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Polymerization of *n*-Hexyl Isocyanate with Rare Earth Catalyst Composed of $Nd(P_{204})_3/Al(i\text{-}Bu)_3$

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Summary

Rare earth catalyst system: lanthanide phosphonate/tri-*i*-butyl aluminum ($Nd(P_{204})_3/Al(i\text{-}Bu)_3$) has been found for the first time as a novel catalyst for the polymerization of *n*-hexyl isocyanate (HNCO). $Nd(P_{204})_3$ and $Nd(P_{507})_3$ are the commercial names of neodymium 2-ethylhexyl phosphonates, their formulas are shown in table 1. The catalyst can be prepared easily by mixing $Nd(P_{204})_3$ and $Al(i\text{-}Bu)_3$. The effects of catalyst, solvent, reaction temperature and time on the polymerization of HNCO were studied. The obtained poly (*n*-hexyl isocyanate) (PHNCO) was characterized by GPC, FT-IR, ^{1}H-NMR and TGA. The resulting PHNCO had molecular weight ($Mn=39.6\times10^4$, $Mv=67.2\times10^4$), molecular weight distribution (MWD=2.44) and yield (82.7%) under the moderate reaction conditions: catalyst concentration $[Nd]=6.65\times10^{-2}$mol/L, Al/Nd=10 molar ratio, [HNCO]/[Nd]=100 molar ratio, at -10°C for 10h in bulk. Relatively high reaction temperature (-10°C) is the most distinct virtue. The IR and NMR analyses show that the polymer obtained is not polyether but polyisocyanate.

Introduction

Polyisocyanates (nylon 1) are stiff polymers. Because of the steric reason, they adopt a stable helical conformation in solution as well as in solid state. They have been studied for application fields such as chiral recognition materials, optical switches and liquid crystal materials [1,2]. In 1960, Shashoua and co-workers reported the polymerization of various isocyanates with NaCN as an initiator in polar solvents [3]. Other anionic initiators, such as sodium naphthalene (Na-Naph) [4～8] and lithium amide of piperidine [9～11] have been used to prepare polyisocyanates. In these reports, the polymerizations of isocyanates were performed at rather low temperatures around -60°C.

Lee et al. reported living anionic polymerization of isocyanates using Na-Naph catalyst with 15-crown-5 or sodium tetraphenylborate ($NaBPh_4$) as an additive [4～8]. They prepared triblock polymer poly(PHNCO-block-styrene-block-PHNCO) [12]. Using Lee's method, Hadjichristidis and coworkers prepared block copolymer of HNCO with styrene or isoprene [13]. Novak et al. found that organotitanium(IV) catalysts were more appropriate for controlling the molecular weight of the polyisocyanates [14~17]. Using Novak's method, Se and coworkers prepared graft copolymers of HNCO and methyl methacrylate [18]. Free radical and cationic initiators failed to prepare high molecular weight polyisocyanates.

Rare earth catalysts have attracted much attention to be used as effective catalysts for polymerization of dienes, alkynes and many other monomers [19~22]. Fukuwatari *et al*. found lanthanum isopropoxide was an effective catalyst for the polymerization of HNCO at very low temperature (-78°C). However, the molecular weight of the PHNCO can not be controlled [23].

We have found for the first time that $Nd(P_{204})_3/Al(i\text{-}Bu)_3$ is an effective catalyst on the polymerization of HNCO at moderate temperature.

Experimental

Materials

Toluene, tetrahydrofuran (THF) and *n*-hexane were distilled over sodium benzophenone ketyl in an argon atmosphere. Chloroform ($CHCl_3$) and carbon tetrachloride (CCl_4) were distilled over calcium hydride (CaH_2). HNCO (Acros) was distilled over CaH_2 under reduced pressure before use. $Al(i\text{-}Bu)_3$ (AKZO Nobel) with purity of 99% were used without further purification. $Ln(P_{204})_3$, $Ln(P_{507})_3$ and other rare earth compounds (table 1) were prepared according to the methods described in reference [24].

