Lanthanide Complexes for Oligomerization of Phenyl Isocyanate

DENG, Ming-Yu(邓明宇) YAO, Ying-Ming(姚英明) ZHOU, Yu-Fang(周玉芳)
ZHANG, Li-Fen (张丽芬) SHEN, Qi* (沈琪)
Department of Chemistry and Chemical Engineering, Suzhou University, Suzhou, Jiangsu 215006, China

A series of lanthanide complexes including $(Ind)_3Sm(THF)$ (1), $[(MeCp)_2Sm(\mu\text{-}SPh)(THF)]_2$ (2), $[(MeCp)_2Y(\mu\text{-}O\text{-}i\text{-}Pr)]_2$ (3), $(MeCp)_3Sm\cdot THF$ (4), $Sm(SPh)_3(hmpa)_3$ (5), $[(MeCp)_2Y(\mu\text{-}OCH_2CF_3)]_2$ (6) and $(CF_3CH_2O)_3Y(THF)_3$ (7) were synthesized and they have good activity for the oligomerization of phenyl isocyanate. Among them 5 shows the highest activity. The conversion is as high as 96.2%, with 1/2500 of the molar ratio of cat./PhNCO. The main components in oligomer were characterized to be a cyclodimer and a cyclotrimer. The ratio of cyclodimer to cyclotrimer depends on the lanthanide complexes used. 7 gave 85.2% cyclotrimer with 1/300 of the molar ratio of cat./PhNCO at 40 ℃ for 0.5 h, while 5 gave 77.6% cyclodimer with 1/300 of the molar ratio of cat./PhNCO at 40 ℃ for 4 h.

Keywords phenyl isocyanate, lanthanide complexes, cyclotrimer, cyclodimer, oligomerization, alkoxide

Introduction

The study on the reactivities of lanthanide complexes toward isocyanates has attracted much attention. It has been reported that lanthanide alkoxides,[1] and divalent diaza-pentadienyl lanthanide complexes[2] can be used as the single component initiators for isocyanates polymerization. Recently our research group has also found that lanthanocene amide,[3] divalent aryloxide of samarium[4,5] and divalent samarocene[6] are all active for the oligomerization of phenyl isocyanate, and the active species for these three systems were all successfully isolated. In our continuing study on the reactivities of lanthanide complexes to phenyl isocyanate, seven complexes with different ligands, such as $(Ind)_3Sm(THF)$ (**1**), $[(MeCp)_2Sm(\mu\text{-}SPh)(THF)]_2$ (**2**), $[(MeCp)_2Y(\mu\text{-}O\text{-}i\text{-}Pr)]_2$ (**3**), $(MeCp)_3Sm\cdot THF$ (**4**), $Sm(SPh)_3(hmpa)_3$ (**5**), $[(MeCp)_2Y(\mu\text{-}OCH_2CF_3)]_2$ (**6**) and $(CF_3CH_2O)_3Y(THF)_3$ (**7**) were synthesized, and their catalytic activities in the oligomerization of phenyl isocyanate were tested. It was found that all the complexes can effectively catalyze the oligomerization of phenyl isocyanate, and the main components in the oligomer were analyzed to be a cyclodimer and a cyclotrimer.

Experimental

General considerations

All operations except the characterization of the oligomerization products were performed under an argon atmosphere using Schlenk techniques. Toluene, hexane, and tetrahydrofuran (THF) were purified by distilling from Na/benzophenone. Anhydrous $LnCl_3$ was made according to the reported procedures.[13] Phenyl isocyanate was distilled from CaH_2 and stored under argon. CF_3CH_2OH was transferred from anhydrous $MgSO_4$ and stored under argon. CF_3CH_2ONa was obtained by the reaction of CF_3CH_2OH with Na in THF.

Melting points were determined in sealed argon-filled capillaries and uncorrected. Lanthanide metal analysis was carried out by complexometric titration. Carbon, hydrogen and nitrogen analyses were performed on a Carlo Erba 1110 spectrometer by direct combustion. The IR spectra were recorded on a MAGNA-550 spectrometer as KBr pellets. The ^1H NMR spectra were obtained on an INOVA-400 MHz apparatus, and referenced to TMS. Mass spectra were obtained on a HP5988A gas chromatograph-mass spectrometer.

