

# Copolymerization of Phenylisocyanate and $\epsilon$ -Caprolactone with Rare Earth Chloride Systems

Xufeng Ni, Xiaoyan Xu, Zhiquan Shen

Key Laboratory of Macromolecule Synthesis and Functionalization (Ministry of Education),  
Institute of Polymer Science, Zhejiang University, Hangzhou 310027, People's Republic of China

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**ABSTRACT:** A copolymer of phenylisocyanate (PhNCO) and  $\epsilon$ -caprolactone (CL) was synthesized by the rare earth chloride systems lanthanide chloride isopropanol complex ( $\text{LnCl}_3 \cdot 3i\text{PrOH}$ ) and propylene epoxide (PO). Polymerization conditions were investigated, such as lanthanides, reaction temperature, monomer feed ratio, La/PO molar ratio, and aging time of catalyst. The optimum conditions were:  $\text{LaCl}_3$  preferable,  $[\text{PhNCO}]/[\text{CL}]$  in feed = 1 : 1 (molar ratio), 30°C,  $[\text{monomer}]/[\text{La}] = 200$ ,  $[\text{PO}]/[\text{La}] = 20$ , aging 15 min, polymerization in bulk for 6 h. Under

such conditions the copolymer obtained had 39 mol % PhNCO with a 78.2% yield,  $M_n = 20.3 \times 10^3$ , and  $M_w/M_n = 1.60$ . The copolymers were characterized by GPC, TGA,  $^1\text{H-NMR}$ , and  $^{13}\text{C-NMR}$ , and the results showed that the copolymer obtained had a blocky structure with long sequences of each monomer unit. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2135–2140, 2007

**Key words:** catalysts; copolymerization; Ziegler-Natta polymerization; block copolymers

## INTRODUCTION

Polyisocyanates are stiff polymers that have a lot of interesting properties, such as light scattering, frictional, electrical, and optical properties. They may be used as chiral recognition materials, optical switches, and liquid crystal materials.<sup>1</sup> Polymerization and copolymerization of isocyanates have attracted great interest. Usually, the polymerizations of isocyanates is carried out by anionic initiators at very low temperatures (from  $-60^\circ\text{C}$  to  $-98^\circ\text{C}$ ).<sup>2–8</sup> Organotitanium (IV) catalysts have been reported to be more effective initiators in controlling the molecular weight of polyisocyanates and accomplishing living polymerization.<sup>9–12</sup> A few rare earth catalysts also have been reported for the polymerization of isocyanates at  $-78^\circ\text{C}$ .<sup>13,14</sup> Recently we found that rare earth catalysts neodymium phosphonate/tri-*i*-butyl aluminum [ $\text{Nd}(\text{P}_{204})_3/\text{Al}(i\text{-Bu})_3$ ] and lanthanum tris(2,6-di-*tert*-butyl-4-methylphenolate) [ $\text{La}(\text{OAr})_3$ ] effectively catalyze the polymerization of isocyanates at mild temperatures.<sup>15,16</sup>

Copolymerization of isocyanates with ketenes, ethylene oxide, aldehydes, and methyl methacrylate was summarized by Bur and Fetters.<sup>17</sup> Recently, triblock copolymers and pentablock copolymers of *n*-hexyl isocyanate with styrene or isoprene prepared in tetrahydrofuran at  $-98^\circ\text{C}$  using sodium naphthalene/sodium tetraphenylborate initiator have been reported.<sup>18</sup> It should be noted that all the copolymerizations of isocyanates were carried out by anionic polymerization at very low temperature. In terms of coordination polymerization, only a block copolymer of *n*-hexylisocyanate and ethylene glycol synthesized using Ti(IV) macroinitiator containing poly(ethylene glycol) has been reported.<sup>19</sup>

Our group found that rare earth halide-epoxide systems exhibited high activity for  $\epsilon$ -caprolactone polymerization.<sup>20</sup> In the present article we report the copolymerization of PhNCO and CL by an easily available novel rare earth coordination catalyst,  $\text{LaCl}_3 \cdot 3i\text{PrOH}$ , in the presence of PO at 30°C. The features of the copolymerization and characterization of the copolymer by NMR, GPC, and TGA were investigated.

