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A Recoverable, Metal-Free Catalyst for the Green Polymerization of ϵ-Caprolactone

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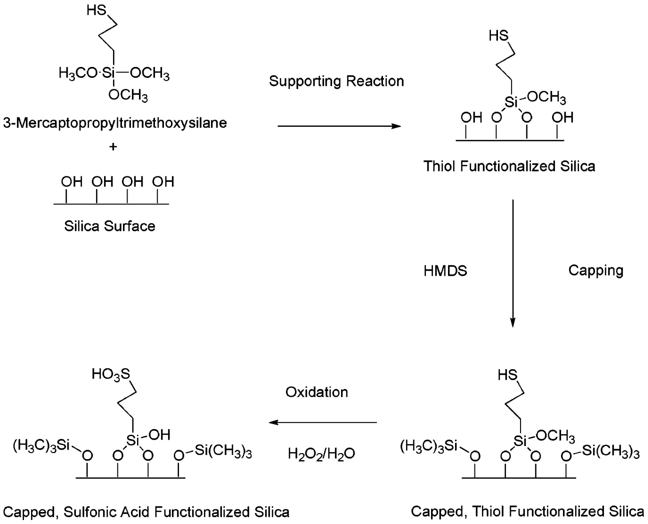
ABSTRACT: *n*-Propylsulfonic acid-functionalized porous and nonporous silica materials are evaluated in the ring-opening polymerization of ϵ-caprolactone. All catalysts allow for the controlled polymerization of the monomer, producing polymers with controlled molecular weights and narrow polydispersities. Polymerization rates are low, with site-time yields generally 1−3 orders of magnitude lower than metal-based systems. The catalysts are easily recovered from the polymerization solution after use and are shown to contain significant residual adsorbed polymer. Solvent extraction techniques are useful for removing most of the polymer, although the extracted solids are not effective catalysts in recycle experiments under the conditions used here. These new materials represent a green alternative to traditional metal-based catalysts, as they are recoverable and leave no metal residues in the polymer.

Introduction

Aliphatic polyesters such as polycaprolactone have garnered much attention lately for their use in biomedical and pharmaceutical applications because of their biodegradable nature.[1−14] Metal complexes are the most commonly explored catalysts for the production of polycaprolactone. Previous examples of metal complexes used as catalysts include tin,[2,6,15−21] aluminum,[6,10,18,19,22−27] iron,[6,18] scandium,[1,12,28] yttrium,[14,18,29−35] zinc,[36−39] and other metals.[1,14,18,19,24,25,30−34,40−43] Although in a few of these systems the metal complex is grafted onto a silica or alumina support,[10,14,35] most are done with homogeneous metal complexes.[44] The downside of using these homogeneous systems is that the resulting polymer is then contaminated by residual metal. Furthermore, even with supported systems, it is possible that the active metal leaches into solution to some degree, contaminating the polymer.

Recent work has shown that the polymerization of aliphatic cyclic esters, such as ϵ-caprolactone, can be catalyzed by organic species. The catalysts reported include various tertiary phosphines,[45] (dimethylamino)-pyridine,[11] and *n*-heterocyclic carbene complexes,[3,46] all functioning as Lewis bases. In these reactions, the catalyst facilitates the opening of the ring. A nucleophile, such as an alcohol, then removes the first monomer from the active site, giving 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.[11] These reactions show characteristics of a controlled, living reaction (e.g., conversion shows a linear relationship to reaction time, molecular weight shows a linear dependence on conversion, and the resulting polymers show a low polydispersity).[3,11,46] Other purely organic systems that display catalytic activity include natural amino acids,[9] organic acids,[47] and acid/alcohol systems.[13] Unfortunately, these catalysts are all homogeneous species[48] that, while not contaminating the polymer with metal residue, are not easily recoverable from the reaction mixture, making catalyst recovery and recycle problematic.

