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Tsuyosi Ikeda[a]; Hiroshi Sugimoto[a]; Shohei Inoue[a]
[a] Department of Industrial Chemistry, Faculty of Engineering, Science University of Tokyo, Shinjuku-ku, Tokyo, Japan

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POLYMERIZATION OF ISOCYANATE AT ROOM TEMPERATURE, LANTHANOID ALKOXIDE AS NOVEL INITIATOR

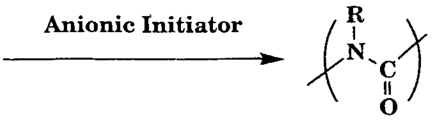
Tsuyosi Ikeda, Hiroshi Sugimoto, and Shohei Inoue*
Department of Industrial Chemistry
Faculty of Engineering
Science University of Tokyo
Kagurazaka, Shinjuku-ku
Tokyo 162, Japan

ABSTRACT

Room temperature polymerization of isocyanate initiated with some lanthanoid alkoxides is demonstrated. Yttrium isopropoxide is an effective initiator for the homopolymerization of hexyl isocyanate at room temperature and affords the polymer a high yield, in contrast to lanthanum isopropoxide (La(O^{i}Pr)$_3$) which produces only cyclic trimer. On the other hand, copolymerization of hexyl isocyanate and 3-phenylpropyl isocyanate initiated with La(O^{i}Pr)$_3$ proceeds even at room temperature. La(O^{i}Pr)$_3$ - active hydrogen compound systems also serve effectively in the polymerization of hexyl isocyanate at room temperature.

INTRODUCTION

In recent years, polyisocyanates have attracted much attention due to their helical structures [1-3], optical activities, [4-6] and liquid crystalline properties [7-9]. For the syntheses of polyisocyanates, sodium cyanide [10-13], lithium alkoxides [14], lithium amides [15], and iron alkoxides [16-18] have been used as initiator for the polymerization of isocyanates (Equation 1). However, these metallic compounds give polymeric products only at low temperature, e.g. -50°C, and form the cyclic trimer at room temperature as a result of the back-biting reaction (Scheme 1). Thus far, only titanium alkoxides have been reported to bring about the polymerization of isocyanates at room temperature [19]. On the other hand, a number of studies the on polymerization of various monomers [20-31] using lanthanoid compounds have been undertaken. We have found that lanthanoid isopropoxides serve as a novel initiator for the polymerization of isocyanates at low temperature, and afford polyisocyanates of very high molecular weight [32]. For example, in the polymerization of hexyl isocyanate (^{n}HexNCO) with lanthanum isopropoxide ($La(O^iPr)_3$) at -78°C, a polymer was obtained in 90% yield ($[La(O^iPr)_3]_0/[^nHexNCO]_0 = 1/100$, 24 hours, $M_n = 685000$, $M_w/M_n = 2.45$). However, at room temperature $La(O^iPr)_3$ produced only cyclic trimer similarly to other initiators. In the present paper, we wish to report the polymerization of isocyanates initiated with lanthanoid alkoxides at room temperature. Yttrium isopropoxide was found to be a particularly effective initiator for the polymerization of ^{n}HexNCO at room temperature.



(1)

EXPERIMENTAL

Materials

Toluene was distilled over sodium benzophenone ketyl in nitrogen atmosphere.

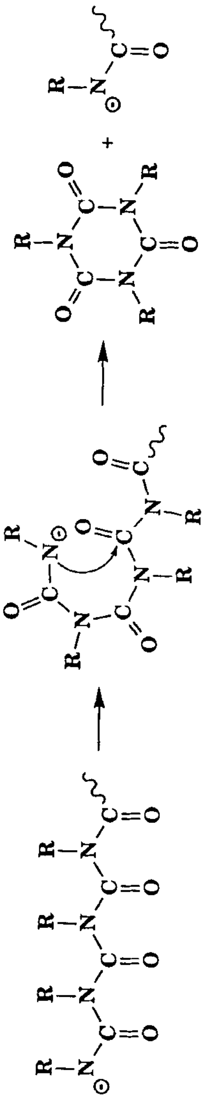
1,1,1,3,3,3-hexafluoro-2-propanol was distilled over a molecular sieve 3A in nitrogen atmosphere.

o-*tert*-Butylphenol was used without further purification.

Yttrium isopropoxide ($Y(O^iPr)_3$), purchased from Kojundo Chemical Laboratory Co., Ltd., was recrystallized from benzene in dry nitrogen.