Preparation of catalysts

1,[7] **2**,[8] **3**,[9] **4**,[10] **5**,[11] and **6**[12] were prepared according to the reported procedure.

Synthesis of **7** To a suspension of anhydrous YCl_3 (1.17 g, 6.0 mmol) in THF (30 mL) was added 16.7 mL of CF_3CH_2ONa (1.08 mol/L, 18.0 mmol) in THF by syringe. The mixture was stirred for 8 h at room temperature, then NaCl was removed by centrifugation. The resulting clear solution was concentrated and cooled to −20 ℃ to gave as colorless crystals (1.99 g, 76.3%). M.p. 153.3—155.0 ℃; ^1H NMR ($CDCl_3$, 400 MHz, 25 ℃) δ: 4.05 (br, 6H, OCH_2CF_3), 3.75 (t, J = 6.4 Hz, 12H, THF), 1.86 (m, 12H, THF); IR (KBr) ν: 2995—2885.7, 1643.5, 1520.0,

* E-mail: qshen@suda.edu.cn; Fax: 0512-65112371
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1280.8, 1161.2, 1099.5, 956.8, 856.5, 829.5, 667.4 cm^{-1}. Anal. calcd for $C_{18}H_{30}O_6F_9Y$: C 35.89, H 4.98, Y 14.77; found C 35.74, H 4.56, Y 14.26.

Oligomerization reaction

A 20 mL Schlenk flask equipped with a stirrer was charged with an appropriate amount of the lanthanide complex, depending upon the monomer-to-initiator ratio. The definite amount of phenyl isocyanate was added by a syringe at the fixed temperature. The white powder precipitated at once. After a definite reaction time, the reaction was terminated by adding 5 mL of petroleum ether including HCl (5%). After centrifugation to move the unreacted phenyl isocyanate and the solvents, the precipitation was washed with petroleum ether and dried *in vacuo*. The total yield of the oligomer was calculated.

Analysis of oligomer

The oligomer obtained above was dissolved in enormously excessive methanol. The contents of cyclodimer and cyclotrimmer of phenyl isocyanate in oligomer were evaluated by HPLC (SHIMADSU LC-8A, MeOH/H_2O: 80:20) on an ODS column (250 mm × 4.6 mm, 7 μm) at a 1 mL/min flow rate with a detector at 254 nm.

Cyclodimer of phenyl isocyanate[5,14,15] M.p. 175—176 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz, 25 ℃) δ: 7.16—7.56 (m, 10H, ArH); IR (KBr) ν: 3059, 2149, 1956, 1771, 1754, 1605, 1505, 1416, 1165, 1103, 1084, 1034, 895, 782, 764, 687, 502 cm^{-1}. Anal. calcd for $C_{14}H_{10}N_2O_2$: C 70.59, H 4.20, N 11.76; found C 70.78, H 4.34, N 11.70.

Cyclotrimer of phenyl isocyanate[5,16] M.p. 280—281 ℃; IR (KBr) ν: 3067, 1875, 1713, 1696, 1593, 1493, 1416, 1292, 1219, 1157, 1073, 1030, 756, 691, 593 cm^{-1}; MS *m/z* (%): 357 (M^+, 0.15), 238 (M^+ − PhNCO, 0.04), 119 (M^+ − 2PhNCO, 100). Anal. calcd for $C_{21}H_{15}N_3O_3$: C 70.59, H 4.20, N 11.76; found C 69.97, H 4.19, N 11.75.

