Synthesis of poly(hydroxyurethane) from 5-membered cyclic carbonate under mild conditions in the presence of bicyclic guanidine and their reaction process

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ABSTRACT

A series of amines are applied as catalysts in the aminolysis reactions of five-membered cyclic carbonate (**5CC**). Kinetic results display that **TBD**, which has a guanidine structure, exhibits the best catalytic efficacy and the reaction rate constant is about 100 times higher than the blank system without catalyst. The reaction medium, NMP is found to be as both solvent and promoter in the aminolysis of **5CC**. Finally, with **TBD** and NMP as catalyst and solvent, respectively, the polymerization of *bis*-functional 5CC (**B5CC**) and *1, 6*-diaminohexane can proceed almost 100% at room temperature in less than 4 hours to obtain poly(hydroxyurethane)s (**PHU**s) with moderate molecular weight.

KEYWORDS: Aminolysis; Five-membered cyclic carbonate; Guanidine; Kinetics; Polyhydroxyurethane

INTRODUCTION The isocyanate-free process for the synthesis of polyurethane is an environmentally benign and safe alternative to the traditional protocol, which involves the reactions of hazardous and toxic isocyanate with polyols.[1-4] Among the various isocyanate-free routes, cyclic carbonates as candidates to react with aliphatic or aromatic amines via aminolysis ring-opening to form poly(hydroxyurethane)s (**PHU**s) is more feasible and appealing, on one hand for the synthetic process is not sensitive to moisture and does not require harsh conditions, and on the other hand, the thus formed **PHU**s, which have pendent primary and secondary hydroxyl groups along the backbone are endowed with better thermal and mechanical properties by the inter-and intra-molecular hydrogen bonding between primary and secondary hydroxyl groups and carbonyl groups in **PHU**s.[1,2]

Various types of cyclic carbonates have thus far been designed and synthesized and amongst all of them, five-, six- and seven-membered cyclic carbonates have received much more attentions than the others.[5-8] Six- and seven-membered cyclic carbonates, often require harmful reagents like phosgene or its derivatives for the synthesis, although they show higher reactivity with amines.[5-8] The less reactive five-membered cyclic carbonate (**5CC**) can be synthesized simply through the carbonation of epoxide with CO_2, which is an effective and promising approach for the valorization of CO_2.[9,10] In order to improve the reactivity of **5CC** toward aminolysis, some parameters like the reaction temperature, the monomer concentration and the type of reaction solvents have already been considered.[11] In addition, some works try to optimize the molecular structures of the **5CC** and indicate that an electron-withdrawing groups attached to the carbonate

ring is able to accelerate the aminolysis reactions.[12] Another study further reveals an inverse relationship between the distance of the electron-withdrawing group from the carbonate ring and the aminolysis reactivity of **5CC**.[13]

The development and application of catalysts is also a viable route on activating the aminolysis reaction of **5CC** and furthermore accelerating the polymerization of *bis*-functional **5CC** (**B5CC**) and poly-functional amines to obtain **PHU**s.[14] A series of organic bases, Brönsted acids, alkali metal salts and organometallic catalysts have already been developed and applied in the amine/carbonate reaction systems.[11] Metal-free catalysts, which are competitive with metal-containing ones on catalytic efficacy, have many advantages in biomedical and electronic applications, for the reason that metal-containing catalysts often result in the deteriorations of the obtained products, like the toxicity and low insulation capability.[15,16] Herein, in order to accomplish the polymerization of **B5CC** and *1, 6*-diaminohexane in a mild condition, the aminolysis of **5CC** at room temperature as the model reaction is adopted firstly and a series of commercial available organic bases are selected, screened and ranked on catalyzing the aminolysis ring-opening of **5CC**; they are triethylamine (**TEA**), *1, 4*-diazabicyclo[2.2.2]octane (**DABCO**), *4*-dimethylaminopyridine (**DMAP**), *1*-methylimidazole (**Mim**), *1, 8*-Diazabicyclo[5.4.0]undec-7-ene (**DBU**), *N, N'*-diphenylthiourea (**Thiourea**) and *1, 5, 7*-Triazabicyclo[4.4.0]dec-5-ene (**TBD**). At the same time, the solvent systems are also screened and optimized. Finally, the catalyst that displays the best catalytic efficacy is used for the synthesis of **PHU**s.

