

## Supporting Information

# Metal-Free Anionic Polymerization of *n*-Hexyl Isocyanate Catalyzed by Phosphazene Bases

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## S1. Experimental Section

### S1.1. Materials

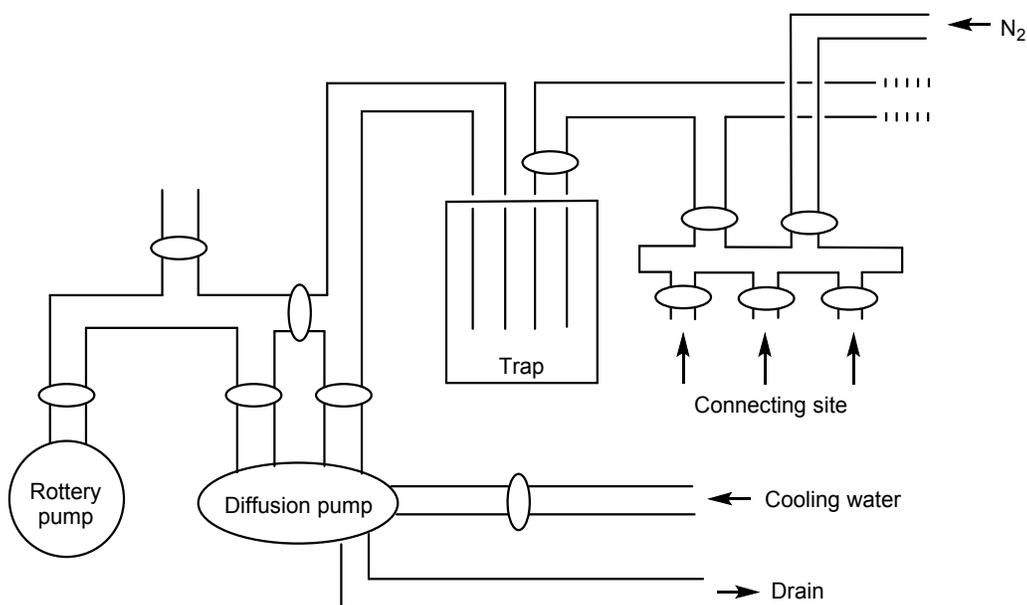
*n*-Hexyl isocyanates (HIC, Aldrich, 97%) was distilled over calcium hydride (CaH<sub>2</sub>) under reduced pressure and then redistilled over CaH<sub>2</sub> under 10<sup>-6</sup> Torr. Tetrahydrofuran (Fisher Scientific, GR grade) was distilled from a sodium naphthalenide solution and degassed two times at room temperature (RT) under 10<sup>-6</sup> Torr. *N*-phenethyl-3-phenylpropanamide (PEPPA) was synthesized by following our prior work.<sup>S1</sup> *tert*-butylimino-tris(dimethylamino)phosphorene (*t*-BuP<sub>1</sub>, Aldrich, >97%), 1-*tert*-butyl-2,2,4,4,4-pentakis(dimethylamino)-2λ<sup>5</sup>,4λ<sup>5</sup>-catenadi(phosphazene) (*t*-BuP<sub>2</sub>, Aldrich, 2M solution in THF) and 1-*tert*-Butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylidenamino]-2λ<sup>5</sup>,4λ<sup>5</sup>-catenadi(phosphazene) (*t*-BuP<sub>4</sub>, Aldrich, 0.8M solution in hexane) was used after degassing at room temperature (RT) under 10<sup>-6</sup> Torr, two times. HIC, PEPPA, *t*-BuP<sub>1</sub>, *t*-BuP<sub>2</sub> and *t*-BuP<sub>4</sub> were appropriately diluted with dried THF and flame-sealed in clean glass ampules equipped with break-seals under 10<sup>-6</sup> Torr.

