crystallites for the former material. Perez reported the in-situ preparation of a hybrid/composite material based on MCM-48 and poly(methyl methacrylate). To provide improved reinforcement of the organic phase, the authors established the importance of a dispersed phase and low concentration of agglomerations. Solvent casting techniques were used by Kim and Marand, to create nano-sized MCM-41 (80nm particle size) / polysulfone composites (mixed matrix membrane) and by Jin, who presented Nafion (sulfonated fluoropolymer-copolymer) / MCM-41 composites. Valsesia and co-workers presented a hybrid material based on mesoporous silica and PS or PMMA via in-situ polymerization. ¹H-²⁹Si NMR experiments were carried out, revealing the proximity of the polymer to the silica walls. However, the catalyst used for the polymerization was not supported onto the silica, but rather it was added separately to the reaction batch with the monomer and mesoporous silica.
This polymer composite did not exhibit a glass transition temperature, attributed to the forbidden combined motion of the polymer chains due to their confinement within the channels of the mesostructure. Rosenholm investigated targeting of cancer cells by labeled mesoporous silica. The mesostructure particles functionalized with poly(ethylene imine) by in-situ polymerization (PEI covalently attached) were labeled with a fluorescent compound. This hybrid material was further modified by the addition of the targeting-ligand.

Micro/mesoporous solids have also been used for organic/inorganic composites with novelty-biodegradable polymers, however, not as extensively as with petroleum-based polymers. Poly(D,L-Lactide) composites based on MCM-41 were prepared to investigate biological processes like calcium phosphate formation. The hybrid material was prepared through solvent casting techniques. Radu reported the use of PLLA coated MCM-41 composites with a fluorescence probe to detect amino-neurotransmitters. The MCM-41 was first functionalized with a thiol group replacing the hydroxyls, then an organo-silane group was grafted onto the surface and further reaction converted them to organol-hydroxy groups. The monomer/catalyst was introduced to the modified MCM-41, and the polymerization was carried out in-situ coating the outside surface of the MCM-41 with PLLA. This PLLA coating was used as a gate-keeping layer for probing molecules through the channels of the hybrid. Zhang investigated the properties of PLA nanocomposites prepared by mixing the PLA with fumed silica in a twin-screw extruder. The composites exhibited an increased glass transition temperature as compared to the pure PLA. Similar to Radu’s approach, Huang reported the preparation of composites based on modified mesoporous silica coated with a PLGA copolymer. The hybrids were used for studying
controlled drug release and drug targeting. The polymerization of lactones, γ-valerolactone and ε-caprolactone to create polymer nanocomposites have been described with the aid of aluminum-containing mesoporous MCM-41.\textsuperscript{143} Polymerizations were carried out with Al-MCM-41, the monomer, and an alcohol (protic chain transfer agent), no other catalyst was used. The authors claim to have generated polymer with average number molecular weights of 1200 and higher. Siliceous MCM-41 and aluminosilicate zeolites did not polymerize the monomers. Concluding from this literature review, a relatively fewer number of reports have targeted enhanced properties of polylactides through composite formation, differing from traditional polymer nanocomposites such as layered clays, a planar host, and the formation of inclusion compounds with small molecule hosts like cyclodextrins or urea.

\textbf{1.5 Experimental Methods}

\textbf{1.5.1 Gel Permeation Chromatography}

Averaged molecular weights presented later on in this investigation were obtained by gel permeation chromatography since this is a powerful and easy technique to use. GPC also known as size exclusion chromatography (SEC) is a type of high performance liquid chromatography (HPLC) that differs from other types by its column, which is able to separate polymer molecules by their size. The stationary phase of the GPC column typically consists of silica particles or polymer beads (5-10\textmu m in diameter) which form a network of pores into which solvent molecules (or the liquid mobile phase) can diffuse through. No chemical or physical interaction is involved between the analytes and the stationary phase of
the column; thus, every attempt is made to avoid these interactions since they lead to impaired column efficiencies. The retention time \( t_r \) of molecules depends on their size. Molecules that are larger than the average pore size of the column packing exhibit no retention; these molecules are the first to appear on the chromatogram (or first to be eluted). In contrast, molecules that are much smaller than the pores can diffuse throughout and be entrapped for the greatest time; hence, these are the last to be eluted. All other molecules in between the upper and lower limits again, depend on their size to penetrate into the pores and hence undergo separation or fractionation. The main parts of a GPC, similar to those of any liquid chromatography instrument are the solvent reservoirs regulated by a pump system, which then in turn carries the sample injected at the sample injection loop valve. This mobile phase then moves through the column or series of columns and then through the detector, as seen on Figure 1.34.\(^5\) A series of columns rather than just one is preferred because this makes the separation more efficient due to the increase in plate count \( N \), which is related to the plate height \( H \) and column length \( L \) by the following equation:

\[
N = \frac{L}{H} \quad (17)
\]

Some of the many different types of detectors employed are fluorescence, ultraviolet, infrared, and refractive index detectors. The GPC instrument used in this investigation has a refractive index detector. In this type of detector the solvent (reference) passes through one half of the cell and the sample through the other half. A glass plate is mounted between these cells at an angle and bending of the incident beam occurs if the two solutions differ in refractive index. This displacement of the beam causes a variation in the output signal,
which is in turn amplified and then recorded. Refractive index is a measurement of a medium’s interaction with light and is defined by:

\[ \eta_i = \frac{c}{v_i} \quad (18) \]

where \( \eta_i \) is the refractive index at a specified wavelength \( i \), \( v_i \) is the velocity of the light in the medium and \( c \) is its velocity in a vacuum.

**Figure 1.34** Scheme of a typical Gel Permeation Chromatography Instrument where (1) is the driving gas, (2) is the solvent valve, (3) is the injection valve loop, (4) is the filter, and (5) is the backpressure regulator.

The total volume \( (V_t) \) of the column is given by:

\[ V_t = V_g + V_i + V_0 \quad (19) \]

where \( V_g \) is the volume occupied by the solid matrix, \( V_i \) is the volume of solvent held in its pores, and \( V_0 \) is the free volume outside the particles. Intermediate size molecules transfer to some fraction \( K \) (distribution constant for the solute) of the solvent in the pores, thus the elution volume \( (V_e) \) for these retained molecules is given by:

\[ V_e = V_0 + KV_i \quad (20) \]
K=0 when the molecules are too large to enter the pores, hence $V_e = V_0$; K=1 for molecules that are considerably smaller than the pores, thus $V_e = V_0 + V_i$. The relationship between concentration and the constant K is obtained by rearranging equation 20 for K:

$$K = \frac{(V_e - V_0)}{V_i} = \frac{c_S}{c_M}$$  \hspace{1cm} (21)

where $c_S$ represents the molar concentration of the solute in the stationary phase and $c_M$ is the molar concentration in the mobile phase. Figure 1.35 depicts the relation between molecular weight and retention volume, $V_R$, which is given by the following equation:

$$V_R = t_R F$$  \hspace{1cm} (22)

where $t_R$ is the retention time and F is the volumetric flow rate. The molecular weight of species beyond which no retention occurs, labeled as A, is defined by the exclusion limit. In a similar way the permeation limit defines the molecular weights below the point of complete penetration of the pores by very small molecules, labeled as D. The separation occurs in the selective permeation region, where the molecules are labeled as B and C.
1.5.2 Differential Scanning Calorimetry

A couple of different instruments which are used to determine the $T_g$ are differential thermal analysis (DTA) and differential scanning calorimetry. DSC was used to determine the glass transition temperatures shown in this investigation. DSC is a thermal technique where differences in heat flow (energy) between the material and reference are observed as a function of the material’s temperature. A typical depiction of the heat cell of this instrument can be seen on Figure 1.36. The sample is placed in an aluminum pan and the reference is an empty pan. The thermoelectric disk, made of a copper and nickel alloy (constantan) and the Chromel (alloy of nickel and chromium) disk are both located below the pans. These
transfer the heat flow into both the sample and reference materials. The difference in heat flow of the sample and reference is determined by thermocouples in between the Chromel-constantan area. The heat flow difference is measured as the sample temperature is changed. Figure 1.37 depicts a typical DSC thermogram where the glass transition temperature, crystallization point, and melting point can be observed.\textsuperscript{5} With this type of analysis, as mentioned earlier, the $T_g$ will only display a change in heat capacitance, and the melting transition will have an energy value in cal/g corresponding to the $\Delta H_{\text{trans}}$.

**Figure 1.36** Typical diagram of a differential scanning calorimetry heat cell\textsuperscript{5}

**Figure 1.37** Example of a DSC thermogram (heat flow versus temperature) for a semi-crystalline material\textsuperscript{5}
1.5.3 Thermal Gravimetric Analysis

The decomposition of polymers into smaller molecules (or degradation temperature) is typically determined by thermal gravimetric analysis (TGA). TGA determines changes in the weight of the material as the temperature is varied. This instrument is not only helpful in obtaining the decomposition temperature of polymers but in addition, it can provide quantitative analysis of the composition of materials, oxidation of materials at different temperatures, loss of water, etc. An example of a TGA thermogram seen on Figure 1.38 shows the weight loss for two samples as the temperature increases. Not all materials show a weight loss, some can gain weight by reacting with the atmosphere. This instrument consists of a high precision balance which holds the sample pan (e.g. platinum or aluminum) (see Figure 1.39). The balance is covered by a heated oven or furnace with a thermocouple to detect the exact temperature. An inert gas is used to purge the system when oxidation or other reactions might be a problem. The temperature is gradually increased and the results are plotted in a temperature versus mass or percent weight change curve as seen on Figure 1.38.
Figure 1.38 Thermal gravimetric analysis curve (thermogram) for Poly(methyl methacrylate) (—) and Poly(vinyl chloride) (---)\textsuperscript{5}

Figure 1.39 Illustration of a typical thermal gravimetric analysis instrument\textsuperscript{5}

1.5.4 X-Ray Powder Diffraction

X-ray powder diffraction (XRD) was also used to characterize the synthesized mesoporous materials presented here. XRD is a non-destructive diffraction technique used to extract the crystallographic structure, crystallite size, and physical properties of polycrystalline or powder solid materials. It is typically used to identify materials by
comparing their diffraction data with the International Centre for Diffraction Data database. X-rays are high frequency, high energy, short wavelength electromagnetic radiation. When an X-ray beam hits a solid sample the X-rays are diffracted through the inspected matter by an angle $2\theta$, producing a deflection spot in the diffraction pattern (Figure 1.40). The angle $2\theta$ is the angle between the beam axis and the plane of the material. The diffracted rays are added constructively in a few specific directions, this has to satisfy Bragg’s law:

$$2d \sin\theta = n\lambda \quad (23)$$

where $d$ is the spacing between the diffracting planes, $\theta$ is the incident angle, $n$ is any integer, and $\lambda$ is the wavelength of the beam. These specific directions appear as spots on the diffraction pattern. The XRD data is typically plotted with intensity as a function of scattering angle, known as a diffractogram.

Figure 1.40 Scheme depicting the diffraction of an X-ray beam by a solid sample
1.5.5 Nuclear Magnetic Resonance

NMR is a non-destructive and non-invasive spectroscopic technique. The Stern-Gerlach experiment (1921) led to the spin angular momentum discovery. Spin angular momentum or simply “spin” is an intrinsic property of a particle, instead of the result of motion by a particle, like angular momentum. Particles like electrons, protons, and neutrons posses spin. Most atomic nuclei also posses spin, denoted as I, however, their net spin is given by the combination of the neutrons and protons spins. Spin, is proportional to the magnetic moment (\(\mu\)) of a species as described by:

\[
\hat{\mu} = \gamma \hat{I} \quad (24)
\]

where \(\gamma\) is the magnetogyric ratio. The magnetogyric ratio is specific to each nucleus with both positive and negative values possible. When the \(\gamma\) is positive, spins are parallel to the magnetic moment of the nucleus, and when it is negative spins are antiparallel to the magnetic moment. When a magnetic field, \(B_0\), is applied the spins begin to move around the field as on a cone. This is called precession and it continues at a constant angle with respect to the field (Figure 1.41).

This precession is possible because in addition to magnetic moment, spins posses angular momentum. The frequency of precession (\(\omega\)) in radians per second is given by:

\[
\omega = - \gamma B_0 \quad (25)
\]

The precession angle of the spins about the magnetic field can change and “wander” around different precession cones. This is brought about by the interaction of microscopic fields such as the magnetic fields of other nuclei and electrons and the rapid movements of molecules. Eventually, this leads to an anisotropic distribution of spins polarizations, in
other words the spins find an energy minimum (thermal equilibrium). This equilibrium means that the entire sample acquires a small net magnetic moment along the field. The re-establishment of thermal equilibrium is determined by the spin-lattice relaxation or longitudinal relaxation ($T_1$).

**Figure 1.41** Depiction of a precessing spin along the magnetic field

The energy of the spin in a magnetic field is given by:

$$E = -\hat{\mu} \times B_0$$  \hspace{1cm} (26)

Substituting the definition $\hat{\mu}$ (equation 24) onto equation 26 gives:

$$E = \gamma \hat{I}_z \times B_0$$  \hspace{1cm} (27)

where $\hat{I}_z$ corresponds to the z axis component of this operator and it is given by:

$$\hat{I}_z = \hbar m_I$$  \hspace{1cm} (28)

where $\hbar$ is Planck’s constant divided by $2\pi$, and $m_I$ is the quantum number of the state of the spin. For example, in the case of a sample containing only one magnetic nucleus, proton, the spin, $I_z = \hbar / 2$, will give quantum number $m_I = \pm \frac{1}{2}$, thus, two energy levels are generated (Figure 1.42). The $m_I = + \frac{1}{2}$ is referred to as $\alpha$ state (lower in energy) and $m_I = - \frac{1}{2}$ is
known as the $\beta$ state (higher in energy). The change in energy or energy of transition between these two quantum states is given by:

$$\Delta E = -\gamma \cdot \hbar \cdot B_0 \cdot \Delta m_I \quad (29)$$

Energy transition selection rules limit the value of $\Delta m_I$ to +1 or -1 for $I_z$ greater than $\frac{1}{2}$. Equation 29 would then be:

$$\Delta E = \pm \gamma \cdot \hbar \cdot B_0 \quad (30)$$

or

$$\Delta E = -\gamma \cdot \hbar \cdot B_0 \quad (31)$$

For positive values of the magnetogyric ratio, equation 30 would be for the absorption of energy between states and equation 31 for the emission of energy. And vice versa for negative values of $\gamma$.

**Figure 1.42** Diagram of energy levels for spin $I_z = \hbar/2$ in a magnetic field

The energy states of the spins within the nuclei are unequally populated. Their spin population is given by the Boltzmann distribution. In the case of the proton with states $\beta$ and $\alpha$, at $T=298K$ and $\omega=900MHz$, the Boltzmann equation gives a population of:

$$\frac{N_\beta}{N_\alpha} = e^{-\Delta E/kT} = 0.999855 \quad (32)$$
where \( N_x \) is the population of the corresponding states and \( k \) is the Boltzmann constant. The proton spin population has roughly no difference at equilibrium. However, a detectible bulk magnetization, \( M_B \), is generated by this slight population difference (Figure 1.43). NMR, then, examines the effects of the bulk magnetization by resonance methods, unlike other forms of spectroscopy (e.g. infrared or visible) which monitor the direct emission or absorption of a photon related with the transition. \( M_B \), which is the sum of all the spin magnetizations, at equilibrium it is aligned with \( B_0 \) field, positive \( z \)-axis.

The net magnetization is altered by a second magnetic field, \( B_1 \), (or radiofrequency pulse) and detected. The signal is then processed by Fourier Transform (FT) to yield a spectrum. Current from a coil surrounding the sample and perpendicular to the \( B_0 \) field induces the applied \( B_1 \) field; this same coil can also receive the signal. Through this method frequencies over a given range may be excited and detected at the same time. A short pulse (short period of time) of a specific radiofrequency stimulates a large range of frequencies, resulting in a broad frequency spectrum after the FT. On the contrary, a long pulse of radiofrequencies stimulates a small range of frequencies. The bandwidth of excited
frequencies is inversely proportional to the pulse durations (time) due to the uncertainty principle:

$$\Delta E \cdot \Delta t \geq \frac{\hbar}{2} \quad (33)$$

During the pulse period the bulk magnetization is rotated as in the absence of $B_0$. For example, if $B_1$ is applied along the $x$-axis for a specific amount of time, the $M_B$ could be rotated $90^\circ$ into the $x$-$y$ plane, along the $-x$ axis (Figure 1.44). This rotated $M_B$ will begin to precess along the $B_0$ field like the individual spins. The precessing $M_B$ induces an oscillating current in the coil, which then detects the signal. This signal is called the free induction decay (FID). This time dependent signal is mathematically transformed through FT, extracting the excited frequencies.