## EXPERIMENTAL

### Materials

PhNCO (Acros 98%), CL (Acros 99%), and PO were distilled over  $\text{CaH}_2$  under reduced pressure prior to use. Toluene was distilled over sodium benzophenone ketyl. Anhydrous rare earth chlorides were prepared

Correspondence to: Zhiquan Shen(zhiquan\_shen@163.com).

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TABLE I  
Copolymerization of PhNCO and CL Using Different Rare Earth Catalysts

| Catalyst system                                  | Ln <sup>3+</sup> radius (pm) | Yield (%)  | PhNCO content (mol %) <sup>b</sup> | M <sub>n</sub> (10 <sup>3</sup> ) <sup>c</sup> | MWD <sup>c</sup> |
|--|------------------------------|------------|------------------------------------|--|------------------|
| LaCl <sub>3</sub> · 3 <i>i</i> PrOH <sup>a</sup> |                              | No polymer | —                                  | —  | —                |
| LaCl <sub>3</sub> · 3 <i>i</i> PrOH/PO           | 103.2                        | 78.2       | 39                                 | 20.3   | 1.67             |
| PrCl <sub>3</sub> · 3 <i>i</i> PrOH/PO           | 99                           | 74.8       | 43                                 | 19.6   | 1.59             |
| NdCl <sub>3</sub> · 3 <i>i</i> PrOH/PO           | 98.3                         | 74.1       | 41                                 | 20.1   | 1.62             |
| SmCl <sub>3</sub> · 3 <i>i</i> PrOH/PO           | 95.8                         | 46.7       | 66                                 | 13.6   | 1.52             |
| GdCl <sub>3</sub> · 3 <i>i</i> PrOH/PO           | 93.8                         | 38.6       | 98                                 | 4.9  | 1.27             |
| TbCl <sub>3</sub> · 3 <i>i</i> PrOH/PO           | 92.3                         | 38.1       | 97                                 | 5.2  | 1.23             |
| DyCl <sub>3</sub> · 3 <i>i</i> PrOH/PO           | 91.2                         | 37.6       | 97                                 | 4.4  | 1.19             |
| ErCl <sub>3</sub> · 3 <i>i</i> PrOH/PO           | 89.0                         | 36.9       | 98                                 | 4.7  | 1.23             |

<sup>a</sup> No PO.

<sup>b</sup> Determined by <sup>1</sup>H-NMR.

<sup>c</sup> Measured by GPC calibrated with standard polystyrenes.

Conditions: [PhNCO]/[CL] in feed = 1 : 1 (molar ratio), [monomer]/[Ln] = [200], [PO]/[Ln] = 20, aging 15 min, polymerized for 6 h in bulk at 30°C.

by heating a mixture of hydrated rare earth chloride and ammonium chloride under reduced pressure.<sup>21</sup> LnCl<sub>3</sub> · 3*i*PrOH was obtained by refluxing excessive isopropanol on anhydrous LnCl<sub>3</sub> until LnCl<sub>3</sub> was entirely dissolved. White crystals of LnCl<sub>3</sub> · 3*i*PrOH precipitated while the solution cooled to room temperature. The superfluous isopropanol was removed under vacuum. All these operations were carried out under an argon atmosphere.

### Polymerization

All polymerizations were carried out under argon using Schlenk techniques. In a typical copolymerization, catalyst was prepared by mixing LaCl<sub>3</sub> · 3*i*PrOH (0.039 g, 0.091 mmol) and PO (0.13 mL, 1.83 mmol) together with a small amount of toluene in a 20-mL ampoule and aging at room temperature for 15 min. A mixture of PhNCO (1 mL, 9.1 mmol) and CL (1 mL, 9.0 mmol) was added to the ampoule by syringe. Copolymerization was carried out at 30°C for 6 h. Ethanol (containing 5% HCl) was added to terminate the copolymerization. The white copolymer precipitate formed was collected by filtration, washed by ethanol three times, and then dried at room temperature at 30°C in vacuum.

### Measurements

The number-average molecular weight (*M<sub>n</sub>*) and molecular weight distribution (*M<sub>w</sub>*/*M<sub>n</sub>*) were determined in THF at 25°C by a Waters 1525 GPC with UV (Waters 2414) and RI (2487) detectors and calibrated with standard polystyrenes. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on a Bruker Avance DMX500 spectrometer in CDCl<sub>3</sub> at 25°C with TMS as internal reference. The compositions of the copolymers (PhNCO mol %) were calculated according to the <sup>1</sup>H-NMR spectra. TGA ther-

mograms were made with a Perkin Elmer Pyris 6 instrument at a heating rate of 10°C/min.