EXPERIMENTAL

Materials

Triethylamine (TCI, >99.0%), *1*-methylimidazole (TCI, >99.0%), *4*-dimethylaminopyridine (TCI, >99.0%), *1, 4*-diazabicyclo[2.2.2]octane (WAKO, 95.0+%), *N, N'*-diphenylthiourea (TCI, >98.0%), *1, 8*-diazabicyclo[5.4.0]-7-undecene (TCI, >98.%), *1, 5, 7*-triazabicyclo[4.4.0]dec-5-ene (TCI, >98.0%), *1*-methyl-2-pyrrolidine (WAKO, special grade), acetone (WAKO, 1st grade), hexylamine (TCI, >99.0%) and *1, 6*-diaminohexane (TCI, 99.0%). These reagents above are used as received. *4*-phenoxymethyl-*1, 3*-dioxolan-*2*-one (**5CC**) and *2, 2-bis*[*p*-(*1, 3*-dioxolan-*2*-one-*4*-yl-methoxy)phenyl]propane (**B5CC**) are synthesized according to the methods reported previously and the synthetic details and characterizations are provided in the supporting information.

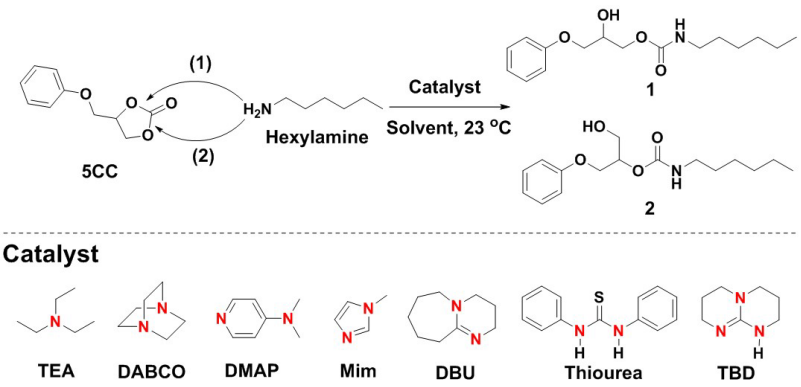
Measurements

Proton nuclear magnetic resonance (^{1}H NMR) measurements were recorded on JEOL JNM ECS 400 in DMSO-*d6* or Chloroform using tetramethylsilane as an internal standard. ATR-FT-IR spectroscopy was conducted on a Thermo Fisher Scientific Nicolet iS10 spectrometer. Number-average molecular weight (M_n) and molecular weight dispersity ($Đ$) were estimated from size exclusion chromatography performed on a Tosoh HLC-8220 chromatograph, equipped with three consecutive polystyrene gel columns [TSK-gels (bead size, exclusion, limited molecular weight); super-AW4000 (6 µm, $>4 \times 10^5$), super-AW3000 (4 µm, $>6 \times 10^4$), and super-AW2500 (4 µm, $>2 \times 10^3$)] and refractive index and ultraviolet detectors. The system was operated using 10 mM LiBr in DMF as eluent at a flow rate of 0.5 mL min^{-1} at 40 °C. Polystyrene standards were employed for calibrations.

Methods

Kinetic studies of aminolysis of 5CC without (blank) or with various organic amines.

In a typical reaction, *4*-phenoxymethyl-*1, 3*-dioxolan-*2*-one (**5CC**) (0.19g, 1 mmol), hexyla



Scheme 1. Aminolysis of **5CC** by hexylamine and the types of amines used as catalysts.

mine (0.10g, 1 mmol) and **TEA** (0.03g, 0.3 mmol) are dissolved in 0.4 mL NMP. The reaction is stirred at room temperature and sampled for ^{1}H NMR after 5 min, 10 min, 15 min, 30min, 1 hour, 3 hours, 6 hours, 12 hours and 24 hours.

Kinetic studies of aminolysis of B5CC by hexylamine without (blank) or with TBD.
In a typical reaction, *2, 2-bis*[*p*-(*1, 3*-dioxolan-*2*-one-*4*-yl-methoxy)phenyl]propane (**B5CC**) (0.21 g, 0.5 mmol), hexylamine (0.10g, 1 mmol) and **TBD** (0.02g, 0.15 mmol) are dissolved in 0.4 mL NMP. The reaction is stirred at room temperature and sampled for ^{1}H NMR after 5 min, 10 min, 15 min, 30min, 1 hour, 3 hours, 6 hours, 12 hours and 24 hours.