![Figure 1.44](Image)

**Figure 1.44** Depiction of the bulk magnetization rotating into the $x$-$y$ plane as a $B_1$ field is applied.

The vector model used up to now has demonstrated that the magnetization induced by the $B_0$ field precesses at a constant frequency, $\omega$, given by equation 25. However, this also restrains the $x$-$y$ plane precession of the rotated $M_B$ to a constant frequency. This point of view is known as the laboratory frame of reference. Another useful way of viewing this is to monitor the precession from the central’s resonance point of view, known as the rotating frame of reference. In the rotating frame the $x$-$y$ axes precesses at the same frequency as the
central frequency of the pulse, the Larmor frequency, \( \omega_1 \) (Zeeman interaction). When the bulk magnetization is on resonance (it is precessing at the same frequency as the x-y axes), it will remain at its position in x-y plane. If the \( M_B \) is off-resonance, then it will precess at:

\[
\omega_{RF} = \omega_1 - \omega_M \tag{34}
\]

where \( \omega_{RF} \) is the precession frequency of \( M_B \) in the rotating frame and \( \omega_M \) is the precession for \( M_B \) in the laboratory frame.

### 1.5.5.1 Internal Interactions

Spins experience both internal and external interactions. Our discussion up to now has been about external interactions originating from the external applied magnetic field. Internal interactions originate from inside the sample (neighboring spins, electrons, etc.). These interactions are quadrupolar coupling, dipole-dipole coupling, scalar coupling, and chemical shift. Quadrupolar coupling represent the electric interactions of the nuclear spins > \( \frac{1}{2} \) with the surrounding electric fields generated by the electron density. This interaction is very strong (second in magnitude to the Zeeman interaction) for most environments, except for highly spherical ones, which average the interaction to zero. The majority of the nuclei in this research are spin \( \frac{1}{2} \).

Direct dipole-dipole coupling is the magnetic interaction through space of a nuclear spin with another. Spins actually interact with the generated magnetic field around the neighboring spin. The magnitude of this interaction is calculated by the secular dipolar Hamiltonian:
\[ \hat{H}_{\text{dd}} = \left( -\frac{\gamma_1 \gamma_2 \hbar \mu_0}{4\pi r^3} \right) (3\cos^2 \theta - 1) \left( \hat{I}_{1z} \hat{I}_{2z} - \frac{1}{4} (\hat{I}_{1-} \hat{I}_{2+} + \hat{I}_{1+} \hat{I}_{2-}) \right) \] (35)

where the subscripts 1 and 2 represent the two nuclei, \( \mu_0 \) is the permeability of free space, \( r \) is the distance between the two spins, \( \theta \) refers to the angle between the line connecting the two spins and the magnetic field, the \( \hat{I}_z \) terms represent the z components of the respective spin, and \( \hat{I}_+ \) and \( \hat{I}_- \) are the step up and step down ladder operators from quantum mechanics. For the homonuclear case, the \( \hat{I}_+ \) and \( \hat{I}_- \) operators give rise to spin diffusion, where the local spins simultaneously flip from high energy to low energy, maintaining the same Boltzmann distribution, and preserving the energy of the system. However, in the heteronuclear case, these spin flips are not equal in energy, since they possess differing magnetogyric ratios. The secular dipolar Hamiltonian on equation 25 is then reduced with the elimination of the energy conserving term.

For both the heteronuclear and homonuclear cases the Hamiltonian possesses the \( 3\cos^2 \theta - 1 \) term. In liquids, due to the rapid tumbling motion of molecules, this term averages to zero. In solids, manipulation of the sample to spin rapidly (simulating tumbling from liquids) at 54.74° causes the term to go to zero. Magic Angle Spinning NMR (MAS NMR) is the technique for performing NMR experiments under these conditions. Also, radiofrequency irradiation applied to the coupled nuclei induces rapid flipping, and can be used to average out the interaction. However, not all dipole-dipole interactions for solids are eliminated, which can lead to broadening of the solid’s NMR spectrum, especially for high density spins.
Scalar or J-coupling is the indirect magnetic interaction of nuclear spins through the bonding electrons. J-coupling occurs through linked chemical bonds, propagating only through a small number of bonds. They produce splitting of the NMR spectrum however this is typically only observed for liquids, since solids exhibit broad line widths masking these fine structures.

Chemical shift is the interaction of the nuclear spins through electrons with the \( B_0 \) field. When placed in a magnetic field, a current is induced in the electron cloud. The circulating current gives rise to a magnetic field (induced field, \( B_{\text{ind}} \)). The spins “feel” the sum of the \( B_{\text{ind}} \) and the applied \( B_0 \) fields:

\[
B_{\text{loc}} = B_0 + B_{\text{ind}} \quad (36)
\]

When substituting the definition of \( B_{\text{loc}} \) onto the frequency of precession definition (equation 25), we obtain:

\[
\omega = -\gamma B_{\text{loc}} = -\gamma (B_0 + B_{\text{ind}}) \quad (37)
\]

The applied external field is related to the \( B_{\text{loc}} \) by the following equation:

\[
B_{\text{ind}} = \delta \times B_0 \quad (38)
\]

where \( \delta \) is the chemical shift tensor of the spin, corresponding to the magnitude of the induced field in a given direction when a magnetic field is applied in a specific direction. The secular approximation eliminates all possible \( \delta \) components, except for \( \delta_{zz} \) (the induced field component in the z direction when a magnetic field is applied along z.) The rapid tumbling motion of an isotropic liquid causes the \( \delta_{zz} \) to be replaced by a new term, \( \delta_{\text{iso}} \):

\[
\delta_{\text{iso}} = \frac{\delta_{xx} + \delta_{yy} + \delta_{zz}}{3} \quad (39)
\]
which in turn causes the Larmor frequency to become:

\[ \omega = -\gamma (B_0 + B_{\text{ind}}) = -\gamma B_0 (1 + \delta_{\text{iso}}) \]  \hspace{1cm} (40)

Nuclei in different environments would possess their own \( \delta_{\text{iso}} \) value, resulting in slightly shifted Larmor frequencies. In solids, there is usually no isotropic tumbling, so the chemical shift does not reach an average value. The sample retains its orientation dependence, known as the chemical shift anisotropy (CSA). For a powder sample, all different orientations are observed at the same time. The sum of all of these causes a broadening of the spectrum, referred to as powder pattern. MAS NMR can eliminate the effects of CSA, which possesses an angular dependence of \( 3\cos^2\theta - 1 \), by spinning rapidly at 54.74°. Similar to dipolar coupling, not all of the CSA can be removed. This results in spinning side bands with residual signal, at the distances of integer multiples of the spinning speed away from the isotropic peak.

**1.5.5.2 NMR Experiments**

A variety of NMR experiments were used for characterizing the materials presented here. The simplest pulse sequence employed was the 90°, or \( \pi/2 \), pulse experiment with and without decoupling depending on the nuclei under study. Figure 1.45 displays this simple one 90° pulse. Here, the square displayed on the acquiring nuclei channel represents the pulse, the period during which the radiofrequency is applied; and the section after the pulse represents the acquisition period, were the oscillating signal from the sample is detected. This pulse sequence was used for \( ^1\text{H} \), \( ^{29}\text{Si} \), and \( ^{119}\text{Sn} \) experiments without decoupling and for \( ^{13}\text{C} \) experiments with \( ^1\text{H} \) decoupling. A similar one pulse sequence was used for \( ^{27}\text{Al} \).
Low natural abundance spins like $^{13}$C exhibit low sensitivity in NMR, as well as long $T_1$ relaxation times, which in turns increases the delay between subsequent NMR pulses. The cross polarization (CP) experiment provides a solution for these types of nuclei. This experiment consists of a polarization transfer from an abundant, high magnetogyric ratio spin, such as $^1$H, to a dilute spin; were the dilute spin gains sensitivity and has pulse delays corresponding to the faster relaxing abundant spin. This polarization transfer between different magnetogyric ratio spins is possible in the rotating frame, were the precession frequencies are adjusted by:

$$\omega_0 = \gamma B_1$$  \hspace{1cm} (41)

The condition for the CP experiment, known as the Hartmann-Hahn match, is given by:

$$\omega_{0,\text{spin A}} = \omega_{0,\text{spin B}}$$  \hspace{1cm} (42)

Substituting the Larmor frequency definition given in equation 26 on to equation 27 gives:

$$\gamma_{\text{spin A}} * B_{1,\text{spin A}} = \gamma_{\text{spin B}} * B_{1,\text{spin B}}$$  \hspace{1cm} (43)

The $\gamma$ for each nucleus is fixed, so the $B_1$ strengths must be adjusted to satisfy the CP condition. Here, the CP experiment was conducted on $^{13}$C nuclei with the nearby abundant $^1$H nuclei. The CP pulse sequence consisted of a 90° pulse on the $^1$H spin; followed by a
contact pulse or irradiation time on both the $^{13}$C and $^1$H spins, where the power levels are determined by the CP match condition. After the contact time, the $^{13}$C signal was acquired, while the $^1$H spin was decoupled (see Figure 1.46). The CP techniques is very useful, however, some limitations to the CP technique are that the samples must be spun slowly (e.g. 2 – 4 KHz) which increases the spinning sidebands, because of the \((3\cos^2\theta-1)\) angular dependence of the chemical shift anisotropy. Also, the CP transfer efficiency decreases with increasing distance between the nuclei, since dipolar coupling scales as the inverse of the distance between the nuclei cubed. In addition, nuclei which are not near an abundant spin, might lose their signals completely.

![Figure 1.46 $^1$H-$^{13}$C cross polarization (CP) pulse sequence](image)

Similar to the CP pulse sequence is another NMR technique, the $^1$H-$T_{1\rho}$ experiment. $T_{1\rho}$ is the longitudinal relaxation in the rotating frame. The experiment measures the $T_1$ while maintaining the magnetization fixed with a spin lock pulse in the rotating frame, then, the poor / broad magnetization from the proton due to homonuclear dipole coupling is transferred to the high resolution carbon nuclei. The $T_{1\rho}$ differs from the $T_1$ values for all but the shortest correlation times. This experiment consists of a 90° pulse on the $^1$H nuclei, followed by a varied spin lock time, after this, the magnetization is transferred to the $^{13}$C
nuclei through the contact pulse, and the signal is acquired on the $^{13}$C channel, while decoupling for proton. **Figure 1.47** displays the $^1$H-$T_{1p}$ pulse sequence. The varied spin lock values are plotted against the determined intensities for the proton nuclei and are fitted to the following exponential decay equation:

$$I(t) = I(0) \times \exp(-t/T) \quad (44)$$

where $t$ is the spin lock period time, $I(t)$ is the intensity at the spin lock period, and $T$ is the longitudinal relaxation value.

**Figure 1.47** $^1$H $T_{1p}$ pulse sequence

The $^1$H - $^{27}$Al TRAPDOR experiment is useful for determining if a detected nucleus is in close proximity to another nucleus. This NMR method takes advantage of the heteronuclear dipolar coupling (~5Å) between the proton and aluminum atoms, allowing for the suppression of the $^1$H signal with a series of aluminum pulses. The larger the coupling between the two nuclei the larger the reduction of the signal will be as compared to the experiment performed without aluminum irradiation. **Figure 1.48** illustrates the $^1$H - $^{27}$Al TRAPDOR pulse sequence with aluminum pulses; where a 90° pulse is applied to $^1$H nuclei, followed by the $\tau$ period, where the $^{27}$Al nuclei are irradiated; then a 180° pulse is applied to
$^1\text{H}$, followed by another $\tau$ period; and then the $^1\text{H}$ signal is acquired. To examine the extent of the reduction of the $^1\text{H}$ signal another experiment is performed without the aluminum pulses, which should have no effect on the proton signal.

![Diagram of TRAPDOR pulse sequence with aluminum pulses](image)

**Figure 1.48 $^1\text{H} - ^{27}\text{Al}$ TRAPDOR pulse sequence with aluminum pulses**

### 1.5.6 Gas Chromatography – Micro-Reactor System

Catalytic studies were performed on a GC micro-reactor system. **Figure 1.49** illustrates this setup. The system is mainly composed of a feed (test gas), which is injected into the line; it will pass through the reactor, which contains the solid catalyst under flowing helium (He); this is surrounded by a furnace, controlled by a temperature control box; and the GC is used to analyze the products of the reaction. Some of the parts illustrated in the diagram and not mentioned above, were not used or simply bypassed for the purposes of our study. Prior to any experiments, each sample was dried overnight inside the reactor at 450 °C under flowing He. The carrier flow gas was maintained at 10 sccm (standard cm$^3$/min) for all runs. Collection times varied depending on the temperature. At 100 and 150 °C, the collection time was 24 seconds; at 450 and 500 °C, the collection time was 18 seconds. The ramp heat on the GC ranged from 40 to 180 °C at 3 °C/min, and a final hold at 180 °C for 12
min. Elution times were calibrated with a variety of gas mixtures; C1-C6 paraffins, C2-C6 olefins, and C4-C6 branched alkenes.

Figure 1.49 Diagram of the GC micro-reactor setup
1.6 Objectives

The main purpose of this research is to investigate and create new organic-inorganic composites based on biodegradable and biocompatible poly(d,l-lactide). Specific emphasis was given to studying the polymer / surface interface of the polymer nanocomposite. From this, other interests surfaced: the comparison of aluminum-containing mesoporous materials prepared by different synthetic routes; the study of mesoporous materials as hosts; and the analysis of known ring opening polymerization catalysts supported onto mesoporous hosts.

To achieve these goals a combination of multiple techniques were employed. Solid-state Magic Angle Spinning and liquid-state NMR characterized the chemical structure of the prepared materials, gave insight to which aluminosilicate mesoporous solid was a superior solid acid, and indicated that the important steps in the composite’s chemistry, for both the catalyst and polymer syntheses occur inside the channels of the hosts. Microscopy and X-ray powder diffraction results confirmed the uniform structure and overall appearance of the mesoporous hosts before / following catalyst and polymer preparation, while elemental analysis revealed chemical compositions. Nitrogen adsorptions surface area determinations and thermal gravimetric analysis provided bulk measurements for comparisons between the polymer composite and its hosts. Physical properties of the biopolymer composites were obtained by molecular weight and glass transition temperatures. To compare the aluminum-containing mesoporous materials, catalytic experiments using a GC micro-reactor systems, were performed. The combination of these techniques provides irrevocable evidence of the formation of an organic-inorganic composite.
Chapter 2: Comparative Study of Synthesis Routes for Aluminum-Containing Mesoporous Materials

2.1 Introduction

Generating acidity in mesoporous materials, analogous to zeolites, requires, for example, the introduction of aluminum to the siliceous material. This creates solid acids, which are useful in a variety of catalytic applications. Direct incorporation and post-grafting are the typical methods used for obtaining mesoporous aluminosilicates. Here, we explore if these known procedures produce true solid acids and determine which specific route generates a superior catalytically active material. This was achieved through multiple experimental results from solid-state NMR, catalytic studies, and nitrogen adsorptions.