## RESULTS AND DISCUSSION

Copolymerization features with various LnCl<sub>3</sub> · 3*i*PrOH/PO catalysts were studied for the copolymerization of PhNCO and CL. The data in Table I show that LnCl<sub>3</sub> · 3*i*PrOH alone could not catalyze the copolymerization of PhNCO and CL. As mentioned in a previous study, rare earth chlorides react with PO and produce chloride rare earth alkoxides, which are active for polymerization of CL via a “coordination-insertion” mechanism.<sup>20</sup> It was found that these catalyst systems also can polymerize PhNCO and cause the copolymerization of CL and PhNCO. The catalytic activity sequence of different lanthanides was La > Pr ~ Nd > Sm > Gd ~ Tb ~ Dy ~ Er. The light rare earths were more favorable for copolymerization than the heavy ones, and the polymers obtained by the latter were almost homopolymers of PhNCO at low polymer yield. Heavy rare-earth metals have a small ionic radius, leading to less electrophilicity than with light rare-earth metals. The differences in the electrophilicity probably cause near homopolymerization of the phenylisocyanate of the copolymerization catalyzed by heavy metals. Therefore, LaCl<sub>3</sub> · 3*i*PrOH was selected for further study.

The preparation, composition of catalysts, and the polymerization conditions of copolymerization were investigated. The results are summarized in Table II. From the data, it could be concluded that copolymer with a yield of around 70% and a PhNCO content of about 35% could be prepared under these conditions: [PhNCO]/[CL] in feed = 1 : 1, [monomer]/[La] = 200, [PO]/[La] = 20, aging 15 min, 30°C, polymerized in bulk for 6 h. At a low reaction temperature (0°C, entry 1 in Table II), the catalyst showed low activity to both

**TABLE II**  
Influence of Polymerization Conditions on Copolymerization of PhNCO and CL

| Entry | Temperature (°C) | PO/La (molar ratio) | Monomer/La (molar ratio) | Aging time (min) | Yield (%) | PhNCO content (mol %) <sup>a</sup> |
|-------|------------------|---------------------|--------------------------|------------------|-----------|------------------------------------|
| 1     | 0                | 20                  | 200                      | 15               | 16.5      | 98                                 |
| 2     | 15               | 20                  | 200                      | 15               | 54.6      | 32                                 |
| 3     | 30               | 20                  | 200                      | 15               | 78.2      | 39                                 |
| 4     | 55               | 20                  | 200                      | 15               | 75.3      | 36                                 |
| 5     | 30               | 10                  | 200                      | 15               | 77.9      | 30                                 |
| 6     | 30               | 30                  | 200                      | 15               | 76.8      | 37                                 |
| 7     | 30               | 40                  | 200                      | 15               | 67.8      | 28                                 |
| 8     | 30               | 20                  | 200                      | 3                | 70.3      | 34                                 |
| 9     | 30               | 20                  | 200                      | 30               | 67.1      | 33                                 |
| 10    | 30               | 20                  | 200                      | 60               | 61.9      | 34                                 |
| 11    | 30               | 20                  | 100                      | 15               | 68.6      | 31                                 |
| 12    | 30               | 20                  | 133                      | 15               | 74.1      | 36                                 |
| 13    | 30               | 20                  | 300                      | 15               | 60.9      | 47                                 |

<sup>a</sup> Determined by <sup>1</sup>H-NMR.

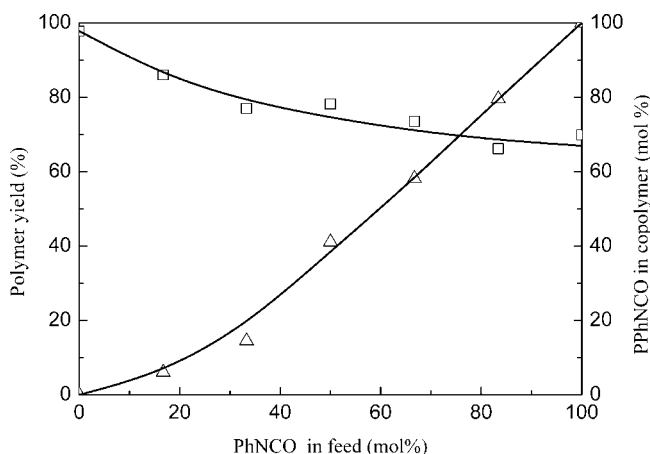
Conditions: [PhNCO]/[CL] in feed = 1 : 1, 6 h in bulk. Catalyst: LaCl<sub>3</sub> · 3iPrOH/PO.

monomers (yield 16.5%), especially to CL, with the resulting copolymer containing almost pure PhNCO unit (98%). The higher the molar ratio of monomer to La, the higher was the PhNCO content in copolymer (entries 11, 12, 3, and 13 in Table II), indicating PhNCO monomer had higher reactivity than CL monomer.