Polymerization

All polymerizations were carried out under argon using Schlenk techniques. $Nd(P_{204})_3/Al(i\text{-}Bu)_3$ catalyst was prepared by mixing $Nd(P_{204})_3$ and $Al(i\text{-}Bu)_3$ together, then ageing at 50°C for 5h. The polymerization started when the catalyst was added into a 20mL ampoule containing HNCO, and terminated by ethanol with 5% HCl. The polymeric product was dissolved in toluene at room temperature, and the solution was added dropwise into ethanol. The white precipitate was collected by filtration, then dried at 30°C in vacuum and weighed.

Measurements

The number- and weight-average molecular weights (Mn, Mw) and molecular weight distributions (MWD) were determined by GPC (Waters 208) in THF at 25°C (calibrated with standard polystyrenes). Viscosity-average molecular weights (Mv) were measured in THF at 25°C with an Ubbelohde viscosimeter according to the equation (1) [25]. FT-IR spectrum was recorded on a Bruker Vector 22 spectrophotometer using KBr pellets. ^{1}H-NMR spectrum was obtained on a Bruker Avance DMX500 spectrometer in $CDCl_3$ at 25°C with TMS as internal reference. TGA thermogram was carried on a Perkin Elmer Pyris 6 TGA instrument with a heating rate of 10°C/min.

$$[\eta]=1.59\times10^{-5}Mv^{1.08} \qquad \textbf{(1)}$$

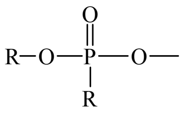
Results and Discussion

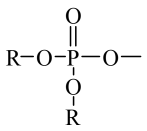
We have examined the polymerization of HNCO by several rare earth compounds combined with Al(*i*-Bu)$_3$. The results are listed in table 1. Neither Nd(P$_{204}$)$_3$ nor Al(*i*-Bu)$_3$ alone can catalyze the polymerization of HNCO. The catalytic activity sequence of different rare earth phosphonates is as follows: Nd > La > Gd > Y > Tm; the catalytic activity of various Nd compounds has the following order: Nd(P$_{204}$)$_3$ > Nd(P$_{507}$)$_3$ >> Nd(naph)$_3$ ≈ Nd(phcoo)$_3$. Therefore Nd(P$_{204}$)$_3$/Al(*i*-Bu)$_3$ catalyst system was selected for the further studies.

Table 1. Bulk polymerization of HNCO with LnR$_3$/Al(*i*-Bu)$_3$.

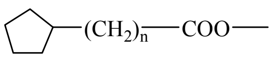
Run	Catalyst system	Yield (%)	Mv (10^4)
1[a]	Nd(P$_{204}$)$_3$	no PHNCO	-
2[a]	Al(*i*-Bu)$_3$	no PHNCO	-
3[b]	Nd(P$_{204}$)$_3$/Al(*i*-Bu)$_3$	82.7	67.2
4[b]	La(P$_{204}$)$_3$/Al(*i*-Bu)$_3$	51.4	28.5
5[b]	Gd(P$_{204}$)$_3$/Al(*i*-Bu)$_3$	40.2	13.6
6[b]	Y(P$_{204}$)$_3$/Al(*i*-Bu)$_3$	27.5	9.22
7[b]	Tm(P$_{204}$)$_3$/Al(*i*-Bu)$_3$	7.48	25.3
8[b]	Nd(P$_{507}$)$_3$/Al(*i*-Bu)$_3$	50.7	25.3
9[b]	Nd(naph)$_3$/Al(*i*-Bu)$_3$	no PHNCO	-
10[b]	Nd(phcoo)$_3$/Al(*i*-Bu)$_3$	no PHNCO	-

Conditions: -10°C, 10h, monomer contentration [HNCO]=6.65mol/L. a: catalyst concentration [Mt]=6.65×10^{-2}mol/L; b: catalyst concentration [Ln]=6.65×10^{-2}mol/L, Al/Ln=10 molar ratio.

