

Total Replacement of Solvent in Polyurethane Synthesis Using Carbon Dioxide Soluble 1,3-Dichlorodistannoxane Catalysts

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ABSTRACT: This work demonstrates catalytic synthesis of polyurethanes using 1,3-dichlorodistannoxane catalysts (**1**) in carbon dioxide (CO₂) and carbon dioxide expanded liquids (CXL). Catalytic polyurethane synthesis was also performed in pure organic solvent (dimethylformamide) for comparison. In this study, mainly, 4, 4'-methylene-bis-(phenyl isocyanate) (MDI) as the diisocyanate precursor and ethylene glycol (EG) as the diol precursor were used for polyurethane synthesis. In addition to MDI, hexamethylene diisocyanate (HDI), toluene diisocyanate (TDI), and *p*-isocyanatobenzylisocyanate (PIBI) were also used for polyurethane synthesis with different diols or triol in CO₂. Polyurethanes with a molecular weight ranging from 3000 to 70,000 were synthesized depending upon the combination of diisocyanate and diol used. Comparable yields of polyurethanes were obtained using an all butyl group substituted (**1a**) catalyst in CO₂ (55 bars, 50°C) and in DMF (50°C). Additionally, the yield and polydispersity index (PDI) of polymer formed in neat CO₂ was comparable with those synthesized in the largely used organic solvent DMF. Interestingly, catalyst **1a** in CXL (55 bars, 50°C) gave higher yields, and polymers with lower PDI (1.19). Reactions carried out in scCO₂ at 145 bars using PIBI and EG were found to be about three times faster than the reaction carried out in DMF. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Since the discovery of polyurethane by Otto Bayer in 1937¹ and the first commercial production by DuPont in 1956, our society is becoming increasingly reliant on their versatile applications. Rigid and light weight foams, elastomers, adhesives, and coatings are forms of polyurethanes which are produced in large quantities.² Several forms of these polyurethanes serve essential functions such as in automotive industries, furniture and bedding, textile, coatings, and building materials, etc. Polyurethane demand in US was projected to be 7.6 billion pounds in 2009 for building insulation, coatings, and adhesives.³ The potential growth in motor vehicle and other industrial sectors that use thermoplastic polyurethane remains steady. The global consumption of polyurethane raw materials was more than 12 million metric tons in 2007, with an average annual growth of 5%.⁴ Therefore, for such highly demanded material, polyurethane synthesis requires continuous development. Particularly, the methodology for polyurethane synthesis still demands

intimate attention in terms of process improvements, such as catalysts and solvents used.

The polyurethane catalyst systems presently practiced in industrial process can broadly be classified as amine and organometallic catalysts.⁵ Amine catalysts, especially in large scale operation, carry hazard concerns.⁶ On the other hand, organometallic catalysts that normally incur costs must be highly efficient. Moreover, recyclability of the catalyst, which is hardly taken into consideration especially in polymerization reactions, is significant from an environmental point of view.⁷ Solvent choice in polyurethane manufacturing also plays a significant role, as it is hard to find a good solvent to provide a homogenous reaction medium comprising of substrates, catalyst and the formed product. In most cases, organic solvents such as dimethylformamide (DMF) are used as the solvent in large quantities. Since many of these solvents are known to have toxic effects, the additional responsibility on solvent replacement must be taken into account.⁸ Thus, it is of highest importance to find a greener

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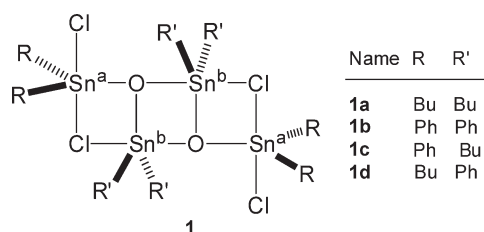


Figure 1. Structure of 1, 3-dichloro-1, 1, 3, 3-tetraalkyldistannoxane (1).

solvent for the replacement of harmful organic solvents in polyurethane synthesis.

