

**SILICA-SUPPORTED ORGANIC CATALYSTS FOR THE SYNTHESIS OF
BIODEGRADABLE POLYMERS**

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Silica-Supported Organic Catalysts for the Synthesis of Biodegradable Polymers

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SUMMARY

Porous and nonporous silica materials functionalized with n-propylsulfonic acid moieties are used as catalysts in the ring-opening polymerization of ϵ -caprolactone. All catalysts facilitate the controlled polymerization of the monomer, yielding polymers with controlled molecular weights and narrow polydispersities. These metal-free catalysts display relatively low polymerization rates, as seen by the site-time-yields for the catalysts, which were generally at least one to three orders of magnitude lower than metal-based systems. The catalysts are recovered by simple techniques from the polymerization solution after use. However, they are shown to contain significant residual adsorbed polymer, most of which can be removed by solvent extraction techniques. Up to this point, the extracted solids are not effective catalysts in recycle experiments. These new materials represent a green alternative to traditional metal-based catalysts, as they are recoverable and leave no metal residues in the polymer.

CHAPTER 1: INTRODUCTION

Biodegradable polymers are normally defined as those polymers whose degradation can be facilitated in some fashion by a biological system. This degradation normally occurs as a result of hydrolysis and oxidation. These degradable polymers have seen use in several areas. Initially they received interest for their use in biomedical applications, and more recently they have seen growth in the area of polymer waste management through biodegradation and bioconversion¹.

For these polymers to reach the level where they are clinically applicable, they need to be measured against four key criteria that can be specifically suited for a particular application. The first criteria is biocompatibility, the biocompatibility of the polymer itself, the compatibility of any leachable species including oligomers, residual monomer, and degradation products, the compatibility of its shape, surface properties and degradation products with the system. The second is biofunctionality, the compatibility of its physical, mechanical, and biological properties with the system. The next is stability, stability in its processing, sterilization for use, and storage. The final is bioresorbability, the control of the degradation rate and resorption of the degradation products into the system. One of the large advantages of biodegradable polymers is that they can be designed specifically for controlled degradation under the stresses commonly found in biological systems. This ability to control this type of polymer has lead to its use in many medical applications including controlled drug release, absorbable surgical implants, skin grafts and bone plates².

Aliphatic polyesters such as polycaprolactone and polylactide have been found to be biodegradable, and as such have garnered much attention lately for their use in biomedical and pharmaceutical applications¹⁻¹⁹. Polymers made from lactic and glycolic acids are generally considered to be the most important aliphatic polyesters. However, polycaprolactone has seen a lot of attention for its use in controlled drug delivery systems^{2, 18, 19}.

In other published works, these polymers have been synthesized using metal complexes of tin^{4, 8, 20-27}, aluminum^{8, 13, 24, 25, 28-32}, iron^{8, 24}, scandium^{3, 11, 15}, yttrium^{17, 24, 33-37}, zinc^{24, 38-40} and other metals^{3, 17, 24, 25, 30, 34-36, 41} as catalysts. Most of these systems use a homogeneous metal complex as the catalyst, although in a few cases^{13, 17, 42} the metal complex is grafted onto a silica or alumina support. The use of these homogeneous systems then can result in residual metal contamination in the polymer produced in the reaction, which can lead to the problematic side effect of toxic metals being released during degradation^{39, 43}. Even though switching to a solid supported metal complex system does exhibit some of the positives associated with heterogeneous catalysis (e.g. recoverability of the catalyst and decreased polymer contamination) it is possible that the active metal still leaches into solution to some degree, contaminating the polymer, a highly undesirable result when producing polymers for possible medical and pharmaceutical uses.

Recent work has shown that the polymerization of aliphatic polyesters, such as ϵ -caprolactone can be catalyzed, albeit less actively, by purely organic species. The catalysts reported include catalysts that function as Lewis bases, such as various tertiary phosphines⁴⁴, dimethylaminopyridine¹⁴, and N-heterocyclic carbene complexes^{5, 45}. In

these reactions, the catalyst facilitates the opening of the ring, as shown in Figure 1.1. The first monomer is then removed from the active site by a nucleophile, such as an

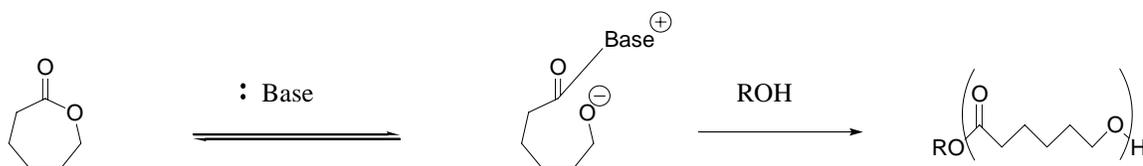


Figure 1.1. General Mechanism for ROP of Aliphatic Polyester by a Lewis Base.

alcohol, giving it an ester functionality at one end, and a hydroxyl functionality on the other end, which becomes the growing end of the chain, adding new monomer units that have been opened by the active site. These reactions show characteristics of a living reaction, (one in which even after initial monomer consumption is complete, the chains remain active to the addition of fresh monomer), such as conversion showing a linear relationship to reaction time, molecular weight showing a linear dependence on conversion, and the resulting polymers having a low polydispersity^{5, 14, 45}. Other purely organic systems that display catalytic activity include natural amino acids¹², organic acids⁴⁶, and acid/alcohol¹⁶ systems. Unfortunately, these catalysts are all homogeneous speciesⁱ that, while not contaminating the polymer with metal residue since they are in fact metal-free, still are not easily recoverable from the reaction mixture making catalyst recovery and recycle problematic.

The ultimate, environmentally benign polymerization catalyst would marry excellent catalytic properties with low cost and no waste. This could potentially be achieved with recoverable, recyclable, metal-free catalysts. This work seeks to combine

ⁱ It is noteworthy that there is a single data point that gives a precedent for a recoverable, solid organic catalyst for lactide polymerization in reference 14. In that work, they presented one instance of DMAP immobilized on polystyrene being used as a catalyst and recovered by filtration. No discussion of residual catalyst in the polymer was presented for that sample.

the advantages of metal-free systems (no possibility of metal contamination in the polymer) and supported systems (a recoverable and possibly recyclable catalyst) to give a new, “greener” polymerization catalyst. Building on the idea of using purely organic basic catalysts for this polymerization, both base and acid catalysts were tested, with an immobilized organic sulfonic acid being the most successful system. It is thus used as the primary catalyst in this work.

Much work has also been done where a sulfonic acid functionality is supported onto an oxidic solid⁴⁷⁻⁵⁷ for use in immobilizing a metal species in later synthetic steps^{47, 57} or for use as a heterogeneous catalyst for small molecule reactions^{50, 54-56}. Here, propylsulfonic acid moieties were immobilized on various silica supports, as shown in Figure 1.2, and were evaluated in the ring-opening polymerization of ϵ -

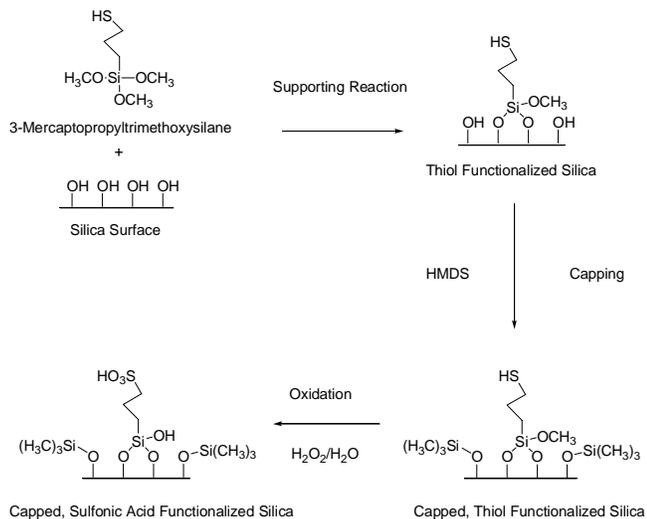


Figure 1.2. Sulfonic Acid Functionalities Immobilized onto a Silica Surface.

caprolactone, with a focus on several key issues, including the effect of physical properties of the support on the course of the polymerization and the properties of the

resulting polymer and the feasibility of first recovering and ultimately recycling the catalyst for repeated use.

CHAPTER 2: REVIEW OF PERTINENT LITERATURE

To gain context for the solid supported organic catalysts presented in this work an understanding of several related areas is important. They include homogeneous, metal-free Lewis base systems for ϵ -caprolactone polymerization, homogeneous metal systems for the polymerization, and grafted metal systems for the polymerization. An understanding of the synthesis and uses of silica supported organic catalysts is also beneficial.

2.1 Organic Lewis Bases as Catalysts

2.1.1 N-Heterocyclic Carbene System for ϵ -caprolactone and Lactide Polymerizations

In an effort to produce polymers free of metal contamination, Connor and coworkers worked to develop a metal-free approach for the ring opening polymerization of cyclic esters to form biodegradable polymers. Some of their first work was on tertiary amines¹⁴ and phosphines⁴⁴ as nucleophilic transesterification catalysts for the catalytic ring opening polymerization of lactide. In both of these cases, the catalyst functions as a Lewis base in facilitating the opening of the ring. Taking from the fact that N-heterocyclic carbenes are replacing electron rich phosphine systems in organometallic chemistry, they investigated the use of N-heterocyclic carbenes as organic catalysts for the living polymerization of lactides and lactones⁵.

The polymerizations were performed in THF at 25°C, using predominantly benzyl alcohol as an initiator. Their findings showed that the carbene was active for

polymerization of both lactide and ϵ -caprolactone, achieving near quantitative conversions for target degrees of polymerization (controlled by monomer to initiating alcohol ratio) from 30 up to 200 within 24 hours. A typical site-time yield (STY)ⁱⁱ for these reactions was 5.0 mol monomer*mol catalyst⁻¹*hour⁻¹, for a reaction with a target degree of polymerization of 60, run at a temperature of 25°C. They further found that they could control molecular weight, as the molecular weight of the polymer tracked closely with the initial monomer to initiator ratio in the system. Furthermore, polydispersities were consistently low for both monomers. They further tested the living nature of the reaction by taking a polylactide with a DP of 92 and a molecular weight of 22,500 g/mol and charging it with an additional 100 equivalents of lactide, whereupon the molecular weight of the sample increased to 39,500 g/mol and the polydispersity underwent a minimal change from 1.15 to 1.17.

They propose an anionic mechanism for this reaction, shown in Figure 2.1, where the nucleophilic carbene activates the ring structure toward attack from the alcohol. The

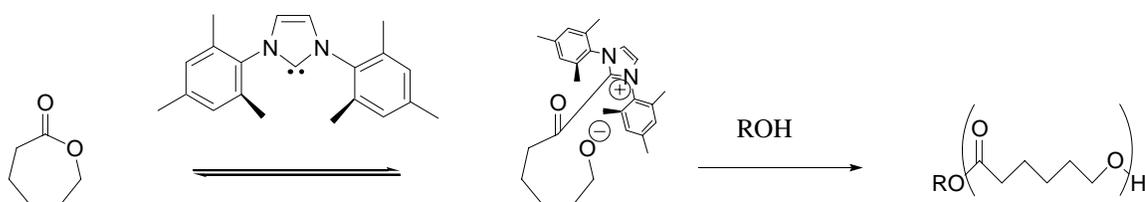


Figure 2.1 Proposed Mechanism of ROP of ϵ -caprolactone by N-Heterocyclic Carbene

ⁱⁱ Site-time-yield is used instead of turnover frequency (TOF) because strong potential transport limitations that vary with degree of polymerization and transport limitations inherent to our solid supported catalysts have not been taken into account. Strictly speaking, TOFs imply the absence of transport limitations. STY was calculated as the amount of monomer consumed per amount of catalyst per time.

initiating alcohol reacts with the monomer-carbene complex to form a ring-opened adduct. This being the case, one end of the chain should show an ester functionality from the initiating alcohol while the other should be a hydroxyl functionality, which would serve as the nucleophile to continue the propagation. NMR studies of polylactide initiated with 1-pyrenebutanol confirm that these two functionalities are present in the polymer. They noted that in anhydrous conditions, the reaction does not proceed in the absence of the alcohol.