P$_{507}$ =

$$R{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle R}{|}}{P}}{-}O{-}$$

P$_{204}$=

$$R{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\underset{\displaystyle R}{|}}{\underset{\displaystyle O}{|}}}{P}}{-}O{-}$$

R=CH$_3$-(CH$_2$)$_3$-CH(C$_2$H$_5$)-CH$_2$-

naph =


n=10-16

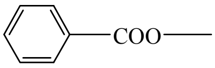
phcoo=


Table 2 illustrates the effect of the solvents on the polymerization. The polarity of solvent influences the Mv of PHNCO obviously. Mv decreases with the increasing of the solvent polarity. The yield of PHNCO keeps around 70% regardless solvent polarity, except the lowest Mv and yield obtained in CHCl$_3$. This phenomenon coincides with coordination polymerization. The effects of the monomer concentration and the polymerization time on Mv and yield are shown in figure 1 and 2. High monomer concentration is favorable for HNCO polymerization in toluene. PHNCO obtained in bulk polymerization gives higher yield and Mv than those in toluene. Long reaction time is preferable to produce PHNCO of high Mv and high yield.

Table 2. Effect of different solvents on the polymerization.

Run	Solvent	Yield (%)	Mv (10^4)
1	CCl4	79.6	78. 6
2	*n*-Hexane	78.9	74.8
3	Toluene	72.8	50.0
4	THF	67.2	39.4
5	CHCl3	20.1	25.0

Conditions: [Nd]=3.33×10^{-2}mol/L, [HNCO]/[Nd]=100 molar ratio, Al/Nd=10 molar ratio, -10°C, 10h.

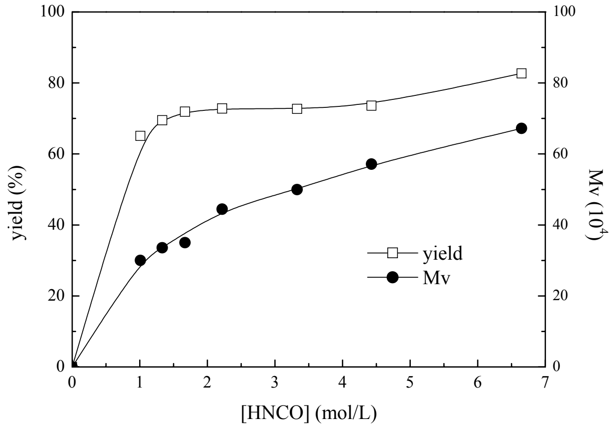


Figure 1. Effect of [HNCO] on the polymerization of HNCO. Conditions: [HNCO]/[Nd]=100 molar ratio, Al/Nd=10 molar ratio, -10°C, 10h, in toluene.

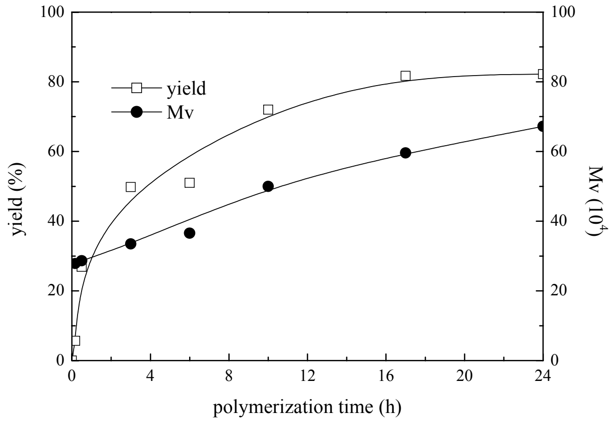


Figure 2. Relationships of polymerization time with PHNCO yield and Mv. Conditions: [Nd]= 3.33×10^{-2}mol/L, [HNCO]/[Nd]=100 molar ratio, Al/Nd=10 molar ratio, -10°C, in toluene.