Our continuing effort in solvent replacement for chemical reactions by CO₂ can be applied to the synthesis of polyurethanes.⁹ However, the extreme insolubility of diisocyanates in most of the solvents makes it very difficult to obtain total solvent replacement during polyurethane synthesis. Catalyst solubility is also one of the key factors that must be taken into consideration. To avoid the occurrence of inhomogeneities in the reaction system that may cause an abrupt drop in the reactivity of the catalyst a soluble catalyst is needed.

Since the introduction in 1959, several tin complexes have been used to synthesize polyurethane from polyhydric alcohols and aromatic diisocyanates.¹⁰ Diorganotin mercaptocarboxylates and mercaptides are widely used to produce relatively hard foams such as for car seats. Tin fatty acid salts, such as dibutyltin, dibutyltin dilaurate and tin(II)-2-ethylhexanoate, are widely used to synthesize polyurethanes especially for the formation of flexible foams.⁵ Tetra-alkyldistannoxanes with the general formula of XR₂SnOSnR₂Y have shown the highest catalytic activity among the catalysts for polyurethane synthesis.^{11,12} Substituents at X, Y, R are determinant factor for the catalytic efficiency. The catalysts with NCS as X and/or Y are noteworthy in this respect. But the solvent issue remained unresolved in these catalyst systems. Moreover, the catalysts are neither recyclable nor separable. There are few reports that disclose the synthesis of polyurethane in CO₂, but these involve either a nonrecyclable catalyst¹³ or copolymer formation.¹⁴

We have recently found that a series of 1,3-dichloro-1,1,3,3-tetraalkyldistannoxane complexes (**1**, Figure 1) are highly soluble in CO₂, a green solvent with low toxicity and high abundance. Catalysts **1** are stable in the presence of air, CO₂ and moisture, excluding the use of specialized equipment such as an inert box, vacuum manifold, etc.¹⁵ The catalysts **1** (Figure 1) are synthesized by a reported single step procedure.^{16–20} Taking the advantage of the high solubility of these catalysts in CO₂, we have found that catalysts are able to execute polyurethane synthesis efficiently both in CO₂ and CO₂ expanded dimethylformamide (CXL).

Herein, we report the synthesis of polyurethane both in pure CO₂ medium and CXL starting with aliphatic as well as aromatic diisocyanates and various diols or triol using **1** as a recyclable catalyst. Different reaction conditions were studied for obtaining optimum reaction yield in pure CO₂. The effect of substituent groups in the Sn catalyst has been studied. These

findings put forward a new “greener” study in the area of polyurethane formation (Scheme 1).

EXPERIMENTAL

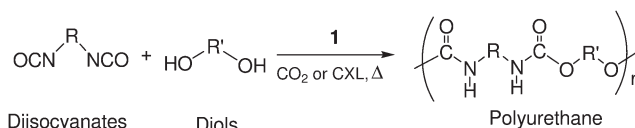
General

Chemicals were purchased from Aldrich chemical company, USA and used without further purifications unless otherwise mentioned. Solvents were purified using standard purification procedures before using in any reaction. All of the high pressure reactions were carried out in 100 mL Parr reactor connected with a 4843 controller. Polyurethane molecular weight was determined by gel permeation chromatography (GPC) method (Prominence LC-20AT, Simazdu RI detector RID-10 A) with JORDI polystyrene standards in DMF. DMF was used as the eluent solvent (flow rate was 1.000 ml/min) for GPC. Thermal degradation of these polyurethane samples was measured by TGA (Mettler TG50, Mettler Toledo) from 35 to 600°C with a heating rate of 10°C/min. The TGA measurements were conducted using 4–11 mg of samples. Weight loss (%) was recorded against temperature. ¹H-NMR spectra were obtained in a 600 MHz Bruker instrument using deuterated solvent as the lock. The spectra were collected at 25°C and chemical shifts (δ , ppm) were referenced to the residual solvent peak (CDCl₃, δ , ¹H, 7.26 ppm). The infrared (IR) spectra of the polyurethane were recorded in between 400 and 4000 cm⁻¹ using a Shimadzu Affinity-1 Fourier transform infrared spectroscopy instruments. The absorption peaks of functional groups present in polyurethane sample were normalized with the characteristic absorption peaks of the isocyanate monomer. The catalysts have been prepared as per previous literature reported single-step procedure.²¹