Kinetic studies of aminolysis of B5CC by 1, 6-diaminohexane without (blank) or with TBD
In a typical reaction, *2, 2-bis*[*p*-(*1,3*-dioxolan-*2*-one-*4*-yl-methoxy)phenyl]propane (**B5CC**) (0.21 g, 0.5 mmol), *1, 6*-diaminohexane (0.06 g, 0.5 mmol) and **TBD** (0.02g, 0.15 mmol) are dissolved in 0.4 mL NMP. The reaction is stirred at room temperature and sampled for ^{1}H NMR after 1 hour, 3 hours, 6 hours, 12 hours and 24 hours.

Polymerizations of B5CC and 1, 6-diaminohexane catalyzed by TBD
In a typical reaction, *2, 2-bis*[*p*-(*1, 3*-dioxolan-*2*-one-*4*-yl-methoxy)phenyl]propane (**B5CC**) (0.43 g, 1 mmol), *1, 6*-diaminohexane (0.12 g, 1 mmol) and **TBD** (0.08g, 0.6 mmol) are dissolved in 0.8 mL NMP. The reaction is stirred at room temperature for 4 hours, then diluted by NMP and finally precipitated in water. The obtained product (**PHU**s) is dried by vacuum oven at room temperature overnight.

RESULTS AND DISCUSSION

Mono-functional five-membered cyclic carbonate *4*-phenoxymethyl-*1, 3*-dioxolan-*2*-one (**5CC**) is firstly applied to react with hexylamine at room temperature as the model reaction for screening the catalyst, as shown in Scheme 1. For the kinetic studies, the characteristic phenyl at 6.85-7.10 ppm (3*H*) in **5CC** or the methyl protons at 0.80-0.95 ppm (3*H*) in hexylamine is used as the internal reference and the integration of methylene protons at 4.50-4.70 ppm (2*H*) adjacent to oxygen in **5CC** is monitored to calculate the conversion of **5CC** with time. The representative ^{1}H NMR spectra of the **5CC**/hexylamine reactions after 30min without and with various catalysts are shown in Figure S3-S10. Thus the kinetic conversion of aminolysis of **5CC** catalyzed by various types of catalysts displayed in Scheme 1 was calculated, summarized and plotted in Figure 1 and Table 1, respectively. It can be found that the time-conversion curves of the systems catalyzed by **TEA**, **DMAP**, **DABCO** and **Mim** are almost superimposed with that of the blank system without catalyst. These results are a little different from

Table 1. Screening of the catalysts for aminolysis reactions of five-membered cyclic carbonate (**5CC**) at 23 °C.

Entry	Solvent	Catalyst (mol %)	Time (h)	Conv. (%)	*k* (L/mol*h)
1	NMP	Blank	24h	87.0	0.34
2	NMP	TEA （30）	24h	89.0	0.31
3	NMP	DMAP (30)	24h	89.5	0.39
4	NMP	DABCO (30)	24h	89.0	0.33
5	NMP	Mim (30)	24h	90.0	0.38
6	NMP	Thiourea (30)	24h	93.0	2.52
7	NMP	DBU (30)	24h	99.5	1.31
8	NMP	TBD (10)	1h	98.3	
9	NMP	TBD (30)	1h	99.5	34.5
10	Acetone	TBD (10)	1h	73.5	
11	Acetone	TBD (30)	1h	88.5	
12	$CHCl_3$	TBD (30)	24h	99.6	

the previous reports. For example, **TEA**[17] and **DABCO**[18] have already been reported to be efficient catalysts in the amine/multi-functional (more than two) five-membered cyclic carbonate reaction, but in the present investigation they have no effects on catalyzing the system. **TBD**, which has a bicyclic guanidine structure, exhibits the best catalytic activity and the conversion of cyclic carbonate reaches nearly 100% after only 1 hour. It is interesting to find that the bicyclic amidine **DBU** displays a much better effect than the monocyclic amidine **Mim** and as shown in Figure 1, **DBU**-catalyzed system has more than 50% conversion of carbonate after 5 mins, while that of **Mim** system is less than 10 %. The time-conversion curve of **thiourea** amine-catalyzed system can be divided into two parts and from 5 min to 1 hour, the aminolysis reaction proceeds very rapidly, faster than the other, except **TBD**-catalyzed system, but after 1 hour, it is obvious that the reaction rate is lower than **DBU**-catalyzed system.