Lanthanum Isopropoxide ($La(O^iPr)_3$) [33]

To a 500-mL round-bottomed flask equipped with a three-way stopcock containing lanthanum metal grains (5.06 g, 36.4 mmol), mercuric chloride (0.070 g, 0.26 mmol), and mercuric acetate (0.084 g, 0.26 mmol), 2-propanol (300 mL) was added by a syringe in nitrogen atmosphere. The suspension was refluxed for 24 h and filtered. Excess alcohol was distilled off to leave the crude isopropoxide as a



Scheme 1.

white powder, which was recrystallized from benzene (1.33 g; yield 11.3%). Samarium isopropoxide ($Sm(O^iPr)_3$) and ytterbium isopropoxide ($Yb(O^iPr)_3$) were prepared in an analogous manner to lanthanum isopropoxide.

n-Hexyl Isocyanate (^{n}*HexNCO) [34, 35]*

In a 500-mL round-bottomed flask immersed in an ice bath, was placed 46.2 g (71.0 mmol) of sodium azide in 150 mL of water. A mixture of 74.7 g (50.2 mmol) of heptanoyl chloride and 150 mL of acetone was added dropwise to the solution of the azide at such a rate that the temperature remains at 10-15°C. The mixture was stirred for 1 hour and allowed to stand. When the mixture was separated in two layers, the upper layer was added slowly to 500 mL of benzene warmed to 60°C. The solution was kept at 60-70°C until no more nitrogen was evolved and evaporated to leave colorless liquid (53.3 g; yield 84%). The crude isocyanate was distilled over CaH_2 under reduced pressure in nitrogen atmosphere (b.p. 78°C/70 mmHg).

3-Phenylpropyl Isocyanate [34, 36]

In a 200-mL round-bottomed flask immersed in an ice bath, is placed 13.2 g (20.3 mmol) of sodium azide in 45 mL of water. A mixture of 45 mL of acetone and 25.5 g (16.9 mmol) of 4-phenylbutryl chloride, prepared from 4-phenylbutyric acid and thionyl chloride, was added dropwise to the solution of the azide kept at 10-15°C. After stirring for 1 hour, the mixture was allowed to stand to be separated in two layers, and the upper layer was added slowly to benzene warmed to 60°C. The solution was kept at 60-70°C until no more nitrogen was evolved and evaporated to leave a colorless liquid. The crude isocyanate was distilled over CaH_2 under reduced pressure in nitrogen atmosphere (15.5 g; yield 62%).

Homopolymerization of n-Hexyl Isocyanate with Yttrium Isopropoxide

To a 50-mL round-bottomed flask with a three-way stopcock and a magnetic stirring bar containing white powder of $Y(O^iPr)_3$ (0.1 mmol), ^{n}HexNCO (1.45 mL, 10 mmol) was added by means of a hypodermic syringe at room temperature in nitrogen atmosphere. After a prescribed time, methanol (3-5 mL) containing concentrated hydrochloric acid (1/20 v/v) was added to the flask at room temperature to stop the polymerization, where white solid was precipitated. The white product was dissolved in chloroform (20 mL) and the solution was added dropwise into methanol (250 mL) containing hydrochloric acid. The white fibrous precipitate formed was collected by filtration. The filtrate was evaporated to leave the mixture of oily and aqueous residues, and the oil was extracted with dichlorometane. When dichloromethane was evaporated, the methanol soluble products were obtained as pale yellow viscous oil. The oil was found to contain cyclic trimer, isopropyl N,N'-dihexyl allophanate (liner dimer), and methyl N-hexylcarbamate (from unreacted isocyanate and methanol) by ^{1}H NMR spectrum. Since the isocyanate, which did not polymerize, is considered to be concerted to the above three products. The yield of cyclic trimer was estimated from the relative intensities of respective signals of the methanol soluble products. Polymerizations of ^{n}HexNCO with other lanthanoid alkoxides were carried out similarly.

Comopolymerization of n-Hexyl Isocyanate and 3-Phenylpropyl Isocyanate with Lanthanum Isopropoxide

To a 50-mL round-bottomed flask with a three-way stopcock and a magnetic stirring bar containing white powder of $La(O^iPr)_3$ (0.1 mmol), a mixture of n-hexyl isocyanate (0.72 mL, 5 mmol) and 3-phenylpropyl isocyanate (0.77 mL, 5 mmol) was added by means of a hypodermic syringe at room temperature in nitrogen atmosphere. After 1 hour, methanol (3-5 mL) containing hydrochloric acid (1/20 v/v) was added to the mixture at room temperature to stop the polymerization. The polymeric products were isolated by a similar manner to that described above.