Polyurethane Synthesis

Polyurethane Synthesis in DMF. 4, 4'methylene-bis-(phenyl isocyanate) (1.32 mmol) and ethylene glycol (1.32 mmol) were taken in a 100-mL round-bottom flask with DMF as solvent. To this mixture **1a** (0.003 mmol) was added. The reaction was carried out at 50°C with continuous stirring for the stipulated time. The reaction mixture was cooled and to this mixture excess methanol was added to precipitate the polyurethane. Polymer was collected by filtration. The unreacted substrates (diisocyanates and diols) were washed off using methanol. As catalyst is also insoluble in methanol, it co-precipitated with the polyurethane. The precipitate was washed with copious amount of hexane to separate the catalyst from the polymer as catalyst is soluble in hexane. The polymer was dried in vacuum at 60°C to obtain the desired polymer and further characterized.

Polyurethane Synthesis in CXL. General methods of polyurethane synthesis in CXL were performed according to the



Scheme 1. Synthesis of polyurethane using diisocyanate and diols catalyzed by **1**.

Table I. Polyurethane Synthesis Using Different Diisocyanates

Catalyst	% Yield			
	MDI + EG	M_n	M_w	PDI
1a	86	4100	5400	1.33
1d	73	5600	9800	1.76
1c	70	6100	10,000	1.64
1b	62	5500	7700	1.41
	PIBI + EG			
1a		13,900	18,900	1.36
1d		14,200	20,100	1.41

Diisocyanate (1.32 mmol), EG (1.32 mmol) Using 0.003 mmol of 1 at 50°C for 10 h, in 55 Bar CO₂.

following procedure. 4, 4'-methylene-bis-(phenyl isocyanate) (1.32 mmol), and ethylene glycol (1.32 mmol) were taken in a Parr reactor (100 mL). To this reaction catalyst **1a** (0.003 mmol) and 2 mL of DMF were added. The reaction mixture was purged with CO₂ and pressure of CO₂ was increased to 55 bar while temperature of the reaction was maintained at 50°C. The reaction mixture was stirred for the desired time (for example 2 or 10 h). After the reaction the Parr reactor was brought back to room temperature and pressure. The polymer was isolated as described previously.

Polyurethane Synthesis in CO₂. General methods of polyurethane synthesis in CO₂ were performed according to the following procedure. MDI (1.32 mmol) and EG (1.32 mmol) were taken in a Parr reactor (100 mL). To this reaction catalyst **1a** (0.003 mmol) was added. The reaction mixture was purged with CO₂ and pressure of CO₂ was increased to 55 bar while temperature of the reaction was maintained at 50°C. The reaction mixture was stirred for the desired reaction time, after which the Parr reactor was brought back to room temperature and pressure. The polymer was isolated as described previously.

Reaction kinetics was followed for experiments carried out in either CO₂ or CXLs. The reactions were stopped at various times and polymer samples were isolated and the conversions were characterized.

