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Efficient Organotin Catalysts for Urethanes: Kinetic and Mechanistic Investigations

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Dibenzyltin bis(2-ethylhexanoate) 1 (4-Y—$C_6H_4CH_2)_2Sn(OC(O)R^1)_2$ [Y = H, 1a; MeO, 1b; Cl, 1c; Me, 1d; and $R^1 = MeCH_2CH_2CH_2$-CH(Et)—] were synthesized either from the reaction of corresponding dibenzyltin dichlorides with silver 2-ethylhexanoate or from the reaction of dibenzyltin oxides with 2-ethylhexanoic acid. Compound 1a was further utilized as a catalyst for the reaction of mono- and di-isocyanates [PhNCO, $CH_3C_6H_3$-2,4-$(NCO)_2$ and $OCN(CH_2)_6NCO$] with alcohols (primary, secondary, tertiary, cyclohexcyl, alkyl, allyl, benzyl and aryl) leading to the formation of the corresponding urethanes. The catalytic efficiencies of 1 vis-à-vis industrially known organotin catalysts have been determined through kinetic studies for the reaction of PhNCO and *n*-BuOH at various temperatures. Compounds 1a, 1c and 1d show higher efficiency than dibutyltin bis(2-ethylhexanoate). FTIR studies further provide mechanistic insights into the catalytic cycle, which comprises pre-coordination of isocyanate to tin(IV), formation of stannyl carbamate and generation of dibenzyl(alkoxy)carboxylate as the active catalyst. Copyright © 2000 John Wiley & Sons, Ltd.

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INTRODUCTION

Urethanes and polyurethanes are of key industrial importance. The addition reaction of alcohols to isocyanates provides an attractive route to their synthesis; however, this requires mediation of a catalyst. (Eqns [1], [2]).[1–3].

$$\mathrm{RNCO} + \mathrm{R^1OH} \rightarrow \mathrm{RNHCOOR^1} \qquad [1]$$

$$\mathrm{OCN{-}X{-}NCO} + \mathrm{HO{-}Y{-}OH} \longrightarrow \left[\mathrm{OOCHN{-}X{-}NHCOO{-}Y}\right]_n \qquad [2]$$

It has been shown that, besides tertiary amines, organolithium,[4] lead[5] and tin[6–9] compounds have good to excellent catalytic activity. Among organometallic catalysts, diorganotin(IV) compounds in general, and esters in particular, show remarkably high activity. Dibutyltin dilaurate (DBTL) and the corresponding dibutyl bis(2-ethylhexanoate) catalysts are used in the industrial production of polyurethanes from di-isocyanates and polyols. As part of our work on tin reagents in organic synthesis,[10–15] we became interested in assessing the catalytic activity of diorganotin(IV) esters where the organic group is other than the butyl group. Towards this, we have earlier reported an efficient synthesis of mono- and di-urethanes via catalysis using diallyltin bis(2-ethylhexanoate).[14] However, comparison of the kinetics showed that the catalyst efficiency was lower than that of DBTL. In this paper we study the synthesis and kinetic of urethane formation catalysed by dibenzyltin diesters, a new group of catalysts.

The mechanism of the urethane-forming reaction has been investigated extensively by various research groups.[16] While the mechanism of the amine-catalysed reaction[17] is well understood, that of the tin-catalysed reaction remains uncertain. We also describe our work towards understanding the

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Table 1 Synthesis of Dibenzyltin bis(2-ethylhexanoate) **1** (4-Y—$C_6H_4CH_2)_2Sn[OC(O)R^1]_2$ [$R^1 = MeCH_2CH_2CH_2$-CH(Et)—]

Entry	Y	Compd no.	M.p. (°C)	Yield (%)[a]	
				Method A	Method B
1	H	**1a**	54	78	86
2	MeO	**1b**	33	82	71
3	Cl	**1c**	101	91	80
4	Me	**1d**	67	68	83

[a] Isolated yield; Method A = reaction of dibenzyltin dichloride and silver (2-ethylhexanoate); Method B = reaction of dibenzyltin oxide with 2-ethylhexanoic acid.

isocyanate–alcohol addition reaction mediated by the new group of organotin catalysts.