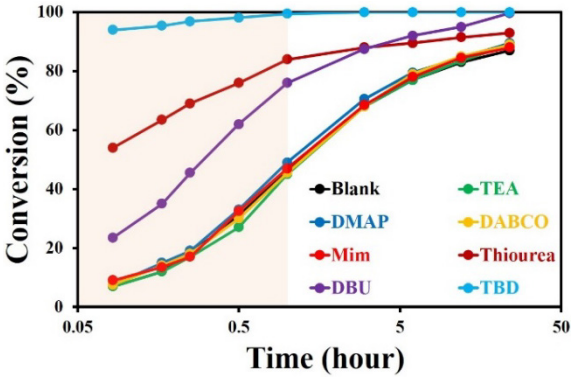
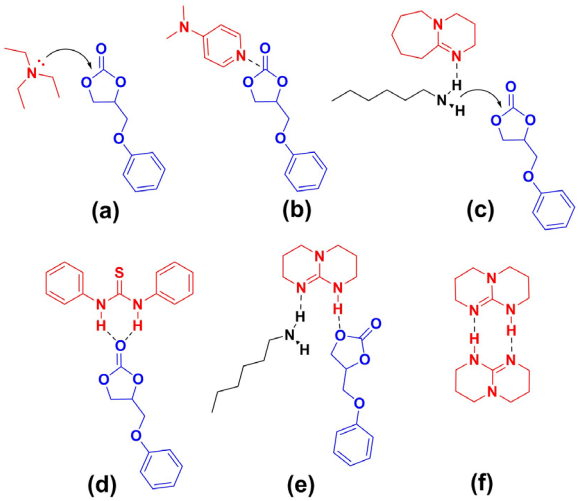


Figure 1. Semi-logarithmic time-conversion plots of the reactions of **5CC** and hexylamine without (Blank) and with a series of catalysts at 23 °C.

The reaction between five-membered cyclic carbonate and primary amine is well known to proceed with overall second-order kinetics – $d[C]/dt = k[C]^2$, wherein $[C]$ = [5CC] = [hexylamine]. Thus the rate constant k in respective systems catalyzed by various types of amines can be calculated from the slope of the linear region of the $1/[C] - 1/[C]_0$ versus time plots in Figure 2, wherein $[C]_0$ and $[C]$ are the initial concentration and concentration at any time, respectively and summarized in Table 1. It can be found that the rate constant of **TBD** is 34.5 L mol^{-1} h^{-1}, almost 100 times higher than the blank system without catalyst, **TEA**, **DMAP**, **DABCO** and **Mim**. As shown in Scheme 2, **TBD** is a kind of bi-functional catalyst, which can inter-

act with amine and **5CC** simultaneously through hydro



Scheme 2. Mechanisms of various amines on catalyzing **5CC**, **TEA** (a), **DMAP** (b), **DBU** (c), **Thiourea** (d), **TBD** (e) and dimeric structure of **TBD** (f).

