Kinetic Evaluation of Tin-POMS Catalyst for Urethane Reactions

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ABSTRACT: We report the activity for a new tin-polyhedral oligomeric metal silsesquioxane (POMS) catalyst in 1-butanol and 2-butanol model reactions with 4,4′-methylenebis(cyclohexylisocyanate) (H_{12}MDI) in toluene and *N,N*-dimethylformamide (DMF). Kinetic rate constants for varying levels of tin-POMS ranging between 100 ppm and 1000 ppm tin are reported. We observed urethane reactions in toluene to follow second order reaction kinetics, whereas similar reactions in DMF followed first order reaction kinetics. We determined tin-POMS is an efficient catalyst system for urethane reactions and found the new catalyst to be easy to handle, soluble, and very effective for catalyzing urethane reactions. By direct comparison of a model reaction between tin-POMS and dibutyltin dilaurate (DBTDL), tin-POMS was found to be quite similar to DBTDL for urethane catalytic activity. In addition, we show the efficacy for tin-POMS to be an excellent polyurethane reaction catalyst through a model reaction of H12MDI with 2000 g/mol poly(ε-caprolactone) diol. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 3683–3689, 2008

Key words: polyurethane; catalyst; POSS; elastomer; kinetics

INTRODUCTION

Polyhedral oligomeric silsesquioxanes (POSS) have been extensively studied for their unique molecular structures and thermomechanical properties as modifiers within polymer matrices.[1,2] POSS molecules are generally viewed as nano-scale reinforcements and have utility in a variety of polymeric matrices associated with controlling functionality and solubility through pendant organic and reactive groups within the molecules. Reactive functionality allows POSS to be covalently bonded through polymerization and grafting reactions. Nonreactive organic substituents provide pathways for controlling solubility within a broadrange of organic media. As a result, POSS molecules have been evaluated in variety of applications including photo-resist coatings,[3,4] interlayer dielectrics and protective coating films,[5,6] liquid crystal displays,[7,8] and gas separation membranes.[9,10]

In addition to POSS molecules being evaluated as thermomechanical and morphological modifiers, their well-controlled chemistries and "tuned" solubilities make them excellent choices for evaluation as metal catalysts. Research has been conducted to evaluate a variety of polyhedral oligomeric metal silsesquioxane (POMS) structures for catalytic activity including gallium-POMS,[11] magnesium-POMS,[12] lanthanide-POMS,[13] zirconium-POMS,[14] and titanium-POMS.[15] We are evaluating the kinetic catalytic efficacy for a new tin-POMS catalyst in model urethane reactions for this research.

EXPERIMENTAL

Materials

4,4′-methylenebis(cyclohexylisocyanate) (H_{12}MDI) 90%, anhydrous 1-butanol 99.8%, anhydrous 2-butanol 99.5%, ACS reagent toluene 99.5%, and ACS reagent *N,N*-dimethylformamide (DMF) 99.8% were purchased from Aldrich and used as received. Tin-POMS JJS5010 was supplied by Hybrid Plastics and used as received. Poly(ε-caprolactone)diol (2000 g/mol) was supplied by DOW and used as received.

Synthetic and kinetic analytical procedures

Isocyanate-hydroxyl reactions were monitored using a Bruker Equinox 55 FTIR spectrometer set at a spectral resolution of 4 cm^{-1} and equipped with a temperature-controlled flow cell with a 20mm diameter aperture equipped with ZnSe windows and 0.20 mm Teflon spacers (64401-2, New Era Enterprises, Vineland, NJ). The flow cell temperature was controlled

using an Ace Glass temperature controller (12111-15, Vineland, NJ). The reaction vessel temperature was controlled with a silicone oil bath and a Therm-O-Watch L6-1000SS temperature controller. The reaction vessel contents were pumped through the flow cell from a 100 mL three-neck round-bottomed flask using a Cole Parmer Master Flex PTFE Tubing Pump Head connected to a digital Cole Parmer Master Flex Drive using 6 mm O.D. PTFE tubing at a pump head speed of 75 RPM.