RESULTS AND DISCUSSION

Dibenzyltin bis(2-ethylhexanoate) **1** (4-Y—$C_6H_4CH_2)_2Sn[OC(O)R^1]_2$ [Y = H, **1a;** MeO, **1b;** Cl, **1c;** Me, **1d;** and $R^1 = MeCH_2CH_2CH_2CH(Et)$—] was synthesized via two different routes (Table 1). The first method relies on the ligand exchange reaction between dibenzyltin dichloride[18] and silver 2-ethylhexanoate in benzene at room temperature (Eqn [3]). The second method comprises

Table 2 Synthesis of urethanes and diurethanes [$PhNHCOOR^1$, entries 1–11; MeC_6H_3-2,4-$(NHCOOR^1)_2$, entries 12–17; $R^1OOCNH(CH_2)_6NHCOOR^1$, entries 18–28] from the reaction of RNCO and R^1OH catalysed by **1a**

Entry	RNCO	R^1	Time (min)	M.p. (°C)	Isolated yield (%)
1	PhNCO	*n*-Butyl	10	60.5	96
2		Isobutyl	10	86	88
3[b]		*tert*-Butyl	55	135	75
4		Isoamyl	10	—	84
5		*n*-Dodecyl	10	73	97
6		2-Chloroethyl	10	50	93
7		Cyclohexyl	10	82	78
8		Allyl	10	70	76
9		Benzyl	10	77	93
10		Phenyl	10	124	84
11		*p*-Tolyl	10	113	90
12	$CH_3C_6H_3$-2,4-$(NCO)_2$	*n*-Butyl	15	117	87
13[b]		*t*-Butyl	60	123	68
14		*n*-Dodecyl	15	80	86
15		Allyl	15	—	82
16		Benzyl	15	95	91
17		*p*-Tolyl	15	192	80
18	$OCN(CH_2)_6NCO$	*n*-Butyl	25	91.5	94
19		Isobutyl	25	116	86
20[b]		*t*-Butyl	60	—	72
21		*n*-Dodecyl	25	110	94
22		2-Methoxyethyl	25	73.5	96
23		2-Chloroethyl	25	112	96
24		Cyclohexyl	25	111	92
25		Allyl	25	—	86
26		Benzyl	25	125	86
27		Phenyl	25	125.5	88
28		*p*-Tolyl	25	162	94

[a] All reactions were carried out in refluxing dichloromethane unless otherwise stated.
[b] Reactions in refluxing benzene.

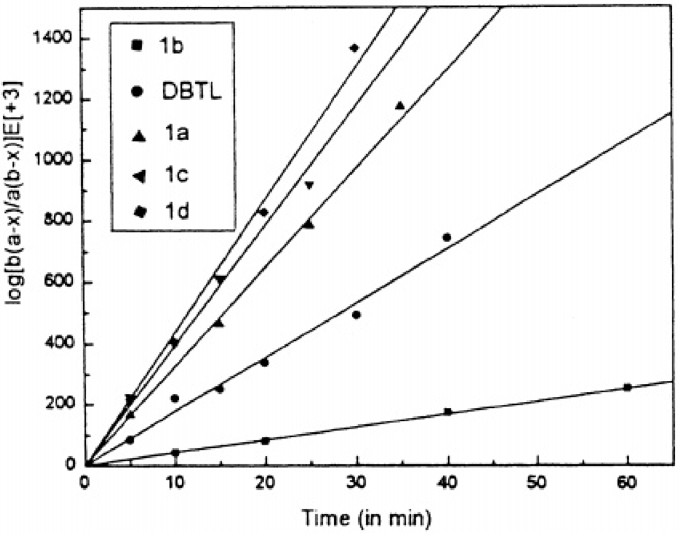


Figure 1 Second-order kinetic plots for the reaction of PhNCO and BuOH in the presence of various catalysts: ■, diallyltin bis(2-ethylhexanoate); ▽, **1b**; ▲, dibutyltin bis(2-ethylhexanoate); ○, dibutyltin dilaurate; ●, **1c**; □, **1a**; ◆, **1d**.