gen bonding, in contrast to the other aliphatic, aromatic, thiourea and amidine type catalysts, which interacts only with amine or cyclic carbonate. At the same time, the cyclic structure of **TBD** also facilitates the aminolysis of **5CC** by reducing the distance between hexylamine and **5CC**, as compared to the other catalysts.[14] A significant difference between the reaction system catalyzed by **TBD** and the others is that the chemical shift of the hydroxyl from both primary and secondary alcohols and the water in ^{1}H NMR can be observed in all of the systems after 24 hours, except in **TBD** (Figure S11-S18). This means that **TBD** has a stronger tendency to interact with active protons by hydrogen bonding and it is reasonable to deduce the stronger interactions of **TBD** with hexylamine and **5CC**, compare to the other catalysts.[19] This result can partly support the excellent catalytic efficacy of **TBD**. Furthermore, when the reaction solvent is changed from NMP to the other polar aprotic solvents, like acetone (entry 10 and 11 in Table 1) and chloroform (entry 12 in Table1). As shown in Figure S19, before 5 mins, the reaction with acetone as the solvent catalyzed by 10% or 30% **TBD** proceeds very rapidly, then the kinetic curves level off. With chloroform as the solvent, the shape and trend of the time-conversion curve is similar to the blank system, with the whole body of the curve moving upward. It is reasonable to deduce that the tertiary amine structure in NMP also contributes to the aminolysis reaction of **5CC**; that is, NMP behaves not only as the solvent, but also as the promoter in this reaction. The polarity of the solvent is another factor that is able to influence the catalytic efficacy of **TBD**, by affecting the molecular state of **TBD** in solution. With strong polar NMP (polarity index, *P'* = 6.5) as solvent[20], it is plausible to accept that **TBD** exists as a monomeric form in NMP for the strong intermolecular interactions between **TBD** and NMP like dipole induction and hydrogen bonding. While in the less polar acetone (*P'* = 5.4)[20] and chloroform (*P'* = 4.4)[20], **TBD** is prone to be as dimeric structure through two N-H···N interactions within the –NH-C=N- portions of guanidine without the presence of the highly competitive interactions of solvents (Scheme 2 (f)).[21] Thus the –NH-C=N- portions of guanidine is not free to interact with amine and cyclic carbonate, respectively and the catalytic efficacy of **TBD** deteriorates correspondingly.

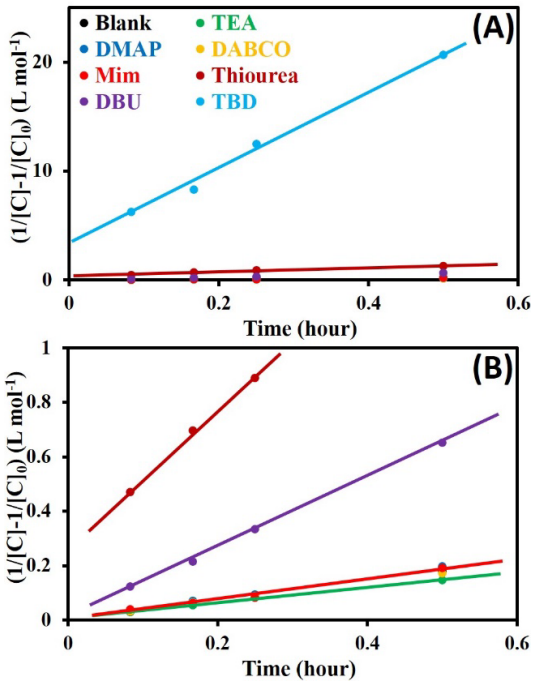
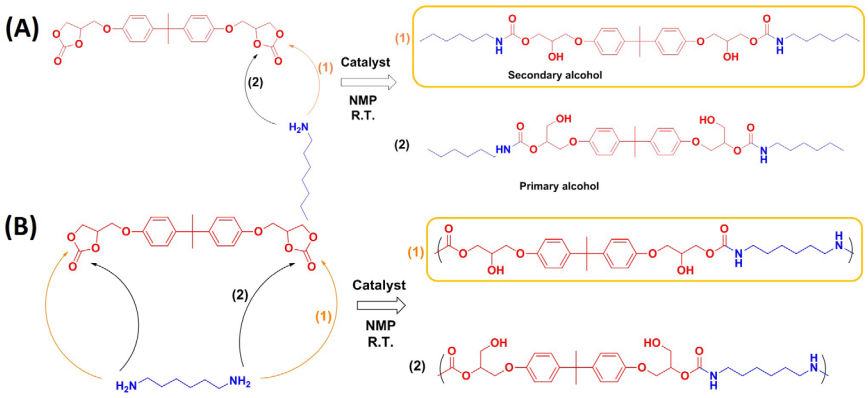


Figure 2. Kinetic plots of the aminolysis reactions of **5CC** at 23 °C, catalyzed by various types of amines at whole scale (A) and regional enlargement (B).



Scheme 3. Aminolysis of **B5CC** by (A) hexylamine (HA) and (B) 1, 6-diaminohexane (DAH) in the presence of **TBD** as catalysts.

Table 2. The aminolysis reactions of bicyclic five-membered cyclic carbonate (**B5CC**) without or with TBD at 23 °C.