RESULTS AND DISCUSSION

Synthesis of Polyurethane

Preparation of polyurethane was executed by reacting diisocyanate and diol using **1** as catalyst and CO₂ as solvent. The final pressure was adjusted to 55 bars, after the desired temperature was attained. The progress of reaction was monitored by FTIR. Thus, the absence of the antisymmetric stretching peak at 2270 cm⁻¹ (ν (O=C=N)) of isocyanate and the presence of peaks at 1660, 1740 cm⁻¹ (ν (O=C-N-)) and 3330 cm⁻¹ (ν (-N-H)) of polyurethane confirms the formation of polyurethane (Figure S1, Supporting Information). ¹H-NMR of polyurethane synthesized using EG showed ethylene hydrogens at δ 4.2. The aromatic H in the MDI were observed at δ 7.0–7.1 (m, 4 H, -C₆H₄-) and δ 7.3 (4 H, -C₆H₄-). The methylene H of the MDI was also seen at δ 3.8 (Figure S4, Supporting Information). The presence of aromatic and aliphatic protons in ¹H-NMR repre-

sents formation of polymer. Moreover, the peak at 9.8 ppm corresponding to N-H instead of NH₂, further supports the formation of polyurethane. The GPC (Figure S2, Supporting Information) of the polymer shows a narrow molecular weight distribution. The low polydispersity index PDI (M_w/M_n), less than 2 indicates the occurrence of step polymerization, Table I. Thermogravimetric analysis (TGA) of the polymer shows thermal degradation at around 280 and 480°C (Figure S3, Supporting Information). The catalyst recovered by extraction into hexane was characterized using FTIR and NMR which showed the same spectra as the original catalyst.

Effect of Cosolvent

Solubility of isocyanates is one of the critical aspects in polyurethane synthesis. Generally highly polar solvents like DMF are employed to get the desired yield. However, as mentioned earlier carrying the reaction out in DMF is a serious concern from environmental aspect. Replacing the solvent as a whole or in part with benign solvent such as CO₂, is one approach to reduce DMF dependence. We initially carried the reaction out in CXL (carbon dioxide expanded DMF here). As seen in Figure 2, addition of small amounts of DMF into the reaction increases the yield. A mere 2% DMF in CO₂ gives high yield of ~100% with a turnover number (TON = the number of moles of substrate that a mole of catalyst can convert) of 400. Thus the reaction implies that a large part of the DMF can be replaced by CO₂. Interestingly this polymerization reaction could be performed in CO₂ with a significant yield of 86% and a TON of 340. Thus total replacement of DMF by CO₂ was achieved and further reactions with variable parameters were performed to see the feasibility of polyurethane synthesis in CO₂ only.

Variation of Reaction Parameters

The optimum amount of catalyst required for the polymerization reaction in CO₂ was checked by varying the amount of **1a** [Figure 3(a)]. Catalyst concentration of up to 0.024 mmols was employed for these reactions. Less than 10% yield was obtained when no catalyst was used with turnover number (TON) less than 40. The TON increased from about 110 to 210 as the mmols of catalyst was increased from 0.0008 to 0.008, with the optimum amount of catalyst required being 0.01 mmol with respect to 4 mmol of isocyanate. At this reaction condition

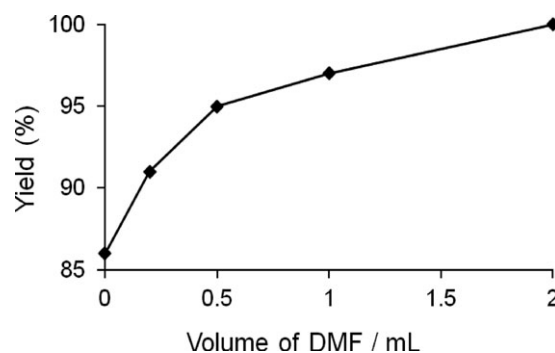


Figure 2. Effect of addition of DMF on yield of polyurethane synthesis in CO₂ (55 bar, 100 mL) in 10 h using MDI (1.32 mmol), EG (1.32 mmol), **1a** (0.003 mmol) at 50°C.