2.1.2 Tertiary Phosphine System for Lactide Polymerization

Connor and coworkers also utilized nucleophilic tertiary phosphines⁴⁴ as a metal-free catalyst for the ring-opening polymerization of lactides. The mechanism, shown in Figure 2.2, is similar to the one shown above for carbene complexes. Again,

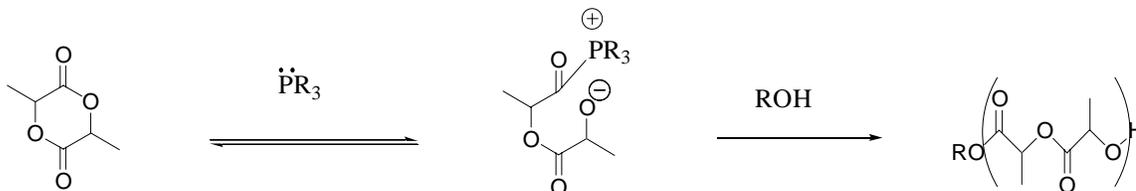


Figure 2.2 Proposed Mechanism of ROP of Lactide by Tertiary Phosphine

the Lewis base, in this case the phosphine, serves to activate the ring structure towards attack by the nucleophilic alcohol, giving a ring opened structure with an ester functionality on one end and a hydroxyl functionality on the other that serves to continue the propagation reaction. Again, under anhydrous conditions, the reaction did not occur in the absence of the initiating alcohol.

The polymerizations were performed in bulk lactide at temperatures of 135°C and 180°C and target degrees of polymerization (controlled by monomer to initiating alcohol ratio) of 30 and 60 with a variety of different phosphines, using benzyl alcohol as an initiator. They found that the substitution on the phosphine played an important role in the reactivity of the reaction. Their most active alkyl substituted phosphines achieved conversions of above 80% in the range of 2 to 5 hours, indicating a site-time yield of roughly 3 to 4 mol monomer*mol catalyst⁻¹*hour⁻¹, while their slower phenyl substituted phosphines took on the order of 24 hours to achieve similar conversions. Polydispersities were generally in the range of 1.10 to 1.30 for these reactions. They investigated the effect of solvent, studying THF at 50°C or toluene at 94°C, and found that activities dropped dramatically. After introducing solvent, the system using THF took 1 week to achieve 60% conversion, and the system using toluene took 1 week to achieve 85% conversion. The site time yield for the reaction done in toluene was calculated to be roughly .06 mol monomer*mol catalyst⁻¹*hour⁻¹. It should be noted that these reactions use lactide as the monomer, not ε-caprolactone as was used in the heterocyclic carbene example.

2.1.3 DMAP System for Lactide Polymerization

Connor and coworkers also used 4-(dimethylamino)pyridine (DMAP)¹⁴ as a metal free Lewis base catalyst for the ring opening polymerization of lactide. The proposed mechanism, shown in Figure 2.3, is again similar to proposed mechanism for carbenes and phosphines shown above. Again, the Lewis base, in this case the DMAP, serves to activate the ring structure towards attack by the nucleophilic alcohol, giving a ring

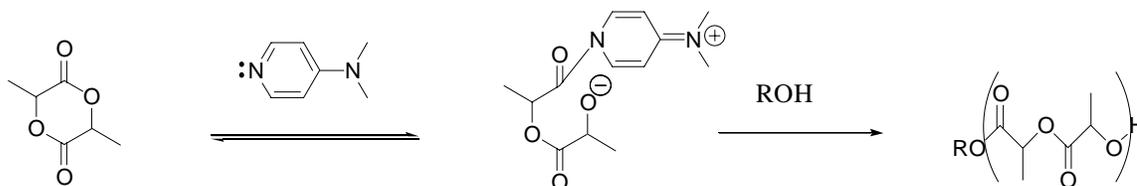


Figure 2.3 Proposed Mechanism of ROP of Lactide by DMAP

opened structure with an ester functionality on one end and a hydroxyl functionality on the other that serves to continue the propagation reaction. Again, the reaction required the initiating alcohol under anhydrous conditions.

The polymerizations were performed several ways. They were first done in dichloromethane at 35°C, with target degrees of polymerization (controlled by monomer to initiating alcohol ratio) of 30, 60, or 100, using different concentrations of DMAP, and using ethanol as an initiator. As expected, increasing DMAP concentration increased the activity of the reaction. Typically, depending on the DMAP concentration, conversions of 80% and above were reached on the order of 24 to 60 hours, for site-time yields on the order of .25 to .65 mol monomer*mol catalyst⁻¹*hour⁻¹. Polydispersities in these cases were around 1.10. Polymerizations were also done in bulk monomer at 135°C or 185°C with target degrees of polymerization of 30, 60, 100, and 140, using benzyl alcohol as an initiator. These reactions were extremely rapid, with conversions of 70% or above reached in 20 minutes or less, depending on DMAP concentration and target degree of polymerization. A typical site-time yield for these bulk reactions was around 180 mol monomer*mol catalyst⁻¹*hour⁻¹. Again, polydispersities were low, 1.20 or less. It should

again be noted that these reactions using DMAP as a catalyst used lactide as a monomer, not ϵ -caprolactone.

The research just covered highlights the possibility of catalyzing the ring-opening polymerization of lactones and lactides with organic species. Along with being metal free, all these catalysts also show the desirable effects of producing polymers with controllable molecular weights and low polydispersities.

2.2 Metal Complex Catalysts

Discussed below are some representative examples of metal complex catalysts for the ring-opening polymerization of lactides or lactones.

2.2.1 Tin Triflate System for ϵ -Caprolactone and Lactide Polymerizations

Hedrick and coworkers also used a tin triflate system²¹ for the ring-opening polymerization of ϵ -caprolactone. They note that switching to a tin triflate instead of the more commonly used tin octoate^{25, 27} provides a reactive center with a higher Lewis acidity. All of their ϵ -caprolactone polymerizations were done using ethanol as an initiator. They were done both in bulk at 0°C, 20°C, and 65°C with target degrees of polymerization of either 30 or 150, and two different catalyst concentrations. The fastest reaction, done in bulk at 65°C with the higher catalyst concentration and a target degree of polymerization of 30 had a site-time yield of 2760 mol monomer*mol catalyst⁻¹*hour⁻¹. The slowest of the bulk reactions, done at 20°C with the lower catalyst concentration and a target degree of polymerization of 30 had a STY of 62.5 mol monomer*mol catalyst⁻¹*hour⁻¹. Polymerizations were also performed in toluene at 0°C, 20°C, and 65°C

with target degrees of polymerization of 30 and 150. The fastest of the solution reactions, done at 65°C with a target degree of polymerization of 150 had a STY of 1590 mol monomer*mol catalyst⁻¹*hour⁻¹. The slowest of the solution polymerizations, done at 0°C with a target degree of polymerization of 150 had a STY of 67.5 mol monomer*mol catalyst⁻¹*hour⁻¹. Polydispersities for the polymers with a target degree of polymerization of 30 were all less than 1.20. Polydispersities for the polymers with a target degree of polymerization were in the range of 1.24 to 1.40.

2.2.2 Homogeneous Scandium Triflate System

Much of the work in the ring opening polymerization of lactones has been done in the areas of anionic and coordinated anionic systems; however, Nomura and coworkers describe a system for the cationic living polymerization of lactones using scandium trifluoromethanesulfonate, Sc(OTf)₃, as a homogeneous catalyst¹⁵. In this system, the scandium triflate is presumed to function as a Lewis acid to facilitate the opening of the ring.

The reactions using ε-caprolactone were run in toluene at 25°C. Various amounts of benzyl alcohol were used as initiators. They found that benzyl alcohol did not suppress the catalytic activity of the scandium triflate, but that the molecular weight of the polymer decreased with increasing amounts of alcohol, indicating that the molecular weight is controlled by the monomer to alcohol ratio. Using 0.10 mol% of scandium triflate, relative to monomer, the reaction proceeded to near quantitative conversion in 120 hours with a target degree of polymerization of 50, for a STY of 8.3 mol monomer*mol catalyst⁻¹*hour⁻¹. The polymers produced show a narrow molecular

weight distribution, and their molecular weights can be controlled by the ratio of monomer to an added nucleophile. The polymerization was assumed to be living because of data showing a linear increase of M_n with conversion, and the fact that low polydispersities were maintained throughout the reaction.

They propose a cationic mechanism for the reaction, as shown in Figure 2.4. The monomer coordinates to the scandium triflate, giving a cationic species that is susceptible

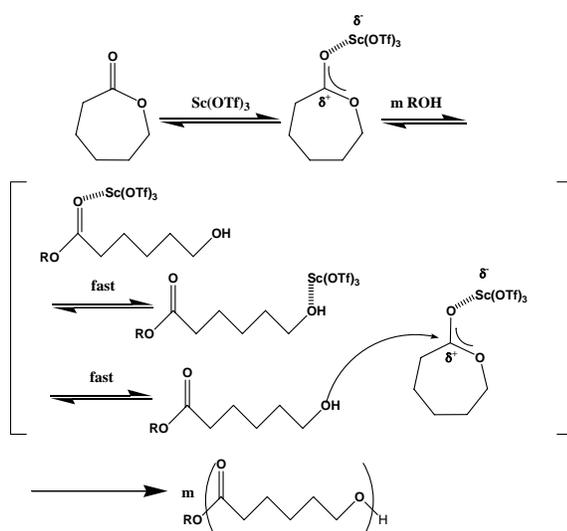


Figure 2.4 Proposed Cationic Mechanism for ϵ -caprolactone Polymerization.

to electrophilic attack by the alcohol, which yields a species with an ester functionality on one end and a hydroxyl functionality on the other. The hydroxyl end then serves to continue propagation by attacking and removing the next coordinated monomer from a scandium triflate.

2.3 Grafted Metal Complexes

2.3.1 Grafted Neodymium Alkoxide System

Rare earth metals, because of their non-toxic nature, are interesting catalysts for the ring opening polymerization of lactides and lactones. Tortosa and coworkers studied the grafting of rare earth metal alkoxides onto silica and alumina and then tested these catalysts in the ring opening polymerization of ϵ -caprolactone and oxiranes¹⁷. The solid supported catalysts were synthesized by grafted a neodymium amide onto the surface, subsequently converting it to a neodymium alkoxide by adding alcohol to the medium.

Polymerizations of ϵ -caprolactone were then performed in toluene at 50°C using benzyl alcohol as an initiator. They were able to achieve quantitative yields with target degrees of polymerization of 10 on the order of 2 hours or less, for a STY of 2200 mol monomer*mol catalyst⁻¹*hour⁻¹. They also found that molecular weight tracked well with initial monomer to alcohol concentration, and that the system produced polymers with narrow polydispersities. They also performed the reaction on two different types of commercial silica and saw different enough results, in terms of reaction rate versus particle size, to conclude that silica particle size has an important influence on the activity of the reaction, with increasing particle size leading to a decrease in their calculated rate constant. They concluded that the main advantages of their heterogeneous system were: the synthesis of the grafted neodymium alkoxide onto porous solids can be done under mild conditions; the short completion time indicated that the new catalyst is efficient for the ϵ -caprolactone polymerization, and the system produces what they term as a well defined oligo(ϵ -caprolactone).

The activities of some of the previous systems are summarized in Table 2.1.

Table 2.1 Activities of Literature Systems for ROP of ϵ -caprolactone.

System	Site-Time Yield ^a	Target DP	Temperature (°C)
N-Heterocyclic Carbene	5.0	60	25
Tin Triflate	1590	50	65
Scandium Triflate	8.3	50	25
Grafted Neodymium Alkoxide	2200	10	50

a. mol monomer consumed / mol catalyst * hour

In general, metal catalysts are obviously several orders of magnitude more active than organic systems. Scandium triflate is somewhat an exception to this rule, as it more on the level of organic systems. More examples are given later in Table 4.5 for comparison.

2.4 Solid Supported Organic Catalysts

2.4.1 Solid Supported Base Catalysts

Basic catalysts have been supported on both inorganic supports like mesoporous silica and onto polymer matrixes. Work has been done in the area of supporting analogues of 4-(dimethylamino)-pyridine (DMAP), a widely used catalyst in organic chemistry, onto polymer matrixes. Klotz and coworkers used polymer-supported DMAP analogues to catalyze the hydrolysis of p-nitrophenyl esters^{58, 59}. Shinkai and coworkers used polymer-supported DMAP analogues to catalyze the methyl ester formation of carboxylic acids⁶⁰. Tomoi and coworkers used them in the acetylation of linalool with acetic anhydride in the presence of triethylamine⁶¹. Menger and McCann tested them in the esterification of secondary and tertiary alcohols⁶². Frechet and coworkers⁶³ and Bergbreiter and coworkers⁶⁴ catalyzed the acetylation of 1-methylcyclohexanol with

them. From these examples, it is clear that supported base catalysts have seen extensive use in the catalysis of small molecule organic reactions for many years.