reaction of dibenzyltin oxide with 2-ethylhexanoic acid in the presence of 4 Å molecular sieve in cyclohexane (Eqn [4]).

$$(4-\mathrm{Y}-\mathrm{C_6H_4CH_2})_2\mathrm{SnCl_2}+\mathrm{Ag[OC(O)R^1]}\longrightarrow (4-\mathrm{Y}-\mathrm{C_6H_4CH_2})_2\mathrm{Sn[OC(O)R^1]} \quad [3]$$

$$(4-\mathrm{Y}-\mathrm{C_6H_4CH_2})_2\mathrm{Sn({=}O)}+\mathrm{R^1COOH}\longrightarrow (4-\mathrm{Y}-\mathrm{C_6H_4CH_2})_2\mathrm{Sn[OC(O)R^1]} \quad [4]$$

The reaction of isocyanate and alcohol follows apparent second-order kinetics.[19,20] Accordingly, the half-life of the reaction depends on initial reactant concentrations. All the reactions in the present study were carried out with initial concentrations of isocyanates and catalyst being kept at 0.1 mol $\mathrm{dm^{-3}}$ and 0.001 mol $\mathrm{dm^{-3}}$ respectively. With these initial concentrations, the reactions of pheny isocyanate with 1 equiv of alcohol or phenol proceeded smoothly in refluxing dichloromethane and were complete within 10 min (inferred via TLC), giving rise to the corresponding *N*-phenylurethanes in 76–97% yields (Table 2, entries 1, 2, 4–11). Similar reactions of toluene-2,4-diisocyanate with 2 equiv of alcohols proceeded to completion in 20 min with the formation of the corresponding diurethanes in 80–91% yield (Table 2, entries 12, 14–17). In all the above cases the uncatalysed reactions under similar conditions showed 6–19% conversion. These results demonstrate the high catalytic activity of the present catalyst.

Unlike primary and secondary alcohols, reactions of tertiary alcohols are slower (Table 2, entries 3 and 13). Earlier studies[20] demonstrated that in urethane-forming reactions the competitive rates of tertiary, secondary and primary alcohols approximated to 1:33:100. Aliphatic isocyanates are less reactive. Reactions of hexamethylene-1,6-di-isocyanate with 2 equiv of alcohols take longer to afford the corresponding diurethanes (Table 2, entries 18–28).

We then sought to determine, via kinetic measurements, the efficiencies of the new catalysts compared with industrial tin(II) and tin(IV) catalysts. Kinetic studies were carried out at 29 ± 0.1 °C using phenyl isocyanate (0.0384 mol $\mathrm{dm^{-3}}$) and *n*-butanol (0.08 mol $\mathrm{dm^{-3}}$) in dry benzene following the literature method[19]. The reaction follows second-order kinetics, in accord with the rate expression shown in Eqns [5] and [6], where a_0 is the initial concentration of alcohol, b_0 is the initial concentration of PhNCO, x is the amount of PhNCO consumed at time interval t and k_2 is the second-order rate constant.

$$-\,\mathrm{d[C_6H_5NCO]}/\mathrm{d}t = k_2[n-\mathrm{BuOH}][\mathrm{C_6H_5NCO}] \quad [5]$$

$$k_2t = [2.303/(a_0-b_0)]\log[b_0(a_0-x)/a_0(b_0-x)] \quad [6]$$

The data of the $\log[b_0(a_0-x)/a_0(b_0-x)]$ against

Table 3 Comparison of catalyst activity: rate constants k_2 for the reaction of PhNCO (0.0384 mol dm^{-3}) and *n*-BuOH (0.080 mol dm^{-3}) in presence of R_2Sn(2-ethylhexanoate)$_2$ (0.0001 mol dm^{-3}) in benzene at 29.0 ± 0.1 °C