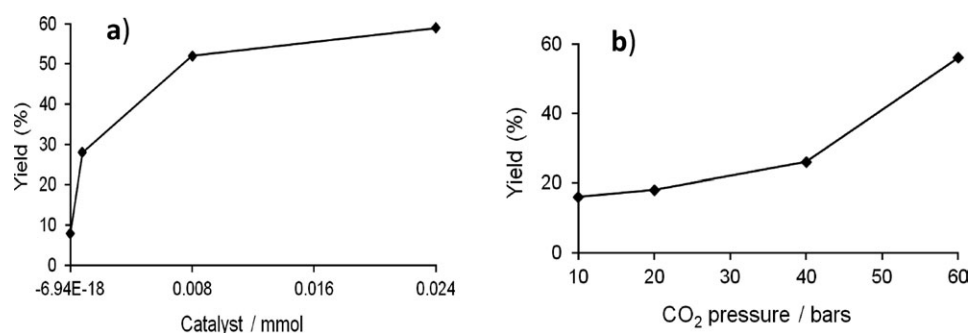


Figure 3. (a) Effect of variation of amount of catalyst on yield (%). MDI (4 mmol), EG (4 mmol), 50°C, CO₂ 55 bar, 2 h, 1a. (b) Effect of CO₂ pressure on % yield of polyurethane. MDI, (4 mmol); EG, (4 mmol); Temperature, 50°C; Time, 2 h; Catalyst (1 a), 0.008 mmol; Volume, 100 mL CO₂; No organic solvent used.

more than 50% yield was obtained which indicates that the TON for the catalyst is ~ 220 .

Yields were found to increase exponentially with increasing CO₂ pressure. Less than 20% yield was observed when reactions were performed at low CO₂ pressures of 10 and 20 bars. However, yield was found to be increasing with an increase in the CO₂ pressure. About 60% yield could be obtained at 60 bar CO₂ pressure [Figure 3(b)]. TON increased from about 70 at 10 bars CO₂ to 240 at 60 CO₂ bars pressure. This may be attributed to the increased solubility of the catalysts as the phase trends to go from the gaseous phase to near critical phase.⁹

Effect of Different Catalysts

The role of Sn metal centers in dichlostannoxanes **1** in the catalysis of polyurethane synthesis in CO₂ was studied by varying the substituents in both the Sn centers. Butyl and phenyl groups were used as substituents as by itself or in combination to see the effect/change in the activity. These alkyl and aromatic substituents govern the electronic and steric environment of the Sn centers which in turn determine the different activity of **1** catalysts. The catalyst with all butyl groups (**1a**) is found to have the highest activity in CO₂ with more than 50% yield of polymerization in 2 h [Figure 4 (a)]. Substitution with phenyl groups in the Sn centers showed a decrease in the catalyst activity. This is attributed to the stronger and shorter Sn—Cl bond at the terminal Sn (Sn^a in Figure 1) because of the weaker nucleophilic phenyl group. The stronger Sn—Cl makes it harder

for the diol to interact with the Sn metal center, which is the mechanism by which the chlorodistannoxane catalyze the reaction,¹² hence decreasing the overall activity.²² While using all phenyl substituted **1b** catalyst, less than 30% polymerization was observed in 2 h. It was further observed that in catalyst **1c** and **1d** which had both butyl and phenyl substituents, position of the phenyl substituent on Sn played deciding factor on the reactivity of **1** too. This variation of activities between **1c** and **1d**, upon the substituents on the two Sn centers showed the nondegeneracy of Sn in **1**. Catalyst **1c** with terminal phenyl group showed less activity when compared with the catalyst **1d**, which had butyl in the terminal position. This is in agreement with our earlier observation regarding the trend of catalytic activity of chlorostannoxanes in sun flower oil methanolysis and ethyl-2,2-dimethylacetoacetate transesterification with benzyl alcohol in CO₂, showing **1a** and **1d** are most and least reactive catalysts, respectively. This implies that the mechanism of reaction is likely to be similar to that of other distannoxane catalyzed reactions.⁹

Another factor that may contribute to this trend of activity of **1** is their solubility in reaction medium CO₂. Differences in the catalytic activity of catalysts in neat CO₂ were observed as shown in Figure 4(a). Effect of various catalysts showed that the catalyst **1a** is most effective while catalyst **1b** is least effective, inferring the reactivity in order **1a** > **1d** > **1c** > **1b**, which was in accordance to the trend of their solubility in CO₂.⁹