### S1.2. Instruments and Analyses

Proton and carbon-13 nuclear magnetic resonance (<sup>1</sup>H and <sup>13</sup>C NMR) spectra were recorded using a JNM-ECX 400 NMR spectrometer (JEOL) in chloroform-*d* (CDCl<sub>3</sub>, 99.8 atom% D, contains 0.03 vol% tetramethylsilane (TMS)) at 25 °C. Number-average molecular weight (*M*<sub>n</sub>) and dispersity (*D*) values of polymers were measured using a size exclusion chromatography-multiangle laser light scattering (SEC-MALLS) instrument equipped with a 515 HPLC pump (Waters), a set of four Styragel columns connected in series (HR 0.5, HR 1, HR 3, and HR 4 with pore sizes of 50, 100, 500, and 1000 Å, respectively, Waters), a miniDAWN TREOS light scattering detector (Wyatt Technology) and an Optilab T-rEX refractive index detector (Wyatt Technology). The SEC-MALLS was operated in THF:triethylamine (98:2 v:v) with an elution rate of 1.0 mL/min at 40 °C. The refractive index increment (*dn/dc*) values of polymers were calculated according to the assumption of 100% mass recovery.<sup>S2,3</sup>

### S1.3. Vacuum System and Preparation of Reaction Apparatus

Schlenk vacuum line consists of diffusion pump, rotary pump, nitrogen line, cooling water and trap like Figure S1. Diffusion pump acts to decrease the air pressure in glass apparatus about 10<sup>-6</sup> Torr. And rotary pump connected to the diffusion pump to discharge the gas from diffusion pump. In order to prevent overheat of diffusion pump, cooling water flows to the surround of diffusion pump. Also, cold trap plays a role to minimize inflow of the chemical toward diffusion pump.



**Figure S1** Shlenk vacuum line for anionic polymerization.

Glass ampule and apparatus were handmade by glass-blowing technique. Glass apparatus made by glass-blowing technique connects to connecting site in vacuum line and then check the pin hole. Pin hole can derive into the breaking glass apparatus in high vacuum. After checking the pin hole, glass apparatus was depressured in high vacuum for 30 min and baked every 10 min 3 times to remove the organic chemical and moisture in glass apparatus. And then glass apparatus was separated from the vacuum line by break-seal technique. The details of high vacuum techniques were noted in reference.<sup>54</sup>

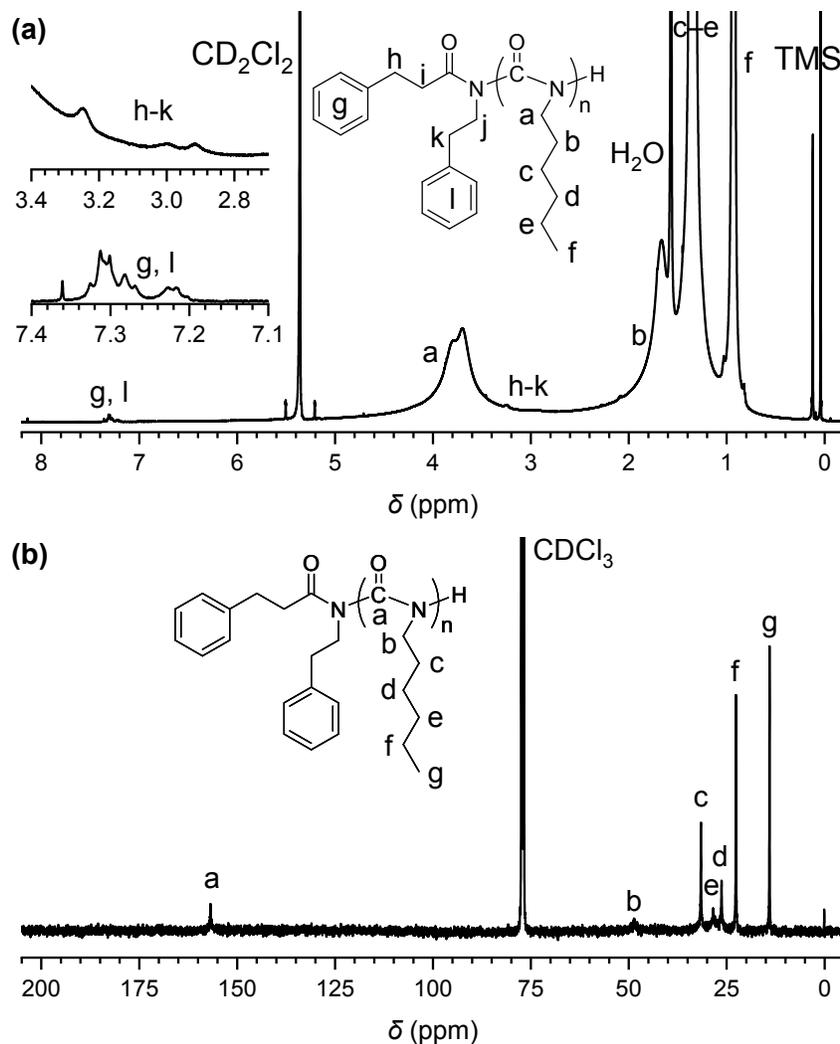
#### **S1.4. Preparation of Solutions of Initiating Ion Pairs in THF**