Polymerization of n-Hexyl Isocyanate with Lanthanum Isopropoxide-Active Hydrogen Compound Systems

To a 50-mL round-bottomed flask with a three-way stopcock and a magnetic stirring bar containing toluene solution of $La(O^iPr)_3$ (0.1 mmol), an active hydrogen compound (0.3 mmol) was added and the mixture was stirred at 100°C for 2 hours. A powder obtained by evaporating this mixture was used as initiator for the polymerization of ^{n}HexNCO.

Measurements

Gel permeation chromatography was performed at 40°C on TOSOH Model 802UR high-speed liquid chromatograph equipped with a UV (280 nm) detector using chloroform as eluent. The molecular weight calibration curve was obtained by using standard poly(hexyl isocyanate)s; M_w by light scattering (M_w/M_n by GPC): 244000 (1.07), 133000 (1.05), 68000 (1.06), 40700 (1.06), and 15200 (1.05).

TABLE 1. Polymerization of Hexyl Isocyanate at Room Temperature with Lanthanoid Isopropoxides as Initiator[a)]

run	$M(O^iPr)_3$	$[^nHexNCO]_0/[M(O^iPr)_3]_0$	Yield in %	$Mn^{b)}$	$Mw/Mn^{b)}$	initiation efficiency in %$^{c)}$
1	$Y(O^iPr)_3$	100	57	59,000	2.19	12
2	$Sm(O^iPr)_3$	100	10	48,000	2.37	3
3	$Yb(O^iPr)_3$	100	10	23,000	2.08	6
4	$La(O^iPr)_3$	100	0	-	-	-
$5^{d)}$	$Y(O^iPr)_3$	1000	46	53,000	2.56	109

a) Without solvent, under nitrogen, r.t., 1 h. b) Estimated by GPC based on standard poly(hexyl isocyanate)s. c) Initiation efficiency = M.W. of ^{n}HexNCO x (yield/100) / *Mn* x 100. d) 24 h.

^{1}H NMR measurements were performed using $CDCl_3$ as solvent on HITACHI R-24B spectrometer, where the chemical shifts were determined with tetramethylsilane as internal standard. IR spectra were recorded on a HORIBA FT210 spectrometer. Elemental analysis was performed on a Heraeus CHN-O=RAPID.

RESULTS AND DISCUSSION

Homopolymerization of n-Hexyl Isocyanate with Lanthanoid Isopropoxide at Room Temperature

Polymerization of n-hexyl isocyanate(^{n}HexNCO) with various lanthanoid isopropoxides at room temperature was examined. A typical example is the polymerization of ^{n}HexNCO initiated with yttrium isopropoxide ($Y(O^iPr)_3$). 100 equiv of ^{n}HexNCO (10 mmol) was added to $Y(O^1Pr)_3$ (0.1 mmol) at room temperature. Polymerization of ^{n}HexNCO started with an immediate rise in viscosity and solidification of the reaction system was observed after 10 minutes. After 1 hour, when methanol containing hydrochloric acid was added to the polymerization mixture at room temperature, white powder was precipitated. By the addition of the chloroform solution of the white powder to methanol, a white fibrous polymer was obtained as a methanol insoluble product in 57% yield. The IR spectrum of the

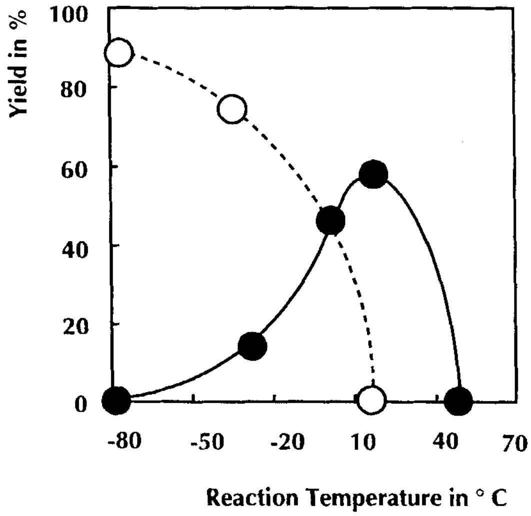


Figure 1. Polymerization of ^{n}HexNCO initiated with $Y(O^{i}Pr)_3$ ●; $[{}^{n}HexNCO]_0/[initiator]_0 = 100$, without solvent, 1 hour. ○ : for $La(O^{i}Pr)_3$ Reference 3.

polymer showed a characteristic carbonyl absorption at about 1701 cm^{-1} corresponding to disubstituted amide [1], which indicated the nylon-1 structure of the polymer main chain. The molecular weight of the polymer, as estimated by gel permeation chromatography (GPC) based on poly(^{n}HexNCO) standards, was 59000 ($M_w / M_n = 2.19$) (Table 1, run 1).