Since their discovery in 1992, ordered mesoporous molecular sieves have attracted much attention due to their excellent properties.\textsuperscript{54,55} Mesoporous materials are ordered porous solids with readily accessible, well defined, and highly ordered pores or channels (with sizes between 20 and 500 Å). In addition, they exhibit large surface areas and pore volumes. Two mesoporous solids of interest are MCM-41\textsuperscript{54,55} and SBA-15\textsuperscript{75,76}. Both of these materials, based on a SiO\textsubscript{2} framework, consist of a hexagonal honeycomb-like array. The pore sizes of MCM-41 range from 20 Å – 100 Å, while SBA-15’s pores range from 40 Å – 300 Å. In addition, the wall of SBA-15 is much thicker than in MCM-41 (~10 – 20 Å), with thicknesses between 20 to 60 Å, leading to a higher thermal and hydrothermal stability. These siliceous materials lack acidity which limits their usefulness in a variety of catalytic applications. Aluminum is typically substituted for silicon into the lattice creating a
Bronsted acid site as seen in Figure 2.1. However, the concentration of Brönsted acid sites in mesoporous materials is lower than in zeolites, which has been attributed to their amorphous pore walls.\textsuperscript{63-67}

The direct synthesis method for obtaining Al-MCM-41 has proved to be challenging. It has been reported that the incorporated aluminum is unstable upon mild thermal treatment, converting the aluminum to non-framework (de-alumination or increase of structural defects).\textsuperscript{68,69,145} In addition, the directly synthesized Al-MCM-41 exhibits moderate acidity, containing both Bronsted and Lewis acid sites.\textsuperscript{70} However, the post-grafting of aluminum onto MCM-41 produces a material with increased surface acidity and improved hydrothermal stability (decreased structural defects) as compared to the direct Al-MCM-41.\textsuperscript{71-73,146} In addition, controlled incorporations of aluminum to MCM-41 are possible.\textsuperscript{74} Al-SBA-15 has also been successfully prepared by post-synthetic methods\textsuperscript{82,147} and direct synthesis\textsuperscript{84}. However, the formation of metal oxides in the channels of Al-SBA-15 and structural disorder have been detected for the post-grafting method.\textsuperscript{80,81} While, the directly synthesized Al-SBA-15 maintained its structural order as compared to SBA-15,\textsuperscript{60} it exhibited higher catalytic activity to cumene than Al-MCM-41,\textsuperscript{83} and it incorporated a higher concentration of tetrahedral aluminum.\textsuperscript{148}

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure2.1.png}
\caption{Depiction of a “mesoporous material” Brönsted acid site}
\end{figure}
We note that extensive studies have been reported in the literature on the different synthetic methods for Al-MCM-41 and Al-SBA-15. However, questions still rise about these materials being true solid acids. Here, we present a comparison study between Al-MCM-41 with a pore size of 40Å synthesized by a post-grafting method and directly synthesized Al-SBA-15 with 80Å channels. These specific methods for preparing Al-MCM-41 and Al-SBA-15 were chosen because according to the literature they produced improved catalysts as compared to the materials synthesized through the opposite methods. Different techniques were performed to further understand and characterize these aluminum-containing mesoporous materials. In addition, these studies will give insight into the true structures (e.g. if tetrahedral aluminum is near an acidic proton) produced by each synthetic method.

2.2 Experimental

Materials. Cetyltrimethylammonium bromide >99% (CTMABr) was purchased from Amresco. Silicon (IV) oxide 99+%, 0.012micron (SiO$_2$) was purchased from Strem Chemicals. Aluminum isopropoxide 98+% was obtained from Alfa Aesar. Tetraethylorthosilicate 98% (TEOS) and Poly(ethylene glycol)-block-Poly(propylene glycol)-block-Poly(ethylene glycol) mw = 5800 g/mol (Pluronic P123) were purchased from Sigma-Aldrich. Amonnium Chloride (NH$_4$Cl), ACS certified was obtained from Fisher. Isobutane, >99% and 1-butene, >99% were purchased from Matheson Tri Gas. Hexane was obtained from Pharmco-AAPER.

Characterization. X-ray diffraction (XRD) patterns were obtained on a Bruker AXS D-8 Advanced X-ray powder diffractometer using copper K$_a$ radiation. Analysis was
completed using a search/match program and the PDF-2 database of the International Center for Diffraction Data. Specific surface area BET measurements were performed on a Quantachrome Nova 1200 Surface Area Analyzer. Microscopy images were obtained from Scanning Electron Microscopy (SEM) (FEI Quanta 600 ESEM) and Transmission Electron Microscopy (TEM) (JEOL JEM-2100) instruments. Magic angle spinning solid-state (MAS SSNMR) experiments were performed on a 300-MHz Bruker DSX-300. A 90° pulse was used for ¹H experiments. The ¹H-²⁷Al TRAPDOR NMR experiment consisted of 90° pulse on the proton channel followed by a τ period of 700 µs where the aluminum is irradiated, followed by a 180° pulse on the proton channel and a second τ period with aluminum irradiation. Prior to all proton experiments, samples were first dehydrated and then loaded into the rotors inside a glovebox to prevent exposure to moisture. Carbon bloch decay (¹³C) experiments were performed on all mesoporous materials to verify template removal by calcination; these consisted of a 90° pulse with a delay time of 20 seconds. A 90° pulse was used for silicon (²⁹Si) experiments with delay times of 20 seconds. Aluminum (²⁷Al) NMR spectra were obtained using a one pulse experiment with a pulse width of 0.60 µsec, power level of 0.60 dB, and a delay time of 300 msec. Catalytic experiments were conducted on a home built micro reactor system with GC FID detection (model HP-5890 GC FID with a Restek 50 meter, 0.53 mm ID Rt-Alumina column). A flow of 10sccm was maintained for the He carrier gas. Before analysis samples were dried inside the micro-reactor at 450 °C for >30 minutes.

**MCM-41.** MCM-41 was synthesized following the procedure described by Zhao.¹⁴⁹ 0.800 g of NaOH, 59.994 g of DI-water, 2.523 g of CTMABr, and 2.403 g of SiO₂ were
thoroughly mixed and aged in a Parr acid digestion bomb for three days at 100 °C. The material was filtered and washed with excess deionized water and calcined at 550 °C for ten hours using a 1 °C/min ramp. In addition to the $^{13}$C NMR results which revealed the absence of the template CTMABr, carbon elemental analysis resulted in <0.5% carbon by weight.

**Post-Synthesis of Al-MCM-41.** Al-MCM-41 was synthesized following the method described by Mokaya. Calcined MCM-41 was treated with aluminum isopropoxide (Al-isoo) in hexanes for 24 hours. The material was filtered and rinsed with hexanes and calcined at 550 ºC for 6-10 hours using a 1 °C/min ramp. Al-MCM-41 was prepared with five different Si/Al ratios (i.e. 5, 10, 15, 20, and 25), where the Si/Al=5 was utilized for most of the studies. NH$_4^+$ exchanged Al-MCM-41 was obtained by treating the calcined material with a 1 M solution of NH$_4$Cl in water for 12-15 hours. To revert back to the protonated material the exchanged material was calcined.

**SBA-15.** SBA-15 was synthesized following the procedure described by Vinu. An acidic solution of Pluronic P123 was stirred for 2 hours. TEOS was added to the Pluronic solution and stirred for 24 hours at 40 ºC. The molar gel composition was 1 TEOS : 0.016 P123 : 5.54 HCl : 190 H$_2$O. The resulting material was filtered and rinsed with excess deionized water and calcined at 550 ºC for 10 hours using a 1 °C/min ramp.

**Direct Synthesis of Al-SBA-15.** Al-SBA-15 was also synthesized following the method described by Vinu. The molar gel composition was 1 TEOS : 0.016 P123 : 0.2-0.1 Al$_2$O$_3$ : 0.46 HCl : 126 H$_2$O (Si/Al = 18). Similar to the SBA-15 synthesis, an acidic solution of Pluronic P123 was stirred for 2 hours. TEOS and Al-isoo were added to the Pluronic solution and stirred for 24 hours at 40 ºC. The material was filtered and rinsed with excess
deionized water and calcined at 550 °C for 6-10 hours using a 1 °C/min ramp. NH$_4^+$

exchanged Al-SBA-15 was obtained by the previously described method for Al-MCM-41.

2.3 Results and Discussion

The synthesized mesoporous materials were characterized by XRD, surface areas, and microscopy. XRD confirmed the crystalline structures of the as-synthesized mesoporous solids by the appearance of their characteristic reflections (Figure 2.2 and 2.3). Apart from the higher 2θ peak observed in MCM-41 (d=35 Å), post-grafted Al-MCM-41 (d=35 Å) maintained its crystalline structure as compared to its siliceous parent. The loss of this high 2θ reflection is possibly due to the multiple calcinations of the material which can reduce its crystallinity. Both SBA-15 (d=80 Å) and Al-SBA-15 (d=70 Å) exhibited higher d-spacing values than MCM-41 and Al-MCM-41. Note the 2θ angles for these materials are smaller than ones detected in the XRD patterns of MCM-41 and Al-MCM-41, not to be confused with the different XRD scales. This 2θ angle reduction is due to a larger space in between the crystal layers, as suggested by the d-spacing value, when compared to the other two materials. As synthesized, MCM-41 surface areas exceeded 1150 m$^2$/g while, a surface area of ~1000 m$^2$/g was obtained for the post-grafted Al-MCM-41. The slightly decreased surface area of Al-MCM-41 as compared to MCM-41 is explained by the incorporated aluminum which decreases the volume of the mesostructure. SBA-15 (~700 m$^2$/g) and Al-SBA-15 (425 m$^2$/g) exhibited lower surface areas than both MCM-41 and Al-MCM-41, with Al-SBA-15 possessing the lowest.
**Figure 2.2** XRD patterns for (a) is MCM-41 and (b) Al-MCM-41
Figure 2.3 XRD patterns for (a) SBA-15 and (b) Al-SBA-15

Microscopy images of the synthesized mesoporous materials revealed their general structure, morphology, and channel sizes (see Figures 2.4, 2.5, 2.6, and 2.7). 7µm-averaged sized particles with a mostly spherical morphology were observed for the MCM-41
structure. In addition, an ordered channel structure with pores of 40 Å in size was determined by TEM. SEM and TEM images confirmed that the structural ordering of MCM-41 was not affected by the aluminum incorporation. We note that two different views of direction are apparent in the TEM images of the mesoporous materials; the view of the long continuous channel structure and the view of the pore entrances. As synthesized SBA-15 exhibited a rod-like morphology where at times it appears like a long continuous bundle of thread. On average at the longest and shortest extremities of the SBA-15 particles, 1 µm and 0.5 µm sizes were determined, respectively. In addition, ordered 80 Å pores were observed on the TEM images of both SBA-15 and Al-SBA-15. Figure 2.7b at 100Kx magnification illustrates the well-known honeycomb-like pore structure of these mesoporous materials. Opposite to SBA-15, Al-SBA-15 exhibited an irregular (mostly spherical) morphology with particle sizes of ~1.5 µm. The morphologies of SBA-15 and Al-SBA-15 are extremely different. However, these materials are synthesized through a similar procedure with only a difference in pH value. The reported literature for SBA-15 has shown this material possesses a rod-like structure of approximately 1 µm in size. However, different Al-SBA-15’s morphologies have been reported varying with the synthesis method and aluminum source. Rod-like, irregular, and spherical structures have been observed for directly synthesized Al-SBA-15. With aluminum isopropoxide as the aluminum source, irregular (mostly spherical) particles have been determined. The results presented here are then similar to the reported literature. In addition, the particle sizes of SBA-15 and Al-SBA-15 are considerably smaller than the MCM-41 and Al-MCM-41 particles, in accordance with the reported literature.
Figure 2.4 SEM images of (a) MCM-41 and (b) Al-MCM-41
**Figure 2.5** SEM images of (a) SBA-15 and (b) Al-SBA-15
Figure 2.6 TEM images of (a) MCM-41 and (b) Al-MCM-41
Figure 2.7 TEM images of (a) SBA-15 and (b) Al-SBA-15
2.3.1 NMR Analysis

**Figure 2.8** Different types of silicon in mesoporous materials: (a) Q$^2$, (b) Q$^3$, and (c) Q$^4$.

$^{29}$Si (59MHz), $^{27}$Al (78MHz), and $^1$H (300MHz) NMR experiments were performed on the mesoporous structures of interest. **Figure 2.9** displays the $^{29}$Si NMR stack-plot of MCM-41, SBA-15, and their corresponding aluminum-containing analogues. The three typical silicon signals at -92, -101, and -110 ppm corresponding to the Q$^2$ (two siloxane bonds and two silanol groups), Q$^3$ (three siloxane bonds and one silanol group), and Q$^4$ (four siloxane bonds) silicons, respectively were detected for all of the mesoporous materials (see **Figure 2.8** for silicon structures).\textsuperscript{124,156} “A loss of resolution can be observed for the Q$^2$ and Q$^3$ silicon signals of **Figures 2.9 b and c** (Al-MCM-41 and Al-SBA-15, respectively) when compared to their siliceous parents. In addition, Al-MCM-41 exhibits a higher loss of resolution when compared to Al-SBA-15. This might be due to aluminum's incorporation reducing the quantity of surface hydroxyl groups. The post-grafting method used to prepare Al-MCM-41 typically incorporates the aluminum through the surface hydroxyls, eliminating water. The reduction of surface hydroxyls increases the silicon atoms with no silanol groups attached to it, or Q$^4$ silicons.”
A single signal at 2.1 ppm was apparent in the $^1$H NMR spectrum of MCM-41 and SBA-15 (Figure 2.10). This signal is assigned to the protons from the surface hydroxyl groups (also known as silanols). We note that the SBA-15 $^1$H spectrum also displays a signal centered at ~6.5 ppm. This signal arises from residual water not removed by the dehydration procedure prior to acquiring the spectrum. The silanol proton signal was also detected for the aluminum-containing counter-parts, as expected. In addition, a small signal or hump centered at ~4.0 and 4.2 ppm for Al-MCM-41 and Al-SBA-15, respectively, was identified. This type of signal, typically observed in an enhanced form in zeolites, is assigned to the acid proton in the Brönsted acid site.$^{157}$ As stated earlier, aluminum-containing mesoporous materials have lower concentrations of Brönsted acid sites when compared to zeolites. Hence, the reduced 4.0 and 4.2 ppm signals could be assigned to the Brönsted acid. Note that the Al-SBA-15 signal is slightly more prominent than the detected signal for Al-MCM-
41, suggesting the former material contains a higher concentration of Brönsted acid sites. To confirm that these protons are in close proximity to an aluminum atom, a $^1$H-$^{27}$Al TRAPDOR NMR experiment was performed on Al-MCM-41 and Al-SBA-15. The $^1$H-$^{27}$Al TRAPDOR experiment allows us to suppress signal from proton atoms in close proximity to an aluminum atom by irradiating the aluminum during the $\tau$ periods. This stimulates proton relaxation, where the longer the $\tau$ periods, the greater the relaxation. Figure 2.11 and 2.12 illustrate the results from the TRAPDOR experiment for both aluminosilicate materials, with a $\tau$ period of 700 $\mu$sec and an irradiation pulse power level (pL2) of 120 dB and -1.0 dB. When pL2 is set to 120 dB the irradiation pulse is turned off. By taking the difference between these two experiments we can determine any proton signal that is affected by a neighboring aluminum. A small signal, at a similar frequency to the one detected on the previously discussed $^1$H plot, is apparent on the difference spectrum of Al-MCM-41. However, the difference for Al-SBA-15 is much larger than the detected signal for Al-MCM-41, in accordance with the previous $^1$H NMR data. The detection of signals for both catalysts suggests that these protons are probably in close proximity to an aluminum atom, and possibly are a Brönsted acid. In addition, the slightly larger acidic signal detected for Al-SBA-15 suggests that this material contains a higher acidity than Al-MCM-41.
Figure 2.10 $^1$H NMR spectra of (a) MCM-41, (b) Al-MCM-41, Si/Al=5, (c) SBA-15, and (d) Al-SBA-15, Si/Al=18. In (c): * denotes residual H$_2$O.

Figure 2.11 $^1$H-$^{27}$Al TRAPDOR NMR stack-plot of Al-MCM-41 (Si/Al=5) with a $\tau$ period of 700 $\mu$sec: (a) no aluminum irradiation, (b) with aluminum pulse of -1.0 dB, and (c) is the difference spectrum of figures a and b
Figure 2.12 $^{1}H^{27}Al$ TRAPDOR NMR stack-plot of Al-SBA-15 (Si/Al=18) with a $\tau$ period of 700 $\mu$sec: (a) no aluminum irradiation, (b) with aluminum pulse of -1.0 dB, and (c) is the difference spectrum of figures a and b

Figure 2.13 $^{1}H$ NMR of (a) Al-MCM-41 and NH$_4^+$ exchanged Al-MCM-41 (b) before calcination and (c) after calcination
To further verify these results, NH$_4^+$-exchanged Al-MCM-41 and Al-SBA-15 were analyzed by $^1$H NMR before and after calcination. The NH$_4^+$ exchanges with the acid proton at the Bronsted acid site, replacing/remove any cations present after the initial calcination. Subsequent calcination of this exchanged material causes the NH$_4^+$ to decompose to ammonia (NH$_3$), which is carried out by the flowing air, regenerating the acid site. The proton acid signal should then be more prominent if there are non acidic cations present after the initial calcination. **Figure 2.13** and **2.14** display the $^1$H spectra before and after calcination for Al-MCM-41 and Al-SBA-15. A slightly larger signal at 4.2 ppm can be observed for the NH$_4^+$ exchanged calcined Al-SBA-15 when compared to the spectrum of the initially calcined material. The NH$_4^+$ exchange procedure enhanced the acidic site of Al-SBA-15 as observed in the $^1$H NMR spectra, indicating that this material might not have been in the acidic form prior to exchange. However, this type of enhancement was not observed in the $^1$H NMR spectra of NH$_4^+$ exchanged calcined Al-MCM-41. Instead, a slight decrease in

**Figure 2.14** $^1$H NMR of (a) Al-SBA-15 and NH$_4^+$-exchanged Al-SBA-15 (b) before calcination and (c) after calcination
the acid signal at 4.0 ppm was apparent when compared to the spectrum of the initially calcined material, suggesting that Al-MCM-41 was in the acidic form prior to exchange.