Table 3, 4 and figure 3 illustrate the effects of Al/Nd molar ratio, polymerization temperature and [Nd] on the bulk polymerization of HNCO. The preferable conditions for bulk polymerization of HNCO are as follows: [Nd]=6.65×10^{-2}mol/L, [HNCO]/[Nd]=100 molar ratio, Al/Nd=10 molar ratio, at -10°C for 10h.

Table 3 shows that the reaction temperature affects HNCO polymerization. As reaction temperature rises from –50°C to –10°C, molecular weights (Mv and Mn) and yield of PHNCO increase. When it is higher than -10^{o}C, Mv, Mn and yield of PHNCO decrease. The fact that no PHNCO is obtained at 60^{o}C may result from that 60^{o}C is above the ceiling temperature of HNCO polymerization. The optimum Al/Nd molar ratio is 10. Both above and below 10, Mv, Mn and yield of the resulting PHNCO decrease (table 4). MWD increases with the growth of the Al/Nd molar ratio. The possible reason may be that the superfluous Al(*i*-Bu)$_3$ induces chain transfer reaction.

Table 3. Bulk polymerization of HNCO at various temperatures.

Run	Temp (^{o}C)	Yield (%)	Mv (10^4)	Mn (10^4)	MWD
1	-50	71.9	58.5	27.2	2.03
2	-30	75.8	63.0	34.0	2.18
3	-10	82.7	67.2	39.6	2.44
4	10	68.8	37.7	23.1	2.70
5	20	51.3	15.5	14.3	3.21
6	40	23.5	13.9	8.97	3.84
7	60	No PHNCO	-	-	-

Conditions: [Nd]=6.65×10^{-2}mol/L, [HNCO]/[Nd]=100 molar ratio, Al/Nd=10 molar ratio, 10h.

Table 4. Effect of Al/Nd molar ratio on bulk polymerization of HNCO.

Run	Al/Nd (molar ratio)	Yield (%)	Mv (10^4)	Mn (10^4)	MWD
1	5	64.4	45.9	24.6	2.01
2	10	82.7	67.2	39.6	2.44
3	20	59.2	51.0	29.9	2.58
4	30	50.2	42.4	26.9	2.70
5	40	32.1	23.9	17.0	3.27

Conditions: [Nd]=6.65×10^{-2}mol/L, [HNCO]/[Nd]=100 molar ratio, -10°C, 10h.

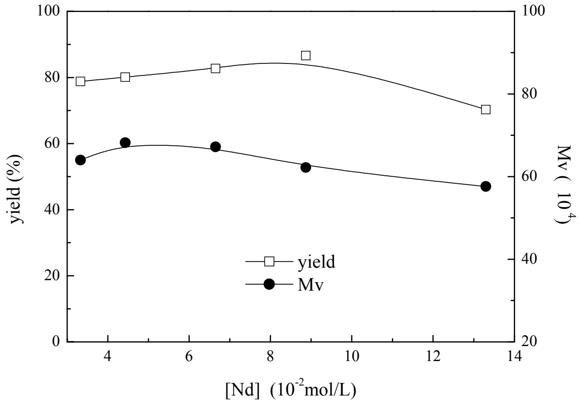


Figure 3. Influence of [Nd] on the bulk polymerization of HNCO, Al/Nd=10 molar ratio, [HNCO]= 6.65mol/L, -10°C, 10h.

The PHNCO obtained has been characterized by FT-IR, ^{1}H-NMR and TGA. The results are shown in figure 4~6. FT-IR spectrum of PHNCO shows that the characteristic peak of N=C=O bond around 2300cm^{-1} disappears. There is an intense peak at about 1700cm^{-1} due to C=O bond. The absence of ether peak of 1100cm^{-1} indicates that the polymer produced is not polyether but polyisocyanate. Therefore the polymerization takes place through N=C double bond, not C=O double bond. The ^{1}H-NMR spectrum also displays the signals of PHNCO: δ=0.89 (3H, H^d), δ=1.31 (6H, H^c), δ=1.59 (2H, H^b), δ=3.70 (2H, H^a). TGA thermogram (figure 6) shows that 210°C is the decomposition point of the PHNCO prepared in table 1 run 3.