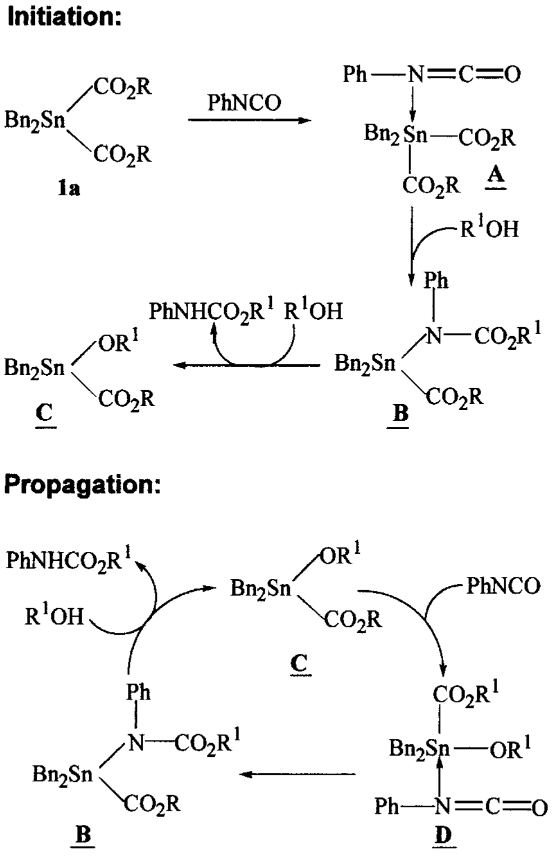
Entry	R	Compd no.	$10^4\ k_2$ (dm mol^{-1} s^{-1})	*R* factor
1	None	—	0.64 ± 0.03	0.9957
2	*n*-Bu	—	165.24 ± 2.36	0.9932
3	*n*-Bu[a]	—	235.89 ± 2.68	0.9969
4	Allyl	—	25.34 ± 0.04	0.9999
4	Benzyl	**1a**	328.89 ± 8.49	0.9952
5	4-OMeBenzyl	**1b**	38.46 ± 0.29	0.9995
6	4-ClBenzyl	**1c**	245.04 ± 1.38	0.9986
7	4-MeBenzyl	**1d**	380.39 ± 2.62	0.9998

[a] Dibutyltin dilaurate.

time relationship from four runs were subjected to linear regression analysis (Fig. 1). The *R* factor, assessed for each regression, was between 0.9932 to 0.9998. The rate constants k_2 were calculated from the slope of the linear plot. The average k_2 values for various catalysts are shown in Table 3. The data reveal that the previously reported diallyltin(IV) catalyst (entry 4) displayed poor efficiency in comparison with dibutyltin(IV) catalysts (entries 2 and 3). Encouragingly, the dibenzyltin(IV) catalysts **1a**, **1c** and **1d** (entries 4 6 and 7) showed comparable or higher efficiency than the dibutyltin catalysts. The reason for the poor efficiency of **1b** is not yet clear.

Kinetic studies on dibutyltin bis(2-ethylhexanoate) and catalyst **1a** at various temperatures led to the evaluation of the thermodynamic parameters (Table 4). The data reveal that **1a** shows a lower enthalpy of activation (E_a) and higher negative entropy of activation ($-\Delta S^{\#}$), suggesting an ordered transition state.