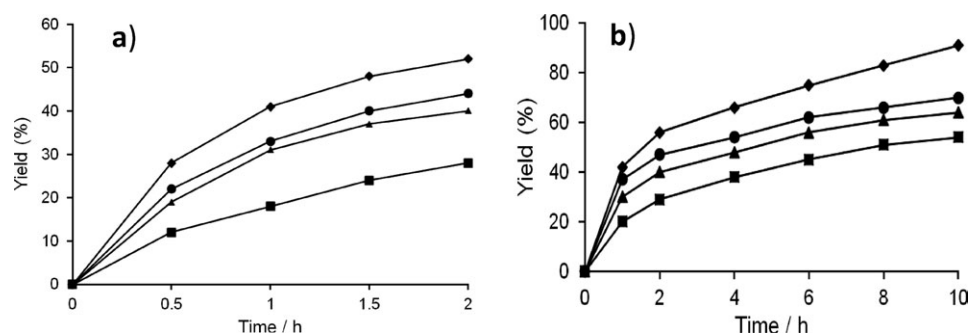


Figure 4. (a) Effect of time on polyurethane synthesis (% yield) with 55 bar CO₂, 50°C, using MDI (330 mg, 1.32 mmol), EG (74 μ L, 1.32 mmol), 0.003 mmol of catalyst: 1a (◆), 1b (■), 1c (▲), and 1d (●). (b) in CXL (2 mL DMF + 98 mL CO₂), (55 bar CO₂), 50°C, using MDI (330 mg, 1.32 mmol), EG (74 μ L, 1.32 mmol), 0.003 mmol of catalyst: 1a (◆), 1b (■), 1c (▲), and 1d (●).

Table II. Comparison of Time vs. % Yield of Polyurethane in DMF for 10 and 18 h (*), in Parr Reactor CXLs (CO₂+DMF) for 10 h and in Pure CO₂ for 10 h Using **1a**, **1b**, **1c**, and **1d**

Catalyst	Yield in solvent		
	DMF	CO ₂	CXL
1a	86	86	91
	91*	-	-
1b	75	56	62
	84*	-	-
1c	79	70	70
	86*	-	-
1d	83	73	73
	88*	-	-

Substrate: MDI and EG.

Similar trend was observed in reactions performed in CXL [Figure 4(b)]. Catalyst **1a** showed a better rate of polymerization as compared to the other catalysts **1b**, **1c**, and **1d**. As seen in Table I, a percentage yield of 91% was obtained within 10 h in CXL at 50°C and 55 bars pressure. Catalyst **1b**, **1c**, and **1d** did not give comparable yields as compared with **1a** with yield of about 60–80%. All of the catalysts gave good yields in DMF with 75–86% yield in 10 h and 80–90% in 18 h at 50°C. Catalyst **1a** gave 91% yield in 10 h in CXL whereas it took 18 h in the DMF to give a similar yield. This was not observed with the other catalyst **1b**, **1c**, and **1d**.

Noticeably, though yield varies with the catalysts, PDI almost remained unchanged. This indicates that the mechanism of polycondensation is not affected by alteration on the catalyst site. The PDI of polyurethane synthesized in CXL was found to be between 1.15 and 1.20 (Supporting Information Table S1), which is less compared with that synthesized in pure organic solvent (1.25–1.30). Polymer weight ranging from 5400 to 9800 were obtained in reactions in neat CO₂ with a PDI of 1.33–

1.76. All of the GPC calibrations were performed using polystyrene standards. It has been observed that the average molecular weight of the polymers reached about 6000 at around 0.5–2 h. The molecular weight then tends to decrease as the reaction time progress.