The two aluminum structures for mesoporous materials are tetrahedral, typically assigned to the Brönsted acid site aluminum, and octahedral, assigned to extra-framework aluminum. $^{27}$Al NMR analysis of Al-MCM-41 revealed a slightly higher content of tetrahedral aluminum as determined by the larger signal at 55 ppm than octahedral aluminum (0 ppm) (Figure 2.15). These two signals were also detected for Al-SBA-15. However, a greater difference was apparent between the tetrahedral and octahedral coordinated aluminum, suggesting a higher concentration of Bronsted acid sites are present in Al-SBA-15 as compared to Al-MCM-41. This is in accordance with the $^1$H NMR results.

Figure 2.15 $^{27}$Al NMR spectra of (a) Al-MCM-41 (Si/Al=5) and (b) Al-SBA-15 (Si/Al=18)
2.3.2 Catalytic Studies

Catalytic experiments were conducted on a GC-micro reactor system to compare the activity of post-grafted Al-MCM-41 and directly synthesized Al-SBA-15 to isobutane and butene. Isobutane is typically used as a test gas for catalytic conversions of zeolites, while, cumene is used for mesoporous materials because of their lower acidity. Although the mesostructures under study contain a much lower concentration of Bronsted acid sites as compared to zeolites, isobutane was chosen as one of our test gases because it was already available to us and nevertheless, there should be sufficient conversion to compare the activity of the materials. SiO$_2$ (100 mesh) and SBA-15, containing no acidity were used as control experiments. Table 2.1 displays percent conversions of the different mesoporous solids at 450 and 500 °C for isobutane and 100 and 150 °C for butene. Isobutane percent conversions for zeolite H-ZSM-5 are also displayed in Table 2.1 as reference. Directly synthesized Al-SBA-15 exhibited the highest conversion for isobutane, approximately 6% at 500 °C. Post-grafted Al-MCM-41, Si/Al=5, displayed a 0.33% conversion at 500 °C. Previous results showed that this material contained a much lower concentration of tetrahedrally-coordinated aluminum as compared to Al-SBA-15 (Figure 2.13). While, Al-MCM-41 with a Si/Al ratio of 25 exhibited a more comparable concentration of tetrahedral aluminum to Al-SBA-15 (discussed in next section), even though, it contains a lower aluminum content as compared to Al-MCM-41 with a Si/Al of 5. Catalytic studies on Al-MCM-41, Si/Al=25, revealed a slightly higher percent conversion at 500 °C to its analogue with a Si/Al=5. Even with these values, both of these materials exhibited much lower conversions than Al-SBA-15. It can be concluded that directly synthesized Al-SBA-15 exhibits a larger concentration of active sites.
as compared to Al-MCM-41 Si/Al=5, which possesses larger aluminum content. This is possibly due to the much higher tetrahedral aluminum concentration of Al-SBA-15, even, when compared to Al-MCM-41 with a Si/Al=25, which exhibited larger amounts of tetrahedral aluminum as compared to the Si/Al=5 analogue. This is in accordance with the NMR results. In the reaction of 1-butene, similar results for both of the aluminosilicate mesoporous solids were observed. This could be expected as the conversion of butene requires much less acidic strength, while the conversion of isobutane requires it to be much higher.

**Table 2.1** Percent conversions of mesoporous materials to isobutane and butene

<table>
<thead>
<tr>
<th>Mesoporous Materials</th>
<th>Isobutane</th>
<th>450 °C</th>
<th>500 °C</th>
<th>100 °C</th>
<th>150 °C</th>
<th>Butene</th>
</tr>
</thead>
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<tr>
<td>SiO₂</td>
<td>0.00</td>
<td>0.09</td>
<td>4.63</td>
<td>4.63</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SBA-15</td>
<td>0.07</td>
<td>0.22</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-MCM-41 (Si/Al=5)</td>
<td>0.17</td>
<td>0.33</td>
<td>27.38</td>
<td>29.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-MCM-41 (Si/Al=25)</td>
<td>0.12</td>
<td>0.45</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-SBA-15 (Si/Al=18)</td>
<td>0.94</td>
<td>5.62</td>
<td>27.07</td>
<td>26.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H-ZSM-5 (Si/Al=12.5)</td>
<td>57</td>
<td>87</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**2.3.3 Grafting Quantification**

Al-MCM-41 was prepared with varied Si/Al ratios ranging from 5 to 25. NMR experiments were performed on these materials to first determine if the acid proton could be detected with lower aluminum contents, and to explore a correlation between the aluminum content and the general aluminum environment in the material. **Figure 2.16** displays the $^1$H spectra for these materials. As the aluminum content decreases with increased Si/Al ratio,
the acid proton centered at 3.9 ppm is less apparent. This is to be expected as this Brönsted acid site is already weak at the low Si/Al ratio of 5. $^1$H-$^{27}$Al TRAPDOR experiments performed on Al-MCM-41 with Si/Al ratios of 10 and 15 displayed no significant difference near the acid proton shift (Figures 2.17 and 2.18). In addition, Figure 2.19 illustrates the $^{27}$Al NMR plots for these materials. As the Si/Al ratio is increased, the octahedral aluminum signal decreases, and the tetrahedral aluminum signal becomes sharper. This implies that with the higher the Si/Al ratio, or lower aluminum content, a higher concentration of the incorporated aluminum will acquire a tetrahedral structure rather than an octahedral form, which typically increases the Brönsted acidity. This is to be expected as there are only a limited number of available silanol surface sites for aluminum to attach to and subsequent aluminum would be in a less well incorporated form (i.e. octahedral). However, $^1$H NMR plots of the higher Si/Al ratios of Al-MCM-41 did not display a detectable signal near the acid proton shift, suggesting the materials posses low Brönsted acidity.
Figure 2.16 $^1$H NMR plots of (a) MCM-41 and Al-MCM-41 with Si/Al ratios of (b) 5, (c) 10, (d) 15, (e) 20, and (f) 25

Figure 2.17 $^1$H-$^{27}$Al TRAPDOR NMR plots of Al-MCM-41, Si/Al=10 with a $\tau$ period of 700 $\mu$sec: (a) no aluminum irradiation, (b) with aluminum pulse of -1.0 dB, and (c) is the difference spectrum of figures a and b
Figure 2.18 $^1$H-$^{27}$Al TRAPDOR NMR plots of Al-MCM-41, Si/Al=15 with a $\tau$ period of 700 $\mu$sec: (a) no aluminum irradiation, (b) with aluminum pulse of -1.0 dB, and (c) is the difference spectrum of figures a and b.

Figure 2.19 $^{27}$Al NMR of Al-MCM-41 with Si/Al ratios of (a) 5, (b) 10, (c) 15, (d) 20, and (e) 25.
2.4 Conclusions

Post-grafted Al-MCM-41 and directly synthesized Al-SBA-15 were prepared, characterized, and their catalytic activity was compared. $^{27}$Al NMR experiments for Al-SBA-15 revealed a greater tetrahedral aluminum environment, which is typically assigned to the Brönsted acid site aluminum, than octahedrally coordinated aluminum, as compared to the post-grafted Al-MCM-41. In addition, the number of Brönsted acid sites was larger in Al-SBA-15 as detected by $^1$H NMR and further verified by the $^1$H-$^{27}$Al TRAPDOR NMR experiment. Higher percent conversions to isobutane were obtained for directly synthesized Al-SBA-15 as compared to post-grafted Al-MCM-41. We can conclude that the direct method produces a material (i.e. Al-SBA-15) with higher Brönsted acidity and catalytic activity towards isobutane as compared to the post-grafting of aluminum onto MCM-41.
Chapter 3: Synthesis and Characterization of Biopolymer Composites from the Inside Out, Part I

3.1 Introduction

Creating new hybrid materials that meet multiple constraints for performance in engineering, medical, and consumer applications while maintaining environmentally attractive waste disposal options requires novel synthesis routes. In this contribution, we demonstrate that known controlled architecture mesoporous hosts may be functionalized to produce an active catalyst for ring-opening polymerizations of biopolymer starting materials. Specifically, a Sn\(^{2+}\) catalyst is supported inside the channels of MCM-41\(^{54}\) or SBA-15\(^{75}\) to generate a spatially unique ring-opening catalyst for the conversion of d,l-lactide to poly(d,l)-lactide, also known as poly(d,l-lactic acid) (PDLLA). The resulting polymer forms inside the host channels, and ultimately is extruded out of the channels as the molecular weight increases. In this way, a biodegradable and biocompatible organic/inorganic nanocomposite is formed in-situ. However, as the polymer chain originates from inside the host channels, they cannot easily segregate from the inorganic component, thereby ensuring intimate contact. In order to demonstrate reproducible synthesis of the polymer originating from within the host, we present multiple experimental results from solid-state NMR, calorimetry, microscopy, nitrogen adsorption, x-ray diffraction, and wet chemical methods indicating that important steps in the chemistry, both for catalyst synthesis and d,l-lactide polymerization, occur inside the host channels versus outside on the crystallite surfaces.

Recent activity in the synthesis and preparation of organic-inorganic composites, or
nanocomposites as they are most often termed, has expanded the materials science field.\(^\text{121}\) Natural layered or pillared clays,\(^\text{103-105}\) carbon nanotubes,\(^\text{115-117}\) carbon and natural fibers\(^\text{118-120}\) have replaced more traditional materials and methods, like physical mixing of fumed silica\(^\text{141}\) or carbon black, as constituents that when placed in polymeric hosts at low volume or weight percents significantly modify the final physical or mechanical properties. Success in these areas depends significantly on the degree to which the inorganic component is homogeneously distributed in the polymeric matrix, and most commonly involves clays where exfoliation is the key step. In more recent work, synthetic micro- and meso-crystalline silicates and aluminosilicates, i.e. zeolitic and crystalline mesoporous MCM-41 materials, have garnered attention.\(^\text{158}\) The microcrystalline channels of zeolite materials, whose cross-sectional channel dimensions typically are less than 1 nm, can pose problems for materials synthesis since many polymers and even their respective monomers encounter diffusion barriers inside the crystalline void volume, although in a recent case, high pore loadings were achieved.\(^\text{126}\) Typically, approaches to date can be categorized as either physical mixing methods, where the polymer (at its final molecular weight) and inorganic reinforcing agent of choice are mixed together as a function of temperature or solvent, or by introducing the monomer and completing the polymerization in the presence of the inorganic reinforcing agent. The latter approach has been particularly successful for petroleum-based and olefin polymers.\(^\text{159-164}\)

Polymers generated from naturally produced monomers, e.g. polylactide, are biocompatible and biodegradable, and could have an increased impact in consumer materials or health field applications given a larger, more flexible range of physical properties. A
relatively fewer number of reports have targeted enhanced properties of polylactides through composite formation. Here, we discuss an in-situ approach using the d,l-lactide monomer and a modified MCM-41 or SBA-15 catalyst that supports the ring-opening Sn$^{2+}$ catalyst. In contrast to a previous report in which an acid functionalized ring-opening mechanism for polymerization of a valerolactone monomer was proposed, we find through additional experiments utilizing Al-functionalized MCM and SBA hosts that this does not occur for lactide monomers. The Sn complex (stannous octoate) must be incorporated into the mesoporous host for d,l-lactide polymerization to occur. Here we also demonstrate that a material formed by simple mixing of the inorganic matrix and the organic poly(d,l-lactide) polymer is not equivalent at the polymer/surface interface to the new material generated by the in-situ polymerization approach. In this contribution we discuss the details of host synthesis, active catalyst preparation, and polymerization of d,l-lactide with our supported catalyst approach to create the final biopolymer composite material, as well as subsequent molecular and physical characterization results for that composite with specific emphasis on polymer that is actually made within the interior of the mesoporous host.

3.2 Experimental

Materials. D,L-Lactide (97 %) was obtained from Alfa Aesar. Tin (II) 2-ethylhexanoate (Sn(Oct)$_2$) (95 %) and 1-dodecanol (98 %) were purchased from Sigma-Aldrich. All organic solvents were obtained from Pharmco-AAPER.

Characterization. Molecular weight ($M_w$) analyses were performed on a Series 1100 HP Size Exclusion Chromatography (SEC) instrument with a polystyrene (PS) column.
Glass transition temperatures $T_g$ were measured using a 5 degree/minute ramp on a Q2000 Thermal Analysis (TA) Differential Scanning Calorimetry (DSC) instrument. Elemental analysis of the final catalysts formulations was performed by Galbraith Laboratories using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). X-ray diffraction (XRD) patterns were obtained on a Bruker AXS D-8 Avance X-ray powder diffractometer using copper $K_a$ radiation. Analysis was completed using a search/match program and the PDF-2 database of the International Center for Diffraction Data. Specific surface area BET measurements were performed on a Quantachrome Nova 1200 Surface Area Analyzer using nitrogen adsorption. Thermal gravimetric analysis (TGA) was performed on a Shimadzu model 50 instrument. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) data were obtained using FEI Quanta 600 ESEM and JEOL JEM-2100 microscopes, respectively. Solid-state NMR experiments were performed on a Bruker DSX spectrometer operating at 7 Tesla, which corresponds to a $^1$H Larmor frequency of 300 MHz. Magic-angle sample spinning (MAS) speeds ranged from 4 to 10 kHz, depending upon the specific experiment. The $^1$H $T_{1p}$ experiments were carried out via indirect detection of the directly attached carbons using cross-polarization. Carbon Bloch decay ($^{13}$C single-pulse) experiments consisted of a 90° pulse with a delay time of 20 seconds. The $^1$H to $^{13}$C cross polarization (CP) pulse sequence consisted of a 3.7 ms 90° pulse on the proton channel followed by a 1-ms contact pulse for heteronuclear polarization transfer.

**Sn Supported Mesoporous Catalyst (Sn/MCM-41).** MCM-41 was synthesized following the procedure described by Zhao. For a typical synthesis, 0.800g of NaOH, 59.994g of deionized water, 2.523g of cetyltrimethylammonium bromide (CTAB), and
2.403g of SiO$_2$ were thoroughly mixed and aged in a Parr acid digestion bomb for three days at 100 °C. The material was filtered and washed with excess deionized water and calcined at 550 °C for ten hours using a 1 °C/min ramp. The supported catalyst was prepared by stirring stannous octoate (Sn(Oct)$_2$) with the calcined MCM-41 material at different Sn/Si ratios for three hours. Excess stannous octoate was filtered and the remaining material was rinsed with 2 L of hexanes and dried overnight. Throughout the remainder of the text, we denote each supported catalyst by the relative amounts of Sn and Si, e.g., Sn/MCM-41_2 indicates a catalyst with a calculated Sn/Si atom ratio of 2 based in the starting ingredient concentrations.