The absorption peak height corresponding to the NCO (2264 cm^{-1}) was monitored to calculate the conversion of isocyanate during the urethane reaction.[16] The energy loss that is observed at a given frequency can be taken as a measure of the reduction in concentration of the absorbing substance and we found the isocyanate absorption to be particularly sensitive to monitor isocyanate concentration using this apparatus. Quantification is based on the Lambert-Beer law[17]:

$$A \propto \varepsilon^* C$$

where A is the measured integrated absorbance, ε is the molar absorptivity of the sample (cm^2 mol^{-1}), and C is the concentration of the sample (mol/cm^3).

A representative procedure for the reaction was as follows: 80 mL of toluene and 0.0049 g (300 ppm) of POMS-Sn were added to a dry three-neck round-bottomed 100 mL flask in a nitrogen purged glovebox. The round-bottomed flask was capped with rubber stoppers, taken out of the glovebox and, subsequently, connected to the FTIR apparatus under the dry N$_2$ purge. Then, the flask was placed into a 40°C oil bath, and the solution was stirred using a magnetic stirring device. After 20 min, the system was considered equilibrated at temperature, and the background spectrum was obtained. Then, 1.104 g (0.0042 mol) of H$_{12}$MDI was weighed into a polypropylene syringe in the glovebox and transferred to the reaction kettle. After the absorption peak height of NCO at 2264 cm^{-1} was observed to be stable (about 20 min), 0.624 g (0.0084 mol) of 1-butanol was weighed into a polypropylene syringe in the glovebox and transferred to the reaction kettle to initiate the urethane reaction. Spectra were collected every 5 min until high isocyanate conversions over the spectral ranges of 1500–2500 cm^{-1} were observed. The reactions were monitored by the observed changes in the peak heights of the 2264 cm^{-1} NCO absorptions.

Polyurethane reactions in DMF and catalyzed with tin-POMS catalyst (300 ppm tin) were synthesized using similar reaction conditions and reaction monitoring techniques described earlier by replacing the hydroxyl stoichiometric equivalent of mono-ol with 2000 g/mol poly(ε-caprolactone diol).
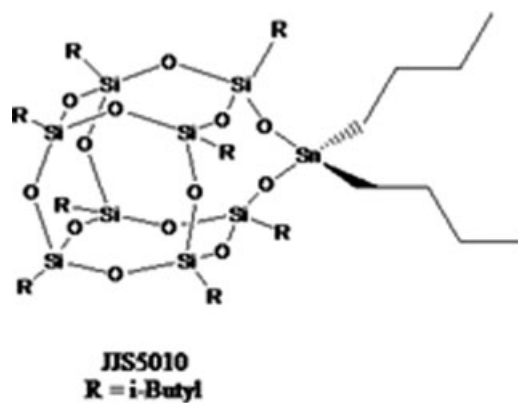
Scheme 1 Tin-POMS catalyst.

RESULTS AND DISCUSSION

Potential advantages for selecting tin-POMS over traditional urethane catalysts such as stannous octoate (Sn(OCT)$_2$) or dibutyltin dilaurate (DBTDL) are associated with hydrophobicity, thermal stability and handlability at room temperature as a crystalline solid making it convenient to use when considering measurement and storage when compared with conventional hydrophilic liquid catalysts. In addition, flexibility in synthesizing tin-POMS provides a multitude of opportunities to "tune" the solubility of these compounds for use in a variety of organic media.

We are reporting our analysis of tin-POMS catalytic activity for urethane model reactions between dicyclohexylmethane diisocyanate with 1-butanol and 2-butanol, and report kinetic rate constants of model primary hydroxyl-isocyanate and secondary hydroxyl-isocyanate reactions in toluene and DMF using tin-POMS catalyst. Tin-POMS catalyst was completely soluble in the common urethane reaction solvents utilized in this research. The chemical structure for the tin-POMS molecule we evaluated is depicted in Scheme 1 and had an FW = 1120.7 g/mol.