2.4.2 Solid Supported Sulfonic Acid Functionalities

Sulfonic acid functionalities have been supported on solids for a variety of uses, including for use as a ligand for supporting metal species in later synthetic steps^{47, 57} and for use as a heterogeneous catalyst for small molecule reactions^{48, 50, 54-56}. Normally, a solid support such as silica is treated with a silating agent like mercaptopropyltrimethoxysilane to immobilize thiol groups on the surface. These thiol functionalities are then oxidized, normally using hydrogen peroxide, as shown in Figure 1.2. Some groups then recommend a final treatment with dilute sulfuric acid to ensure complete protonation, although not all groups use this step.

Sreekanth and coworkers⁵⁷ use supported sulfonic acid sites as a ligand for coordinating lanthanum metal species. They take a sulfonic acid functionalized SBA-15 and treat it with the chloride form of a lanthanum metal, then treat that with triflic acid to yield a lanthanum triflate species supported on the solid. These solids were then used as catalysts for C-C bond forming reactions, such as the allylation of carbonyl compounds with tetraallytin.

Cano-Serrano and coworkers⁴⁸ used the basic procedure outlined above of immobilizing thiol groups onto amorphous silica and then oxidizing using hydrogen peroxide to create acid-functionalized amorphous silica. They then used the supported acid species as a catalyst for a small molecule reaction, the esterification of acetic acid with methanol, done in the liquid phase.

2.5 Literature Conclusion

The work summarized here shows that both Lewis bases and acidic metals can be used to catalyze the ring-opening polymerization of lactides and lactones to produce polymers of controlled molecular weights and low polydispersities. Knowing how to support both metal-free Lewis bases and metal-free acids, we set out to expand upon this work by investigating the creation of a solid supported, metal-free system for the ring-opening polymerization of ϵ -caprolactone.

CHAPTER 3: IMMOBILIZED LEWIS BASES

Two silica-immobilized Lewis bases were investigated as catalysts for the polymerization of ϵ -caprolactone and lactide. A system where a tertiary phosphine was immobilized on the silica surface was developed, as was one using a supported methylaminopyridine (MAP). Preliminary work, involving catalyst synthesis and attempted use in polymerizations, was done on both of these basic systems. However, neither of the systems proved to be effective catalysts under the conditions used.

3.1 Phosphines

3.1.1 Experimental

3.1.1.1 *Chemicals*

Benzyl alcohol (Acros, 99%) and ϵ -caprolactone (Acros, 99%) were dried over 4-Å molecular sieves and stored under nitrogen in a glovebox. L-lactide (Aldrich, 98%) was sublimed *in vacuo* at 80°C for several hours and stored in a glovebox. Toluene for polymerization (Acros, 99.8%) was dried over sodium benzophenone and stored under nitrogen in a glovebox. Anhydrous toluene (Acros, 99.8%), 2(diphenylphosphino)ethyltriethoxysilane (Gelest), triphenylphosphine (Aldrich, 99%), and 1,1,1,3,3,3-hexamethyldisilazane (HMDS, Acros, 98%) were used as received and stored under nitrogen in a glovebox. CPG240 (Millipore) and Cab-O-Sil EH5 (Cabot) were dried *in vacuo* at 150 °C and stored under nitrogen in a glovebox. Poly(ethylene glycol)-*block*-

poly(propylene glycol)-*block*-poly(ethylene glycol) (EO-PO-EO; Aldrich), hydrochloric acid (HCl; JT-Baker), tetraethyl orthosilicate (TEOS; Acros; 98%), and 1,3,5-trimethylbenzene (TMB; Aldrich; 97%) were used as received.

3.1.1.2 Characterization Techniques

3.1.1.2.1 Materials Characterization

Thermogravimetric analysis (TGA) was carried out with a Netzsch STA 409 PC Luxx simultaneous thermal analyzer (TGA/differential scanning calorimetry) with heating to 1000 °C at 20 K/min. The silica pore diameters and surface areas were determined with nitrogen physisorption data obtained with a Micromeritics ASAP 2010 system. The samples were dried at 70 °C for 1 h and at 150 °C overnight *in vacuo*. The surface areas were analyzed by the Brunauer-Emmett-Teller (BET) method, and the pore size distribution was determined with the Barrett-Joyner-Halenda (BJH) method applied to the adsorption side of the isotherm.

3.1.1.2.2 Polymer Characterization

Attempts were made to determine the polymerization reaction conversion using ¹H NMR and gravimetric methods. ¹H NMR measurements were performed with a Mercury Vx 300-MHz instrument with CDCl₃ as a solvent. A gel permeation chromatograph, GPC, with American Polymer Standards columns (10⁵, 10³, and 10² Å) was used to determine molecular weights and molecular weight distributions of the polymers. It was equipped with a Waters 510 pump and a Waters 410 differential refractometer. The eluent was

THF at a flow rate of 1 mL/min. Polymer molecular weights and molecular weight distributions were measured against 11 linear polystyrene standards (580 – 189,300).

3.1.1.3 Synthesis and Reactions

3.1.1.3.1 SBA-15 (105 Å pores)

A nonionic surfactant (EO-PO-EO) was used as the structure-directing agent in the synthesis of mesoporous SBA-15⁶⁵. In a typical experiment, 12.1 g EO-PO-EO was combined with 320.2 g deionized H₂O and 69.4 g 38% HCl and stirred at room temperature for at least 3 hours until all the surfactant was dissolved. Next, 25.3 g TEOS was added and allowed to stir for 10 minutes. Finally, 1.5 g TMB was added and allowed to stir for a further 10 minutes before the solution was portioned into 10 Parr Teflon-lined autoclaves. These were then agitated at 35°C for 20 hours and allowed to age without stirring at 100°C for 24 hours. The solid product was then recovered by filtration, washed with deionized water, and air dried at 50°C for several hours. Calcination was then performed, with the temperature increasing from room temperature to 200°C at 1.2 K/min; the temperature was then maintained at 200°C for 2 hours before increasing to 550°C at 1.2 K/min, which was then maintained for 4 hours. This final product was then dried *in vacuo* at 150°C for 3 hours and stored in a glovebox under nitrogen.

3.1.1.3.2 Preparation of phosphine functionalized silica

Typically ~1.1 g of 2(diphenylphosphino)-ethyltriethoxysilane was combined with ~ 1.0 g of silica (SBA-15, CPG 240, or Cab-O-Sil) in ~15-20 g anhydrous toluene in the

glovebox. The solution was then stirred under Ar at reflux conditions for approximately 24 hours. The solid was then recovered by filtration and washed with anhydrous toluene in the glovebox. The solid was finally dried *in vacuo* at room temperature overnight and placed in the glovebox for further use.

3.1.2 Results and Discussion

Three different silica supports, SBA-15, CPG-240, and Cab-O-Sil EH5 were used in this study. Their properties are further enumerated in section 4.2.1. As an analog to the homogeneous tertiary phosphines used a Lewis base catalyst in literature examples⁴⁴, 2(diphenylphosphino)-ethyltriethoxysilane, a commercially available phosphine with two attached phenyl groups and an ethyl linker to an alkoxy silane was used as the supportable species. The supporting reaction was a simple one-step procedure as seen in Figure 3.1. Typical loadings are shown in Table 3.1 and would seem to track with the

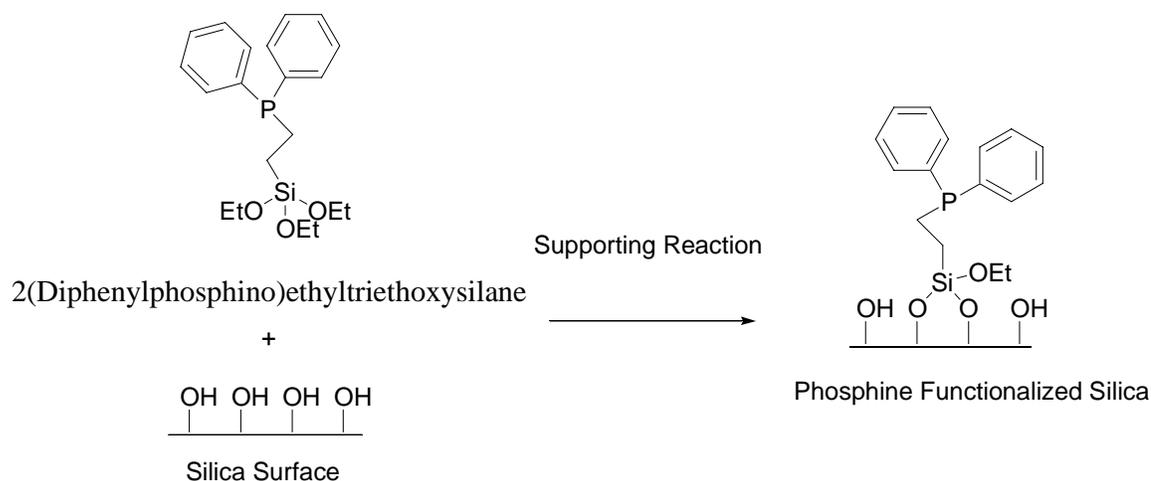


Figure 3.1 Phosphine Supporting Reaction

Table 3.1 Phosphine Loading

Sample	Phosphine Loading (mmol / g silica)	Surface Area (m ² / g)	Phosphine Loading (mmol / m ²)
Phos-SBA	0.516	798	6.47E-04
Phos-CPG	0.129	79.6	1.62E-03
Phos-Cab	0.367	335	1.10E-03

surface area of the support, with SBA-15 having the highest surface area and the highest loading and CPG having the lowest surface area and the lowest loading. It should be noted that at this point, solids were washed only with toluene after the supporting reaction. It was later discovered during the work on sulfonic acids that washing the solid with a more polar solvent like THF or DCM lowered the apparent loading on the solid.

Polymerizations were run at a variety of conditions: with lactide and ϵ -caprolactone as monomers, heterogeneously and homogeneously, in solution and in bulk monomer, with different catalyst concentrations, and different temperatures. Typical results are summarized in Table 3.2. As seen by the data, polymerizations using

Table 3.2 Phosphine Polymerizations

Catalyst	Monomer	Solvent	[M]:[C]:[I] ^a	Time (h)	Temperature (°C)	Mn ^b
PPh ₃	ε-caprolactone	Toluene	100:5:1	97	95	<1200
PPh ₃	L-lactide	Toluene	100:5:1	90	100	<1400
PPh ₃	L-lactide	Neat	100:1:1	26	135	3500
PPh ₃	L-lactide	Toluene ^c	60:1:1	67	135	<1400
PBu ₃	L-lactide	Toluene ^c	60:1:1	52	135	<1400
SBA-PPh ₂	L-lactide	Toluene	60:1:1	72	135	**
SBA-PPh ₂	L-lactide	Toluene	60:1:1	97	135	<700

a. Monomer : Catalyst : Initiator Ratio

b. Determined by GPC

c. Low solvent concentration, 1:1 monomer to solvent, mass:mass

phosphines were largely unsuccessful. Any reactions done with solvent present resulted in oligomers with a degree of polymerization of 10 or less even at prolonged reaction times. The only reactions that gave a higher molecular weight were done in bulk monomer, which would be unsuitable for a supported catalyst since it would not provide the necessary liquid volume for good mixing and would also suffer from viscosity issues as molecular weight grows, further inhibiting good mixing.

At this time, we attempted to determine conversion via ¹H NMR analysis by comparing relative intensities of proton signals in the monomer to their counterpart shifted signals in the polymer. Unfortunately, this method appeared unreliable for several reasons. For example, when two reactions with the same target degree of polymerization were analyzed, the reaction showing a higher molecular weight as determined by GPC, showed lower conversion as determined by NMR. Simple gravimetric calculations for conversion were also impossible as it was almost always impossible to precipitate and recover polymer from these solutions due to low molecular weights being produced.

And, at this time, we had not investigated GC as a method for determining reaction conversion, so no reliable conversion data exists for these reactions.