The glass apparatus with frame seal to prepare the solution of initiating ion pairs in THF conducted 3 times baking under  $10^{-6}$  Torr was prewashed by sodium naphthalenide solution in THF. And then, sodium naphthalenide solution ampule was separated from glass apparatus by using a break-seal technique. PEPPA and *t*-BuP<sub>2</sub> solution in THF was transferred into a reaction flask. PEPPA solution was reacted with *t*-BuP<sub>2</sub> solution at room temperature for 10 min. transparent PEPPA and *t*-BuP<sub>2</sub> solution in THF was changed into a pale brown color. This solution was divided into appropriate numbers of clean glass ampules equipped with break-seals under  $10^{-6}$  Torr and stored in the freezer at  $-30^{\circ}\text{C}$ . PEPPA:*t*-BuP<sub>1</sub> and *t*-BuP<sub>4</sub> solution in THF for initiation also followed to this procedure.

#### **S1.5. Anionic Polymerization of HIC Using PEPPA Catalyzed by Phosphazene Bases**

Anionic polymerization promoted by phosphazenebase was also carried out by using a break-seal technique in a sealed glass apparatus. The glass apparatus was maintained at  $-98^{\circ}\text{C}$  by putting in a frozen methanol bath. PEPPA:*t*-BuP<sub>2</sub> solution in THF was transferred into a reaction flask for polymerization from a sealed ampule and cooled down to  $-98^{\circ}\text{C}$  for 2 min. and then HIC solution in THF was fastly added into the PEPPA:*t*-BuP<sub>2</sub> solution in a reaction flask. The polymerization was terminated by adding 4 ml solution of HCl:methanol in THF (HCl:MeOH:THF = 1:20:30 ml) as a terminator after a specific reaction time, *t*. The resulting polymer was precipitated in cool methanol, filtered, and dried under vacuum. The homopolymerization of HIC using PEPPA promoted by *t*-BuP<sub>1</sub> and *t*-BuP<sub>4</sub> also followed to this procedures. The conversion to the polymer was determined by the gravimetric yield and the conversion to the cyclotrimer was calculated by <sup>1</sup>H NMR. In order to calculate the conversion of cyclotrimer, sample which used to calculate the conversion of cyclotrimer by <sup>1</sup>H NMR was filtered. And then it dried by evaporator. The concentrated solution was used to calculate the conversion of cyclotrimer by <sup>1</sup>H NMR. Size exclusion chromatography-multiangle laser light scattering (SEC-MALLS) measurements were implemented to determine the number-average molecular weight ( $M_n$ ) and the dispersity ( $\mathcal{D}$ ) of the polymer. Each  $M_n$  value was compared to the corresponding  $M_{n,\text{theo}}$  value to evaluate the initiation efficiency (*f*).