The influence of monomer feed ratio is illustrated in Figure 1. The copolymer yield decreased gradually with the increasing of the PhNCO mol % in the monomer feed ratio. The PhNCO mol% in the copolymer was always lower than that in the feed. A possible reason for this could be that the formed PhNCO dimer or trimer could not copolymerize with CL and was washed out in the polymer treatments. Thus, copolymer with various PhNCO contents could be prepared by controlling the monomer feed ratio.

Table III depicts that the reaction time had a remarkable influence on the copolymerization of PhNCO and

CL with the LaCl<sub>3</sub> · 3iPrOH/PO catalyst system. The polymer yield increased slowly when the polymerization time was less than 2 h. In this procedure, the PhNCO mol % in the copolymer was more than 95% from <sup>1</sup>H-NMR analysis. The products were of low molecular weight:  $M_n < 6000$  (entries 1 and 2 in Table III). After being polymerized for 2 h, the yield rose sharply from less than 20% to more than 70%. At the same time, the proportion of PhNCO segment in the copolymer fell from above 90% to around 30%. This means that PhNCO polymerized first, within the first 2 h, followed by polymerization of the monomer CL. In this regard, the copolymer obtained had a blocky structure with long sequences of each monomer unit. To confirm this, the copolymer was characterized by GPC, NMR, and TGA. In addition, the copolymers of phenylisocyanate and caprolactone were synthesized by the sequent addition of the two monomers. The results of copolymerization are shown in Table IV and Figure 2.



**Figure 1** Effects of monomer feed ratio on the yield ( $\Delta$ ) and PhNCO mol % ( $\square$ ) of the copolymer. Conditions: [monomer]/[La] = 200, [PO]/[La] = 20, aging 15 min, 30°C, 6 h in bulk; catalyst: LaCl<sub>3</sub> · 3iPrOH/PO.

**TABLE III**  
Effect of Polymerization Time on Copolymerization of PhNCO and CL

| Entry          | Time (h) | Yield (%) | PhNCO content (%) <sup>b</sup> | $M_n$ (103) <sup>c</sup> | MWD <sup>c</sup> |
|----------------|----------|-----------|--------------------------------|--------------------------|------------------|
| 1 <sup>a</sup> | 0.5      | 3.95      | 100                            | —                        | —                |
| 2              | 1        | 7.30      | 99                             | 5.51                     | 1.26             |
| 3              | 2        | 17.3      | 95                             | 7.74                     | 1.23             |
| 4              | 2.5      | 36.7      | 83                             | 13.6                     | 1.49             |
| 5              | 3        | 70.0      | 37                             | 18.5                     | 1.52             |
| 6              | 4.5      | 75.4      | 38                             | 19.7                     | 1.60             |
| 7              | 6        | 78.2      | 39                             | 20.3                     | 1.67             |

<sup>a</sup>  $M_n$  is too low to be detected by GPC.

<sup>b</sup> Determined by <sup>1</sup>H-NMR.

<sup>c</sup> Measured by GPC calibrated with standard polystyrenes.

Conditions: [PhNCO]/[CL] in feed = 1 : 1, [monomer]/[La] = 200, [PO]/[La] = 20, aging 15 min, 30°C in bulk. Catalyst: LaCl<sub>3</sub> · 3iPrOH/PO.