Scheme 1. Silica Functionalization Procedure with the Optional Silanol Capping Step



Much work has been done where a sulfonic acid functionality is supported onto an oxidic solid[49−60] for use in immobilizing a metal species in later synthetic steps[51,52] or for use as a heterogeneous catalyst for small molecule reactions.[53,56,58,60] Building on the feasibility of using organic base and acid catalysts for this polymerization, an immobilized sulfonic acid is used as the catalyst in this work. Propylsulfonic acid moieties were immobilized on various silica supports (Scheme 1) and were evaluated in the ring-opening polymerization of ϵ-caprolactone, with a focus on potential catalyst recovery and reuse.

Experimental Section

Chemicals and 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. *p*-Toluenesulfonic acid monohydrate (TsOH, Aldrich, 98.5+%) was dried in vacuo at 100 °C for 4 h and stored under nitrogen in a glovebox. Toluene for polymerization (Acros, 99.8%) was dried over sodium benzophenone and stored under nitrogen in a glovebox. Tetrahydrofuran (THF, Aldrich,

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>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 Corp.) 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; J.T. Baker), tetraethyl orthosilicate (TEOS; Acros, 98%), and 1,3,5-trimethylbenzene (TMB; Aldrich, 97%) were used as received.

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 Brunaer−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 CaF_2 beam splitter. ^1H NMR measurements were performed with a Mercury Vx 300 MHz instrument with $CDCl_3$ as a solvent. 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 and then from 140 to 300 °C at 40 K/min under constant pressure with a constant inlet and detector temperature of 330 °C. 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). Elemental analysis was performed by Galbraith Laboratories (Knoxville, TN).

Materials Synthesis. SBA-15 (105 Å Pores). A nonionic surfactant (EO−PO−EO) was used as the structure-directing agent in the synthesis of mesoporous SBA-15.[61] In a typical experiment, 12.1 g of EO−PO−EO was combined with 320.2 g of deionized H_2O and 69.4 g of 38% HCl and stirred at room temperature for at least 3 h until all the surfactant was dissolved. Next, 25.3 g of TEOS was added and allowed to stir for 10 min. Finally, 1.5 g of TMB was added and allowed to stir for a further 10 min before the solution was portioned into 10 Parr Teflon-lined autoclaves. These were then agitated at 35 °C for 20 h and allowed to age without stirring at 100 °C for 24 h. 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 h before increasing to 550 °C at 1.2 K/min, which was then maintained for 4 h. This final product was then dried in vacuo at 150 °C for 3 h and stored in a glovebox under nitrogen.

Synthesis of Sulfonic Acid Functionalized Catalysts. Sulfonic acid functionalized solids were made by routes adapted from literature methods as described below.[49,50,52,58]

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

Silanol Capping on Thiol Functionalized SBA-15 (SBA-SH-Cap). Typically, 1.1 g of HMDS was added to a slurry of 1.0 g of SBA-SH in ~20 g of anhydrous toluene in a 100 mL round-bottom flask in the glovebox. The mixture was then stirred at room temperature under an Ar atmosphere for ~24 h. The product was recovered and washed with copious amounts of toluene and THF, again in a glovebox. The solid product was then dried in vacuo at 150 °C overnight before being stored in a glovebox.

Oxidation of SBA-SH or SBA-SH-Cap to Sulfonic Acid Functionalized SBA (SBA-SO_3H/SBA-SO_3H-Cap). In a typical experiment, 1.0 g of SBA-SH was combined with 10.0 g of MeOH and 20.0 g of 30% H_2O_2 in a 100 mL round-bottom flask. The mixture was stirred at room temperature for 24 h. The product was subsequently recovered and washed with copious amounts of deionized H_2O. The solid product was then dried in vacuo at 150 °C overnight before being stored in a glovebox.

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-SO_3H/Cab-SO_3H/MS−SO_3H) using the same procedures outlined above for SBA-15. All resulting catalysts were recovered, washed, and stored under the same conditions.

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

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 three-neck flask fitted with a glass stopper and a rubber septum. To this was added 30.6 μL 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 (0.57 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 a glovebox.