PHIC:  $dn/dc = 0.086 \text{ mL/g}$  (in THF at  $40^\circ\text{C}$ ).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$  with 0.03% v/v TMS, 600 MHz):  $\delta$  (ppm) 7.35-7.20 (br), 4.21-3.22 (br), 1.59-1.51 (br), 1.44-1.06 (br), 0.97-0.73 (br).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$  with 0.03% v/v TMS, 400 MHz):  $\delta$  (ppm) 156.8, 77.1, 48.5, 31.6, 28.5, 26.3, 22.6, 14.0.

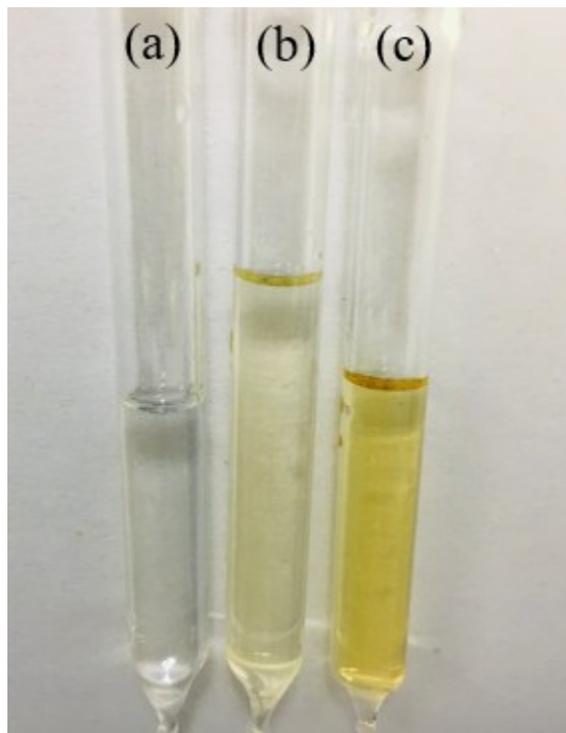


**Figure S2** (a)  $^1\text{H}$  NMR spectrum of PHIC ( $M_n = 54.3 \text{ kDa}$ ,  $D = 1.76$ ) in  $\text{CD}_2\text{Cl}_2$  and (b)  $^{13}\text{C}$  NMR spectrum of PHIC ( $M_n = 21.4 \text{ kDa}$ ,  $D = 1.34$ ) in  $\text{CDCl}_3$ .

### S1.6. Chain-extension of HIC using PEPPA promoted by phosphazenebase.

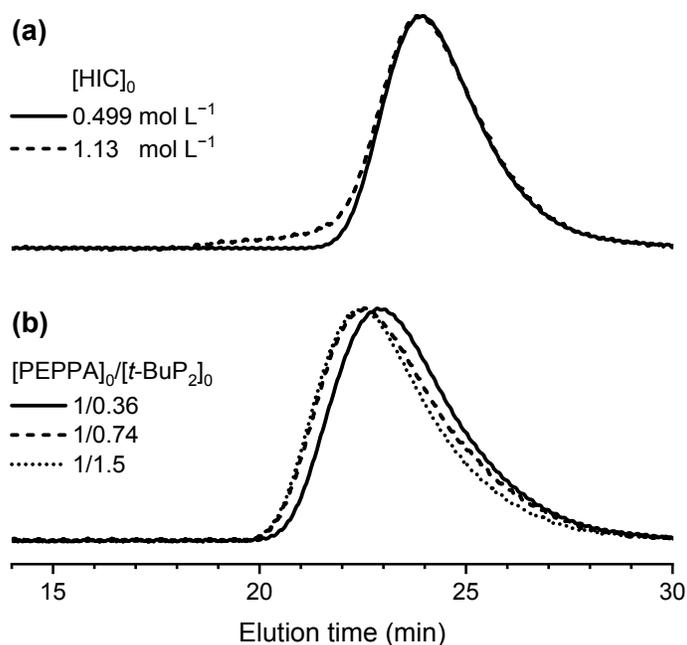
A solution of PEPPA: $t\text{-BuP}_2$  as initiator in THF was transferred into a reaction flask prewashed by sodium naphthalendie solution and then cooled down to  $-98^\circ\text{C}$  for 2 min. The polymerization was performed by adding the solution of HIC in THF to the initiation solution. The mixture of HIC:PEPPA: $t\text{-BuP}_2$  solution was maintained at  $-98^\circ\text{C}$ . Before adding the second HIC solution for chain-extension, second HIC solution was made it cool to  $-98^\circ\text{C}$  for 2 min. Second HIC solution in THF was added into the mixture of HIC:PEPPA: $t\text{-BuP}_2$  for chain-extension at  $t$ . After  $t$ , Solution of HCl:methanol in THF as a terminator was quenched in the solution of HIC:PEPPA:  $t\text{-BuP}_2$ . The resulting polymer was precipitated in cool methanol, filtered, and dried under vacuum. The conversion to the polymer was determined by the gravimetric yield and the conversion to the cyclotrimer was calculated by  $^1\text{H}$  NMR.