Initially, as seen in the first two entries in Table 3.2, reactions were done with a homogeneous catalyst in solution. After prolonged reaction times at elevated temperatures, GPC analysis indicated that all that had been produced was oligomers perhaps up to a degree of polymerization of 10, with little control, as evidenced by multimodal GPC trace. A typical GPC trace is shown in Figure 3.2. After these initial

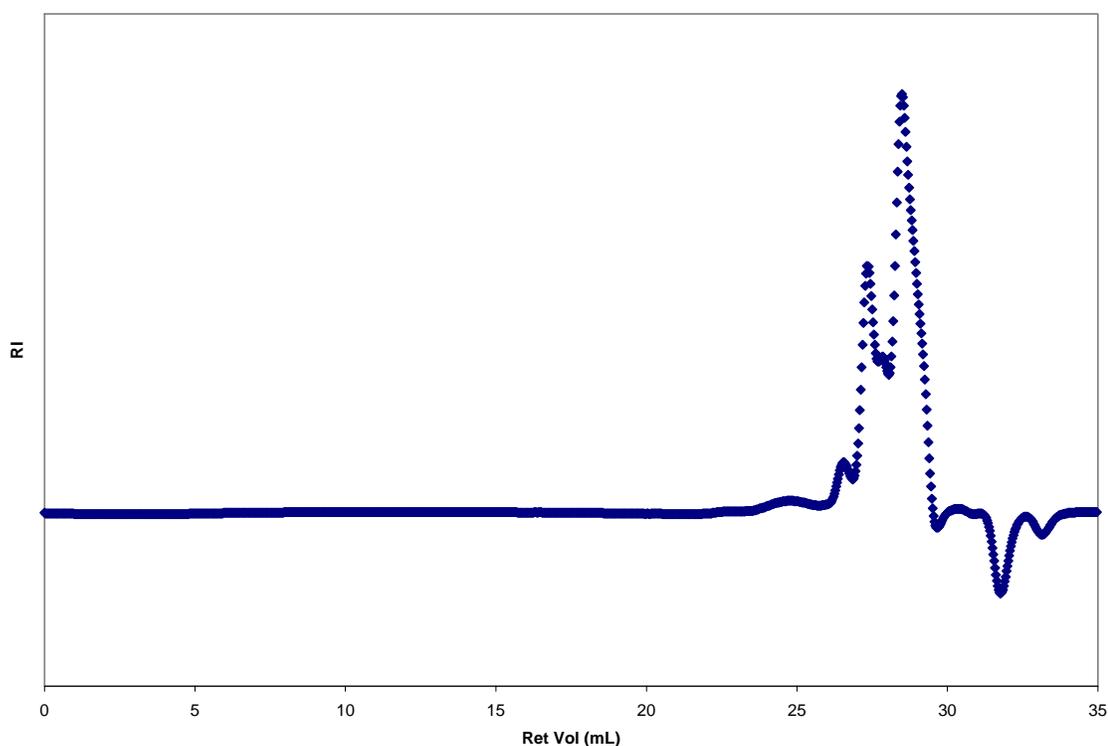


Figure 3.2 Phosphine GPC Trace Showing Typical Multi-Modal Pattern

unsuccessful attempts, efforts were concentrated solely on L-lactide, the predominant monomer used in the literature for this system. The next attempt, as seen in the third

entry in Table 3.2 was to try a homogeneous reaction in bulk monomer. This was somewhat successful as a polymer with a Mn of around 3500 was produced after 26 hours. However, a bulk reaction was hypothesized to be unfeasible with a solid-supported catalyst. Based on catalyst loading, solid-supported catalyst would need to be added on the order of 100's of milligrams to produce the desired catalyst concentration, and without solvent, that amount of solid catalyst would not be able to mix uniformly into the system. So, the next step was to try several reactions with lower solvent contents than the initial tests, as seen in the fourth and fifth entries of Table 3.2. In these trials, solvent was added in a 1:1 mass ratio with the monomer. Again after prolonged reaction times at elevated temperatures, GPC showed nothing more than uncontrolled oligomerization, again seen in the multimodal GPC traces. Lastly, for sake of completeness, SBA supported phosphines were attempted, as seen in the sixth and seventh entries of Table 3.2. As expected, these trials suffered from a similar low activity to the previous homogeneous trials.

While disappointing, these results were not unexpected as phosphines were the least active system of the Lewis base systems in the literature. And, by supporting the phosphines onto a solid, the problems of low activity seen in the homogeneous system were only exacerbated. So, efforts were switched to a more promising system, one based around dimethylaminopyridine.

3.2 DMAP

3.2.1 Experimental

3.2.1.1 Chemicals

Benzyl alcohol (Acros, 99%) and ϵ -caprolactone (Acros, 99%) were dried over 4-Å molecular sieves and stored under nitrogen in a glovebox. L-lactide (Aldrich, 98%) was sublimed *in vacuo* at 80°C for several hours and stored in a glovebox. Toluene for polymerization (Acros, 99.8%) was dried over sodium benzophenone and stored under nitrogen in a glovebox. Anhydrous toluene (Acros, 99.8%) and 1,1,1,3,3,3-hexamethyldisilazane (HMDS, Acros, 98%) were used as received and stored under nitrogen in a glovebox. Allyl bromide (Acros, 99%) was dried over calcium hydride and stored in the glovebox. 4-(Methylamino)pyridine (Aldrich, 99%) was dried *in vacuo* and stored in the glovebox. 4-(Dimethylamino)pyridine (Aldrich, 99%+) was recrystallized from methanol, dried *in vacuo* and stored in the glovebox. Butyl lithium (BuLi, Aldrich, 1.6M in hexanes) was used as received. CPG240 (Millipore) and Cab-O-Sil EH5 (Cabot) were dried *in vacuo* at 150 °C and stored under nitrogen in a glovebox. Poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*poly(ethylene glycol) (EO–PO–EO; Aldrich), hydrochloric acid (HCl; JT-Baker), tetraethyl orthosilicate (TEOS; Acros; 98%), and 1,3,5-trimethylbenzene (TMB; Aldrich; 97%) were used as received.

3.2.1.2 Characterization Techniques

3.2.1.2.1 Materials Characterization

Thermogravimetric analysis (TGA) was carried out with a Netzsch STA 409 PC Luxx simultaneous thermal analyzer (TGA/differential scanning calorimetry) with heating to

1000 °C at 20 K/min. The silica pore diameters and surface areas were determined with nitrogen physisorption data obtained with a Micromeritics ASAP 2010 system. The samples were dried at 70 °C for 1 h and at 150 °C overnight *in vacuo*. The surface areas were analyzed by the Brunauer–Emmett–Teller (BET) method, and the pore size distribution was determined with the Barrett–Joyner–Halenda (BJH) method applied to the adsorption side of the isotherm.

3.2.1.2.2 Polymer Characterization

Attempts were made to determine the polymerization reaction conversion using gravimetric methods. A gel permeation chromatograph, GPC, with American Polymer Standards columns (10^5 , 10^3 , and 10^2 Å) was used to determine molecular weights and molecular weight distributions of the polymers. It was equipped with a Waters 510 pump and a Waters 410 differential refractometer. The eluent was THF at a flow rate of 1 mL/min. Polymer molecular weights and molecular weight distributions were measured against 11 linear polystyrene standards (580 – 189,300).

3.2.1.3 Synthesis

3.2.1.3.1 SBA-15 (105 Å pores)

A nonionic surfactant (EO-PO-EO) was used as the structure-directing agent in the synthesis of mesoporous SBA-15⁶⁵. In a typical experiment, 12.1 g EO-PO-EO was combined with 320.2 g deionized H₂O and 69.4 g 38% HCl and stirred at room temperature for at least 3 hours until all the surfactant was dissolved. Next, 25.3 g TEOS

was added and allowed to stir for 10 minutes. Finally, 1.5 g TMB was added and allowed to stir for a further 10 minutes before the solution was portioned into 10 Parr Teflon-lined autoclaves. These were then agitated at 35°C for 20 hours and allowed to age without stirring at 100°C for 24 hours. The solid product was then recovered by filtration, washed with deionized water, and air dried at 50°C for several hours. Calcination was then performed, with the temperature increasing from room temperature to 200°C at 1.2 K/min; the temperature was then maintained at 200°C for 2 hours before increasing to 550°C at 1.2 K/min, which was then maintained for 4 hours. This final product was then dried *in vacuo* at 150°C for 3 hours and stored in a glovebox under nitrogen.

3.2.1.3.2 Preparation of methylaminopyridine (MAP) ligand

Typically, 0.45 g of 4(methylamino)pyridine was dissolved in ~16.0 of dry THF in the glovebox. Roughly 1.1 equivalents, 0.79g, of allyl bromide were combined with a small amount of dry THF in a syringe in the glove box as well. The flask was then placed under Ar in an ice bath. Approximately 1.1 equivalents of 1.6M BuLi in hexanes was then added to the MAP/THF mixture and allowed to stir for 30 minutes under Ar. The allyl bromide/THF mixture was then injected into the solution which was allowed to warm to room temperature as it stirred overnight. After stirring overnight, ethanol was added to the solution to quench the BuLi. Excess solvent was pumped off under vacuum. Approximately 50mL of deionized water was then added to the solution, which was mixed and poured into an extraction funnel. Approximately 100 mL of dichloromethane was then added the funnel. The solution was agitated and then allowed to separate. The dichloromethane layer was removed into a flask and magnesium sulfate was added to dry

the solution. The magnesium sulfate was then filtered off and the liquid collected in another flask. Excess dichloromethane was then removed on the rotovap and the remainder was dried *in vacuo* leaving the 4(methylamino)pyridine species with an attached allyl functionality. The MAP/Allyl species was then combined with approximately 5 equivalents of 3mercaptopropyltrimethoxysilane and a catalytic amount of AIBN in ~20 g of chloroform. The solution was stirred under Ar at reflux overnight. The excess chloroform was then pumped off under vacuum and the excess MPTMS removed by distillation, leaving the supportable MAP/alkoxysilane ligand.

3.2.1.3.3 Preparation of silica supported MAP

Typically ~1.1 g of MAP ligand was combined with ~ 1.0 g of silica (SBA-15, CPG 240, or Cab-O-Sil) in ~15-20 g anhydrous toluene in the glovebox. The solution was then stirred under Ar at reflux conditions for approximately 24 hours. The solid was then recovered by filtration and washed with anhydrous toluene in the glovebox. The solid was finally dried *in vacuo* at room temperature overnight and placed in the glovebox for further use.

3.2.2 Results and Discussion

Three different silica supports, SBA-15, CPG-240, and Cab-O-Sil EH5 were used in this study. Their properties are further enumerated in section 4.2.1. As an analog to the homogeneous DMAP used a Lewis base catalyst in literature examples¹⁴, a method for supporting a methylaminopyridine functionality onto silica was developed. The

immobilization scheme is shown in Figure 3.3. In the procedure, 4-(methylamino)pyridine was used a starting compound. BuLi was used to deprotonate the

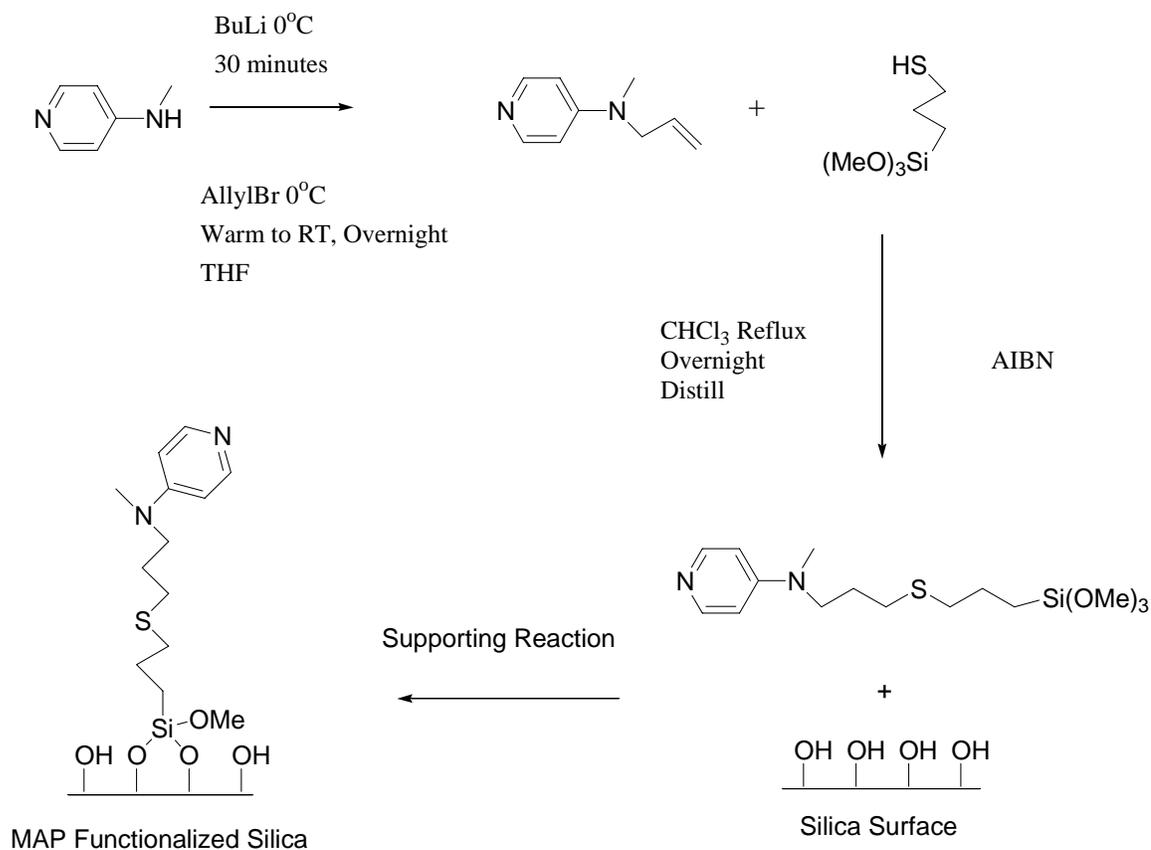


Figure 3.3 MAP Immobilization Procedure

amine, which could then be coupled with allyl bromide to introduce an allyl functionality into the compound. The allyl functionality was then coupled with the thiol functionality on 3(mercaptopropyl)trimethoxysilane using a radical reaction to give a methylaminopyridine functionality tethered to a supportable alkoxy silane. Typical loadings are shown in Table 3.3 and would seem to track with the surface area of the

Table 3.3 MAP Loadings

Sample	MAP Loading (mmol / g silica)	Surface Area (m ² / g)	MAP Loading (mmol / m ²)
MAP-SBA	2.06	798	2.58E-03
MAP-CPG	0.3	79.6	3.77E-03

support, with SBA-15 having the highest surface area and the highest loading and CPG having the lowest surface area and the lowest loading. It should again be noted that these solids were washed only with toluene before it was discovered that washing with more polar solvents lowered the apparent loading in the case of sulfonic acid, so it is once again a possibility here that some of the loading may be due to physisorbed species not removed by toluene in the wash process.