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 three-neck flask fitted with a glass stopper and a rubber septum. To this was added 30.6 μL 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 precipitated with cold hexanes, then recovered, and washed with cold hexanes. The resulting polymer was then dried under vacuum and stored in a glovebox.

Results and Discussion

Catalyst Synthesis and Characterization. Four different silica supports were studied. Hexagonal mesoporous SBA-15 was synthesized in the lab. The other three silica sources, mesoporous CPG 240 and MS-3030 and fumed, nonporous Cab-O-Sil EH5, were commer-

Table 1. Porosity and Surface Area of Silica Supports

material	BET surf. area (m^2/g)	mean pore diam (Å)
SBA15	970	105
CPG240C	76.6	237
Cab-O-Sil EH5	335	
MS-3030	300	400

Table 2. TGA Results for Solid Catalysts

sample	thiol loading (mmol/g silica)	sample	sulfonic acid loading (mmol/g silica)
SBA-SH	0.31	SBA-SO_3H	0.30
Cab-SH	0.33	Cab-SO_3H	0.26
CPG-SH	0.37	CPG-SO_3H	0.25
MS-SH	0.68	MS−SO_3H	0.37

cially available. CPG 240 is a controlled pore glass with interconnected mesopores with a narrow pore size polydispersity and low surface area. MS-3030 is a commercially available, mesoporous, microspherical silica with an average particle size of 90 μm. SBA-15 is a hexagonal mesoporous silica material with unidimensional mesopores connected by small micropores. Using multiple types of silica facilitated the investigation of the effects of the support's porosity and structure on the polymerization reaction. Porosity and surface area of SBA-15 were 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 1.

Propylsulfonic acid sites were immobilized on the silica surfaces using a protocol (Scheme 1) based on literature methods. First, propylthiol moieties were grafted onto the surface by reacting the silica source with 3-mercaptopropyltrimethoxysilane. Next, if a support with the surface silanols removed 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. Thus, HMDS is expected to only react 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 2. Thiol loadings range from 0.31 to 0.68 mmol thiol ligand per gram of silica. Sulfonic acid loadings were found to range from 0.25 to 0.37 mmol of sulfonic acid ligand per gram of silica after oxidation, as determined by TGA. These results indicate that oxidation of the thiol sites is incomplete under the conditions used. The results imply 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. The oxidation of the thiol groups on SBA-15 was also tracked using FT-Raman spectroscopy, as shown in Figure 1. The FT-Raman spectrum of SBA-SH shows the characteristic signal of the S−H bond of the thiol group at around 2600 cm^{-1}. After oxidation, the spectra of SBA-SO_3H show no corresponding signal, indicating the loss 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.

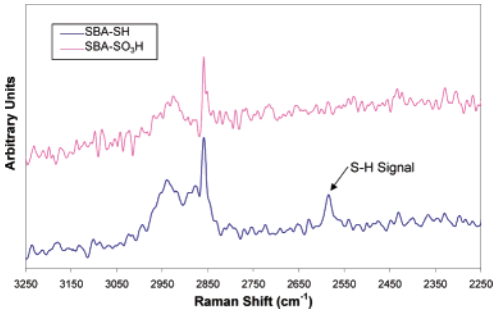
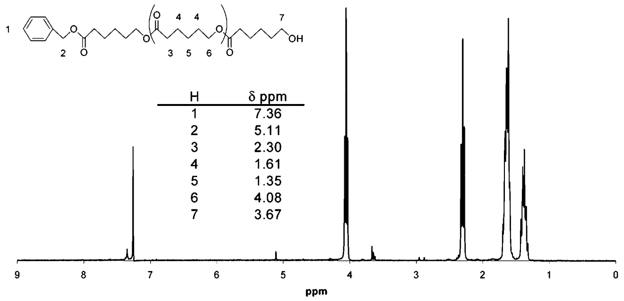


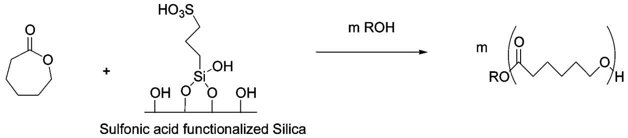
Figure 1. FT-RAMAN spectra of functionalized SBA-15 samples.