**Poly(D,L-Lactide)/Sn/MCM-41 Hybrids.** Pure poly(d,l-lactide) was synthesized following established methods.$^{13,20,25,167-169}$ The monomer was recrystallized with toluene and kept under vacuum. The monomer, catalyst, and dodecanol co-initiator were placed in a round bottom flask equipped with a stir bar, and the reaction was carried out for two hours at 175 °C in an oil bath. Excess monomer was removed by dichloromethane addition and precipitating in methanol. The molar composition was: 1 mol D,L-lactide to 7.11×10$^{-5}$ mol Sn(Oct)$_2$ to 3.87×10$^{-5}$ mol of 1-dodecanol. The organic-inorganic hybrid was obtained by stirring the monomer, Sn/MCM-41 supported catalyst, and 1-dodecanol for two hours at 175 °C. The molar gel composition was: 1 mol D,L-lactide to 7.11×10$^{-3}$ mol Sn(Oct)$_2$ to 3.87×10$^{-3}$ mol of 1-dodecanol. Washes of the hybrid material were obtained by rinsing with 15 to 30 mL of dichloromethane. A physical mixture of the Sn/MCM-41 catalyst and the pure PDLLA (control sample; $M_w = 50,000$) was prepared by stirring the two together in dichloromethane for two hours at room temperature. The resulting blend was dried overnight.
3.3 Results and Discussion

3.3.1 Mesoporous Host with Supported Sn Catalyst

As-synthesized MCM-41 exhibited the well-defined x-ray powder pattern previously reported, with four characteristic (including the 100) reflections between \(2 < 2\theta < 6\) and BET surface areas in excess of 1000 \(\text{m}^2/\text{g}\).\(^{54,149}\) Solid state \(^{29}\text{Si}\) MAS and \(^1\text{H}\) to \(^{29}\text{Si}\) CP/MAS NMR experiments revealed characteristic chemical shifts for Si atoms at -92, -101, and -110 ppm, corresponding to Si atoms in Q\(^2\), Q\(^3\), and Q\(^4\) lattice positions, respectively.\(^{124,156}\)

Figure 3.1a shows SEM images for the pure MCM-41 typical of the type used as a basis for further modification to make the final composite; average particle dimensions are ca. 5 \(\mu\text{m}\). While a majority of recent work has focused on making smaller particle dimensions, we favor the larger crystallites for this initial investigation since the interior volume to exterior surface area ratio is maximized. Incorporation of the Sn(Oct)_2 into the MCM-41 to create the supported ring-opening catalyst, followed by washing to remove excess Sn-catalyst, did not alter the SEM data as shown in Figure 3.1b. Indeed, TEM reveals that the one-dimensional crystalline channel structure of MCM-41 is preserved after the final Sn(Oct)_2/MCM-41 composite catalyst is made, as observed by comparing Figure 3.2b to 3.2a. The microscopy data indicates that the catalyst morphology and channel structure were not altered by preparation of the Sn(Oct)_2 modified catalyst. However, BET surface area measurements showed a decrease in surface area from >1000 \(\text{m}^2/\text{g}\) for the starting MCM-41 material to 400 \(\text{m}^2/\text{g}\) for the Sn/MCM-41 catalysts, independent of whether the initial Sn/Si atomic ratio in the synthesis mixture ranged from a value of 2 to 35.
Figure 3.1 SEM images of (a) pure MCM-41, and of (b) MCM-41 containing the supported Sn(Oct)$_2$ ring-opening catalyst, i.e., the Sn/MCM-41$_2$ sample.

Figure 3.2 TEM images of (a) pure MCM-41, and of (b) the Sn/MCM-41$_2$ catalyst.
We verified the Sn concentrations in several Sn/MCM-41 catalyst formulations via elemental analysis, as summarized in Table 3.1. The results indicate that the background level of Sn as an impurity in the synthesis of pure MCM-41 is very low, and as confirmed by control experiments, too low to effect any polymerization of the d,l-lactide monomer. Most importantly, one observes that varying the initial amount of Sn in the synthesis by over an order of magnitude (2 to 35 Sn/Si ratio) has relatively little effect on how much Sn survives with the MCM host following the synthesis and subsequent washings. Obviously, our initial Sn/Si compositions represent significant Sn excess. This is in agreement with the BET surface area measurements, indicating that the stable incorporation of Sn(Oct)₂ in MCM-41 reaches an upper limit. We obtained very similar results from elemental and surface area measurements in separate catalyst formulations, where MCM-41 and SBA-15 each contained framework Al atoms were used as the inorganic host material. While detailed experiments on the Al-containing MCM-41 and Al-containing SBA-15 materials are not the subject of this contribution, the fact that the presence of Al in the framework does not alter the amount of Sn(Oct)₂ that can be incorporated in the mesoporous host relative to purely siliceous hosts indicates that a charged host framework is not required to support the Sn(Oct)₂ (vide infra).

Table 3.1 Comparison of Sn concentrations in several initial synthesis mixtures to that in the final catalyst. The data in the column Sn/Si (exp) is from elemental analysis on the final washed catalyst.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Si (wt%)</th>
<th>Sn (wt%)</th>
<th>Sn/Si (calc.)</th>
<th>Sn/Si (exp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCM-41</td>
<td>28.4</td>
<td>&lt; 371 ppm</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sn/MCM-41_35.4</td>
<td>21.9</td>
<td>27.0</td>
<td>35.4</td>
<td>0.291</td>
</tr>
<tr>
<td>Sn/MCM-41_10.9</td>
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<td>16.4</td>
<td>10.9</td>
<td>0.143</td>
</tr>
<tr>
<td>Sn/MCM-41_2</td>
<td>26.7</td>
<td>19.6</td>
<td>2.0</td>
<td>0.173</td>
</tr>
<tr>
<td>washed PDLLA_Sn/MCM-41_35.4</td>
<td>17.6</td>
<td>19.3</td>
<td>0.291</td>
<td>0.259</td>
</tr>
</tbody>
</table>
**Figure 3.3** summarizes results from quantitative $^{13}$C Bloch decay single-pulse MAS NMR experiments. The spectrum of the pure Sn(Oct)$_2$ (a viscous liquid) is shown for reference in **3.3a**. Even with excessive washings using 1 to 2 L of solvent, a fixed amount of the Sn(Oct)$_2$ catalyst remains in the MCM-41 host, and the differential peak intensities and widths for similar carbons in the octanoate ligands indicates that the complex has adopted a constrained geometry, i.e. the Sn(Oct)$_2$ resides in a specific location in the channels of the MCM-41. This is particularly evident when comparing 3.3b, the supported but unwashed catalyst complex, with 3.3d or 3.3e. If the spectra for the catalyst complex are generated via cross-polarization from $^1$H’s in the ligand to $^{13}$C nuclei in the ligand, this requires an immobile, constrained catalyst in order for the requisite dipolar interactions to persist. The $^1$H to $^{13}$C CP/MAS data in **Figure 3.4** shows that indeed the octanoate ligands in the washed Sn/MCM-41 catalyst meet this requirement, and strong signals are obtained for contact times as short as 100 $\mu$s. Comparing the quantitative Bloch decay spectrum in 4a to the 1-ms contact time CP experiment in 4b indicates, by virtue of the similar peak intensities and chemical shifts, that the CP/MAS data does not reflect a minor fractional component of the catalyst complex, but is representative of the majority of the supported catalyst. One key difference is that the carbonyl signal centered near 180-185 ppm exhibits a larger linewidth in the CP/MAS result of 4b, and its center of mass is shifted downfield by 2-3 ppm relative to 4a, suggesting that the CP/MAS experiment is emphasizing that fraction of the catalyst complex ligands that interact most strongly with the host surface.
**Figure 3.3** $^{13}$C MAS NMR spectra of (a) pure Sn(Oct)$_2$ prior to catalyst formulation; and various Sn/MCM-41_35.4 catalysts following the indicated solvent washings: (b) unwashed, (c) 600 mL wash, (d) 1200 mL wash, and (e) 2000 mL wash. Spectra were acquired with 70 kHz $^1$H decoupling r.f. field strengths during acquisition, and with MAS speeds = 6 kHz. The broad central hump in 3.3c-3.3e is a residual carbon background signal from the probe.

**Figure 3.4** Comparison of $^{13}$C results for the same Sn/MCM-41_35.4 catalyst sample in 3.3e: (a) Bloch decay/MAS spectrum; (b) CP/MAS spectrum acquired with a 1-ms polarization transfer time.
The combined results from the BET, microscopy, elemental, and solid-state NMR analyses indicate that the Sn(Oct)$_2$ complex is supported inside the MCM-41 channels, which is critical to our original goal of generating poly(d,l-lactide) from the monomer inside the host channels. As mentioned previously, the purely siliceous MCM-41 is a charge neutral framework, and therefore one can ask if and how the Sn(Oct)$_2$ interacts with the channel walls of the host to form a stable catalyst for the subsequent ring-opening polymerization. Recall that dodecanol is added simultaneously with the monomer in the polymerization step, but is not present when making the supported Sn(Oct)$_2$ / MCM-41 catalysts described in the preceding data. Figure 3.5 shows possible schemes based on hydrogen bonding or dipole-dipole interactions between MCM-41 surface hydroxyls and the Sn$^{2+}$ catalyst complex. There is experimental evidence for the scheme in 3.5a; a 183-ppm peak is detected in the liquid $^{13}$C NMR spectrum of the solvent washes, characteristic of the 2-ethylhexanoic acid byproduct of the catalyst complex formation.
Figure 3.5 Reactions/structures depicting possible modes of interaction between the Sn(Oct)$_2$ complex and the interior walls of the MCM-41 channels. (a) proton-transfer to yield a free carboxylic acid ligand and the tethered Sn catalyst complex; (b) hydrogen bonding association, which could between either geminal (shown) and/or vicinal hydroxyl groups on the surface; (c) dipole-dipole interaction between the metal atom and surface oxygens, which could also involve non-protonated bridging oxygens from the surface (not shown).

3.3.2 Poly(d,l-lactide)/MCM-41 Composites

Kageyama and coworkers reported the polymerization of ε-caprolactone and γ-valerolactone using an Al-MCM-41 catalyst and butanol co-initiator. The reaction was carried out at 50 °C under nitrogen atmosphere, and presumably, the Al-MCM-41 acted as a Lewis acid in the initiation step. In order to generate proper control data, we explored if
aluminum-containing mesoporous materials or their purely silicious analogues, each in the presence of an alcohol co-catalyst, could polymerize d,l-lactide. Amorphous SiO₂ as well as crystalline MCM-41, Al-MCM-41, SBA-15, and Al-SBA-15 were each stirred together with the monomer and co-initiator 1-dodecanol for two hours at 175 °C in an oil bath. Carbon NMR experiments indicated that polymerization did not occur, consistent with the physical characteristics of the final product mixture. These combined results confirm that the supported Sn(Oct)₂ complex is a required component for the active mesoporous d,l-lactide polymerization catalyst.

Two catalysts with different as-prepared Sn concentrations, i.e., Sn/Si = 2 and Sn/Si = 35, were evaluated for their d,l-lactide polymerization activity according to the procedure described in the Experimental section. As previously mentioned in Table 3.1 and the supporting discussions, these catalysts are denoted as Sn/MCM-41_2 and Sn/MCM-41_35, respectively. Figure 3.6 shows TGA results for all materials used at each stage of catalyst synthesis, as well as that for a final composite made using a Sn/MCM-41_2 catalyst. Compared to the pure MCM-41, we observe that the water absorption capacity after Sn(Oct)₂ incorporation is reduced by a factor of 2, indicating that the catalyst complex is incorporated inside the MCM channels, as previously suggested, and in agreement with previous BET results for the catalyst. More importantly, water absorption within the MCM channels is precluded in the polymer composite materials, clearly demonstrating that the polymer which is being made, and removed by thermal decomposition in the TGA experiment, is polymer which originates inside the channels of the Sn/MCM-41_2 catalyst. All catalyst and composite samples were prepared in the presence of ambient moisture, i.e., there were no
special sample handling or inert atmosphere preparation steps to preclude exposure to moisture.

![Graph showing TGA results for pure MCM-41, Sn/MCM-41_2, a PDLLA_Sn/MCM-41_2 composite washed with 15 mL CH₂Cl₂ (wash 1), and PDLLA_Sn/MCM-41_2 washed with 30 mL CH₂Cl₂ (wash 2).]

**Figure 3.6** TGA results for pure MCM-41, Sn/MCM-41_2, a PDLLA_Sn/MCM-41_2 composite washed with 15 mL CH₂Cl₂ (wash 1), and PDLLA_Sn/MCM-41_2 washed with 30 mL CH₂Cl₂ (wash 2).

The TGA results for both of the washed polymer composite samples in **Figure 3.6** agree with further reductions in accessible surface area relative to the pure MCM-41 or the Sn/MCM-41 catalyst complex. BET measurements on the polymer composite yielded, on average, 25 m²/g surface area, which is lower than that of the Sn/MCM-41 catalyst (400 m²/g) but still larger than the 5 m²/g measured on pure poly(d,l-lactide) prepared via conventional routes. SEM and TEM data for the polymer composites revealed that MCM-41 particle morphology and channel integrity was unchanged following polymerization (data not shown).
While the TGA and BET experiments are bulk measurements, Figure 3.7 shows solid-state CP/MAS spectra for the polymer composites, as well as results from an important control experiment. Solid-state NMR can provide much more local length scale information compared to TGA or BET experiments. The spectrum for the as-prepared composite, but prior to solvent washing to remove any extractable polymer components, is shown in 3.7a. Except for the increased linewidths, the result looks in every way similar to the CP/MAS spectrum for bulk amorphous poly(d,l-lactide) prepared via conventional methods. Note that all three chemical shifts for chemical moieties in the polymer are different by 2-6 ppm than their respective peak in the d,l-lactide monomer, so polymerization has definitely occurred. In other words, simply absorbing monomer in the host materials cannot generate the spectra shown in Figure 3.7. After washing with 600 mL of CH$_2$Cl$_2$, the spectrum in 3.7b is obtained in which we see the clear appearance of broad downfield shoulders on both the polymer C=O and CH$_3$ signals. Vertical expansion of the spectrum in 3.7a (not shown) reveals that these features are also present in the unwashed sample, but at a much lower fraction of the total polymer chains. The broad downfield shoulder on the washed polymer composite (3.7b) indicates that the polymer has significant hydrogen bonding contacts with hydroxyl groups in the channels of the MCM-41 host. Further, it is known that pendant methyl groups are excellent reporters of conformational inequivalence in polymer chains, and the strong shoulder at 21 ppm on the main 18-ppm CH$_3$ peak supports this assignment. Clearly, the solid-state CP/MAS NMR results indicate that there is a strongly interacting polymer chain inside the host channels of the MCM-41. $^1$H rotating frame spin-lattice relaxation rate time constants $T_{1\rho H}$ decreased by a factor of four (48 ms to 12 ms) in going
from pure poly(d,l-lactide) to the washed polymer composite sample of \textbf{Figure 3.7b}. By comparison, \textbf{Figure 3.7c} and \textbf{3.7d} show results for identical experiments to that in \textbf{3.7a} and \textbf{3.7b}, except that the sample is a blend of poly(d,l-lactide) and the Sn/MCM-41 composite catalyst. In other words, the polymer itself was not generated from the monomer in-situ in the presence of the catalyst host complex, but mixed with the catalyst complex at the same temperature (175\textdegree C) that the polymerizations were done for the in-situ prepared composites, and then cooled. The as-prepared unwashed spectrum in 3.7c looks almost identical to that in 3.7a. However, following the same 600-mL CH\textsubscript{2}Cl\textsubscript{2} wash procedure for this blend as was used to generate the spectrum in 3.7b, the spectrum in 3.7d shows that essentially all of the poly(d,l-lactide) is completely removed from the MCM-41 host. Indeed, the strongest signals in the spectrum for the washed blend sample come from the octanoate ligands of the supported Sn catalyst, denoted by asterisks in the figure.
Figure 3.7 $^{13}$C CP/MAS NMR spectra of PDLLA_Sn/MCM-41_35.4 polymer composites: (a) the composite as prepared in-situ using the procedure outlined in the text, but prior to washing; (b) same sample as in (a) after washing with 600 mL of CH$_2$Cl$_2$; (c) a blend of poly(d,l-lactide) and the Sn/MCM-41 catalyst complex prepared as described in the Experimental section, prior to washing; (d) same sample as in (c) after washing. Spectra were acquired with 70 kHz $^1$H decoupling r.f. field strengths during acquisition. In (d), * denotes signals from the ligands of the supported Sn complex. Spinning sidebands are indicated by “ssb”.

Molecular weight analysis of the resulting poly(d,l-lactide)/MCM-41 composites by GPC is problematic due to relatively high MCM-41 composition in the washed samples. As stated earlier in the manuscript, our emphasis on identifying and characterizing the polymer that originates and remains within the host channels after a strong solvent extraction step requires a higher mass fraction of the host than one might choose to employ for applied work. On average, the GPC results indicate that the polymer chains have approximately one-fifth
the molar mass of bulk, as-synthesized pure polymer (10,000 vs. 50,000). However, one should regard molecular weight data by GPC for these composites with some skepticism, since the hydrodynamic properties of the washed polymer composites are much different than that of bulk polymer chains. The use of relatively high concentrations of Sn-catalyst complex in this study, as needed to adequately characterize interior-channel surface interactions, results in lower polymer molecular weights.