According to the literature on Lewis bases, DMAP was a more active catalyst than the tertiary phosphines, so these trials were expected to yield better results than the phosphine work. Polymerizations were run at a variety of conditions: heterogeneously and homogeneously, in solution and in bulk monomer, with different catalyst concentrations, and different temperatures, using lactide as a monomer. Typical results are summarized in Table 3.4. The first two entries are homogeneous experiments, and entries three and four are two of the more successful heterogeneous reactions. By using

Table 3.4 MAP Polymerizations

Catalyst	Monomer	Solvent	[M]:[C]:[I] ^a	Time (h)	Temperature (°C)	Conversion (%) ^b	Mn ^c	PDI ^c
DMAP	L-lactide	DCM	60:2:1	24	35	50	2290	1.09
DMAP	L-lactide	DCM	60:4:1	24	35	60	2520	1.09
MAP-SBA	L-lactide	DCM	60:4:1	45	37	35	8600	**
MAP-CPG	L-lactide	DCM	60:2:1	65	37	**	3780	**

- Monomer : Catalyst : Initiator Ratio
- Gravimetric Conversion (when precipitated polymer exists)
- As Determined by GPC

a homogeneous DMAP complex, conversions of 50% or greater, as determined gravimetrically by the weight of polymer precipitated using cold methanol divided by the weight of initial monomer used, were achieved in 24 hours. Molecular weights of over 2000 were achieved and polydispersities were low, 1.09, as determined by GPC. As expected, increasing the catalyst concentration also appeared to increase the rate of the reaction. With these successful homogeneous trials in hand, efforts to catalyze the reaction with the solid-supported catalysts were made. These reactions were more successful than the work on supported phosphines, but unfortunately still did not meet all of the goals we were hoping to meet for a solid-supported catalyst. As seen in the entry for MAP-SBA, an isolated conversion of 35% was achieved in 45 hours reaction time. However, the reaction was unsuccessful from a control standpoint, because the molecular weight listed is the Mn for the highest molecular weight signal on the trace, but the GPC trace was multimodal. A typical multimodal GPC trace from a supported-MAP polymerization is shown in Figure 3.4. So, it was impossible to determine a polydispersity for this sample. The MAP-CPG showed even more problems. No

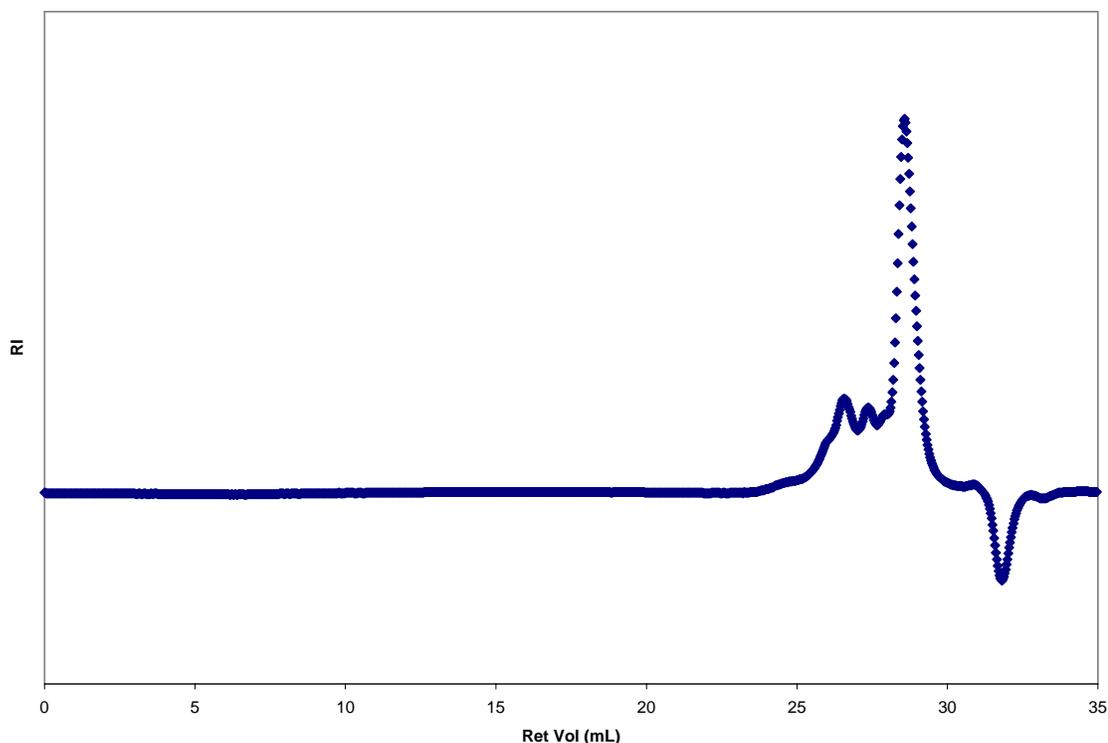


Figure 3.4 Supported-MAP GPC Trace Showing Typical Multi-Modal Pattern

polymer precipitated for gravimetric conversion. The GPC did indicate a molecular weight of 3780, but again the trace was multimodal, so only the Mn of the highest molecular weight peak is shown and polydispersity was impossible to determine. Several more trials with supported MAP complexes were run, but these results are indicative of the best results with this system.

The work on silica-supported basic catalysts showed several things. First, immobilizing a Lewis base onto a silica surface was easily accomplished. However, using them as polymerization catalysts was not as simple. Both homogeneous and silica-supported phosphine catalysts, when used in solution, showed problems with activity, yielding low molecular weight products after prolonged reaction times. This was not

unexpected as phosphines were the least reactive Lewis base catalyst for lactide polymerizations and supporting them onto a solid would probably only function to lessen their reactivity. The drop in activity due to immobilizing the phosphine could be attributed decreased access to the active site once they are tethered close to a surface and to mass transport issues inherent to solid supported systems. Moving to a silica-supported MAP catalyst appeared to alleviate the problems with low activity, as higher molecular weights products were achieved; however, these reactions appeared to suffer from poor control, as GPC traces of the polymers produced were generally multimodal. A probable reason for the multi-modal pattern seen in the GPC traces could be because different types of sites are present on the silica surface. In addition to the desired type of site for supported-MAP seen in Figure 3.3, it is possible that the basic pyridine ring could bend over to associate with the acidic silanols on the silica surface, causing a different type of active site with a different reactivity. Now knowing that supported basic catalysts were largely unsuccessful, efforts were then concentrated in acid systems instead of base systems to catalyze the reaction.

CHAPTER 4: SOLID SUPPORTED SULFONIC ACID CATALYSTS

After the initial work with supported Lewis base catalysts was set aside, efforts were concentrated on other areas. Metal complexes, functioning as Lewis acids, had already been shown to be active for the ring-opening polymerization of ϵ -caprolactone. So, the idea was to use a supported, metal free acid as a possible catalyst. A silica-supported sulfonic acid was the catalyst chosen for evaluation.

4.1 Experimental Concerns

4.1.1 Chemicals and Other Materials

Benzyl alcohol (Acros, 99%), dodecane (Acros, 99%), and ϵ -caprolactone (Acros, 99%) were dried over 4-Å molecular sieves and stored under nitrogen in a glovebox. Paratoluenesulfonic acid monohydrate (TsOH, Aldrich, 98.5+%) was dried *in vacuo* at 100°C for 4 hours and stored under nitrogen in the glovebox. Toluene for polymerization (Acros, 99.8%) was dried over sodium benzophenone and stored under nitrogen in a glovebox. Tetrahydrofuran (THF, Aldrich >99%) was dried and deoxygenated with a purification system and stored under nitrogen in a glovebox. Anhydrous toluene (Acros, 99.8%), 3-mercaptopropyltrimethoxysilane (MPTMS, Aldrich, 95%), and 1,1,1,3,3,3-hexamethyldisilazane (HMDS, Acros, 98%) were used as received and stored under nitrogen in a glovebox. Hydrogen peroxide (Acros, 30% in water) was used as received and stored in a refrigerator. CPG240 (Millipore), Cab-O-Sil EH5 (Cabot), and MS-3030 (PQ Corporation) were dried *in vacuo* at 150 °C and stored under nitrogen in a glovebox.

Poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*poly(ethylene glycol) (EO-PO-EO; Aldrich), hydrochloric acid (HCl; JT-Baker), tetraethyl orthosilicate (TEOS; Acros; 98%), and 1,3,5-trimethylbenzene (TMB; Aldrich; 97%) were used as received.

4.1.2 Characterization Techniques

4.1.2.1 *Materials Characterization*

Thermogravimetric analysis (TGA) was carried out with a Netzsch STA 409 PC Luxx simultaneous thermal analyzer (TGA/differential scanning calorimetry) with heating to 1000 °C at 20 K/min. The silica pore diameters and surface areas were determined with nitrogen physisorption data obtained with a Micromeritics ASAP 2010 system. The samples were dried at 70 °C for 1 h and at 150 °C overnight *in vacuo*. The surface areas were analyzed by the Brunauer-Emmett-Teller (BET) method, and the pore size distribution was determined with the Barrett-Joyner-Halenda (BJH) method applied to the adsorption side of the isotherm. FT-Raman spectroscopy was performed with a Bruker IFS 66 v/S equipped with dual Fourier transform infrared (FTIR) and Fourier transform/Raman (FT-Raman) benches and a CaF₂ beam splitter.

4.1.2.2 *Polymer Characterization*

The polymerization reaction conversion was determined by monomer consumption as measured by a Shimadzu GC 14-A gas chromatograph with a flame-ionization detector and a HP-5 column (length=30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). The column was first heated from 50 to 140 °C at 30 K/min, then from 140 to 300

°C at 40 K/min under constant pressure with a constant inlet and detector temperature of 330 °C. ¹H NMR measurements were performed with a Mercury Vx 300-MHz instrument with CDCl₃ as a solvent. A gel permeation chromatograph, GPC, with American Polymer Standards columns (10⁵, 10³, and 10² Å) was used to determine molecular weights and molecular weight distributions of the polymers. It was equipped with a Waters 510 pump and a Waters 410 differential refractometer. The eluent was THF at a flow rate of 1 mL/min. Polymer molecular weights and molecular weight distributions were measured against 11 linear polystyrene standards (580 – 189,300). Elemental analysis was performed by Galbraith Laboratories (Knoxville, TN).

4.1.3 Synthesis

4.1.3.1 *SBA-15 (105 Å pores)*

A nonionic surfactant (EO-PO-EO) was used as the structure-directing agent in the synthesis of mesoporous SBA-15⁶⁵. In a typical experiment, 12.1 g EO-PO-EO was combined with 320.2 g deionized H₂O and 69.4 g 38% HCl and stirred at room temperature for at least 3 hours until all the surfactant was dissolved. Next, 25.3 g TEOS was added and allowed to stir for 10 minutes. Finally, 1.5 g TMB was added and allowed to stir for a further 10 minutes before the solution was portioned into 10 Parr Teflon-lined autoclaves. These were then agitated at 35°C for 20 hours and allowed to age without stirring at 100°C for 24 hours. The solid product was then recovered by filtration, washed with deionized water, and air dried at 50°C for several hours. Calcination was then performed, with the temperature increasing from room temperature to 200°C at 1.2

K/min; the temperature was then maintained at 200°C for 2 hours before increasing to 550°C at 1.2 K/min, which was then maintained for 4 hours. This final product was then dried *in vacuo* at 150°C for 3 hours and stored in a glovebox under nitrogen.