H	δ ppm
1	7.36
2	5.11
3	2.30
4	1.61
5	1.35
6	4.08
7	3.67

Figure 2. ^1H NMR spectrum of poly(ϵ-caprolactone).

Scheme 2. General Mechanism of ROP of ϵ-Caprolactone Initiated by an Alcohol



Catalytic Activity. The polymerization of ϵ-caprolactone was carried out using sulfonic acid species immobilized on the four different supports, both with and without the surface silanols capped. The general procedure (Scheme 2) was to combine the ϵ-caprolactone monomer, benzyl alcohol (the initiating nucleophile), dodecane (the internal GC standard), and the solid catalyst in toluene. The reactions were then performed under an argon atmosphere at 52 °C. After reaction, the 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 ± 2 °C, in good agreement with listed values of ~60 °C.[62,63] A typical ^1H NMR spectrum of the resulting polymer is shown in Figure 2, along with a tabulation of the characteristic signals.

The polymerizations were performed with two different target degrees of polymerization, 43 and 70. Full results of these trials are shown in Tables 3 and 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 h. Control experiments were performed, using bare SBA-15 and SBA-SH as possible catalysts, both of which showed no measurable activity. This indicates that the catalytic activity was associated with the sulfonic acid sites only. Also, TsOH was used as a homogeneous catalyst for comparison. Polymers produced from supported cata-

Table 3. Polymerization Results for Target DP of 43

catalyst type	catalyst sample	[M]/[I]	mol % cat.	time (h)	conv (%)[a]	STY[b]	M_n(theor)[c]	M_n[d]	M_w[d]	PDI[d]
TsOH	TsOH	43	0.3	5.5	82	49.8	4000	9470	15240	1.61
SBA-SO3H	171	43	0.3	27	96	13.7	4690	6210	6850	1.1
SBASO3H-Cap	171Cap	43	0.3	101.5	95	6.8	4640	5270	6230	1.18
CPG-SO3H	182	43	0.3	116	70	6.2	3420	5080	6120	1.2
CPG-SO3H-Cap	182Cap	43	0.3	116	38	1.2	1860	2410	3580	1.49
Cab-SO3H	178	43	0.3	60	84	4.7	4100	4770	5520	1.16
Cab-SO3H-Cap	176Cap	43	0.3	136.5	84	4.7	4100	5900	6960	1.18

[a] Determined by GC. [b] Site time yield: (mol of monomer consumed)/(h mol of active sites at low conversion). [c] Assuming a linear relationship between molecular weight and conversion. [d] Determined by GPC.

Table 4. Polymerization Results for Target DP of 70

catalyst type	catalyst sample	[M]/[I]	mol % cat	time (h)	conv (%)[a]	STY[b]	M_n (theor)[c]	M_n[d]	M_w[d]	PDI[d]
TsOH	TsOH	70	0.3	9	64	23.5	5110	5750	11500	2
SBA-SO3H	171	70	0.3	49.5	83	6.6	6330	6130	7200	1.17
CPG-SO3H	182	70	0.3	112	77	3.5	6150	6440	7790	1.21
Cab-SO3H	177	70	0.3	166.5	34	1.4	2720	2440	2910	1.19
MS-SO3H	185	70	0.3	142.5	39	1.6	3120	3420	4560	1.33

[a] Determined by GC. [b] Site time yield: (mol of monomer consumed)/(h mol of active sites at low conversion). [c] Assuming a linear relationship between molecular weight and conversion. [d] Determined by GPC.

lysts had PDI's in the range of 1.1–1.3, while the homogeneous reaction produced polymers with a PDI's of 1.6 and 2.0, implying much better control in the supported reactions. 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 the PDIs of the polymers derived from the supported catalysts all appear to be in the same range, polymers derived from MS-3030 had a slightly higher PDI, perhaps an indication of less control using this solid.