It was necessary to determine the functional relationship between the apparent FTIR absorption peak height at 2264 cm^{-1} and H$_{12}$MDI concentration to generate a calibration curves for each solvent in generating kinetic rate data using this method. We compared peak heights using four known quantities of H$_{12}$MDI in toluene equilibrated at 40°C. Figure 1 shows the plot of the peak height for the 2264 cm^{-1} absorption versus H$_{12}$MDI concentration which confirms the peak height is effectively proportional to H$_{12}$MDI concentration. The following calibration equation was generated on the basis of line fit and used in our analysis.
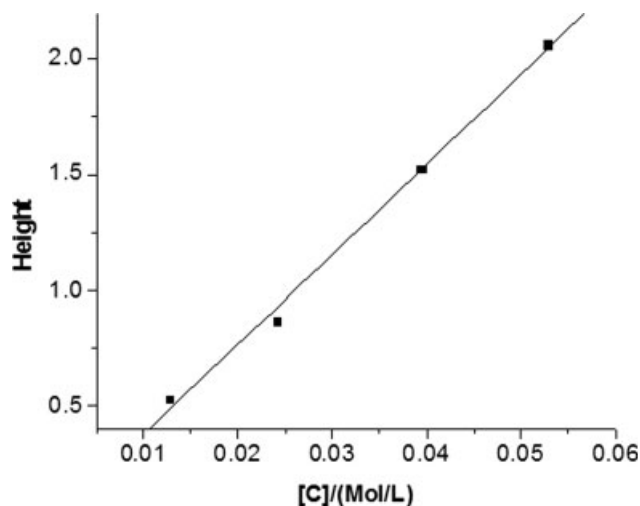
$$H = 38.945[C] - 0.01122 \tag{1}$$

Figure 1 Absorption peak height versus measured concentration: $H_{12}MDI$ in toluene.

Figure 3 NCO absorption during 1-butanol reaction in toluene with tin-POMS.

where H is the 2264 cm^{-1} absorption peak height, and [C] is the concentration of H12MDI (mol/L).

Kinetic study of $H_{12}MDI$ with 1-butanol and 2-butanol in toluene

The kinetic efficacy of tin-POMS based upon $H_{12}MDI$ model reactions with 1-butanol and 2-butanol in toluene was conducted. We selected four concentrations of tin-POMS catalyst based upon 100 ppm, 300 ppm, 500 ppm, and 1000 ppm of tin for this research. In addition, we ran control experiments based upon 0 ppm of tin which were performed to confirm no reactivity under our reaction conditions and used as references for comparative purposes. Figure 2 depicts the NCO absorption peak of $H_{12}MDI$ ran 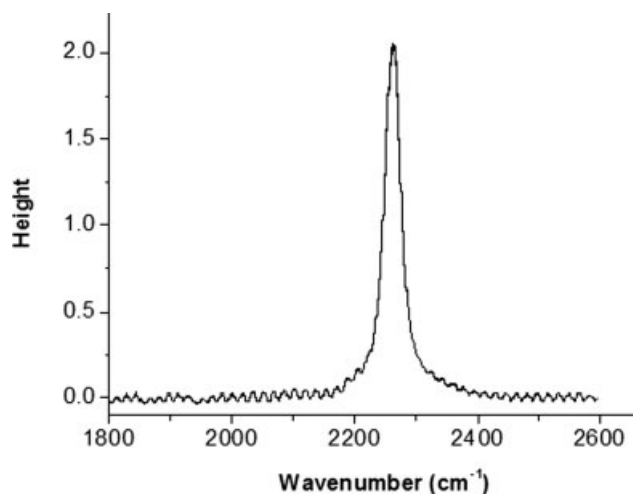over a 6 h period under reaction conditions and confirms that 1-butanol does not react at 40°C in toluene without catalyst. Figure 3 depicts typical spectral changes during a urethane reaction used to monitor NCO conversions over time as the reactions progressed in the presence of tin-POMS. The peak height for the NCO absorption decreases with time showing the continuous consumption of NCO during the reaction. We used eq. (1) to directly relate the changes of the NCO absorption peak heights to the reduction of $H_{12}MDI$ concentrations. Figure 4 shows the changes in $H_{12}MDI$ concentration for 0 ppm, 100 ppm, 300 ppm, 500 ppm, and 100 ppm tin catalyst over time. It is apparent from these results that tin-POMS effectively catalyzes the primary hydroxyl-isocyanate urethane reaction typical to what one would expect when considering catalyst concentration behavior. We plotted ln[C] versus time as depicted in Figure 5 and 1/[C] versus time as