Based on the evidence presented above, we propose a mechanism for how polymerization occurs within the channels of the MCM-41 host, in which the Sn\textsuperscript{2+} catalyst is supported. As discussed earlier in Figure 3.5, we cannot specify the exact structure of the supported Sn catalyst complex, but two reasonable possibilities exist as a starting point for polymerization. Figure 3.8 shows the same ring-opening mechanism of the d,l-lactide monomer in the presence of the dodecanol initiator, but starting from two different Sn complex structures. Proposed mechanisms for the polymerization of lactones using stannous octanoate catalysts have been published in the literature and suggest a coordination-insertion mechanism\textsuperscript{8,15}. Irrespective of whether the reaction initiates as shown in Figure 3.8a or 3.8b, the main barrier to propagation and generation of higher molecular weight polymer (\( > M_w = 10,000 \)) is diffusion of monomer to the active catalyst site in the presence of a growing polymer chain in the limited channel dimensions.
Figure 3.8 Scheme depicting the introduction and subsequent reaction of 1-dodecanol and d,l-lactide monomer into the channels of Sn/MCM-41; (a) via the proposed ion-exchanged supported catalyst, and (b) via the proposed catalyst with a weak bond association between the Sn atom and the surface hydroxyl groups.
3.4 Conclusions

A stable ring-opening polymerization catalyst can be prepared within the channels of the mesoporous hosts MCM-41 and SBA-15. Using Sn(Oct)$_2$ catalyst supported inside MCM-41, we have demonstrated that the d,l-lactide polymerization occurs within the host channels to produce poly(d,l-lactide). More importantly, the characteristics of the resulting organic/inorganic polymer composite cannot be replicated by simple blending methods involving the polymer and MCM-41. Clear experimental evidence from a variety of methods, most notably solid-state NMR, indicate that polymer chains grow inside the channels and can only be removed by extensive washing with a good solvent. Mechanisms describing chemical interactions between the ring-opening catalyst and the host channel walls, as well as the subsequent polymerization steps, have been proposed based on experimental evidence. Future work will target optimized catalyst compositions, e.g., different hosts and reduced Sn$^{2+}$ concentrations, for higher molecular weight organic fractions in the composite.
Chapter 4: Synthesis and Characterization of Biopolymer Composites with Aluminum-Containing Mesoporous Hosts

4.1 Introduction

The design of environmentally attractive organic-inorganic hybrid materials that meet specific constraints for multiple applications requires novel synthesis routes. Biopolymers are attractive alternate materials for market dominant petroleum-based polymers because they offer unique properties like excellent biodegradability and biocompatibility. However, their physical properties (e.g. elongation, tensile moduli, etc.) need further modification to tailor their use to specific applications. The innovative research on organic-inorganic hybrids/polymer nanocomposites has led to materials with enhanced properties as compared to the traditional macroscale composites and conventional materials.121

The well-known micro/mesoporous materials (e.g. MCM-4154,55 and SBA-1575,76) have been recently used as inorganic components to polymer composites.126-128,139-142 Mesoporous materials offer attractive properties like a regular and uniform framework structure containing highly ordered pores. Different research groups have successfully obtained polymer/mesoporous hybrids by physical mixtures and extrusions;139,141 or have modified mesoporous materials to be used as catalysts for the in-situ synthesis of polymers.126-129 The in-situ approach to polymer hybrids is desirable, since it creates a polymer which “grows” out of the crystallites, generating a composite structure with inorganic reinforcement distributed throughout the polymer (see Figure 4.1). We have previously reported in much detail the design of Sn/MCM-41 supported catalysts for the in-
situ polymerization of D,L-lactide composites. Here we also explore the in-situ preparation of PDLLA composites, however, using Sn supported catalysts based on Al-MCM-41 and Al-SBA-15 hosts. In this chapter we discuss the details of the catalyst preparation and polymerization to create the biopolymer nanocomposite materials, as well as subsequent characterization results.

**Figure 4.1** Scheme depicting the in-situ approach idea including the design of the supported catalyst and the polymerization to obtain a polymer which “grows” out of the crystallites generating the composite structure

### 4.2 Experimental

**Materials.** D,L-Lactide 97% and aluminum isopropoxide 98% were obtained from Alfa Aesar. Tin (II) 2-ethylhexanoate 95%, 1-dodecanol 98%, tetraethylorthosilicate 98%, and PEG-block-PPG-block-PEG mw = 5800 g/mol were purchased from Sigma-Aldrich. All organic solvents were obtained from Pharmco-AAPER. Cetyltrimethylammonium bromide
>99% (CTMABr) was purchased from Amresco. Silicon (IV) oxide 99+%, 0.012micron (SiO$_2$) was purchased from Strem Chemicals.

**Characterization.** Molecular weight analysis was performed on a Series 1100 HP Size Exclusion Chromatography instrument with a polystyrene column. Glass transition temperatures were determined on a Q2000 Thermal Analysis Differential Scanning Calorimetry instrument. Elemental analysis was performed by Galbraith Labs using an Inductively Coupled Plasma – Atomic Emission Spectroscopy instrument. X-ray diffraction patterns were obtained on a Bruker AXS D-8 Advanced X-ray powder diffractometer using copper K$_\alpha$ radiation. Analysis was completed using a search/match program and the PDF-2 database of the International Center for Diffraction Data. Specific surface area BET measurements were performed on a Quantachrome Nova 1200 Surface Area Analyzer. Scanning Electron Microscopy and Transmission Electron Microscopy images were obtained on a FEI Quanta 600 ESEM and a JEOL JEM-2100, respectively. Magic angle spinning solid state experiments were performed on a 300-MHz Bruker DSX-300. Prior to $^1$H T1$\rho$ experiments, samples were first dehydrated and then loaded into the rotors inside a glovebox to prevent exposure to moisture. The $^1$H T1$\rho$ experiment consisted of a 90° pulse on the $^1$H channel followed by a varied $\tau$ period (spin lock) and a contact pulse, acquiring on the carbon channel. Carbon Bloch decay experiments consisted of a 90° pulse with a delay time of 20 seconds.

**MCM-41.** MCM-41 was synthesized following the procedure described by Zhao, X.S., et al.$^{149}$ 0.800g of NaOH, 59.994g of DI-water, 2.523g of CTMABr, and 2.403g of SiO$_2$ were thoroughly mixed and aged in a Parr acid digestion bomb for three days at 100 °C.
The material was filtered, washed with excess deionized water, and calcined at 550 °C for ten hours using a 1 °C/min ramp. In addition to the $^{13}$C NMR results which revealed the absence of the template CTMABr, carbon elemental analysis resulted in <0.5% carbon by weight.

**Post-Synthesis of Al-MCM-41.** Al-MCM-41 was synthesized following the method described by Mokaya, R., et al..$^{71,74}$ Calcined MCM-41 was treated with Al-iso in hexanes for 24 hours. The material was filtered and rinsed with hexanes and calcined at 550°C for 6-10 hours using a 1°C/min ramp. Al-MCM-41 was prepared with a target Si/Al ratio of 5.

**SBA-15.** SBA-15 was synthesized following the procedure described by Vinu, A., et al..$^{60}$ An acidic solution of Pluronic P123 was stirred for 2 hours. Tetraethylorthosilicate (TEOS) was added to the Pluronic solution and stirred for 24 hours at 40°C. The molar gel composition was 1 TEOS : 0.016 P123 : 5.54 HCl : 190 H$_2$O. The resulting material was filtered and rinsed with excess deionized water and calcined at 550°C for 10 hours using a 1°C/min ramp.

**Direct Synthesis of Al-SBA-15.** Al-SBA-15 was also synthesized following the method described by Vinu, A., et al..$^{60}$ The molar gel composition was 1 TEOS : 0.016 P123 : 0.2-0.1 Al$_2$O$_3$ : 0.46 HCl : 126 H$_2$O (Si/Al = 18). Similar to the SBA-15 synthesis, an acidic solution of Pluronic P123 was stirred for 2 hours. TEOS and Al-iso were added to the Pluronic solution and stirred for 24 hours at 40°C. The material was filtered and rinsed with excess deionized water and calcined at 550°C for 6-10 hours using a 1°C/min ramp.

**Sn Supported Mesoporous Catalysts.** The supported catalysts were prepared by stirring stannous octoate with calcined MCM-41, SBA-15, and their aluminum-containing analogous at different Sn/Si ratios for three hours. Excess stannous octoate was filtered and
the remaining material was rinsed with ~2L of hexanes and dried overnight. Supported catalysts were also prepared in solution. A similar procedure to the described bulk synthesis was used here however the reactants were mixed in hexanes. Throughout this chapter, we denote each supported catalyst by the relative amounts of Sn and Si and include the solvent used, e.g. Sn/MCM-41_2_hex indicates a catalyst synthesized in hexanes with a calculated Sn/Si ratio of 2 based on the starting ingredient concentrations.

**Poly(D,L-Lactide) Composites.** Pure PDLLA was synthesized following the established methods.\textsuperscript{13,20,25,167-169} The monomer was recrystallized with toluene and kept under vacuum. The monomer, catalyst, and co-initiator were placed in a round bottom flask equipped with a stir bar. The reaction was carried out for two hours at 175 °C in an oil bath. Extra monomer was removed by dissolving in dichloromethane and precipitating in methanol. The molar composition was: 1mol D,L-lactide : 7.11 \times 10^{-5} \text{ mol Sn(Oct)$_2$} : 3.87 \times 10^{-5} \text{ mol of 1-dodecanol}. The organic-inorganic hybrid was obtained by stirring together the monomer, supported catalyst, and 1-dodecanol for two hours at 175 °C. The molar gel composition was: 1 \text{ mol D,L-lactide} : 7.11 \times 10^{-3} \text{ mol Sn(Oct)$_2$} : 3.87 \times 10^{-3} \text{ mol of 1-dodecanol}. Washes of the hybrid material were obtained by rinsing with 15mL and 30mL of dichloromethane. Physical mixtures of the Sn/MCM-41 and Sn/Al-MCM-41 catalysts with the pure PDLLA (control sample) were prepared by stirring the supported catalyst and polymer together in dichloromethane for two hours at room temperature. The resulting blend was dried overnight.
4.3 Results and Discussion

The initial idea for preparing the supported catalysts was to use aluminum-containing mesoporous materials, which through cationic exchange with their Brönsted acid sites, could assist the incorporation or anchor the stannous octoate catalyst. The catalyst would then be used to prepare the composite material by introducing D,L-lactide into the Sn supported catalyst. Figure 4.2 illustrates a possible reaction scheme for the proposed catalyst preparation chemistry. Ion-exchange occurs between the acid proton and the stannous octoate, liberating octanoic acid, and producing the anchored stannous octoate supported catalyst. The reaction mechanism seems plausible, however, it will be demonstrated here that this is not the case for the Sn supported aluminum-containing mesoporous catalysts. Instead, the mechanism that takes place is attributed to the surface hydroxyl groups present throughout the mesoporous hosts, as suggested in the previous chapter (Figure 3.5).
Figure 4.2 Scheme depicting the use of the aluminum-containing mesoporous material’s Brønsted acid site to anchor the stannous octoate catalyst, followed by the introduction of monomer D,L-lactide into the channels, and its polymerization to produce a polymer composite with inorganic reinforcement.

4.3.1 Aluminum-Containing Mesoporous Hosts with Supported Sn Catalysts

The mesoporous hosts where characterized by XRD, BET surface area, microscopy, and NMR techniques. As synthesized, Al-MCM-41 (Si/Al=5) and Al-SBA-15 (Si/Al=18) exhibited their characteristic reflections as determined by XRD and surface areas (obtained by nitrogen adsorption) of ~1000 m²/g and ~450 m²/g, respectively. SEM and TEM images revealed their regular structure. In addition, NMR experiments of both of these materials revealed their characteristic proton, aluminum, and silicon environments. All of these results can be found in chapter 2.
Table 4.1 BET specific surface areas for the mesoporous hosts, supported catalysts, and polymer composites.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Specific Surface Area (m²/g)</th>
<th>Correlation Coefficient</th>
</tr>
</thead>
<tbody>
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<td>MCM-41</td>
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</tr>
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<td>Sn/Al-MCM-41_35.4</td>
<td>281.4438</td>
<td>0.9958</td>
</tr>
<tr>
<td>SBA-15</td>
<td>692.8867</td>
<td>0.9989</td>
</tr>
<tr>
<td>Sn/SBA-15_35.4</td>
<td>220.8329</td>
<td>0.9999</td>
</tr>
<tr>
<td>PDLLA_bulk</td>
<td>5.5537</td>
<td>0.8962</td>
</tr>
<tr>
<td>Washed PDLLA_Sn/Al-MCM-41_35.4</td>
<td>26.0436</td>
<td>0.9999</td>
</tr>
</tbody>
</table>

No crystallinity was detected by XRD for the Sn supported catalysts. One would conclude that these materials are amorphous. However, stannous octoate incorporated into the mesoporous hosts would fill the surface and pores/channels. Thus, the XRD instrument could not detect a contrast between the different crystal layers. As suggested by the microscopy analysis to follow, these materials are in fact crystalline. In addition, decreased surface areas by a factor of three were determined for the Sn supported catalysts as compared to the parent mesoporous hosts (Table 4.1). Once again, this is due to the incorporation of the stannous octoate. Table 4.2 displays theoretical and experimental elemental compositions of the supported Sn catalysts given as Sn/Si ratios. Two different Sn/Al-MCM-41 catalysts were studied, in addition to Sn/Al-SBA-15, and the siliceous mesoporous solids. The aluminum-containing mesoporous Sn-catalysts displayed decreased Sn/Si ratios as compared to the siliceous analogue catalysts. This suggests that the aluminum does not assist in anchoring the stannous octoate to the mesoporous hosts as displayed in the reaction
scheme seen on Figure 4.2. As stated in the preceding chapter, a charged host framework is not required to support stannous octoate. If the siliceous Sn/MCM-41 and Sn/SBA-15 catalysts contain higher amounts of incorporated stannous octoate, it would then be attributed to their higher surface areas (leading to more hydroxyl groups), as compared to the aluminum-containing catalysts. Moreover, it suggests that incorporation of stannous octoate takes place through the surface hydroxyl groups of the hosts, in accordance with the previous chapter findings. The incorporation of Al is actually detrimental to the anchoring of tin as it consumes available SiOH. SEM and TEM images of Sn/Al-MCM-41_35.4 revealed a similar morphology and channel structure, as compared to the host Al-MCM-41 (Figure 4.3b and 4.4b). The addition of the stannous octoate did not affect the uniform structure of the hosts, as suggested in the XRD results discussion.