Results and discussion

All the complexes tested show good catalytic activities for the oligomerization of phenyl isocyanate. The effect of the lanthanide complexes on the oligomerization of phenyl isocyanate was observed, for instance, when the molar ratio of lanthanide complex to phenyl isocyanate was 1:300, the conversions were ranged from 100% to 36.7% at 25 ℃ for 4 h, depending on the complexes used (Table 1, Runs 1—4 and Runs 9—10). It seems that the replacement of SPh or OCH_2CF_3 groups by methyl cyclopentadienyl results in the decrease of the activity (Runs 2, 4, 9, 10). Among these complexes, **5** shows the highest activity, for example, when the catalyst/substrate ratio decreases from 1:300 to 1:2500 molar ratio, the reaction conversion can still reach as high as 96.2% at 40 ℃ for 1.5 h (Run 7). The activity order of the lanthanide complexes can be described as follows: **5** > **7** > **1** > **2** > **6** > **3** > **4** (Runs 1—5, 9—10).

The main components in the oligomer have been separated by HPLC, and characterized fully to be a cyclodimer and a cyclotrimer respectively. It is interesting that the ratio of cyclodimer to cyclotrimer depends on the lanthanide complexes used. For example, **7** gave cyclotrimer as main product while **5** afforded cyclodimer (Runs 10—13 and Runs 5—8). As we can see from Table 1, reaction temperature also has effect on the reaction selectivity. The increasing of reaction temperature results in the increasing of cyclotrimer content for **7** (Runs 12 and 13), and the increasing of cyclodimer content for **5** (Runs 6 and 7).

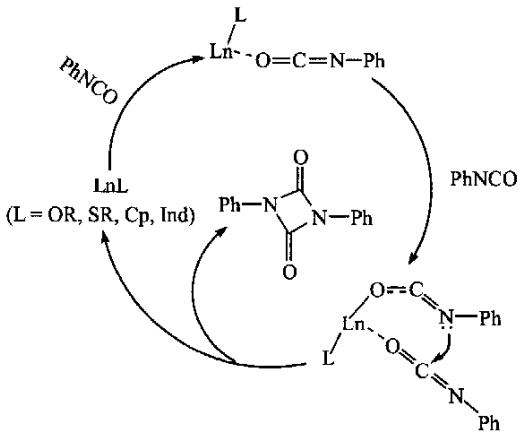
Table 1 Oligomerization of phenyl isocyanate with different lanthanide complexes

Run	Catalyst	The catalyst-to-monomer molar ratio	Time (h)	Temp. (℃)	Conversion (%)	Cyclodimer (%)	Cyclotrimer (%)	Others[a] (%)
1	**1**	1:300	4	25	91.1	38.5	5.2	56.3
2	**2**	1:300	4	25	85.5	63.0	11.0	26.0
3	**3**	1:300	4	25	41.3	71.4	5.9	22.7
4	**4**	1:300	4	25	36.7	60.1	6.7	33.2
5	**5**	1:300	4	40	100	77.6	13.7	8.7
6	**5**	1:2500	1.5	30	86.3	53.4	3.0	43.6
7	**5**	1:2500	1.5	40	96.2	59.7	16.0	24.3
8	**5**	1:2500	0.5	50	100	70.3	22.7	7.0
9	**6**	1:300	4	25	63.6	54.6	11.8	33.6
10	**7**	1:300	4	25	100	6.7	79.1	14.2
11	**7**	1:300	0.5	40	100	1.3	85.2	13.5
12	**7**	1:1000	0.5	40	100	4.5	74.6	20.9
13	**7**	1:1000	0.5	50	96.5	7.6	81.0	11.4

[a] Others = the content of oligomer.

According to the mechanism of dimerization of isocyanate catalyzed by Lewis acid,[17] it can be proposed as follows. At first, phenyl isocyanate coordinates to lanthanide metal to activate the carbon-oxygen bond of phenyl isocyanate, followed by nucleophilic attack of N atom of second phenyl isocyanate molecule, which results in the formations of cyclodimer and the generation of catalyst LnL (Scheme 1). The similar mechanism can be proposed for the formation of cyclotrimer.

Scheme 1



Conclusion

All the lanthanides tested can catalyze the oligomerization of phenyl isocyanate effectively and the lanthanide complexe has great effect on the activity of oligomerization of phenyl isocyanate. **5** shows the highest activity. Cyclotrimer and cyclodimer can be obtained selectively, for example, **7** gave cyclotrimer as main product while **5** afforded cyclodimer. A possible mechanism was proposed.

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