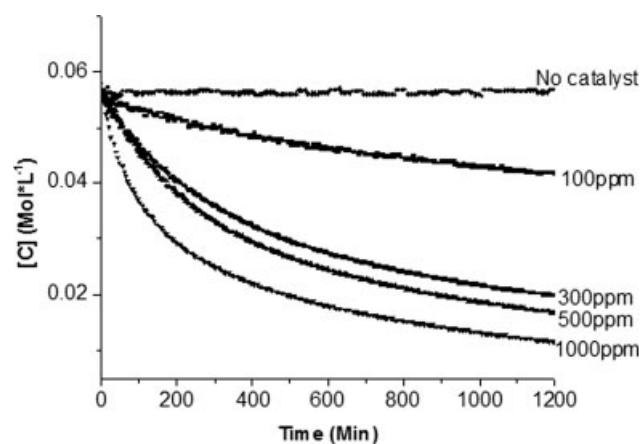**Figure 2** A 6-h FTIR NCO absorption without catalyst in toluene.

Figure 4 $H_{12}MDI$ concentration versus time: 1-butanol in toluene with tin-POMS.

Figure 5 ln[C] versus time: 1-butanol in toluene with tin-POMS.

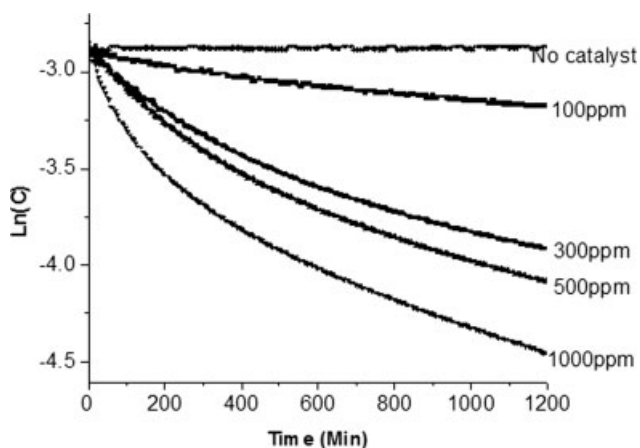**Figure 7** $H_{12}MDI$ concentration versus time: 2-butanol in toluene with tin-POMS.

depicted in Figure 6 to determine the reaction rate order for the tin-POMS catalyzed primary hydroxyl-isocyanate reaction in toluene. It is apparent from these plots that the reaction in toluene follows second order rate kinetics. The rate constants were calculated from $(\Delta(1/[C]))$ divided by the elapsed time (Δt) as the slope of the line for each corresponding catalyst concentration from Figure 6.

It is well known that primary and secondary alcohols react at different rates with isocyanates under the same conditions, with secondary hydroxyls being kinetically slower than primary hydroxyls using metal catalysts.[18] We determined the catalytic activity of tin-POMS on the reaction of 2-butanol with $H_{12}MDI$ to study the efficacy and behavior of the catalyst on secondary hydroxyl reactions with isocyanates. We elected to assess three levels of tin concentration (100 ppm, 300 ppm, 500 ppm) to evaluate the new catalyst's performance on secondary hydroxyl reactions. Following similar procedures
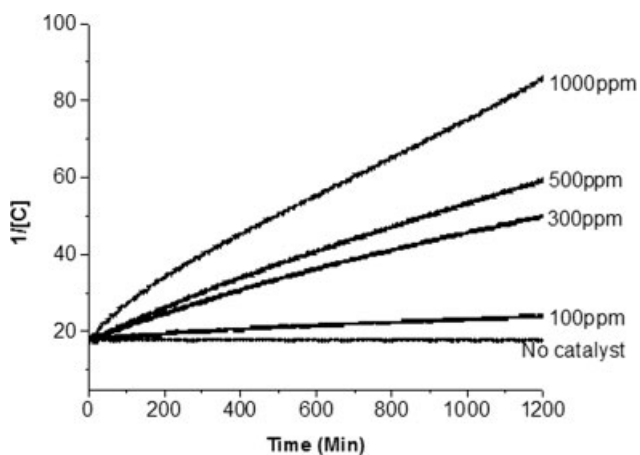
employed for the primary hydroxyl reactions we observed tin-POMS to behave similar to other metal catalysts reported for these reactions.