Kinetically speaking, the supported catalysts are, as expected, inferior to the homogeneous catalyst. The homogeneous TsOH catalyst was able to achieve high conversions in reaction times of 10 h or less. Using identical reaction conditions, the supported catalysts took at least 1 day and up to 7 days to achieve similar conversions. Furthermore, in some cases, for example, the Cab-O-Sil supported catalyst with a target DP of 70, conversion over 50% was not achieved in reactions lasting 7 days. Reasons behind the decreased activity of the supported catalysts could include 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. The polymerization rates look relatively linear, although it is difficult to conclusively determine this with the limited number of data points in the initial activity screening experiments shown in Figure 3. 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, although this phenomenon would be undetectable with the current data if it occurred very early on in the experiments. In the case of low polymerization rates with Cab-O-Sil, internal transport limitations cannot be an issue, as the catalysts are nonporous. However, the Cab-O-Sil support has the smallest primary particles size, and these solids 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 lower rates over this support.

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.[64,65] In these cases, moieties supported on SBA-15 gave the poorest control over the polymerization, indicating that transport issues may exist on the time scale 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 catalysts in this study).

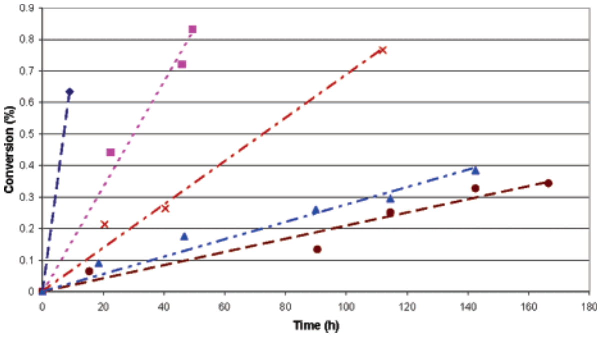


Figure 3. Conversion vs time for DP of 70. (TsOH = ♦, SBA = ■, CPG = X, Cab = ●, MS = ▲).

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 5. Most metal catalysts show much higher activity, although occasionally some are reported with productivities similar to the organic systems. For example, in the case of homogeneous scandium triflate catalysts,[12] the catalytic productivity is in line with that of the sulfonic acid catalysts. However, the reactions in that case were run at 25 °C instead of the 52 °C used here, so a lower activity would be expected in that system. For further comparison, the polymerization rates with four examples of grafted lanthanide alkoxide systems (two neodymium alkoxide systems,[14,30] one yttrium alkoxide system,[30] and a samarium alkoxide system[30]) are listed in Table 5. All of these were run at 50 °C, roughly equivalent to the temperature used here; however, they use a lower target DP in the range of 10–13. Regardless, activities in these systems were several orders of magnitude higher than the work presented here. Two homogeneous neodymium complexes are also

Table 5. Comparison of Site-Time Yields[a]

system	site-time yield[b]	temp (°C)	target DP
scandium triflate[12]	8.3	25	50
grafted neodymium alkoxide[14]	2200	50	10
grafted yttrium alkoxide[30]	1530	50	12.8
grafted neodymium alkoxide[30]	770	50	12.8
grafted samarium alkoxide[30]	1530	50	12.8
neodymium allyl complex[41]	25700	50	500
neodymium amidinate[40]	4000	40	1000
tin triflate[16]	1590	65	50
N-heterocyclic carbene[3]	5.0	25	60
L-leucine[9]	4.1	160	100
TsOH	49.3	52	43
TsOH	23.5	52	70
SBA-SO_3H	13.7	52	43
SBA-SO_3H	6.6	52	70

[a] All literature STYs are from final conversion; experimental STYs are from initial kinetic data. [b] In (mol of monomer consumed)/(h mol of catalyst).