Table 4.2 Elemental analysis of the different Sn supported catalysts

<table>
<thead>
<tr>
<th>Materials</th>
<th>Si (wt%)</th>
<th>Al (wt%)</th>
<th>Sn (wt%)</th>
<th>Sn/Si (calc.)</th>
<th>Sn/Si (exp.)</th>
<th>Si/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn/MCM-41_35.4</td>
<td>21.9</td>
<td>-</td>
<td>27.0</td>
<td>35.4</td>
<td>0.291</td>
<td>-</td>
</tr>
<tr>
<td>Sn/MCM-41_10.9</td>
<td>27.1</td>
<td>-</td>
<td>16.4</td>
<td>10.9</td>
<td>0.143</td>
<td>-</td>
</tr>
<tr>
<td>Sn/MCM-41_2</td>
<td>26.7</td>
<td>-</td>
<td>19.6</td>
<td>2.0</td>
<td>0.173</td>
<td>-</td>
</tr>
<tr>
<td>Sn/Al-MCM-41_35.4 (Si/Al=5)</td>
<td>21.9</td>
<td>4.4</td>
<td>16.6</td>
<td>35.4</td>
<td>0.124</td>
<td>4.80</td>
</tr>
<tr>
<td>Sn/Al-MCM-41_21.8 (Si/Al=25)</td>
<td>24.9</td>
<td>1.00</td>
<td>21.3</td>
<td>21.8</td>
<td>0.203</td>
<td>23.9</td>
</tr>
<tr>
<td>Sn/SBA-15_35.4</td>
<td>27.0</td>
<td>-</td>
<td>23.0</td>
<td>35.4</td>
<td>0.202</td>
<td>-</td>
</tr>
<tr>
<td>Sn/Al-SBA-15_22.2 (Si/Al=18)</td>
<td>26.4</td>
<td>1.37</td>
<td>17.9</td>
<td>22.2</td>
<td>0.161</td>
<td>18.5</td>
</tr>
<tr>
<td>Sn/MCM-41_35.4_hex</td>
<td>14.2</td>
<td>-</td>
<td>13.7</td>
<td>35.4</td>
<td>0.228</td>
<td>-</td>
</tr>
<tr>
<td>Sn/MCM-41_2_hex</td>
<td>11.5</td>
<td>-</td>
<td>10.9</td>
<td>2.0</td>
<td>0.220</td>
<td>-</td>
</tr>
<tr>
<td>Sn/MCM-41_0.2_hex</td>
<td>16.1</td>
<td>-</td>
<td>16.6</td>
<td>0.2</td>
<td>0.244</td>
<td>-</td>
</tr>
<tr>
<td>Sn/Al-MCM-41_0.2_hex (Si/Al=5)</td>
<td>23.1</td>
<td>5.15</td>
<td>13.8</td>
<td>0.2</td>
<td>0.141</td>
<td>4.31</td>
</tr>
<tr>
<td>Washed PDLLA_Sn/MCM-41_35.4</td>
<td>17.6</td>
<td>-</td>
<td>19.3</td>
<td>0.291</td>
<td>0.259</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 4.3 SEM images of (a) Al-MCM-41 and (b) Sn/Al-MCM-41_{35.4}

Figure 4.4 TEM images of (a) Al-MCM-41 and (b) Sn/Al-MCM-41_{35.4}

$^{29}$Si and $^{27}$Al NMR results revealed the characteristic signals of the aluminosilicate mesoporous hosts, suggesting the general chemical structure has not been altered. Figures 4.5 and 4.6 summarize the results from $^{13}$C Bloch decay NMR. The spectrum of the pure
Sn(Oct)$_2$ is shown as reference in 4.5a and 4.6a. Similar to the Sn/MCM-41 results discussed in chapter 3, Sn/Al-MCM-41 and Sn/SBA-15 catalysts displayed fixed amounts of octoate catalyst remaining in the hosts, even after extensive washing. The differential peak widths (broader) for similar carbons in the octoate ligands indicate that the complex has adopted a constrained geometry. Though, The S/N of Sn/Al-MCM-41_35.4 and Sn/SBA-15_35.4 are lower in comparison to the previously shown carbon spectrum of Sn/MCM-41_35.4 (Figure 3.3), consistent with the lower Sn/Si ratio. Figure 4.7 illustrates a $^{13}$C comparison between the Bloch decay and cross-polarization experiments of the same sample Sn/Al-MCM-41_35.4 (2L wash). The cp experiment requires an immobile / constrained catalyst for the effective dipolar interactions between $^1$H and $^{13}$C nuclei in the ligand to be maintained. The figure shows strong, similar peak intensities and chemical shifts, reflecting that indeed the catalyst must be in a constrained environment.

Figure 4.5 $^{13}$C MAS NMR spectra of (a) pure Sn(Oct)$_2$; and various Sn/Al-MCM-41_35.4 washings: (b) 600mL wash, (c) 1200mL wash, and (d) 2000mL wash
Figure 4.6 $^{13}$C MAS NMR spectra of (a) pure Sn(Oct)$_2$; and various Sn/SBA-15$_{35.4}$ washings: (b) 600mL wash, (c) 1200mL wash, and (d) 2000mL wash.

Figure 4.7 Comparison of $^{13}$C results for the same Sn/Al-MCM-41$_{35.4}$ catalyst in 4.5d: (a) Bloch decay/MAS spectrum; (b) CP/MAS spectrum acquired with a 1 ms polarization transfer time.
$^1$H T$_{1p}$ NMR experiments were also performed on Sn/Al-MCM-41_35.4; the values for each carbon signal can be observed in Table 4.3; where the letters are referenced to the stannous octoate diagram in Figure 4.5. From the 600mL to the 1200mL wash the rate constants remains similar. After extensive washing the stannous octoate appears to decay faster. However, we have no starting point to compare with. The unwashed catalyst and pure stannous octoate (viscous liquid) would need to be analyzed as well, to better understand these results. $^{119}$Sn NMR experiments for Sn/Al-MCM-41_35.4 and Sn/SBA-15_35.4 did not detect any Sn signal; whereas for the Sn/MCM-41_35.4 catalyst a broad signal was apparent. Sn/MCM-41_35 displayed a single broad signal centered at -600ppm relative to standard tetramethyltin, (CH$_3$)$_4$Sn. Large changes in the lineshape and the number of peaks were observed relative to the neat catalyst stannous octoate liquid.

Table 4.3 $^1$H T$_{1p}$ values in msec for supported catalyst Sn/Al-MCM-4_35.4

<table>
<thead>
<tr>
<th>Hexane Washings</th>
<th>CH (50ppm)</th>
<th>CH$_2$-A+B (30-32ppm)</th>
<th>CH$_2$-C (26.5ppm)</th>
<th>CH$_2$-D (23.5ppm)</th>
<th>CH$_3$-E+F (11-13ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600mL</td>
<td>7.237</td>
<td>7.496</td>
<td>7.407</td>
<td>7.432</td>
<td>7.407</td>
</tr>
<tr>
<td>1200mL</td>
<td>7.870</td>
<td>7.603</td>
<td>6.981</td>
<td>7.408</td>
<td>7.224</td>
</tr>
</tbody>
</table>

Examining the most important results shown here, nitrogen adsorption, elemental, microscopy, and solid-state NMR, indicates that Sn(Oct)$_2$ is indeed supported inside the hosts channels, and that the charged framework is not required for its incorporation. These results are in agreement with the initially stated idea of creating a biopolymer composite which grows from the inside to out of the crystallites.
4.3.2 Poly(d,l-lactide)/Aluminum-Containing Mesoporous Composites

Evidence of the formation of PDLLA using catalysts Sn/Al-MCM-41_35.4 and Sn/Al-SBA-15_35.4 was given by $M_w$, $T_g$, and NMR experiments. Pure PDLLA displayed a weight average $M_w$ of ~45,000 g/mol and an averaged glass transition temperature of 42 °C (Table 4.4). The composite’s molecular weights varied between 14,000 g/mol and 4,000 g/mol, with decreased polydispersity, as previously observed for the Sn/MCM-41 composites. The composite’s decreased molecular weights, as compared to the pure polymer, are expected; due to their higher catalyst concentration in the reaction mixture, which decreases the molecular weight of the polymer.\(^{31}\) In addition, the determined glass transition temperatures of the composite’s varied greatly. It should be noted, as stated in chapter 3, that the molecular weight analysis should be regarded with some skepticism, since the properties of the composite are different than the bulk polymer. SEM and TEM images of the polymer synthesized from Sn/Al-MCM-41 illustrated that the polymerization procedure did not affect the general channel structure of the mesoporous host (Figure 4.8).
Table 4.4 Weight averaged molecular weights and glass transition temperatures for pure PDLLA and different PDLLA nanocomposites

<table>
<thead>
<tr>
<th>Samples</th>
<th>$M_w$ (g/mol)</th>
<th>$M_n$ (g/mol)</th>
<th>$D$</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PDLLA</td>
<td>45,000</td>
<td>30,000</td>
<td>1.6</td>
<td>42.00</td>
</tr>
<tr>
<td>PDLLA_Sn/MCM-41_35.4</td>
<td>12,000</td>
<td>10,000</td>
<td>1.3</td>
<td>40.0</td>
</tr>
<tr>
<td>Washed PDLLA_Sn/MCM-41_35.4</td>
<td>12,000</td>
<td>10,000</td>
<td>1.2</td>
<td>49.0</td>
</tr>
<tr>
<td>PDLLA_Sn/MCM-41_35.4</td>
<td>6,000</td>
<td>4,000</td>
<td>1.2</td>
<td>30.0</td>
</tr>
<tr>
<td>PDLLA_Sn/MCM-41_10.9</td>
<td>3,500</td>
<td>3,000</td>
<td>1.2</td>
<td>10.0</td>
</tr>
<tr>
<td>PDLLA_Sn/MCM-41_2</td>
<td>3,000</td>
<td>3,000</td>
<td>1.2</td>
<td>10.0</td>
</tr>
<tr>
<td>PDLLA_Sn/SBA-15_35.4</td>
<td>7,000</td>
<td>5,000</td>
<td>1.3</td>
<td>30.0</td>
</tr>
<tr>
<td>PDLLA_Sn/SBA-15_10.9</td>
<td>5,500</td>
<td>4,000</td>
<td>1.3</td>
<td>20.0</td>
</tr>
<tr>
<td>PDLLA_Sn/Al-MCM-41_35.4</td>
<td>14,000</td>
<td>12,000</td>
<td>1.3</td>
<td>44.0</td>
</tr>
<tr>
<td>Washed PDLLA_Sn/Al-MCM-41_35.4</td>
<td>14,000</td>
<td>12,000</td>
<td>1.1</td>
<td>48.0</td>
</tr>
<tr>
<td>PDLLA_Sn/Al-MCM-41_35.4</td>
<td>6,500</td>
<td>5,000</td>
<td>1.3</td>
<td>30.0</td>
</tr>
<tr>
<td>PDLLA_Sn/Al-SBA-15_22.2</td>
<td>2,000</td>
<td>2,000</td>
<td>1.0</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 4.8 TEM image of PDLLA_Sn/Al-MCM-41_35.4
The three characteristic carbon signals of PDLLA; carbonyl, methine, and methyl; were detected for the PDLLA composite with supported catalyst Sn/Al-MCM-41_35.4, and these frequencies differed from the chemical shifts detected for monomer, d,l-lactide. Figure 4.9 displays this $^{13}$C spectrum with each signal assigned to the specific carbons of PDLLA. The $^1$H MAS NMR spectrum of this composite exhibited two broad signals, assigned to the methyl and methine protons. In addition, $^1$H T1ρ NMR experiments were conducted on this same composite and its washed analogue. These values are displayed in Table 4.5. The unwashed composite exhibited similar values to the pure PDLLA. However, the washed composites displayed a decreased rate constant / faster decay as compared to the pure PDLLA and unwashed composite. This implies that the unwashed polymer composite is somewhat rigid / solid as the pure PDLLA. After washing, this rigidity is lost and a more mobile material is apparent. This strongly suggests that the bulk polymer is removed with subsequent washes of the composite and the polymer threaded inside the channels with different properties, remains. Similar results were obtained for the PDLLA composite with Sn/MCM-41_35.4.
4.3.3 Solution Assisted Sn Supported Mesoporous Catalyst

Addition of a solvent (i.e. hexanes) to the synthesis of the supported catalysts was investigated. If a solvent could facilitate the diffusion of stannous octoate through the channels of the mesoporous materials, a more controlled incorporation of the catalyst into the hosts could be achieved. However, similar results to the bulk synthesis were obtained. Table 4.2 displays the elemental compositions obtained for the hexane assisted syntheses. For example, the Sn/MCM-41_35.4_hex material exhibited a lower Sn/Si ratio as compared to Sn/MCM-41_35.4 (bulk synthesis), even though, it started with the same calculated values.
In addition, the highest experimental Sn/Si ratio determined for the hexanes syntheses was exhibited by the catalyst with the lowest calculated Sn/Si of 0.2. No evident correlation is apparent between the calculated and experimental values, as previously suggested. However, all three hexane assisted Sn/MCM-41 catalysts tested exhibited in general increased experimental Sn/Si values. In addition, the Sn/Al-MCM-41_hex catalyst displayed an increased experimental Sn/Si ratio as compared to its bulk analogue. Although no correlation was detected, it appears that the solvent might help in diffusing the stannous octoate through the mesoporous host, thus incorporating an increased amount of Sn into the mesoporous materials. Figure 4.10 displays the $^{13}$C NMR plot for the unwashed hexane-assisted catalysts. Similar to the previously shown carbon plots of other supported catalysts, these solution-assisted materials also illustrate the characteristic carbon signals from the stannous octoate (labels seen in Figure 4.5).

**Figure 4.10** $^{13}$C NMR of (a) Sn(Oct)$_2$ and the unwashed hexane prepared catalysts (b) Sn/MCM-41_35.4_hex, (c) Sn/Al-MCM-41_35.4_hex, and (d) Sn/Al-SBA-15_22.2_hex
4.4 Conclusions

The formation of Sn supported catalysts based on Al-MCM-41, SBA-15, and Al-SBA-15 mesoporous hosts was confirmed by elemental analysis, NMR, and microscopy techniques, indicating that stannous octoate was indeed supported inside the hosts channels, and that the charged framework is not required for its incorporation. These supported catalysts exhibited decreased Sn content as compared to the Sn/MCM-4_35.4 supported catalyst; possibly due to the lower surface areas of the mesoporous hosts and reduced quantity of available silanol groups. Molecular weight, DSC, and NMR analyses confirmed the formation of PDLLA with the use of the studied Sn supported catalysts. In addition, evidence of a threaded-polymer within the channels of the host different than the bulk / outside polymer was given by the $^1\text{H} T_1$ NMR experiment. Microscopy images revealed the intact general structure of the mesoporous hosts after polymerization.
Chapter 5: Acid Catalyzed Condensation Polymerization of Lactic Acid

5.1 Introduction

Poly(lactic acid), a biodegradable and biocompatible polymer produced from renewable sources, has been of considerable interest in applications for medicine, environmentally friendly packaging materials, agriculture, etc. PLA produced from the ring opening polymerization of cyclic monomer, lactide, produces high molecular weight polymer, while, the condensation polymerization of lactic acid, has been shown to produce low molecular weight PLA. For this reason, the majority of research has focus on the ROP procedure. However, fairly recent reports have claimed the production of high molecular weight PLA by solution polycondensation and by bulk / melt polycondensation methods. Polymerization of PLA by solution condensation typically uses large volumes of solvent with high boiling points to aid in the water removal process by azeotropic distillation. Molecular sieves with Brönsted and Lewis acidity have been used to keep a low concentration of water in the solvent used for the distillation. Bulk condensations of PLA benefit from the absence of azeotropic solvents. To produce high molecular weight PLA, bulk condensations have been carried out with the aid of catalysts. In addition, high vacuum systems have been employed in the polycondensation reaction of PLA for the removal of water.

The use of well known micro/mesoporous molecular sieves for aiding in the removal of water in direct condensation polymerizations, as previously reported, is an interesting concept. Condensation polymerizations consist of the constant removal of the water
produced by the reaction, as to allow larger chains of polymer to be formed. If a monomer is placed with a hydrophilic material such as micro/mesoporous solid acids, in a reaction vessel and heated up, the solid acid could remove or trap water molecules formed by the condensation reaction. The additional application of high vacuum to this type of system could also aid in the removal of water from the reaction. This process would create an organic-inorganic composite containing no impurities (i.e. metal catalysts). Here, we explore the possibility of a bulk condensation polymerization of lactic acid with the aid of solid acid catalysts (i.e. H-ZSM-5 and Al-MCM-41) under atmospheric pressure and high vacuum.

**Figure 5.1** displays a proposed mechanism for this type of reaction. The mechanism starts by the activation of the alcohol through protonation by the solid acid, generating a much better leaving group. Next, there is a nucleophilic attack by another monomer unit substituting the water and forming the polymeric chain. The synthesized polymers were analyzed by GPC, DSC, melting temperature apparatus, and NMR techniques.

![Proposed mechanism scheme for the acid catalyzed condensation polymerization of lactic acid](image)

**Figure 5.1** Proposed mechanism scheme for the acid catalyzed condensation polymerization of lactic acid

### 5.2 Experimental

**Materials.** Lactic acid, 85% in water was obtained from Sigma-Aldrich. Cetyltrimethylammonium bromide, >99% was purchased from Amresco. Silicon (IV) oxide,
99+%, 0.012micron was purchased from Strem Chemicals. Aluminum isopropoxide, 98+% was obtained from Alfa Aesar. All organic solvents were obtained from Pharmco-AAPER. H-ZSM-5, Si/Al=15 was purchased from Zeolyst. Some PLA syntheses used 100mesh SiO₂.