Figure 7 shows the change in NCO concentration over time for the secondary hydroxyl-isocyanate reaction in toluene for varying levels of catalyst. We observed high catalytic activity for the secondary hydroxyl reactions with isocyanate consumption behavior expected for a solubilized and efficient metal catalyst system. Figure 8 plots the inverse concentration versus time data and confirms the secondary hydroxyl-isocyanate reaction in toluene also follows second order rate kinetics using the tin-POMS catalyst. Also evident from Figure 8 is the confirmation that the secondary hydroxyl reaction is indeed kinetically slower than the primary hydroxyl reaction under the same conditions in toluene. We plotted the corresponding rate constants for the primary and secondary hydroxyl-isocyanate reactions in toluene using the various tin-POMS catalyst concentrations as shown in Figure 9. General trends that would be expected for an efficient and soluble catalyst
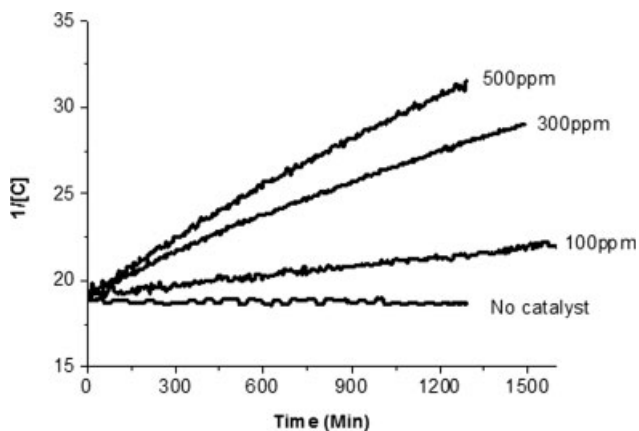

Figure 6 1/[C] versus time: 1-butanol in toluene with tin-POMS.

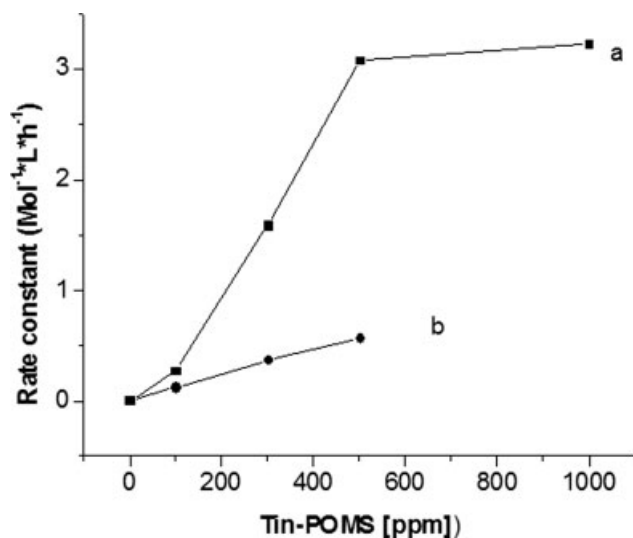**Figure 8** 1/[C] versus time: 2-butanol in toluene with tin-POMS.

Figure 9 Rate constant versus [catalyst] in toluene: (a) 1-butanol and (b) 2-butanol.

system for these reactions were observed with higher catalyst concentrations leading to progressively higher rate constants, and in the case of the primary hydroxyl reaction reaching a concentration level (above 500 ppm tin) where catalytic activity leveled off. In addition, we observed specific kinetic rate differences for the primary versus secondary hydroxyl reaction. For example, at a concentration of 500 ppm tin the kinetic rate constant for the $H_{12}MDI$ and 1-butanol reaction in toluene was 3.08 mol^{-1} L h^{-1} and the secondary hydroxy reaction for 2-butanol under the same reaction conditions was 0.57 mol^{-1} L h^{-1} similar to the previously reported values discussed above.