Much literature exists on the mechanistic aspects of tin(IV)-catalysed isocyanate–alcohol addition reactions.[21,22] Contrasting evidence on the activation of either the alcohol or the isocyanate, or both, by tin(IV) has been reported. Recent work of Houghton and Mulvaney[23] confirmed the prior activation of isocyanate in the DBTL-catalysed reaction between PhNCO and *n*-butanol. On the other hand, in a model polyurethane reaction between isocyanate (N-100) and a polyether polyol, Luo *et al.*[24] provided evidence for the simultaneous activation of isocyanate and alcohol by DBTL. From kinetics, and *in-situ* NMR and FTIR evidence, we propose the mechanism in Scheme 1 for the benzyltin-catalysed urethane-forming reactions.



Scheme 1

Table 4 Kinetic parameters for the reaction of PhNCO (0.0384 mol dm^{-3}) and *n*-BuOH (0.080 mol dm^{-3}) in presence of R_2Sn(2-ethylhexanoate)$_2$ (0.0001 mol dm^{-3}) in benzene

R	$10^4\ k_2$ (dm mol^{-1} S^{-1})			E_a (kJ mol^{-1})	$-\Delta S^{\#}$ (eU)
	29.0 ± 0.1 °C	35.0 ± 0.1 °C	41.0 ± 0.1 °C		
n-Bu	165.24 ± 2.36	305.76 ± 0.76	471.27 ± 7.39	67.2 ± 6.2	13.63 ± 4.78
Benzyl	328.89 ± 8.49	433.00 ± 2.55	663.59 ± 8.73	44.1 ± 6.4	30.66 ± 4.94

Briefly, this mechanism consists of two stages, an initiation step and a propagation step. In the initiation stage, the active catalyst **C** is generated from **1a** via intermediates **A** and **B**. We propose the prior activation of isocyanate by tin(IV) from the following key evidence: (a) as opposed to earlier observations, we could not find any change in the FTIR and ^{1}H NMR spectra of **1a** before and after the addition of *n*-butanol; (b) the FTIR spectra of both 1:1 and 1:2 mixtures of **1a** and PhNCO were found to be identical, with complete disappearance of the isocyanate peak at 2269 cm^{-1}. A strong peak at 1733 cm^{-1} is observed and assigned to stannyl carbamate **B** (R^1 = *n*-Bu). Formation of **B** would be much faster in the presence of an alcohol having a nucleophilic oxygen. Transformation of **B** to the active catalyst **C** is suggested, owing to the high degree of reactivity of stannyl carbamates.[8] The propagation step delineated here involves regeneration of **B** from the isocyanate activation of the active catalyst **C** via intermediate **D**. Direct activation of alcohol is ruled out by the experimental observation that an increase in alcohol concentration did not show any appreciable change in the rate of the reaction. For example, at [PhNCO]/[*n*-BuOH] ratios of 1:4, 1:8 and 1:12, the values of 10^4k_2 were 318.22 ± 6.07, 325.44 ± 8.01 and 337.62 ± 4.92 l mol^{-1} s^{-1}, respectively.

In summary, we have demonstrated an efficient catalyst system for addition reactions of isocyanates to alcohol. The catalysts could be of potential further interest.

EXPERIMENTAL

Tin metal powder (200-mesh, Loba Chemie, India) was activated by treatment with 10% sodium hydroxide solution. Benzyl chloride (Loba Chemie, India), 4-chlorobenzyl chloride, 4-methylbenzyl chloride, 4-methoxybenzyl chloride, 2-ethylhexanoic acid and dibutyltin dilaurate (Aldrich) were used as received. *n*-Butanol (HPLC grade, s.d. fine-chem, India) was stored over 3 Å molecular sieve. Phenyl isocyanate and *n*-butylamine (Aldrich) were distilled before use. Thiophene-free toluene was distilled before use. Cyclohexane was dried by refluxing over phosphorus pentoxide for 6 h followed by distillation. Benzene was distilled over sodium wire. Dibenzyltin dichloride and ring-substituted dibenzyltin dichlorides were prepared according to literature methods.[18]

Melting points were determined using a digital melting point instrument, model Mettler-FP51, the accuracy of which is ±0.5 °C. The melting points reported are uncorrected. ^{1}H NMR and ^{119}Sn NMR spectra were recorded on Varian-Gemini 200 and Bruker 300 DRX instruments respectively. IR spectra were obtained using a Nicolet-740 FTIR instrument. (EI-MS) (70 eV) was recorded using a Finnigen MAT-1020 instrument. Analyses were performed using an Elementar Analyzer VARIO EL instrument.