Polyurethane Synthesis in Supercritical CO₂ (scCO₂)

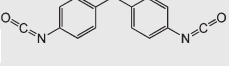
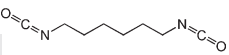
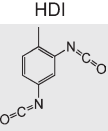
Polymerization reactions using PIBI and EG were also performed using **1a** and **1d** at 55 bars pressure at 50°C. Polyurethane with M_w in the range of 18,800 to 20,100 with PDI between 1.36 and 1.41 was obtained (Table II). Using PIBI and EG in scCO₂ (**1a**) at 90 bars pressure and 35°C, the molecular weight was found to increase to ~40,000. When the CO₂ pressure in the reaction was further increased to 145 bars scCO₂ and 50°C, polymer with (M_w) 41,000 and polydispersity index ($PDI = M_w/M_n$) of 2.59 was obtained. Remarkably the reaction at 145 bars scCO₂ was almost complete within 7 h, whereas in case of DMF the reaction took 19 h to get similar 91% yield of polyurethane. Low viscosity and fast mass transfer in scCO₂ generally attribute to higher reaction rates in scCO₂.

Polymerization Using Different Substrate Combination

Polymerization reactions were also carried out using different combinations of diisocyanate and diols/polyol to see the feasibility of this process in CO₂. Methylene diphenyl diisocyanate (MDI), hexamethylene diisocyanate (HDI), and toluene diisocyanate (TDI) were used as the diisocyanate in combination of hydroxyl containing molecules ethylene glycol (EG), 1,4-butane-diol (BD), and glycerol (GLY).

As seen in Table III, lower molecular weight polymers (molecular weight ranging from 3300 to 7400) were synthesized when EG was used with the various diisocyanates. Polymer with M_w 7300 was synthesized using HDI with EG. Nevertheless the % yield of polyurethane synthesized was as high as 93%. Lower yield in the range of 64–72% was observed when the diisocyanates were used with BD. Higher M_w polymers with an average molecular weight ranging from 36,000–69,000 were observed when BD and GLY were used instead of EG. An average M_w of

Table III. Polyurethane Synthesis Using Different Diisocyanates and Diols/Triols Combinations

Entry	Diisocyanate	Diol	% Yield	M_n	M_w	PDI
1	 MDI	EG	86	4100	5400	1.33
2		BD	69	10,100	53,800	5.35
3		GLY	84	7200	62,600	8.65
4	 HDI	EG	83	4600	7300	1.58
5		BD	72	4000	47,900	12.06
6		GLY	74	9600	37,100	3.85
7	 TDI	EG	93	1600	3400	1.99
8		BD	64	10,100	43,200	4.25
9		GLY	82	9000	68,700	7.63

Diisocyanate (1.32 mmol), diol (1.32 mmol) using 0.003 mmol of **1a** at 50°C for 10 h, in 55 bar CO₂.

69,000 was obtained when GLY was used with TDI. The PDIs were high ranging from around 4 to 12. However, using EG with the different diisocyanates gave polymers with better molecular weight distribution (PDI) ranging from 1.3 to 2. Thus a variety of substrates could be polymerized in CO₂ to give polyurethane with diverse molecular weight profiles and properties.

CONCLUSIONS

In conclusion, we have demonstrated that chlorostannoxanes can be used in synthesizing polyurethane in CO₂ and CXLs, which are environmentally benign. Various combinations of the diisocyanate and polyols could be successfully polymerized to polyurethanes in CO₂ media. Compared with pure organic solvents, the yield of polyurethane was found to be comparable in neat CO₂ and even higher in CXL using the **1a** catalyst. The rate increase is due to several facts including high solubility of the catalyst and high mass transfer in the solvent medium. After the reaction, the precipitated product can be washed with methanol and separated by filtration. Thus, we have shown that chlorostannoxanes can be used efficiently in a green solvent like CO₂ and CXL. In fact, the catalysts we used improved in both of these areas compared to organic solvent based methods. These factors make this a subject for more research because of the environmental benefits, as well as, the increased efficiency and the goal of greater sustainability.

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