4.1.3.2 Synthesis of acid-functionalized catalysts

Solid supported acid functionalized catalysts were prepared by routes adapted from literature methods as described below^{48, 50, 57}.

4.1.3.3 Synthesis of immobilized thiol functionalities on SBA-15 (SBA-SH)

Typically, 2.0 g MPTMS was added to a slurry of 2.0 g of SBA-15 in ~40 g of anhydrous toluene in a 100mL round bottom flask in the glovebox. The mixture was stirred under an Ar atmosphere at reflux conditions for ~ 24 hours. The product was recovered and washed with copious amounts of anhydrous toluene and THF, again in the glovebox. The solid product was then dried at *in vacuo* at 150°C overnight before being stored in the glovebox.

4.1.3.4 Silanol capping on thiol functionalized SBA-15 (SBA-SH-Cap)

Typically, 1.1 g HMDS was added to a slurry of 1.0 g SBA-SH in ~ 20 g anhydrous toluene in a 100mL round bottom flask in the glovebox. The mixture was then stirred at room temperature under an Ar atmosphere for ~ 24 hours. The product was recovered and washed with copious amounts of toluene and THF, again the glovebox. The solid product was then dried *in vacuo* at 150°C overnight before being stored in the glovebox.

4.1.3.5 Oxidation of SBA-SH or SBA-SH-Cap to sulfonic acid functionalized SBA (SBA-SO₃H / SBA-SO₃H-Cap)

In a typical experiment, 1.0 g of SBA-SH was combined with 10.0 g MeOH and 20.0 g 30% H₂O₂ in a 100 mL round bottom flask. The mixture was stirred at room temperature for 24 hours. The product was subsequently recovered and washed with copious amounts of deionized H₂O. The solid product was then dried *in vacuo* at 150°C overnight before being stored in the glovebox.

4.1.3.6 Preparation of sulfonic acid functionalized CPG240, Cab-O-Sil, and MS-3030

Sulfonic acid sites were immobilized onto CPG240, Cab-O-Sil, and MS-3030 (CPG-SO₃H / Cab-SO₃H / MS-SO₃H) using the same procedures outlined above for SBA-15. All resulting catalysts were recovered, washed, and stored under the same conditions.

4.1.4 Polymerization reactions

All polymerization reactions were set up in the glovebox under a nitrogen atmosphere and conducted under argon using standard Schlenk line techniques.

4.1.4.1 Homogeneous polymerization of ϵ -caprolactone with TsOH

Typically, ~7 g of dry toluene was combined with 0.4-0.7 g of dodecane (GC standard) in a 3-neck flask fitted with a glass stopper and a rubber septum. To this was added 30.6 μ L of benzyl alcohol (70:1 [M]:[I]). 2.32 g of ϵ -caprolactone was added to solution, which was then mixed vigorously. Finally 10.6 mg of TsOH (.57 g of a 1.9 wt% solution of TsOH in toluene) was added to the solution (0.3 mol% catalyst to monomer). The

reaction solution was then stirred under Ar at 52°C, while GC was used to monitor the conversion. When the desired conversion was reached, the reaction was quenched by adding excess MeOH, followed by excess THF. Excess solvent was then removed by rotovap, leaving an oily, yellow liquid. The polymer was then precipitated with cold hexanes, then recovered and washed with cold hexanes. The resulting polymer was then dried under vacuum and stored in the glovebox.

4.1.4.2 Polymerization of ϵ -caprolactone with supported catalysts.

In a typical reaction, ~7 g of dry toluene was combined with 0.4-0.7 g of dodecane (GC standard) in a 3-neck flask fitted with a glass stopper and a rubber septum. To this was added 30.6 μ L of benzyl alcohol (70:1 [M]:[I]). 2.32 g of ϵ -caprolactone was added to solution, which was then mixed vigorously. Finally, supported catalyst, corresponding to 0.3 mol% active sites relative to monomer, was added. The reaction solution was then stirred under Ar at 52 °C while GC monitored the conversion. When the desired conversion was reached, the reaction was quenched by adding excess MeOH, followed by excess THF. The solution was then centrifuged to concentrate the solid catalyst and the supernatant solution was poured off. Excess solvent was then removed from this solution by rotovap, leaving an oily, yellow liquid. The polymer was then precipitated with cold hexanes, then recovered and washed with cold hexanes. The resulting polymer was then dried under vacuum and stored in the glovebox.

4.1.5 Attempted recycle procedure

After centrifugation, the solid catalyst was recovered. It was first washed with excess amounts of dichloromethane and THF, both good solvents for poly(caprolactone). A Soxhlet extraction was then performed overnight, again using dichloromethane and THF. The solid was then collected and dried overnight at 150°C, then placed in the glovebox for further use.

4.2 Results and Discussion

4.2.1 Catalyst Synthesis and Characterization

Four different silica supports, with differing pore sizes and structures, were studied. Hexagonal mesoporous SBA-15 was synthesized in the lab via published literature methods⁶⁵. The other three silica sources, mesoporous CPG 240 and MS-3030, and fumed, non-porous Cab-O-Sil EH5 were commercially available. SBA-15 is a hexagonal mesoporous silica material with unidimensional mesopores connected by small micropores. CPG 240 is a controlled pore glass with interconnected mesopores with a narrow pore size polydispersity and relatively lower surface area. MS-3030 is a commercially available, mesoporous, microspherical silica with an average particle size of 90 μm . Cab-O-Sil EH5 is, as noted, a non-porous silica. The reason for using multiple types of silica was to investigate the effects of the support's porosity and structure on the polymerization reaction. Porosity and surface area of SBA-15 was determined by nitrogen physisorption. The corresponding properties for the commercial

supports were taken from the product data sheet and the surface areas and pore volumes were verified in our laboratory via nitrogen physisorption as well. The characteristics of each support are shown in Table 4.1.

Table 4.1. Porosity and Surface Area of Silica Supports.

Material	BET Surface Area (m ² /g)	Pore Diameter (Å)
SBA15	970	105
CPG240C	76.6	237
MS-3030	300	400
Cab-O-Sil EH5	335	--

Propylsulfonic acid sites were immobilized on the silica surfaces using a protocol, shown earlier in Figure 1.1, based on literature methods. First, propylthiol moieties were grafted onto the surface by reacting the silica support with 3-mercaptopropyltrimethoxysilane. Next, if a support without surface silanol functionality was desired, a capping step was performed by reacting the solid with 1,1,1,3,3,3-hexamethyldisilazane. ¹H NMR spectra of mercaptopropyl species and HMDS (not shown) indicated that little or no reaction occurred between the thiol and the HMDS. So, it could be assumed that HMDS reacts only with silanols on the silica surface, and not tethered thiols. Finally, oxidation of the thiol functionalities to sulfonic acid functionalities was carried out by contacting the solid with aqueous hydrogen peroxide. Organic loadings were estimated using TGA and are shown in Table 4.2. Thiol loadings range from 0.31 to 0.68 mmol thiol ligand per gram of silica. In early studies, there were higher apparent values for thiol loadings when using only a toluene wash after the

Table 4.2 TGA Results for Functionalized Catalysts

Sample	Thiol loading (mmol / gram silica)	Sample	Sulfonic acid loading (mmol / gram silica)
SBA-SH	0.313	SBA-SO ₃ H	0.303
Cab-SH	0.329	Cab-SO ₃ H	0.263
MS-SH	0.682	MS-SO ₃ H	0.367
CPG-SH	0.369	CPG-SO ₃ H	0.248

immobilization reaction. Then after oxidation there was a large drop from thiol loading to sulfonic acid loading. An explanation for this seemed to be that perhaps being exposed to more polar solvents, water and methanol, in the oxidation process served to remove some thiol groups that were not chemically bound, but only physically absorbed and not removed by washing with toluene. After that, a washing step was added after the immobilization reaction using more polar THF or dichloromethane. This brought the apparent thiol loadings down and produced much better agreement between the thiol numbers and subsequent sulfonic acid loadings. Sulfonic acid loadings were found to range from 0.25 to 0.37 mmol sulfonic acid ligand per gram of silica after oxidation, as determined by TGA. These results imply that oxidation of the thiol sites is incomplete under the conditions used. The results indicate an oxidation efficiency of about 55% (as defined as sulfonic acid loading / starting thiol loading) for MS-3030, around 70% for CPG 240C, 80% for Cab-O-Sil, and 95% for SBA-15. FT-Raman spectroscopy was also used to track the oxidation of the thiol groups on SBA-15, as shown in Figure 4.1. The FT-Raman spectrum of SBA-SH shows the characteristic signal of the aliphatic C-H bonds in the propyl linker and the characteristic signal of the S-H bond of the thiol group at around 2600 cm⁻¹. After oxidation, the spectrum of SBA-SO₃H shows no

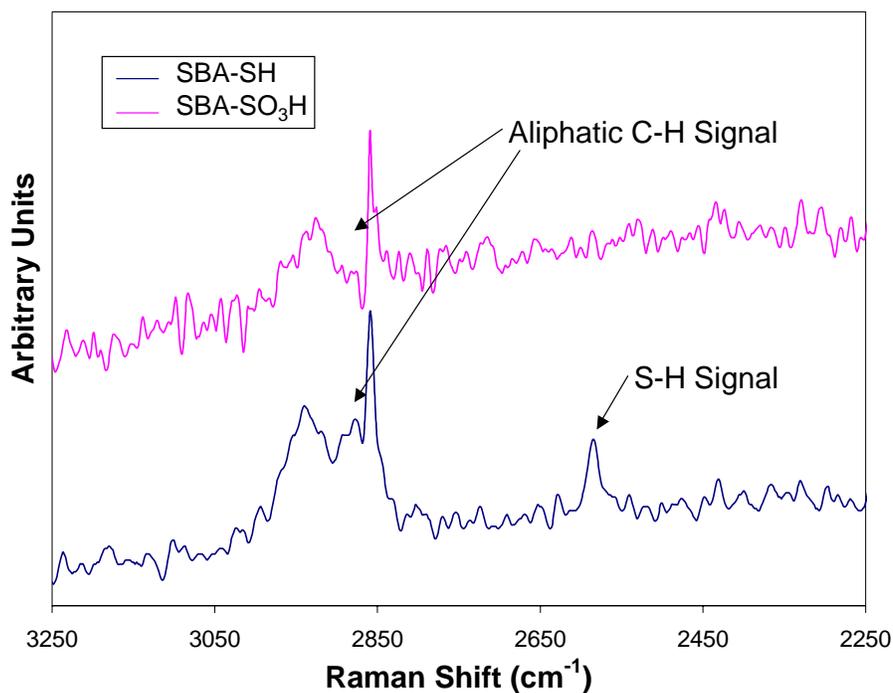


Figure 4.1. FT-Raman Characterization of Functionalized SBA-15 Sample

corresponding signal, indicating the disappearance of the thiol groups. This is of course not evidence of total oxidation, only that the amount of thiols present on the solid has dropped to a level that is undetectable after oxidation. These characterization tests would indicate a silica surface functionalized predominantly with sulfonic acid sites and a small amount of unoxidized thiol sites.

4.2.2 Catalytic Activity

Preliminary work was done using both ϵ -caprolactone and L-lactide as monomers. However, early on, the system appeared to be more suited for caprolactone as opposed to lactide work, so efforts were concentrated in that area. The polymerization of ϵ -

caprolactone was carried out using four different sulfonic acid-functionalized silica supports, both with and without the surface silanols capped. The general procedure, shown in Figure 4.2, was to combine the ϵ -caprolactone monomer, benzyl alcohol (the initiating nucleophile), dodecane (the internal GC standard), and the solid catalyst in toluene. Polymerization reactions were then performed under an argon atmosphere at

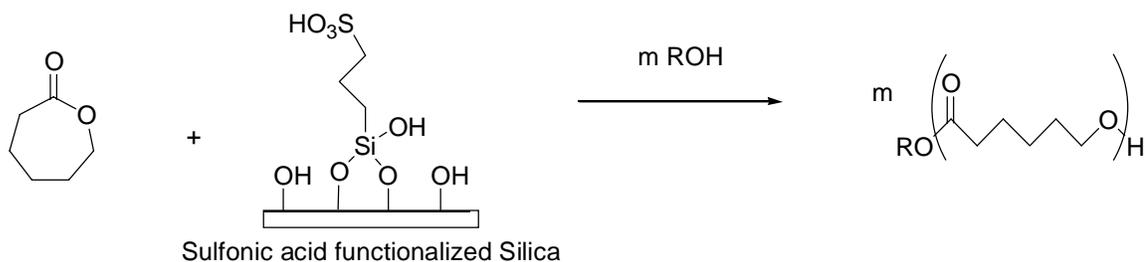


Figure 4.2 Overall Mechanism of ROP of ϵ -caprolactone Initiated by an Alcohol

52°C. After quenching the reaction, the solid catalysts were recovered and the resulting polymers were collected and analyzed by GPC, TGA/DSC, and ^1H NMR. The polymers were identified as poly(ϵ -caprolactone) by a combination of melting point analysis and proton NMR. DSC analysis showed the melting point to be 60°C +/- 2°, in good agreement with listed values of ~ 60°C^{66, 67}. A typical ^1H NMR spectrum of the resulting polymer is shown in Figure 4.3, along with a listing of the characteristic signals.