Entry	Amine	Catalyst (mol %)	Time (h)	Conv. (%)	*k* (L/mol*h)
1	HA	Blank	24h	85.0	0.20
2	HA	TBD (30)	1h	99.0	19.2
3	DAH	Blank	24h	77.0	-
4	DAH	TBD (30)	1h	95.2	-

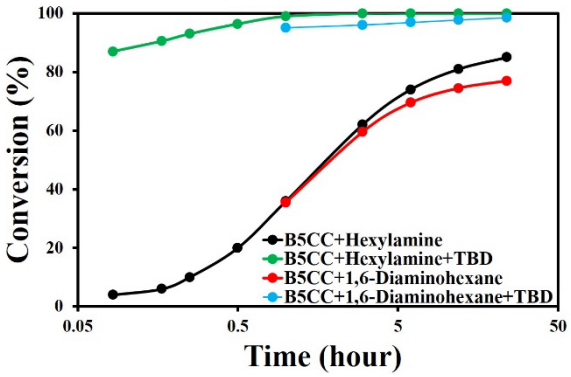


Figure 3. Semi-logarithmic time-conversion plots of the aminolysis reactions of **B5CC** without or with **TBD** at 23 °C.

Furthermore, **TBD**, which has already shown the best catalytic efficacy is chosen for the kinetic studies of bis-functional five-membered cyclic carbonate (**B5CC**) with hexylamine (Scheme 3A) and *1, 6*-diaminohexane (Scheme 3B), respectively. For kinetic investigations, the characteristic phenyl at 6.75-6.85 ppm (2*H*) in **B5CC** is used as the internal reference and the integration of methylene protons at 4.50-4.70 ppm (2*H*) adjacent to oxygen in **B5CC** is monitored to calculate the conversion of **B5CC** with time. The representative ^{1}H NMR spectra of the **B5CC**/hexylamine (*1, 6*-diaminohexane) systems without (Blank) or with **TBD** after reacting for 1 hour are shown in Figure S20-23. The plots of

Table 3. Step-growth polymerization of B5CC and 1, 6-diaminohexane catalyzed by TBD at 23 °C.[a]

Entry	TBD (mol %)	Yield (%)	M_n (g mol^{-1})	$Đ$
1	30	93	7400	1.5
2	60	88	7500	1.4

[a] The polymerization performed in NMP at room temperature for 4 h.

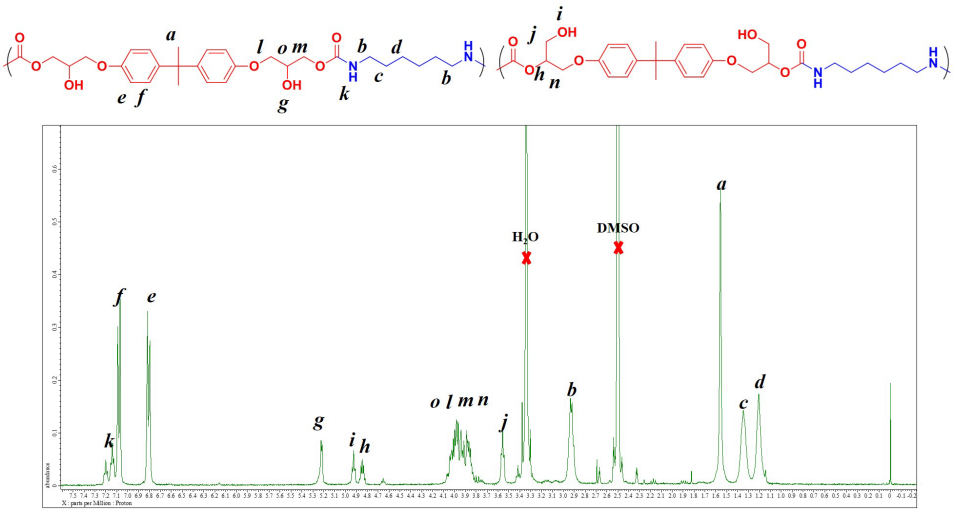


Figure 4. ^{1}H NMR spectrum ($CDCl_3$) of **PHU** (Table 3, entry 1)