According to our previous study [20], the active species might be formed by the exchange of phosphonate and alkyl groups between $Nd(P_{204})_3$ and $Al(i\text{-}Bu)_3$. The polymerization of HNCO was proposed to take place via a coordination-insertion mechanism.

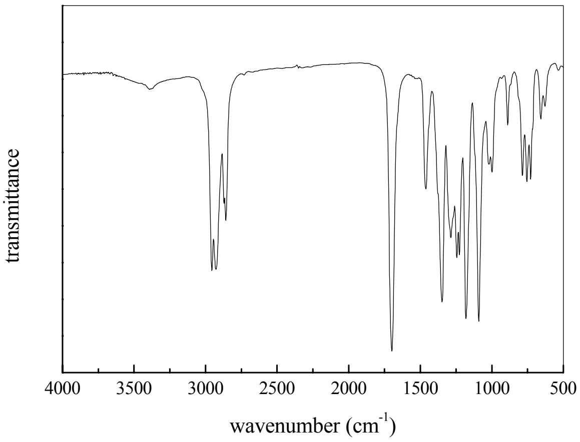


Figure 4. FT-IR spectrum of PHNCO obtained in table 1 run 3.

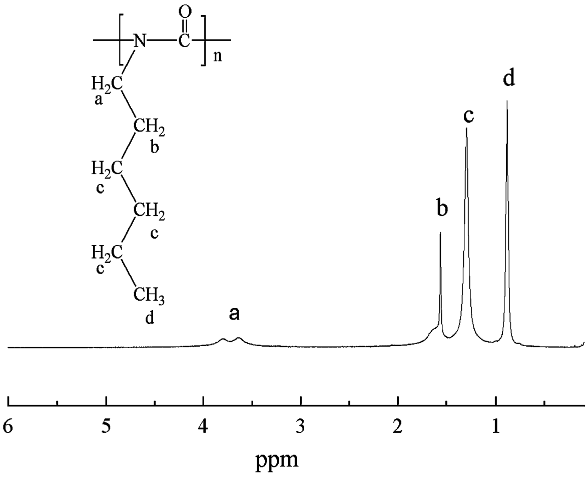


Figure 5. ^{1}H-NMR spectrum of PHNCO obtained under conditions: [HNCO]=3.33mol/L, [HNCO]/[Nd]=10, Al/Nd=10 molar ratio, -10°C, 5 minute, in toluene.

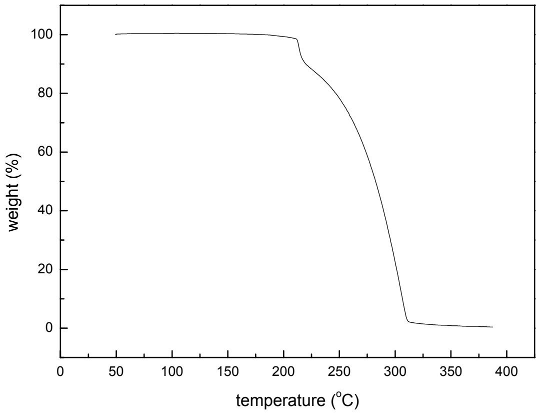


Figure 6. TGA thermogram of PHNCO obtained in table 1 run 3.

Conclusions

The characteristics of HNCO polymerization by $Nd(P_{204})_3/Al(i\text{-}Bu)_3$ catalyst system were studied. The moderate reaction conditions were as follows: $[Nd]=6.65\times10^{-2}$ mol/L, [HNCO]/[Nd]=100 molar ratio, Al/Nd=10 molar ratio, at -10°C for 10h in bulk. Under such conditions, the resulting PHNCO was of molecular weight ($Mn=39.6\times10^4$, $Mv=67.2\times10^4$), molecular weight distribution (MWD=2.44) and yield (82.7%). The IR and NMR analyses show that the polymer obtained is not polyether but polyisocyanate.

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