To further investigate the secondary hydroxyl reaction and have a direct comparison for tin-POMS to a more conventional urethane catalyst such as DBTDL we ran a comparative study. Figure 10 shows a direct comparison between DBTDL and tin-POMS at 300 ppm tin. The rate constant of the reaction for $H_{12}MDI$ with 2-butanol in toluene with DBTDL under our conditions was 0.55 mol^{-1} L h^{-1} compared with 0.40 mol^{-1} L h^{-1} for tin-POMS. Although our results do show a slightly lower activity for the tin-POMS in this study, our practical experience when considering the larger scope of and range of catalytic activity for these reactions confirms these catalysts are very similar in efficiency. We feel the additional benefits of tin-POMS when considering water and oxygen sensitivity, handling, measuring, and storage make it a very attractive alternative for practical use.

The influence of reaction solvent on the rates and mechanisms of polymerization reactions are well documented.[19,20] It is possible for solvent to alter the rate of reaction without influencing the mechanism, but it would be coincidental for a solvent to change

the reaction mechanism without altering the kinetic rate of reaction. Solvents are known to change the reaction rates by altering the forces between molecules and willingness with which they interact with each other kinetically. Solvents will influence rate constants by altering a variety of reaction parameters including nucleophilicity, electrophilicity, cohesion, hydrogen bonding, and etc. We determined the kinetic rate constants for the reaction of $H_{12}MDI$ with 1-butanol and 2-butanol in (essentially) nonpolar toluene to be second order and determined it worthwhile to evaluate the effect of solvent polarity on the catalytic efficiency of tin-POMS in a more polar solvent.

Kinetic study of $H_{12}MDI$ with 1-butanol and 2-butanol in DMF

To explore the effects of solvent polarity, we elected to run a series of reactions in DMF similar to the conditions and methods employed for toluene. We generated a plot of the peak height for the 2264 cm^{-1} absorption versus $H_{12}MDI$ concentration in DMF similar to that depicted in Figure 1 for toluene and determined the calibration equation on the basis of line fit to be:

$$H = 37.309[C] - 0.0381 \qquad (2)$$

Figure 11 shows the decreases of $H_{12}MDI$ concentration versus time with the reaction of 1-butanol in DMF at various levels of tin-POMS concentration and again follows trends expected from a well solubilized and efficient catalyst system. The 0 ppm tin control sample was a noteworthy observation for the DMF reaction and identified a slight reaction between 1-butanol and $H_{12}MDI$ in DMF without catalyst present. The reaction between 1-butanol and $H_{12}MDI$ in toluene was essentially undetectable at
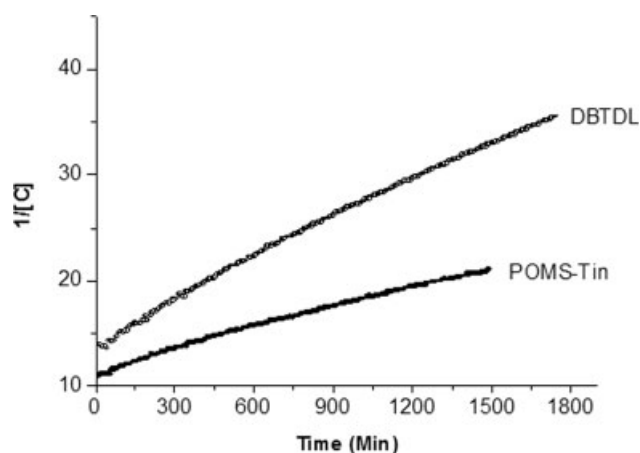

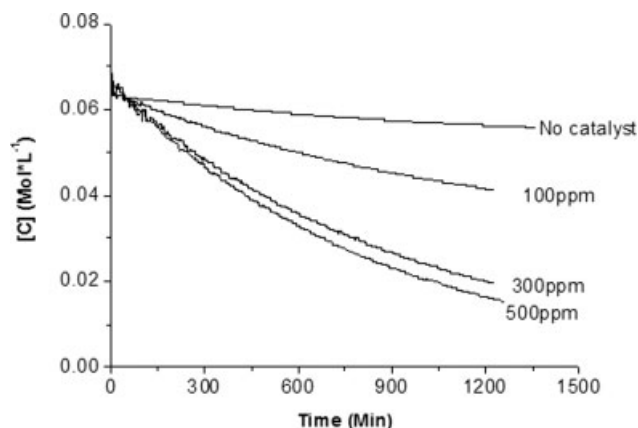**Figure 10** Tin-POMS versus DBTDL: 2-butanol in toluene (300 ppm tin).