TABLE IV  
Copolymerization of PhNCO and CL by Sequential Addition of Monomers

| Entry | Sequence of monomer addition | Yield (%) | PhNCO content (%) <sup>c</sup> | $M_n$ ( $10^3$ ) <sup>d</sup> | MWD <sup>d</sup> | $M_n$ ( $10^3$ ) <sup>e</sup> | MWD <sup>e</sup> |
|-------|------------------------------|-----------|--------------------------------|-------------------------------|------------------|-------------------------------|------------------|
| 1     | CL+PhNCO <sup>a</sup>        | 71.9      | 14                             | 8.2                           | 1.26             | 7.2                           | 1.17             |
| 2     | PHNCO+CL <sup>b</sup>        | 64.7      | 18                             | 26.2                          | 1.90             | 15.4                          | 1.84             |
| 3     | Mixed                        | 78.2      | 39                             | 20.3                          | 1.67             | 18.6                          | 1.54             |

<sup>a</sup> CL was polymerized for 6 h in toluene first, [CL] = 2.5M; then PhNCO was added.

<sup>b</sup> PhNCO was polymerized first in toluene for 6 h [PhNCO] = 2.5M; then CL was added.

<sup>c</sup> Determined by <sup>1</sup>H-NMR.

<sup>d</sup> Measured by GPC calibrated with standard polystyrenes, by RI detector.

<sup>e</sup> By UV (254 nm) detector.

Conditions: [PhNCO]/[CL] in feed = 1 : 1, [monomer]/[La] = 200, [PO]/[La] = 20, aging 15 min, 30°C in bulk. Catalyst: LaCl<sub>3</sub> · 3*i*PrOH/PO.

The GPC elution curve of the copolymer shown in Figure 2 indicates the copolymer (entry 3 in Table IV) also had a unimodal MWD curve, and the MWD curve by the UV detector ( $\lambda = 254$  nm), which was sensitive to the PhNCO unit, was inconsistent with the MWD curve by the RI detector. Thus, it can be assumed that the copolymer obtained by the mixed addition of two monomers did not contain either homopolymer. The copolymers synthesized by the other two monomer addition sequences containing small amounts of homopolymers of the two monomers. Although the copolymer obtained with first polymerization of CL (entry 1 in Table IV) was found to have a narrow MWD by both RI and UV detection, there was a shoulder on the high-molecular-weight side. The absence of the corresponding signal in the UV detector indicated it could be attributed to the polycaprolactone. Poly-PhNCO is some kind of crystal that cannot dissolve well in CL monomer (entry 2 in Table IV). The resulting copolymer had a broad MWD and a shoulder on the low-molecular-weight side

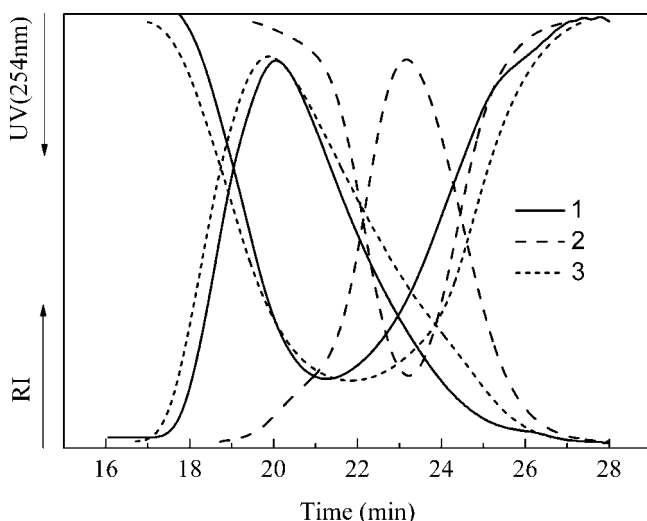


Figure 2 GPC curves of copolymers synthesized by various monomer addition sequences (1, 2, and 3 correspondence to entries 3, 1, 2, respectively, in Table IV).

attributed to poly-PhNCO. This copolymer also had low PhNCO unit content and yield because of the low molecular weight of the poly-PhNCO, which was soluble in ethanol during purification.

The copolymer of PhNCO and CL by LaCl<sub>3</sub> · 3*i*PrOH/PO had clear <sup>1</sup>H-NMR (Fig. 3) and <sup>13</sup>C-NMR (Fig. 4) spectra. The chemical shifts of protons were assigned as follows:  $\delta = 7.4$ – $7.5$  ppm ( $H^{a3}$ ,  $H^{a4}$ , and  $H^{a5}$ , proton of phenyl in PhNCO segment);  $\delta = 4.06$  ppm ( $H^{b6}$ ,  $OCH_2$ );  $\delta = 2.30$  ppm ( $H^{b2}$ ,  $CH_2C=O$ );  $\delta = 1.65$  ppm ( $H^{b5}$ ,  $H^{b3}$ ,  $COCH_2CH_2CH_2CH_2CH_2O$ );  $\delta = 1.38$  ppm ( $H^{b4}$ ,  $COCH_2CH_2CH_2CH_2CH_2O$ ). In addition to the backbone signals of copolymer, doublet signals at 1.32 ppm ( $H^{c5}$ ), assigned to  $OCH(CH_3)CH_2$ , triplet signals, at 3.91 ppm ( $H^{b7}$ ), assigned to  $HO-CH_2-(CH_2)_4$ , and about 5.1 ppm ( $H^{c1}$ ), assigned to  $COOCH(CH_3)CH_2O$ , were present, which were attributed to the proton of the polymer terminals.