Samarium isopropoxide ($Sm(O^{i}Pr)_3$) and ytterbium isopropoxide ($Yb(O^{i}Pr)_3$) also brought about the polymerization of ^{n}HexNCO at room temperature ($[\text{lanthanoid isopropoxide}]_0/[{}^{n}HexNCO]_0 = 1/100$, 1 hour), although the polymer yield was lower than that using $Y(O^{i}Pr)_3$. However, the reaction of $La(O^{i}Pr)_3$ with ^{n}HexNCO at room temperature gave only cyclic trimer of the isocyanate. Thus, the yield of polymer obtained by lanthanoid isopropoxides at room temperature was in the order Y > Sm ≥Yb >> La. This is in contrast to the polymerization at -78°C, where $La(O^{i}Pr)_3$ gave the best result [32].

In contrast to $La(O^{i}Pr)_3$ where the polymer yield decreased at higher temperature in the range of -78 ~ 10°C (Figure 1, ○), in the polymerization with $Y(O^{i}Pr)_3$ the polymer yield increased at higher temperature in the range of -78 ~ 10°C (Figure 1, ●). However, the cyclic trimer was the sole product in the reaction at 50°C.

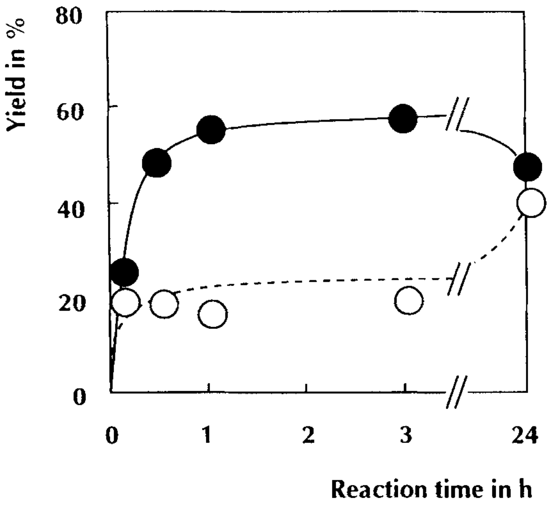


Figure 2. Polymerization of ^nHexNCO initiated with $Y(O^iPr)_3$; r.t., $[^nHexNCO]_0/[initiator]_0 = 100$, without solvent, 1 hour. Effect of the reaction time on the yields of polymer (●) and cyclic trimer (○).

In the polymerization of ^nHexNCO with $Y(O^iPr)_3$ at room temperature, the polymer yield increased rapidly within 1 hour. However, in the period of 1 hour to 3 hours, polymer yield increased little and decreased after 24 hours (Figure 2 , ●). On the other hand, although cyclic trimer was formed in 20% yield in 5 minutes, and the yield did not change within 3 hours. After 24 hours, the yield of cyclic trimer increased to 40% (Figure 2, ○), corresponding to the decrease of polymer yield. These results indicate that the propagation reaction prevails within 1 hour, and that the participation of back-biting reaction becomes apparent at the later stage of polymerization (Scheme 1).

In the polymerization of ^nHexNCO at a low temperature such as -78°C, lanthanoid isopropoxides, e.g., $La(O^iPr)_3$, afford poly(^nHexNCO) with very high molecular weight, but the initiation efficiency is very low, e.g., 0.8% [32]. However, in the polymerization of ^nHexNCO with $Y(O^iPr)_3$ at room temperature, a polymer with lower molecular weight ($M_n = 59000$) was obtained in 57% yield ($[Y(O^iPr)_3]_0/[^nHexNCO]_0 = 1/100$, 1 hour), and the initiation efficiency was 12%. Furthermore, in the polymerization with a high monomer to initiator ratio ($[Y(O^iPr)_3]_0/[^nHexNCO]_0 = 1/1000$, 24 hours), the number of the polymer molecule was almost equal to the number of initiator molecule (yield 46%, $M_n = 53000$, initiation efficiency 109%) (Table 1, run 5). The initiation efficiency exceeding 100% suggests that more than one isopropoxide group of $Y(O^iPr)_3$ initiate the polymerization under these conditions.