Figure 11 H$_{12}$MDI concentration versus time: 1-Butanol in DMF with tin-POMS.

Figure 13 ln[C] versus time: 1-butanol in DMF with tin-POMS.

0 ppm catalyst but showed a slow (but certain) reaction in DMF. We attribute this uncatalyzed urethane reaction in DMF to increased polarity of DMF which must favor a slight reaction between H$_{12}$MDI and 1-butanol under our reaction conditions. To account for the uncatalyzed reaction between 1-butanol and H$_{12}$MDI in DMF we subtracted the concentration changes over time of the 0ppm reaction from the 100 ppm, 300 ppm, and 500 ppm curves when calculating kinetic rate constants and reaction order.

We plotted 1/[C] versus time as depicted in Figure 12 and ln[C] versus time as depicted in Figure 13 to determine the reaction rate order for the tin-POMS catalyzed primary hydroxyl-isocyanate reaction in DMF. It is apparent from these plots the 1-butanol reaction in DMF follows first order kinetics indicating a different reaction mechanism than observed in toluene under the same conditions.

We also ran a series of 2-butanol reactions in DMF to further explore catalyst activity and reaction kinetics. We plotted the corresponding rate constants
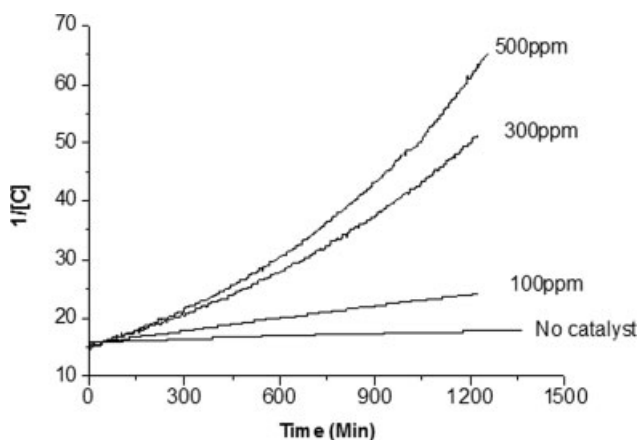
for the primary and secondary hydroxyl-isocyanate reactions in DMF at various tin-POMS catalyst concentrations as shown in Figure 14. Again, we observed general trends that would be expected for an efficient and soluble catalyst system for these reactions with higher catalyst concentrations leading to progressively higher rate constants. We also observed kinetic rate differences for the primary versus secondary hydroxyl reactions as would be expected.

To confirm the efficacy of the tin-POMS catalyst for polyurethane synthesis, we conducted a series of reactions between H12MDI and 2000 g/mol poly(ε-caprolactone)diol in DMF. In every case, we observed a strong catalytic effect for tin-POMS catalyzing polyurethane reactions. As expected, polymerization rates were slightly lower using the polyester polyol when compared with low-molecular weight mono-ol, but the general trends regarding
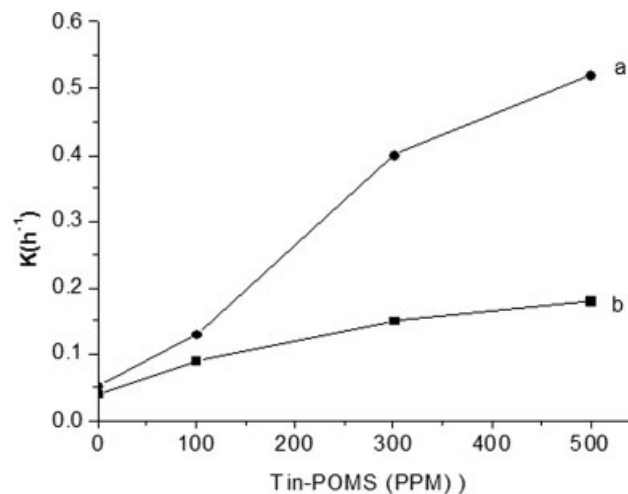

Figure 12 1/[C] versus time: 1-butanol in DMF with tin-POMS.

Figure 14 Rate constant versus [catalyst] in DMF: (a) 1-butanol and (b) 2-butanol.