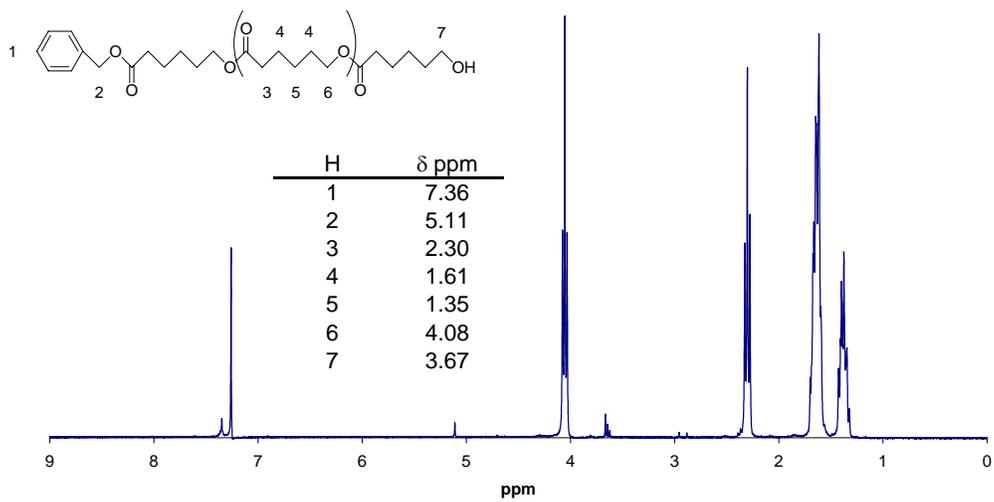


Figure 4.3. ^1H NMR of Poly(ϵ -caprolactone)

Two different target degrees of polymerization, 43 and 70, were used for the polymerizations. The results of these trials are found in Tables 4.3 and 4.4. As indicated by the data, all supported acid catalysts were active for the ring-opening polymerization of ϵ -caprolactone, achieving conversions up to 90% as determined by GC in time ranges from 24 to 160 hours. Control experiments were performed in an attempt to isolate the sulfonic acid functionality as the active species. Bare SBA-15 and SBA-SH were used as possible catalysts and both showed no measurable activity. This indicates that the catalytic activity was associated with the sulfonic acid sites only. Also, a homogeneous catalyst, TsOH, was used for comparison. The supported catalysts showed better control than the homogeneous catalyst, with polymers produced from supported catalysts having PDI's in the range of 1.1 to 1.3, while the homogeneous catalyst produced polymers with

Table 4.3. Polymerization Results for Target DP of 43.

Catalyst Type	Catalyst		Mol % cat	Time (h)	Conversion (%) ^a	STY ^b	Mn (theoretical) ^c	Mn ^d	Mw ^d	PDI ^d
	Sample	[M]/[I]								
TsOH	TsOH	43	0.3	5.5	82	49.8	4000	9470	15240	1.61
SBA-SO ₃ H	171	43	0.3	27	96	13.7	4690	6210	6850	1.1
SBA-SO ₃ H-Cap	171Cap	43	0.3	101.5	95	6.8	4640	5270	6230	1.18
Cab-SO ₃ H	178	43	0.3	60	84	4.7	4100	4770	5520	1.16
Cab-SO ₃ H-Cap	176Cap	43	0.3	136.5	84	4.7	4100	5900	6960	1.18
CPG-SO ₃ H	182	43	0.3	116	70	6.2	3420	5080	6120	1.2
CPG-SO ₃ H-Cap	182Cap	43	0.3	116	38	1.2	1860	2410	3580	1.49

- Determined by GC.
- Site Time Yield: mol monomer consumed / hour * mol active sites at low conversion.
- Assuming a linear relationship between molecular weight and conversion.
- Determined by GPC.

Table 4.4. Polymerization Results for Target DP of 70.

Catalyst Type	Catalyst Sample	[M]/[I]	mol % cat	Time (h)	Conversion (%) ^a	STY ^b	Mn (theoretical) ^c	Mn ^d	Mw ^d	PDI ^d
SBA-SO ₃ H	171	70	0.3	49.5	83	6.6	6330	6130	7200	1.17
Cab-SO ₃ H	177	70	0.3	166.5	34	1.4	2720	2440	2910	1.19
CPG-SO ₃ H	182	70	0.3	112	77	3.5	6150	6440	7790	1.21
MS-SO ₃ H	185	70	0.3	142.5	39	1.6	3120	3420	4560	1.33

- Determined by GC.
- Site Time Yield: mol monomer consumed / hour * mol active sites at low conversion.
- Assuming a linear relationship between molecular weight and conversion.
- Determined by GPC.

PDI's of 1.6 and 2.0. In all cases, the supported catalysts produced a polymer whose molecular weight, as determined by GPC, tracked closely with the theoretical molecular weight, as determined by conversion assuming a linear relationship between conversion and molecular weight. Although generally the PDI's of the polymers derived from the supported catalysts all appear to be in the same range, polymers derived from MS-3030 appear to have a slightly higher PDI, perhaps an indication of less control with catalysts supported on this solid.

Kinetically speaking, as expected, the supported catalysts are, inferior to the homogeneous catalyst. The homogeneous TsOH catalyst was able to achieve high conversions in reaction times of 10 hours or less. The supported catalysts took at least 1 day, and up to 7 days to achieve similar conversions, using identical conditions. Furthermore, in some cases, for example, the Cab-O-Sil supported catalyst with a target DP of 70, a reaction lasting 7 days did not achieve 50% conversion. A lower acidity of the supported sulfonic acid site as compared to the homogeneous catalyst or internal diffusional limitations that would be inherent to the porous solid catalysts that the homogeneous catalyst would not experience could be reasons for the decreased activity of the supported catalyst. The polymerization rates look relatively linear, although it is difficult to conclusively determine this with the limited number of data points in the kinetic plots, seen in Figure 4.4 and 4.5. If pore clogging and diffusion were to play a decisive role in reducing the rates over the porous catalysts, the rates would be expected to decrease as the reaction proceeds. In the case of low polymerization rates with Cab-O-Sil, internal transport limitations cannot be an issue, as the catalysts are non-porous. However, the Cab-O-Sil support has the smallest primary particles size and these solids

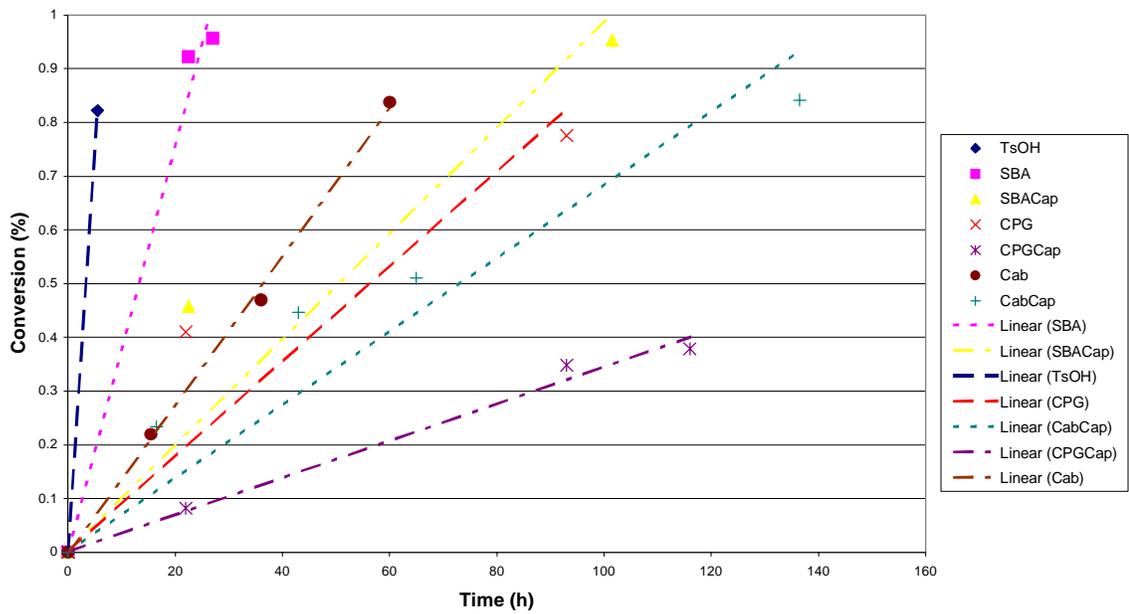


Figure 4.4. Plot of Conversion versus Time for Target DP of 43

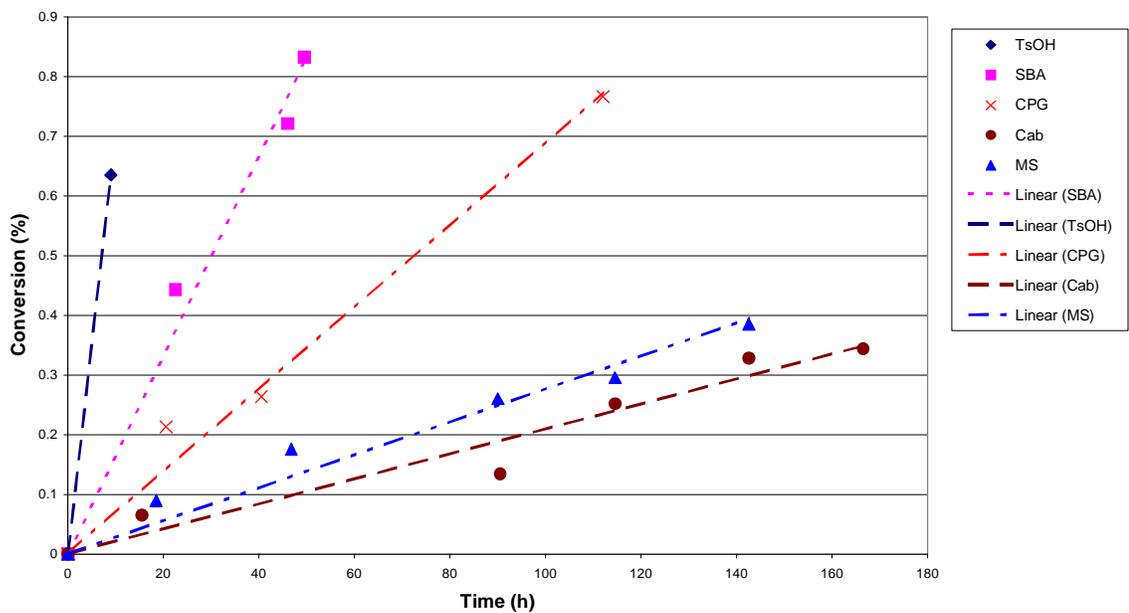


Figure 4.5. Plot of Conversion versus Time for Target DP of 70.

are known to make very viscous solutions. As polymer is formed, viscosity issues only become exacerbated and this may be a key cause for the low rates over this support.

Unfortunately, the data does not really give strong enough evidence to make many conclusions about the influence of the support on the catalytic activity or resulting polymer. On the issue of control of the reaction, all of the polymers produced had polydispersities in the same range. Kinetically speaking, some conclusions can be made. Looking at the data for a DP of 43, it appears that in all cases, the uncapped support is more active than its capped counterpart. This could possibly be due to steric issues. The active site is attached to the surface by a propyl linker, so it is immobilized fairly close to the surface. Upon capping, surface silanols are now capped with $\text{Si}(\text{CH}_3)_3$ groups as seen in Figure 1.2. Adding these new groups on to the surface would serve to place the active site even closer to the surface, perhaps limiting the monomer and growing polymer's access to the sight and thus slowing the reaction. Also, the plots for the capped samples appear to show the decrease in activity as time progresses that might be indicative of pore clogging or diffusional issues, while the uncapped samples appear to remain more linear. This could again indicate that increased steric hindrance that occurs with the active site being immobilized closer to the surface serves to increase the mass transport difficulties, slowing the reaction as it proceeds. Another possibility is that the hydrophobic environment created by capping the silanols would preferentially keep a higher concentration of the more hydrophobic solvent around the active site, excluding the more hydrophilic monomer. Looking at the data for a target DP of 43, it would appear that SBA is the most active catalyst, followed by Cab-O-Sil and lastly CPG. However, this

does not hold true when the target DP was 70, as there, SBA was the most active, followed by CPG, then MS-3030 and Cab-O-Sil, with the MS and Cab-O-Sil having nearly identical plots.