Kinetic measurements were performed by mixing phenyl isocyanate (typically 10 ml of 0.096 mol dm^{-3}), *n*-butanol (typically 10 ml of 0.08 mol dm^{-3}) and catalyst (typically 5 ml of 0.0005 mol dm^{-3}) solutions in dry benzene in a two-necked double-walled glass vessel, with water circulation around the outer wall. The temperature of the solution was measured with a Beckman thermometer connected to a thermostatic water circulator (B. Braun, Melsungen, Germany). The solution was well stirred. Aliquots (2 ml) were removed from the solution at regular time intervals (5 or 10 min) and added to a known excess of *n*-butylamine solution (typically 1 ml of 0.094 mol dm^{-3} in benzene). Amine was back-titrated using standard sulphuric acid solution (typically 0.02 mol dm^{-3}) to a methyl red end-point. The reactions were followed to 60–80% conversion. A blank experiment was always conducted with phenyl isocyanate alone, to ensure that phenyl isocyanate was stable in the solution over the time period (typically 60–80 min) for the actual runs.

Synthesis of silver (2-ethylhexanoate)

2-Ethylhexanoic acid (7.21 g, 50 mmol) was added to a solution of sodium hydroxide (2.2 g, 55 mmol) in water (5 ml). The solution was warmed to 60 °C for 15 min, cooled and diluted to 250 ml with water. The resulting solution was added dropwise to a stirred solution of silver nitrate (8.5 g, 50 mmol) in 250 ml water. The precipitate was filtered, washed with acetone (2 × 50 ml) and finally dried in vacuum in an aluminium-foil wrapped flask. The yield of silver (2-ethylhexanoate) was 11.5 g (91%).

Typical procedure for the synthesis of dibenzyltin dicarboxylate (1a)

Method A

To a stirred suspension of silver 2-ethylhexanoate (1.5 g, 6.0 mmol) in dry benzene, dibenzyltin dichloride (1.11 g, 2.98 mmol) was added and stirring was continued under nitrogen for 3 h at ambient temperature. The solution was filtered and concentrated under vacuum to yield 1.75 g of crude dibenzyltin bis(2-ethylhexanoate) **1a** as a white solid. This solid was dissolved in cyclohexane (25 ml) and washed successively with 20% aq. sodium bisulphite (3 × 25 ml), 20% aq. sodium bicarbonate (3 × 25 ml), water (2 × 25 ml) and brine (3 × 25 ml), and dried over anhydrous magnesium sulphate. After filtration, the solution was passed through a short column of Celite, the solvent was removed under vacuum and the solid was recrystallized from *n*-pentane to yield 1.43 g (78%) of **1a** as a white crystalline solid.

Method B

Aqueous sodium hydroxide solution (3.5 g in 10 ml) was added dropwise to a stirred solution of dibenzyltin dichloride (15.317 g) in acetone (70 ml), resulting in the precipitation of dibenzyltin oxide. After complete addition, acetone was distilled out. The mixture was digested at 80 °C for 2h, and filtered. The moist solid was dried in an oven at 70 °C for 6h. The yield of dibenzyltin oxide was 12.20 g, which was directly used for the next step.

A mixture containing 10.0 g of dibenzyltinoxide, 15.0 g of powdered molecular sieves (4 Å) and 9.152 g of 2-ethylhexanoic acid in 100 ml of dry cyclohexane was stirred at ambient temperature for 6 h. The mixture was filtered, and the residue was washed twice with 20-ml portions of dry cyclohexane. The washings and filtrate were combined and purified as described for Method A. The yield of dibenzyltin bis(2-ethylhexanoate) was 16 g (86%).