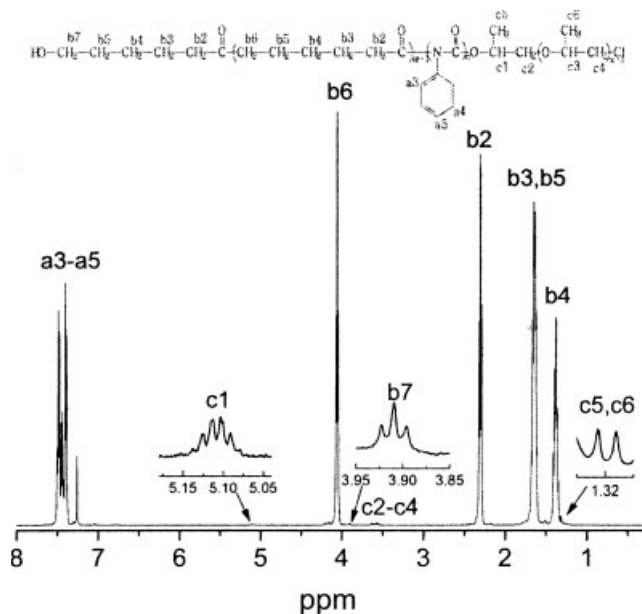
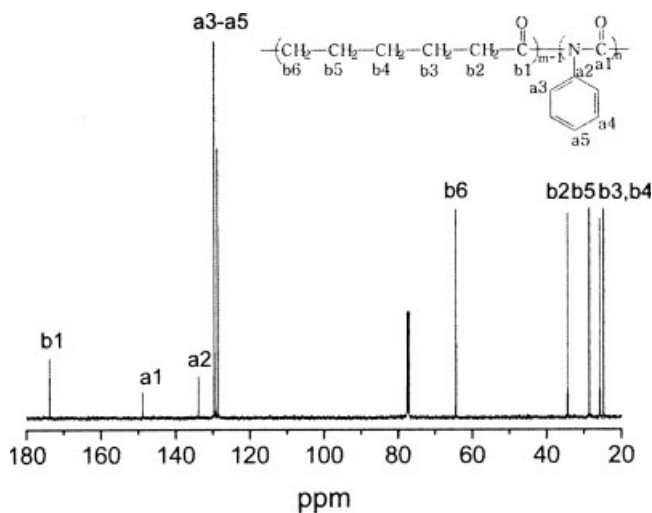


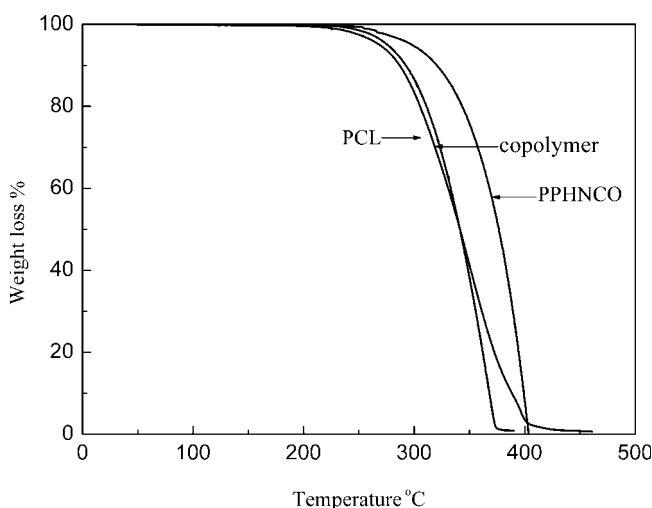
Figure 3 <sup>1</sup>H-NMR spectrum of copolymer (entry 6 in Table III).