TABLE I
The Summary of Rate Constant and Corresponding R

		DMF		Toluene	
		k (h^{-1})	R	K (mol^{-1} L h^{-1})	R
1-Butanol	100 ppm	0.13	0.999	0.28	0.998
	300 ppm	0.4	0.998	1.74	0.995
	500 ppm	0.52	0.997	3.08	0.997
	1000 ppm			3.23	0.993
2-Butanol	100 ppm	0.09	0.998	0.12	0.998
	300 ppm	0.15	0.998	0.38	0.997
	500 ppm	0.18	0.999	0.57	0.998
PCL diol	300 ppm	0.054	0.993		

catalyst concentration and order were confirmed. A summary of the catalytic results for all tin-POMS catalyzed primary and secondary hydroxyl reactions with H$_{12}$MDI in toluene and DMF, and a comparative polyurethane reaction of poly(e-caprolactone) diol in DMF (at 300 ppm tin) are presented in Table I with linear regression R-values.

CONCLUSIONS

We have investigated a new tin-POMS catalyst to study primary and secondary hydroxyl-isocyanate reactions and focused upon the effects of catalyst concentration and solvent polarity. We found tin-POMS to be an efficient urethane catalyst under the traditional urethane reaction conditions that we employed in our study, and feel it has specific advantages over conventional tin catalyst compounds when considering handling, moisture, and oxidative stability. We also found the catalyst efficiency of tin-POMS is comparable with dibutyltin dilaurate activity, and feel it is valid for continued investigation in applications which require careful tin concentration loading levels, such as those found in biomaterials.

References

1. Baney, R. H., Itoh, M., Sakakibara, A., Suzuki, T. Chem Rev 1995, 95, 1409.
2. Li, G.; Wang, L.; Li, H.; Pittman, CU, Jr. J Inorg Org Polym 2002, 11, 123.
3. Gozdz, A. S. Polym Adv Tech 1994, 5, 70.
4. Adachi, H.; Hayashi, O.; Okahashi, K. Jpn. Pat. Kokoku-H-2–15863 (1990).
5. Chen, W. Y.; Wang, Y. Z.; Kuo, S. W.; Huang, C. F.; Tung, P. H.; Chang, F. C. Polymer 2004, 45, 6897.
6. Lee, Y. J.; Huang, J. M.; Kuo, S. W.; Chang, F. C. Polymer 2005, 46, 10056.
7. Shoji, F.; Sudo, R.; Watanabe, T. Jpn. Pat. Kokai-S-56–146120 (1981).
8. Azuma, K.; Shindo, Y.; Ishimura, S. Jpn. Pat. Kokai-S-56820 (1982).
9. Mi, Y.; Stern, S. A. J Polym Sci Part B: Polym Phys 1991, 29, 389.
10. Satio, Y.; Tsuchiya, M.; Itoh, Y. Jpn. Pat. Kokai-S-58–14928 (1983).
11. Feher, F. J.; Budzichowski, T. A.; Ziller, J. W. Inorg Chem 1997, 36, 4082.
12. Ukrainczyk, L.; Bellman, R. A.; Anderson, A. B. J Phys Chem Part B 1997, 101, 531.
13. Annad, J.; Aspinall, H. C.; Steiner, A. Inorg Chem 1999, 38, 3941.
14. Duchateau, R.; Abbenhuis, H. C. L.; Van Santen, R. A.; Meetsma, A.; Thiele, S. K. H.; Van Tol, M. F. H. Organometallics 1998; 17; 5663.
15. Duchateau, R.; Abbenhuis, H. C. L.; Van Santen, R. A.; Meetsma, A.; Thiele, S. K. H.; Van Tol, M. F. H. Organometallics 1998, 17, 5222.
16. Elwell, M. J.; Ryan, A.J. Polymer 1996, 37, 1353.
17. Griffith, P. R.; Haseth, J. A. FT-IR Spectrometry; Wiley Interscience: New York, 1986.
18. Rand, L.; Thir, B.; Reegen, S. L.; Frisch K. C. J Appl Polym Sci 1965, 9, 1787.
19. Li, X. B.; Song, Q. H. Heteroatom Chem 2007, 18, 203.
20. Reichardt, C. Solvents and Solvent Effect in Organic Chemistry; Wiley Interscience: New York, 2002.