**S2. The color of solution of PEPPA with each phosphazene bases.**

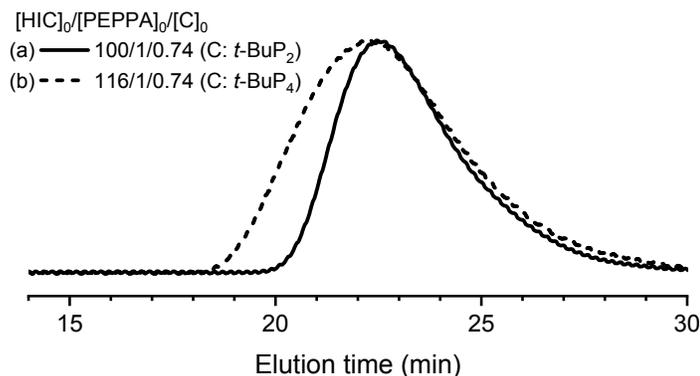


**Figure S3** Solution of PEPPA with each phosphazene bases in THF (a)  $t\text{-BuP}_1$ , (b)  $t\text{-BuP}_2$  and (c)  $t\text{-BuP}_4$ .

**S3. The SEC-dRI traces of PHICs yielded from the anionic polymerization of HIC using PEPPA catalyzed by  $t$ -BuP<sub>2</sub>.**



**Figure S4** SEC-dRI traces of PHICs yielded from the anionic polymerization of HIC using PEPPA catalyzed by  $t$ -BuP<sub>2</sub> in THF at  $-98$  °C under  $10^{-6}$  Torr. Variables: (a) [HIC]<sub>0</sub> = 0.499 and 1.13 mol L<sup>-1</sup> (Table 2, entry 13,16) and (b) [PEPPA]<sub>0</sub>/[ $t$ -BuP<sub>2</sub>]<sub>0</sub> = 1/0.36, 1/0.74, and 1/1.5 (Table 2, entry 17–19).



**Figure S5** SEC-dRI traces of PHICs obtained by the anionic polymerization of HIC using PEPPA catalyzed by (a)  $t$ -BuP<sub>2</sub> (Table 1, entry 6) and (b)  $t$ -BuP<sub>4</sub> (Table 1, entry 9) in THF at  $-98$  °C under  $10^{-6}$  Torr. PHICs: (a)  $M_n$  = 21.1 kDa and  $\mathcal{D}$  = 1.34 and (b)  $M_n$  = 24.9 kDa and  $\mathcal{D}$  = 1.82.

**S4. References of SI**

- S1 C. G. Chae, I. G. Bak and J. S. Lee, *Macromolecules*, 2018, **51**, 10083–10094.
- S2 C. G. Chae, P. N. Shah, J. Min, H. B. Seo and J. S. Lee, *Macromolecules*, 2014, **47**, 1563–1569.
- S3 C. G. Chae, I. G. Bak and J. S. Lee, *Macromolecules*, 2018, **51**, 6771–6781.
- S4 K. Ratkanthwar, N. Hadjichristidis and J. W. Mays, in *Anionic polymerization : Principle, Practice, Strength, Consequences and Applications*, eds. N. Hadjichristidis and A. Hirao, Springer, Japan, 2015, pp. 19-60.