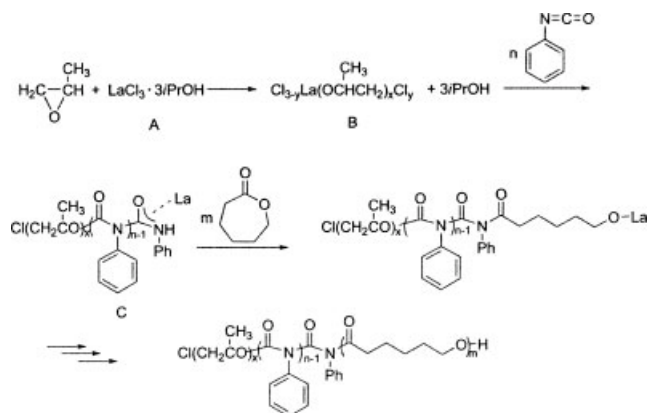
**Figure 4**  $^{13}\text{C}$ -NMR spectrum of copolymer (entry 6 in Table III).

In the  $^{13}\text{C}$ -NMR spectrum (Fig. 4), signals were attributed as follows:  $\delta = 149$  ppm assigned to  $\text{C}^{\text{a}1}$  (CO in PhNCO);  $\delta = 134$  ppm assigned to  $\text{C}^{\text{a}2}$  (NCC=O in PhNCO);  $\delta = 128\text{--}129$  ppm ( $\text{C}^{\text{a}3}\text{--}\text{C}^{\text{a}5}$ ) because of  $\text{C}^{\text{a}3}\text{--}\text{C}^{\text{a}5}$  in PhNCO;  $\delta = 172$  ppm because of ( $\text{C}^{\text{b}1}$ ) ( $\text{C}=\text{O}$  in PCL segment);  $\delta = 64$  ppm because of ( $\text{C}^{\text{b}6}$ ) ( $\text{C}\text{--}\text{O}\text{--}$  in PCL);  $\delta = 34$  ppm because of ( $\text{C}^{\text{b}2}$ ) ( $\text{CH}_2\text{C}=\text{O}$  in PCL);  $\delta = 28.5$  ppm because of ( $\text{C}^{\text{b}5}$ ) ( $\text{OCH}_2\text{CH}_2$  in PCL);  $\delta = 25.7$  ppm because of ( $\text{C}^{\text{b}3}$ ) ( $\text{CH}_2\text{CH}_2\text{C}=\text{O}$  in PCL);  $\delta = 24.7$  ppm because of ( $\text{C}^{\text{b}4}$ ) ( $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$  in PCL).

The intensive degradation temperature of polymers is a criterion of heat stability of polymers. The TGA curves for thermal degradation of the copolymer (entry 3 in Table II), PPhNCO, and PCL are plotted in Figure 5. The heating rate was  $10^\circ\text{C}/\text{min}$ . PhNCO had



**Figure 5** TGA curves of the copolymer (entry 6 in Table III), PPhNCO, and PCL. The PPhNCO and PCL were formed under PhNCO : CL feed ratios of 1 : 0 and 0 : 1, respectively (in Fig. 1).



**Scheme 1** Mechanism of copolymerization.

better heat stability than PCL. Below  $350^\circ\text{C}$ , the curves of the copolymer and PCL were very close. It is a reasonable possibility that the PCL-rich segments of copolymer had lower heat stability than the PhNCO-rich segments. In the following stage the TGA curve of the copolymer (PPNCO-rich segments) had the same currency as that of PPhNCO.

From the polymerization results,  $^1\text{H}$ -NMR analysis of the copolymer, and a previous study,<sup>20</sup> a polymerization mechanism was assumed as shown in Scheme 1. When propylene oxide was added to the starting catalyst A, because of the steric and inductive effects, dissociation of isopropanol and association of propylene oxide occurred. Compound B formed and provided an active site for polymerization. Because of the higher reactivity of PhNCO, it polymerized first, followed by CL polymerization, which led to a blocky copolymer structure.

## CONCLUSIONS

Rare earth coordination catalyst system composed of  $\text{LaCl}_3 \cdot 3\text{iPrOH}/\text{PO}$  led to the copolymerization of PPhNCO and PCL and produced a copolymer with a blocky structure. At the optimum conditions, the copolymer contents could be controlled conveniently by adjusting the monomer feed ratio.

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