Surprisingly, the SBA-15 support gave catalysts with the largest productivity. In contrast, other recoverable polymerization catalysts that we have studied such as CuBr-bipyridine complexes that are tethered to silica supports for atom transfer radical polymerization (ATRP) gave different trends^{68, 69}. In those studies, moieties supported on SBA-15 gave the poorest control over the polymerization, indicating that transport issues may exist on the timescale of the reaction. In contrast, because the reaction rates in ϵ -caprolactone polymerization are much slower, the potential transport issues associated with SBA-15 seem to be inconsequential and good polymer control is observed with high reaction rates (relative to the other supported species).

In general, the catalysts presented here are less active than literature examples of metal catalysts for the ring opening polymerization of ϵ -caprolactone, as shown in Table 4.5. It should be noted that for the literature examples, the site-time yields listed are from final conversion data since full kinetic data was not available; however, for the site-time yields for the sulfonic acid catalysts, the first kinetic data point was used, as a measure of an “initial rate.” Using the first kinetic point for the sulfonic acid catalysts would perhaps

Table 4.5. Comparison of Site-Time Yields between Literature and Studied Systems ^a

System	Site-Time Yield ^b	Target DP	Temperature (°C)
Scandium Triflate ¹⁵	8.3	50	25
Grafted Neodymium Alkoxide ¹⁷	2200	10	50
Grafted Neodymium Alkoxide ⁴²	770	12.8	50
Grafted Yttrium Alkoxide ⁴²	1530	12.8	50
Grafted Samarium Alkoxide ⁴²	1530	12.8	50
Neodymium Allyl Complex ⁷⁰	25700	500	50
Neodymium Amidinate ⁷¹	4000	1000	40
Tin Triflate ²¹	1590	50	65
N-Heterocyclic Carbene ⁵	5.0	60	25
L-leucine ¹²	4.1	100	160
TsOH	49.3	43	52
TsOH	23.5	70	52
SBA-SO ₃ H	13.7	43	52
SBA-SO ₃ H	6.6	70	52

- a. All literature STYs are from final conversion, experimental STYs are from initial kinetic data.
 b. mol monomer consumed / hour * mol catalyst.

help cut down on the influence of mass transport issues which become more prevalent as the reaction proceeds, and would explain why for example capped and uncapped Cab-O-Sil have identical initial site-time yields, but the capped Cab-O-Sil appears to be less active when looking at final conversion in Figure 4.4, as it underwent a significant decrease in rate over time. A homogeneous scandium triflate system¹⁵ was the only metal catalyst reported in the literature that came close to matching the sulfonic acid catalysts in activity. However, a lower activity would be expected in that system since the reactions in that case were run at 25°C instead of the 52°C used here. There are four examples of grafted lanthanide alkoxide systems, two of which are neodymium alkoxide systems^{17, 42}, one yttrium alkoxide system⁴², and a samarium alkoxide system⁴². Although these are run at 50°C, roughly equivalent to the temperature used here, they use a lower target DP in the range of 10 to 13. Regardless, activities in these systems are several orders of magnitude higher than the work presented here, an activity difference

that cannot simply be explained by different target degrees of polymerization. Two homogeneous neodymium complexes are also shown, a neodymium allyl complex⁷⁰, run at 50°C with a target DP of 500, and a neodymium amidinate complex⁷¹, run at 40°C with a target DP of 1000. Again, both of these systems are considerably more active than the sulfonic acid catalysts reported here. The last example of a more active metal system is a tin triflate system²¹ run at 65°C with a target DP of 50. Two examples of metal free catalysts are also given. A system using N-heterocyclic carbenes⁵ run at 25°C with a target DP of 60 and a system using natural amino acids, in this case L-leucine¹² run at 160°C with a target DP of 100. Both systems have activities comparable to the sulfonic acid catalysts presented here. The fact that both these organic catalysts have activities that are on par with the sulfonic acid catalysts indicates that the lower activity of the silica/n-propylsulfonic acid system here may be an inherent feature of organic catalysis rather than rate limitations that are associated with solid systems.

Although the rates are low with all the supported sulfonic acid catalysts, the reactions appear to have characteristics of a controlled system as conversion proceeds roughly linearly with respect to time as seen in Figures 4.4 and 4.5. Molecular weights closely follow the theoretical values and PDIs are narrow, two other indicators of a controlled system. Further evidence of the controlled characteristics of the system is shown in Figure 4.6, a plot of molecular weight against conversion for SBA and CPG supported catalysts. In this plot, M_n is plotted against conversion for SBA-SO₃H and

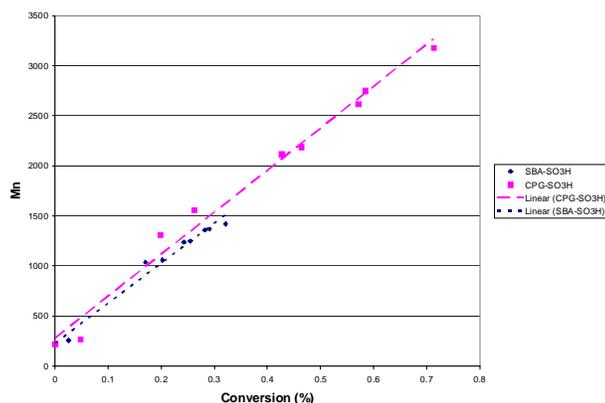


Figure 4.6 Molecular Weight Versus Conversion for SBA-SO₃H and CPG-SO₃H

CPG-SO₃H samples. The figure shows that molecular weight proceeds linearly with conversion, an indicator of a controlled system.

The reaction mechanism for this polymerization was not rigorously investigated, but, based upon other published works, possible mechanisms can be suggested. In their work on the ring-opening polymerization of lactones by homogeneous organic acids, Cordova and co-workers suggest a mechanism in which a nucleophile such as an alcohol reacts with the proton activated monomer to form a ring-opened mono ester adduct. The polymerization then proceeds as the terminal hydroxyl group of the growing chain acts as the nucleophile for other activated monomers.⁴⁶ Other work, specifically using sulfonic acid catalysts in small molecule reactions such as the liquid phase addition of acetic acid to camphene⁵⁰, the esterification of acetic acid⁷², and the hydrolysis of diazinon and triphenyl-methyl fluoride⁷³, all suggest similar mechanisms where the sulfonic acid functions as a Bronsted acid by donating a proton to catalyze the respective reaction. The level of dissociation of the sulfonic acid in organic toluene might call this possibility into

question, but a mechanism in which the sulfonic acid serves to protonate the carbonyl, making the carbonyl carbon more electrophilic and open to attack by the nucleophilic alcohol seems at least plausible.

4.2.3 Attempted Recycle

A recycle procedure was also attempted on all catalysts. The solutions were centrifuged to remove the solid catalyst after the polymerization reaction was quenched. After the supernatant was poured off for polymer recovery, the solid catalyst was kept and steps were taken to try to render it active for further reaction cycles. Elemental analysis of the precipitated polymer showed that silicon and sulfur contents were very small (~65 ppm S and 0.1 wt% Si on average). Pore clogging and surface coverage by the polymer resulting from the first polymerization reaction were hypothesized to be the main hurdles to catalyst recyclability. Hence, steps were taken to attempt to remove any residual polymer from the solid, as noted in the experimental section. First, the recovered solid was washed with THF and methylene chloride, two good solvents for poly(ϵ -caprolactone). Then, a Soxhlet extraction was performed overnight with THF and methylene chloride. The solids were then recovered and dried *in vacuo* at 150°C overnight before being placed in the glovebox for reuse. Analysis was done with TGA throughout the cleaning process and is shown in Table 4.6 for a MS-SO₃H sample. It indicated that for all catalysts, substantial organic matter was removed during each step.

Table 4.6. Monitoring Organic Content During MS-SO₃H Regeneration

Step	Organic (%) ^a	Silica (%) ^b
Before Use	4.8	93.9
After Use	51.4	46.9
After Wash	21.1	77
After Extraction	12.6	86.3

a. Determined by organic loss from 200°C to 650°C divided by non-volatile sample mass.

b. Determined by residual mass at 1000°C divided by non-volatile sample mass.

However, even after extraction and drying, all supports showed substantially more organic loss, roughly two and a half times more in the MS catalyst case shown, than before they were used in the polymerization reaction, indicating that the extraction was unable to remove all the residual polymer from the pores and or surface. So, in any attempted recycle experiment, a commensurate loss in activity would be expected due to the blocking and subsequent loss of active sites. And in fact, upon reuse of catalysts recovered in this manner, site-time-yields were 0.70 mol monomer*mol catalyst⁻¹*h⁻¹ for a SBA-SO₃H sample and 0.76 mol monomer*mol catalyst⁻¹*h⁻¹ for a MS-SO₃H sample, much lower than the initial runs. Furthermore, conversions were low, generally less than 10% for reaction times up to 4 or 5 days, and it was nearly impossible to recover any solid polymer from these reactions. In the few cases where solid material did precipitate, GPC analysis showed it to be nothing more than multimodal oligomers. Thus, using the experimental procedures outlined here, the catalysts are recoverable but not recyclable.

CHAPTER 5: CONCLUSIONS AND FUTURE WORK

Both organic base and acid sites were immobilized onto silica supports of differing porosities and structures using a multi-step grafting procedure. Supported base catalysts, in the form supported phosphines or MAP, suffered from problems which ultimately make them unattractive as polymerization catalysts at this time. Both homogeneous and supported phosphines suffered from a lack of activity and generally produced only low molecular weight products. The lack of activity of supported phosphines was not surprising. Phosphines were the least active Lewis base system for lactide polymerization according to the literature. Supporting the catalyst would probably only serve to lessen its effectiveness as a polymerization catalyst as access to the active site would be hindered by being attached to a solid surface, and the presence of a solid catalyst would lead to mass transport problems not seen with a homogeneous catalyst. Moving to homogeneous DMAP and supported-MAP catalysts did allow for the creation of higher molecular products; however, reaction control was still an issue with the supported-MAP catalysts, as seen in multi-modal GPC traces for polymers made with the supported-MAP. A probable reason for the lack of reaction control seen with these supported-MAP catalysts is the presence of different types of active sites. It is possible, especially with the extended length of the linker used in the supported-MAP work, that the active Lewis base site could bend back over and interact with the acidic silanols on the silica surface, leading to different types of active sites with different reactivities.

Employing a supported, metal-free acid, in the form of a sulfonic acid served to solve both the activity and control problems. Multiple methods including TGA/DSC, FT-

Raman spectroscopy, and nitrogen physisorption were used to characterize these solids. They were evaluated in the ring-opening polymerization of ϵ -caprolactone and demonstrated to be effective catalysts for the polymerization of this monomer, although the reaction rates were slow compared to both grafted and homogeneous metal systems. The resulting polymers were characterized by GPC, melting point analysis and ^1H NMR, and the results indicated that all of the supported sulfonic acid catalysts were found to exhibit good control over the polymerization as evidenced by the low PDIs in the polymers produced. All supported catalysts were less active than a homogeneous analog, although they did show better control. Catalyst recovery is facilitated by using a solid catalyst, and is easily performed. Unfortunately, catalyst regeneration and recycle was unsuccessful using the methods described here.

The materials presented here represent an important new ϵ -caprolactone polymerization technique, as it represents the first recoverable, metal-free system for lactone polymerization. Further work could serve to elucidate several key issues not fully answered in this work though.

First, more work could be done in the area of correlating solid properties to kinetic performance. I believe the conclusions reached on all catalysts producing polymers with roughly the same control over the reaction are fairly valid and would probably only be reinforced with further work. However, further trials could provide a better understanding on the role of solid support on the kinetics of the reaction. I believe there may be clear conclusions to be drawn there, rather than some of the contradictory findings we have seen on the kinetic side of the issue, but the time scale of our work did

not allow for enough trials to either clarify the issue or conclusively say that the solid support does not necessarily have a reproducible effect.

Also, more extensive works might allow for the determination of a definite mechanism for the reaction.

Lastly, more work could be done in the area of catalyst recycling. The methods used here to try to regenerate and recycle the catalyst were fairly rudimentary. Further work could uncover either a physical or chemical methodology either the quenching process or cleaning process that would render the solid active for more than one cycle of polymerization.

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