Copolymerization of n-Hexyl Isocyanate and 3-Phenylpropyl Isocyanate with Lanthanoid Isopropoxide at Room Temperature

The studies on copolymers of isocyanates have been undertaken with respect to their liquid crystalline properties [7, 38], thermal stabilities [38, 39] and helical structures [40-42], but all these copolymers were obtained by the polymerization with NaCN at low temperature, and the studies on details of copolymerization of isocyanates are lacking. We attempted the copolymerization of n-butyl isocyanate (^nBuNCO) and n-octyl isocyanate (^nOctNCO) with $La(O^iPr)_3$ at -30°C ($[La(O^iPr)_3]_0/[^nBuNCO]_0/[^nOctNCO]_0$ = 1/50/50, bulk, 24 hours), and obtained a copolymer in 25% yield (^nBuNCO:^nOctNCO = 27:73). Moreover, when we tried the degradation of the copolymer in the presence of $La(O^iPr)_3$ (polymer 50 mg, $La(O^iPr)_3$ 0.1 mmol, toluene 5 mL, 100°C, 24 hours) in order to investigate the sequence of monomer units in the copolymer, it was found that the degradation did not proceed completely, though homopolymers of ^nBuNCO and ^nOctNCO were degraded to cyclic trimers perfectly under the identical conditions. Thus, a copolymer of isocyanates is more stable than homo-polymers against the degradation to cyclic trimer in the presence of base.

Since the back-biting reaction in the polymerization of isocyanate and the degradation of poly(isocyanate) to cyclic trimer in the presence of base is considered to proceed by the same reaction mechanism of intramolecular attack of growing anion to the third amide group from the terminal [12, 43] (Scheme 1), higher stability of copolymer against degradation suggests the possibility of copolymerization at room temperature even by $La(O^iPr)_3$. Thus, we attempted the copolymerization of ^nHexNCO with 3-phenylpropyl isocyanate ($PhCH_2CH_2CH_2NCO$) with $La(O^iPr)_3$ at room temperature.

As soon as the mixture of ^nHexNCO and $PhCH_2CH_2CH_2NCO$ (5 mmol, respectively) was added to $La(O^iPr)_3$ (0.1 mmol) at room temperature, polymerization started with an immediate rise in viscosity. After 1 hour, methanol containing hydrochloric acid was added to the polymerization mixture at room temperature to stop the polymerization, then white precipitate was formed. When a chloroform solution of the white precipitate was added to methanol, a white fibrous product was obtained as a methanol insoluble part in 48% yield (M_n = 75000, M_w/M_n = 2.53) (Table 2, run 1). GPC curve of the product was broad but

TABLE 2. Copolymerization of Hexyl Isocyanate (**1**) and 3-Phenylpropyl Isocyanate (**2**) at Room Temperature Initiated with Lanthanoid Isopropoxides[a)]

run	$M(O^iPr)_3$	**1** in mmol	**2** in mmol	Yield in %	*M*n[b)]	*M*w/*M*n[b)]	**1**: **2**
1	$La(O^iPr)_3$	5	5	48	75,000	2.53	42:58
2	$La(O^iPr)_3$	10	0	0	-	-	-
3	$La(O^iPr)_3$	0	10	18	-[c)]	-[c)]	-
4	$Y(O^iPr)_3$	5	5	44	86,000	2.38	41:59

a) Without solvent, under nitrogen, r.t., 1 h. b) Estimated by GPC based on standard poly(hexyl isocyanate)s.

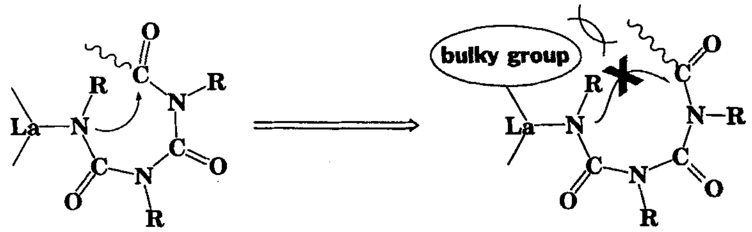
c) Insolble in chloroform, toluene, ethyl acetate, tetrahydrofuran, N,N-dimethylformamide.