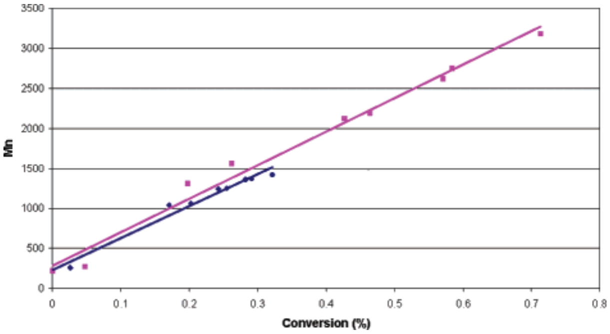


Figure 4. Molecular weight vs conversion for SBA-SO_3H and CPG-SO_3H. (SBA = ♦, CPG = ■).

Table 6. Tracking Organic Content during MS-SO_3H Regeneration

step	organic (%)[a]	silica (%)[b]
before use	4.8	93.9
after use	51.4	46.9
after wash	21.1	77.0
after extraction	12.6	86.3

[a] Determined by organic loss from 200 to 650 °C divided by nonvolatile sample mass. [b] Determined by residual mass at 1000 °C divided by nonvolatile sample mass.

shown: a neodymium allyl complex,[41] run at 50 °C with a target DP of 500, and a neodymium amidinate complex,[40] run at 40 °C with a target DP of 1000. Again, both of these systems are considerably more active than the sulfonic acid catalysts. Another example of a more active metal system is a tin triflate system[16] run at 65 °C with a target DP of 50. Data for two metal free catalysts are also given. One system is an *n*-heterocyclic carbene[3] run at 25 °C with a target DP of 60, while the other uses L-leucine[9] at 160 °C with a target DP of 100. Both systems had activities comparable to the sulfonic acid catalysts presented here. The fact that both these organic catalysts had 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 living characteristics as molecular weights are near their theoretical values and PDIs are narrow. To further probe the nature of the polymerizations, more detailed kinetic and GPC data were obtained for the SBA and CPG systems. As shown in Figure 4, the molecular weight increases linearly with conversion in both cases. This gives further evidence that these polymerizations proceed in a controlled manner, with some of the characteristics of a living polymerization.

A recycle procedure was also attempted on all catalysts. After the polymerization reaction was quenched, the solutions were centrifuged to remove the solid catalyst. 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 the silicon and sulfur contents were very small (~65 ppm S and 0.1% wt Si on average).

The main hurdle to catalyst recyclability was hypothesized to be pore clogging and surface coverage by the polymer resulting from the first polymerization reaction. Hence, steps were taken to attempt to remove any residual polymer from the solid. 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 a glovebox for reuse. Analysis with TGA throughout the cleaning process, shown in Table 6 for a MS-SO_3H sample, indicated that for all catalysts substantial organic matter was removed during each step. However, even after extraction and drying, all supports showed substantially more organic loss, roughly $2^1/_2$ 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.[66] Thus, upon reuse, 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 lower, with values of 0.70 for a SBA-SO_3 H sample and 0.76 mol monomer/mol site − h for a MS-SO_3H sample. Furthermore, conversions were generally less than 10% for reaction times up to 4 or 5 days, and it was very difficult to recover any solid polymer from these reactions. In rare cases where solid material did precipitate, it was determined to be nothing more than multimodal oligomers based on GPC analysis. Thus, using the experimental procedures outlined here, the catalysts are recoverable yet not recyclable. Additional studies are needed to improve the recyclability of these systems. Nonetheless, the present materials represent an important new ϵ-caprolactone polymerization technique, as it represents the first well-characterized, recoverable, metal-free system for lactone polymerization.[48]

Conclusions

Sulfonic acid sites were immobilized onto silica supports of differing porosities and structures using a multistep grafting procedure. These solids were then characterized by multiple methods including TGA/DSC, FT-Raman spectroscopy, and nitrogen physisorption. 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. 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 analogue but exhibited narrower PDIs. Catalyst recovery is facilitated by using a solid catalyst, although catalyst regeneration and recycle was unsuccessful using the methods described here.

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