**Characterization.** Molecular weight (Mₘ) analysis was performed on a Series 1100 HP Size Exclusion Chromatography (SEC) instrument with a polystyrene (PS) column. Glass transition temperatures (Tᵥ) were determined on a Q2000 Thermal Analysis (TA) Differential Scanning Calorimetry (DSC) instrument. Elemental analysis was performed by Galbraith Labs using an Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-OES) instrument. X-ray diffraction (XRD) patterns were obtained on a Bruker AXS D-8 Advanced X-ray powder diffractometer using copper Kᵢ radiation. Analysis was completed using a search/match program and the PDF-2 database of the International Center for Diffraction Data. Specific surface area BET measurements were performed on a Quantachrome Nova 1200 Surface Area Analyzer. Magic angle spinning solid state (MAS SSNMR) experiments were performed on a 300-MHz Bruker DSX-300. Prior to any ¹H experiments, samples were first dehydrated and then loaded into the rotors inside a glovebox to prevent exposure to moisture. A 90° pulse was used for ¹H experiments. The ¹H T₁ρ experiment consisted of a 90° pulse on the ¹H channel, followed by a varied τ period (spin lock), and then a contact pulse, acquiring on the carbon channel. Carbon bloch decay (¹³C) experiments consisted of a 90° pulse with a delay time of 20 seconds with ¹H decoupling during acquisition. The carbon cross polarization (cp) pulse sequence consisted of a 90° pulse on the proton channel followed by a contact pulse with 1 msec contact times.
MCM-41. MCM-41 was synthesized following the procedure described by Zhao, X.S., et al.\textsuperscript{149} 0.800g of NaOH, 59.994g of DI-water, 2.523g of CTMABr, and 2.403g of SiO\textsubscript{2} were thoroughly mixed and aged in a Parr acid digestion bomb for three days at 100 °C. The material was filtered and washed with excess deionized water, then calcined at 550 °C for ten hours using a 1 °C/min ramp. In addition to the $^{13}$C NMR results which revealed the absence of the template CTMABr, carbon elemental analysis resulted in <0.5% carbon by weight.

Post-Synthesis Grafting of Al-MCM-41. Al-MCM-41 was synthesized following the method described by Mokaya, R., et al.\textsuperscript{71,74} Calcined MCM-41 was treated with Al-iso in hexanes for 24 hours. The material was filtered and rinsed with hexanes, then calcined at 550 ºC for 6-10 hours using a 1 ºC/min ramp. Al-MCM-41 was prepared with a target Si/Al ratio of 5.

Condensation Polymerization of Lactic Acid with Micro/Mesoporous Materials. To produce poly(lactic acid) two pressures were used; vacuum and atmospheric pressure. Similar methods to ones reported in the literature were followed for the vacuum synthesis of PLA.\textsuperscript{174,175} Lactic acid or lactic acid and the micro/mesoporous material were placed in a 2-neck round bottom flask equipped with a flow of nitrogen and under vacuum. The flask was connected to a glass / liquid nitrogen (LN\textsubscript{2}) trap, which was emmersed in a dewar filled with LN\textsubscript{2}. The outlet of the trap was connected to a vacuum pump. The reaction was stirred for three hours at 110 °C. The temperature was increased to 150 °C, and after two hours, the nitrogen flow was stopped. The reaction was kept at 150 °C under vacuum for 40 hours. The PLA prepared under atmospheric conditions (no vacuum) was obtained by mixing only lactic
acid, or lactic acid and the micro/mesoporous materials, for 24 hours at 120 °C. The temperature was raised to 150 °C and maintained there for 72 hours. A control experiment was prepared by mixing lactic acid with a 1.0 M solution of HNO$_3$. All final products were purified by dissolving in dichloromethane and precipitating in methanol; purification gave a yellow-brown powder. The molar composition for the reactions was 272.172 mol of Lactic acid / mol of acid site. Siliceous samples were given equivalent amounts per weight as the H-ZSM-5 as there is no acidity for stoichiometric amount determination. Throughout the remainder of the text, we denote each poly(lactic acid) by the micro/mesoporous solid and pressure used for the synthesis, e.g. PLA/SiO$_2$-v indicates poly(lactic acid) was prepared under vacuum in the presence of SiO$_2$.

5.3 Results and Discussion

The purified polymers were characterized by molecular weight, melting and glass transition temperatures, and NMR analyses. Initial evidence of the formation of PLA was given by GPC, where a weight averaged molecular weight of approximately 6,500 g/mol and a polydispersity of 1.3 was obtained for the pure PLA synthesized under atmospheric pressure (Table 5.1). PLA synthesized by the solid acids exhibited slightly larger molecular weights than the pure PLA. However, one of the polymers prepared with a siliceous material (i.e. MCM-41), which was used as a control as it does not contain acidity, also produced a polymer with similar molecular weight to the acid catalyzed reactions. These results might be due to the lactic acid being protonated by the surface hydroxyl groups, since it was previously reported that MCM-41 can be modified through its large concentration of surface
hydroxyl groups.\textsuperscript{121,122} Another explanation might be that the reaction is thermally, not catalytically, driven. The pure PLA exhibited a melting temperature of \(137 ^\circ \text{C}\) and a glass transition of \(30 ^\circ \text{C}\). The acid catalyzed polymers displayed increased melting temperatures between 142-147 \(^\circ \text{C}\), and an increased \(T_g\) of 38 \(^\circ \text{C}\) (determined for the PLA/H-ZSM-5 material), as compared to the pure PLA. Once again, the PLA/MCM-41 material which displayed a high \(M_w\) exhibited similar \(T_m\)’s and \(T_g\)’s to the acid catalyzed polymers. The molecular weights and melting temperatures of poly(lactic acid) synthesized under vacuum are also displayed on \textbf{Table 5.1}. The pure PLA synthesized under vacuum exhibited an increased molecular weight, polydispersity (i.e. \(\sim 15,000 \text{ g/mol, D=1.6}\)), and melting temperature (i.e. \(\sim 148 ^\circ \text{C}\)), when compared to the pure PLA synthesized under atmospheric pressure. However, all other vacuum prepared polymers displayed decreased molecular weights, as compared to the pure PLA\textsubscript{v}. When comparing the siliceous and acid catalyzed vacuum polymers, the latter materials exhibited slightly higher molecular weights and melting temperatures, with the exception of PLA\textsubscript{SiO2}, which displayed an increased \(M_w\) and \(T_g\), as compared to the acid catalyzed polymers. Overall, under atmospheric pressure, one might conclude that the acid catalyzed PLA’s exhibited slightly enhanced properties, as compared to the pure PLA, but the differences are not large. However, under the vacuum conditions, the acid catalyzed polymers displayed decreased properties, when compared to the pure PLA\textsubscript{v}, and similar properties to the polymers synthesized under atmospheric pressure. A second pure PLA sample was prepared under vacuum (PLA\textsubscript{v (II)}), were the reaction setup was adjusted by shortening the connection between the reaction vessel and the LN\textsubscript{2} trap to ensure maximum water removal. This polymer exhibited a molecular weight of
~30,000 g/mol with a very high polydispersity of 1.9 and a similar melting temperature to the original PLA_v. The vacuum setup worked best for the condensation polymerization of lactic acid with no added catalysts or solid acids, producing high molecular weights of up to 30,000 g/mol, though with high polydispersities. On the contrary, for the acid catalyzed polymers, the atmospheric pressure setup produced materials with slightly enhanced molecular weights and melting temperatures as compared to the pure PLA prepared through the same method, and to the acid catalyzed polymers prepared under vacuum conditions.

**Table 5.1** Averaged molecular weights and melting and glass transition temperatures of pure PLA and PLA/micro-mesoporous materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>M_w (g/mol)</th>
<th>M_n (g/mol)</th>
<th>D</th>
<th>T_m (°C)</th>
<th>T_g (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>6,673</td>
<td>5,174</td>
<td>1.3</td>
<td>137.0</td>
<td>30.0</td>
</tr>
<tr>
<td>PLA_v</td>
<td>15,052</td>
<td>9,446</td>
<td>1.6</td>
<td>147.5</td>
<td>-</td>
</tr>
<tr>
<td>PLA_v (II)</td>
<td>29,440</td>
<td>15,762</td>
<td>1.9</td>
<td>147.5</td>
<td>-</td>
</tr>
<tr>
<td>PLA/SiO_2</td>
<td>6,224</td>
<td>4,889</td>
<td>1.3</td>
<td>130.0</td>
<td>25.0</td>
</tr>
<tr>
<td>PLA/SiO_2_v</td>
<td>8,052</td>
<td>5,989</td>
<td>1.3</td>
<td>146.5</td>
<td>-</td>
</tr>
<tr>
<td>PLA/H-ZSM-5</td>
<td>8,228</td>
<td>5,975</td>
<td>1.4</td>
<td>142.0</td>
<td>38.8</td>
</tr>
<tr>
<td>PLA/H-ZSM-5_v</td>
<td>6,294</td>
<td>4,831</td>
<td>1.3</td>
<td>146.5</td>
<td>-</td>
</tr>
<tr>
<td>PLA/MCM-41</td>
<td>8,243</td>
<td>5,902</td>
<td>1.4</td>
<td>147.0</td>
<td>-</td>
</tr>
<tr>
<td>PLA/MCM-41_v</td>
<td>4,523</td>
<td>3,594</td>
<td>1.3</td>
<td>136.5</td>
<td>-</td>
</tr>
<tr>
<td>PLA/Al-MCM-41</td>
<td>7,057</td>
<td>5,384</td>
<td>1.3</td>
<td>146.5</td>
<td>-</td>
</tr>
<tr>
<td>PLA/Al-MCM-41_v</td>
<td>6,230</td>
<td>4,800</td>
<td>1.3</td>
<td>146.0</td>
<td>-</td>
</tr>
<tr>
<td>PLA/HNO_3</td>
<td>4,947</td>
<td>3,981</td>
<td>1.2</td>
<td>132.5</td>
<td>-</td>
</tr>
<tr>
<td>PLA/HNO_3_v</td>
<td>5,809</td>
<td>4,466</td>
<td>1.3</td>
<td>138.5</td>
<td>-</td>
</tr>
</tbody>
</table>

Proton, carbon (both Bloch decay and cross polarization), and ^1^H T_1ρ NMR experiments were used to further characterize the pure PLA and acid catalyzed polymers. The majority of the materials analyzed were synthesized under atmospheric pressure, since this method worked best for the acid catalyzed polymers. **Figure 5.2** illustrates the ^1^H NMR
plots for the polymers synthesized under atmospheric pressure. The spectra display the two signals encountered for poly(lactic acid), though they are very broad, assigned to the methyl (1.8 ppm) and methine (5.3 ppm) protons. Pure PLA samples prepared by both the vacuum and the atmospheric pressure conditions were packed and run in a 2.5mm probe, capable of reaching spinning speeds of up to 30 KHz, thus reducing the CSA interactions and dipolar interactions, making the signals sharper. Figure 5.3 illustrates $^1$H NMR plots for the pure PLA’s ran at spinning speeds of 28-29 MHz in a 2.5 mm MAS probe. The high spinning speeds allows better averaging of the dipolar interactions. Very sharp signals, as compared to the previously shown $^1$H stack-plot, are apparent, centered at similar frequencies to the ones stated earlier. However, the pure PLA synthesized under atmospheric pressure conditions exhibited an additional signal centered at ~5.7 ppm. This signal could be assigned to residual monomer.

Figure 5.2 $^1$H NMR of polymers prepared under atmospheric pressure conditions; (a) pure PLA, (b) PLA/SiO$_2$, (c) PLA/H-ZSM-5, (d) PLA/MCM-41, and (e) PLA/Al-MCM-41
Figure 5.3 $^1$H NMR plots obtained at a spinning speed of 29 MHz (in a 2.5 mm MAS probe) for (a) pure PLA, (b) pure PLA$_{hv}$, and (c) pure PLA$_{hv}$ (II)

Figure 5.4 displays the $^{13}$C-CP NMR plots for the polymer synthesized under atmospheric pressure conditions. Three signals are apparent in the spectra assigned to the methyl, methine, and carbonyl carbons of poly(lactic acid). $^1$H $T_{1p}$ NMR experiments were performed on the polymers prepared by both vacuum and atmospheric pressure conditions. Results for the vacuum prepared polymers were inconclusive. However, the atmospheric pressure prepared polymers displayed the expected increase in $T_{1p}$ (meaning decaying slower) by an increase in correlation time, from being occluded inside an inorganic host.
The polymers prepared with the use of Al-MCM-41 and H-ZSM-5 under atmospheric condition exhibited slightly different molecular weights and melting temperatures when compared to the materials synthesized without them. For H-ZSM-5, this is to be expected, since its small channels (dimension of ~5Å) would constrain the polymer. This is not the case for Al-MCM-41, however, as the results from chapter 2 suggest, this catalyst exhibits a very low catalytic activity, meaning it contains a low acid concentration. Al-MCM-41, then, would not be a good acid catalyst for the condensation polymerization presented here. Chapter 2 findings lead to Al-SBA-15 as a potential catalyst for this type of reaction. The acidic strength is higher than Al-MCM-41 and it possesses much bigger channels than H-ZSM-5. For future work, this acid catalyst should be tested for the acid catalyzed polycondensation of lactic acid.
5.4 Conclusions

Poly(lactic acid) was prepared by condensation polymerization of lactic acid with and without the presence of micro/mesoporous materials containing acidity. The initial proposed acid catalyzed polycondensation of lactic acid produced polymers with fairly similar properties as to the polymers prepared without the solid acids. The vacuum setup worked best for the condensation polymerization of lactic acid, with no added catalysts or solid acids, to produce high molecular weights of up to 30,000 g/mol, though with high polydispersities. On the contrary, for the acid catalyzed polymers, the atmospheric pressure setup produced materials with slightly increased molecular weights and melting temperatures, as compared to the pure PLA prepared through the same method, and to the acid catalyzed polymers prepared under the vacuum conditions. These slight changes might indicate that the polycondensation of lactic acid is not acid catalyzed.
Chapter 6: Conclusions and Future Work

Overall, with the use of multiple techniques an organic-inorganic composite based on poly(D,L-lactide) has been created in-situ and characterized.\textsuperscript{176} A known ring-opening polymerization catalyst (i.e. Sn(Oct)\textsubscript{2}) was incorporated within the channels of the mesoporous hosts MCM-41, SBA-15, and their aluminum-containing analogues. Elemental and solid state NMR evidence indicated that stannous octoate was indeed supported inside the host channels, and that a charged framework is not required for its incorporation. Proposed mechanisms for the Sn supported catalysts are based on hydrogen bonding or dipole-dipole interactions between the hosts surface hydroxyls and the Sn\textsuperscript{2+} complex.

Sn(Oct)\textsubscript{2} catalysts supported inside the mesoporous hosts were used to prepare poly(d,l-lactide) composites. Specifically, for the Sn supported MCM-41 catalyst, it was demonstrated in detail that the d,l-lactide polymerization occurs within the host channels to produce poly(d,l-lactide). The characteristics of the resulting organic-inorganic polymer composite cannot be replicated by simple blending methods involving the polymer and MCM-41. The polymer chains grow inside the channels and can only be removed by extensive washing. For the remainder of Sn(Oct)\textsubscript{2} supported catalysts, the formation of PDLLA was also detected, and the composite’s were characterized to an extent.

Future work on poly(d,l-lactide) composites prepared with the Sn(Oct)\textsubscript{2} catalyst supported within the channels of mesoporous hosts will target optimized catalyst compositions (e.g. different hosts and reduced Sn\textsuperscript{2+} concentrations) for higher molecular weight organic fractions in the composite. The future applications of the polymer composites will be studied by investigating their mechanical properties.
Poly(lactic acid) composites were also prepared by the acid catalyzed condensation polymerization of lactic acid. Micro/mesoporous materials containing acidity, i.e. H-ZSM-5 and Al-MCM-41, were used. These composites exhibited small differences in their properties when compared to the pure / bulk polymer. For H-ZSM-5, this is to be expected, since its small channels (dimensions of ~5Å) would constrain the growth of the polymer. However, Al-MCM-41 possesses much larger channels than H-ZSM-5.

To address the problem, solid-state NMR and catalytic experiments were performed to compare post-grafted Al-MCM-41 and directly synthesized Al-SBA-15. Al-MCM-41 exhibits a lower tetrahedral aluminum environment or Brönsted acidity when compared to Al-SBA-15. In addition, higher percent conversions of isobutane were obtained for directly synthesized Al-SBA-15. These results suggest that the direct method produces a material (i.e. Al-SBA-15) with higher Brönsted acidity and catalytic activity as compared to the post-grafting of aluminum onto MCM-41.

With these catalytic findings for Al-MCM-41, we can look back at the poly(lactic acid) composite with Al-MCM-41 and conclude that the poor results are then expected, since Al-MCM-41 contains a low acid concentration. Furthermore, the results from the comparative study between the two solid acids suggest that Al-SBA-15 is a good potential catalyst for the acid catalyzed condensation polymerization of lactic acid, since its acidic strength is higher than Al-MCM-41, and it possesses much bigger channels than H-ZSM-5.

The acid catalyzed condensation polymerization approach is desirable, since the main goal would be to create an organic-inorganic composite containing no impurities (i.e. metal
catalysts). In addition, the step to create the supported catalyst would be eliminated, creating a one-pot synthesis method for obtaining polymer composites. Future work on the acid catalyzed polycondensation of lactic acid will include testing Al-SBA-15 as the catalyst.
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