unimordal. IR spectrum showed both absorptions observed in homopolymers. ^1H NMR spectrum of the product showed the signals of aromatic protons due to $PhCH_2CH_2CH_2NCO$ unit. In addition, although poly($PhCH_2CH_2CH_2NCO$) is insoluble in chloroform, this product was soluble in chloroform similarly to poly(^nHexNCO). These results indicate that the product is the copolymer of ^nHexNCO and $PhCH_2CH_2CH_2NCO$. Elemental analysis indicated that the copolymer contained more units of $PhCH_2CH_2CH_2NCO$ than that of ^nHexNCO (^nHexNCO: $PhCH_2CH_2CH_2NCO$ = 42:58). It seems that homopolymers of isocyanate were liable to undergo the back-biting reaction due to their helical structure. On the other hand, the coexistence of different side-chains in a copolymer probably loosens the helical structure, and the back-biting reaction would be prevented.

$Y(O^iPr)_3$ also afforded a copolymer in the copolymerization of ^nHexNCO and $PhCH_2CH_2CH_2NCO$ in 44% yield (M_n = 86000, M_w/M_n = 2.38, ^nHexNCO: $PhCH_2CH_2CH_2NCO$ = 41:59) (Table 2, run 4).

Homopolymerization of n-Hexyl Isocyanate with Lanthanum Isopropoxide- Active Hydrogen Compound Systems at Room Temperature

As described above, the reaction of $La(O^iPr)_3$ with ^nHexNCO at room temperature affords no polymer probably due to back-biting reaction. However, if a



Scheme 2. Expected hindrance of back-biting by the presence of a bulky group on growing polymer end.

TABLE 3. Polymerization of Hexyl Isocyanate at Room Temperature with $La(O^iPr)_3$ - Active Hydrogen Compound Systems a)

run	active hydrogen compound	Yield in %	*M*n b)	*M*w/*M*n b)
1	none	0	-	-
2	$CF_3CH(OH)CF_3$	34	20,000	2.5
3	*o-tert*-butylphenol	26	80,000	3.95

a) Reaction between $La(O^iPr)_3$ and active hydrogen compound: $[\text{active hydrogen compound}]_0/[La(O^iPr)_3]_0 = 3$, 100 °C, 2 h, Toluene as solvent, under nitrogen. Polymerization: $[^nHexNCO]_0/[La(O^iPr)_3]_0 = 100$ r.t., 1 h, without solvent, under nitrogen. b) Estimated by GPC based on standard poly(hexyl isocyanate)s.

intramolecular attack of terminal active anion to polymer is prevented, e.g., by bulky groups on La, poly(isocyanate) would be formed even at room temperature (Scheme 2). We attempted to use the reaction mixture of $La(O^iPr)_3$ with a bulky active hydrogen compound, which is expected to allow bulky lanthanum complex as an initiator for the polymerization of ^{n}HexNCO. Hexafluoro-2-propanol and o-tert-butylphenol were used as active hydrogen compounds.

3 equiv of hexafluoro-2-propanol (0.3 mmol) was added to a toluene solution of $La(O^iPr)_3$ (0.1 mmol), the mixture was stirred at 100°C for 2 hours, and evaporated to give a white powder. As soon as 100 equiv of ^{n}HexNCO (10 mmol) was added to the white powder at room temperature, the viscosity of the system rose rapidly. After stirring for 1 hour, methanol containing hydrochloric acid was added to the polymerization mixture at room temperature, then white powder was

precipitated. By pouring the chloroform solution of the white powder into methanol, a white fibrous polymer was obtained in 34% yield (M_n = 20000, M_w/M_n = 2.55) (Table 3, run 2). When o-tert-butylphenol was used instead of hexafluoro-2-propanol, the polymer was obtained also in 26% yield (M_n = 80000, M_w/M_n = 3.95) (Table 3, run 3).

CONCLUSION

The present study demonstrates the polymerization of isocyanate at room temperature initiated with lanthanoid alkoxides. $Y(O^iPr)_3$ serves effectively in the homopolymerization of ^{n}HexNCO at room temperature and affords the polymer in high yield, in contrast to $La(O^iPr)_3$ which produces only cyclic trimer. On the other hand, copolymerization of ^{n}HexNCO and $PhCH_2CH_2CH_2NCO$ initiated with $La(O^iPr)_3$ proceeds even at room temperature. $La(O^iPr)_3$ - active hydrogen compound systems are also effective for the polymerization at room temperature.

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