Spectra of organotin catalysts

Dibenzyltin bis(2-ethylhexanoate) (1a)

M.p. 54 °C; IR (KBr): 1700, 1578, 1485, 1450, 1415, 1280, 1233, 1208, 1058, 810, 758, 690 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.76–1.06 (2t, 12 H), 1.08–1.70 (m, 16 H), 2.20 (m, 2 H), 2.90 (s, $PhCH_2$, J_{Sn-H} 96 Hz), 6.95–7.25 (m, aromatic, 10 H); ^{119}Sn NMR ($CDCl_3$): δ −247.8. Analysis: calcd for $C_{30}H_{44}O_4Sn$: C, 61.34; H, 7.55; found: C, 61.40; H, 7.46%.

Di(4-methoxybenzyl)tin bis(2-ethylhexanoate) (1b)

M.p. 33 °C; IR (neat): 2960, 2940, 2892, 2592, 1510, 1424, 1241, 1043, 839, 769 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.86–0.97(2t, 12 H), 1.13–1.66 (m, 16 H), 2.18–2.33 (m, 2 H), 2.88 (s, $ArCH_2$; J_{Sn-H} 92 Hz), 3.74 (s, 6 H), 6.63–7.35 (aromatic, 8 H); Analysis: calcd for $C_{32}H_{48}O_6Sn$: C, 59.36; H, 7.47; found: C, 59.60; H, 7.31%.

Di(4-chlorobenzyl)tin bis(2-ethylhexanoate) (1c)

M.p. 101 °C, IR(KBr): 2956, 2933, 2870, 2855, 2584, 1498, 1467, 1412, 1294, 1098, 1020, 831, 760 cm^{-1}, ^1H NMR ($CDCl_3$): δ 0.68–0.90 (2t, 12 H), 1.05–1.58 (m, 16 H), 2.15–2.25 (m, 2 H), 2.74 (s, $ArCH_2$; J_{Sn-H} 98 Hz), 6.85–7.08 (m, aromatic, 8 H); ^{119}Sn NMR ($CDCl_3$): δ −256.3; Analysis: calcd for $C_{30}H_{42}Cl_2O_4Sn$: C, 54.90; H, 6.45; found: C, 54.78; H, 6.41%.

Di(4-methyl)benzyltin bis(2-ethylhexanoate) (1d)

M.p. 67 °C; IR (KBr): 2980, 2950, 2878, 1710, 1581, 1510, 1479, 1408, 1279, 812, 745 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.83–0.95 (2t, 12 H), 1.21–1.65 (m, 16 H), 2.22–2.39 (m, 8 H), 2.88 (s, $ArCH_2$; J_{Sn-H} 90 Hz), 6.86–7.33 (m, aromatic, 8 H); ^{119}Sn NMR ($CDCl_3$): δ −247.0; Analysis: calcd for $C_{32}H_{48}O_4Sn$: C, 62.45; H, 7.86; found C, 62.35; H, 7.81%.

Typical procedure for the synthesis of urethanes

A mixture containing phenyl isocyanate (0.475 g, 4.0 mmol) and *n*-butanol (0.296 g, 4.0 mmol) in 20 mL dry dichloromethane was refluxed for 10 min. After solvent removal in a rotary evaporator, the crude product was purified by column chromatography to yield phenyl(*n*-butyl)urethane (0.740 g, 96%) as a crystalline white solid. M.p. 60 °C; IR (KBr) 3297, 2955, 1705, 1550, 1235, 1065, 760 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.98 (t, 3 H, $J = 8.5$ Hz), 1.37–1.52 (m, 2 H), 1.58–1.73 (m, 2 H), 4.15 (t, 2 H, $J = 8.0$ Hz), 6.50 (bs, 1 H), 6.97–7.36 (m, aromatic, 5 H); MS: 193 (M^+).

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