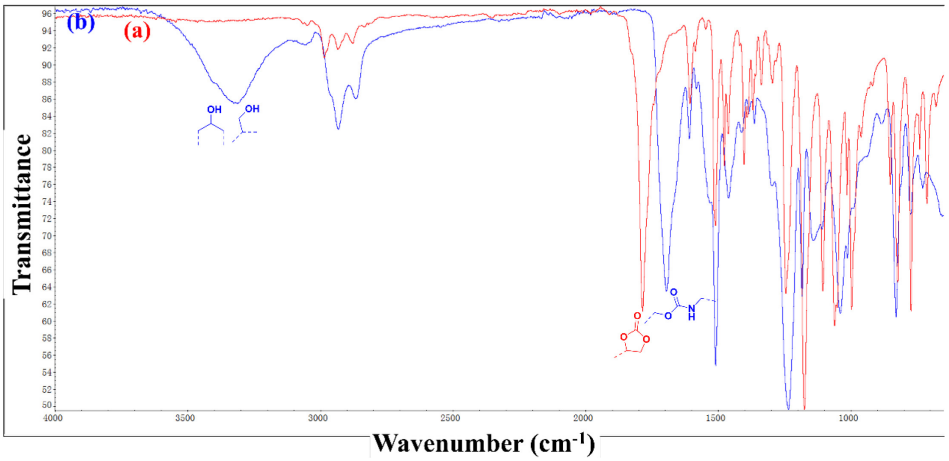


Figure 5. ATR-FT-IR spectra of **B5CC** (a) and the polymerization product PHU (Table 3, entry 1).

time-conversion are displayed in Figure 3, which indicate that **TBD** is also an excellent catalyst on the aminolysis reaction of **B5CC** and the reactions of **B5CC** with hexylamine proceed a little faster than those with *1, 6*-diaminohexane, whether with or without **TBD** and this phenomenon is more obvious at high conversions. This can be ascribed to the viscosity effect in the polymerization system of **B5CC** and *1, 6*-diaminohexane, wherein the diffusion of monomers is gradually hindered by the building-up of the viscosity of the system. As shown in Table 2, the reaction rate constants of **B5CC**/hexylamine without or with **TBD** are cal-

culated as second-order reaction, which are a little lower than those of **5CC**/hexylamine, and this can be ascribed to the more sluggish motions of **B5CC**, compared to **5CC** in the solution state. It has been reported that some side reactions might happen during the ring-opening of **5CC** by amines, especially in the absence of catalyst at high temperature (80 °C).[22] With TBD as catalyst at high temperature (higher than 120 °C), the undesired formation of by-product diol has no contributions on the polymerization of **B5CC** with a series of diamines.[23] Recently, it has been found that room temperature (around 20 °C) can be a compromise on both the selective formation of carbamate structure in urethane and avoiding formation of diol structure.[24] The ^{1}H NMR spectrum (Figure S24) of the model reaction of **5CC** with hexylamine show the absence of the diol (3-phenoxy-1, 2-propanediol[25]) structure, which reveals that the optimization condition with TBD as catalyst and NMP as solvent at room temperature (around 23 °C) can be applied for the polymerization of **B5CC** with diamine.

According to Figure 3, the optimized reaction time 4 hours is chosen for the polymerization of **B5CC** with *1, 6*-aminohexane on considering both the monomer conversion and batch efficiency. The ^{1}H NMR spectrum of the obtained polymerization product poly(hydroxyurethane)s (**PHU**s) (Table 3, entry 1) is shown in Figure 4, the chemical shifts corresponding to the monomer **B5CC** (Figure S2) have totally disappeared in the obtained **PHU**. The newly-appeared chemical shifts indicate the successful aminolysis of **B5CC** with *1, 6*-diamonohexane catalyzed by **TBD** at room temperature in only 4 hours. The ^{1}H NMR spectrum is consistent with our previous report that the ring-opening of **B5CC** to form secondary hydroxyl (path 1 in Scheme 3B) is the major route for the reason of thermodynamics.[12] The ATR-FT-IR spectrum discloses that the characteristic carbonyl bands at 1785 cm^{-1} from the cyclic carbonate has completely disappeared after 4 hours, which is in accordance with the kinetic results by ^{1}H NMR and the newly formed amide bands by the aminolysis of cyclic carbonate appears at 1695 cm^{-1}. The wide absorption around 3300 cm^{-1} can be ascribed to the primary and secondary hydroxyls from the ring-opening reaction of cyclic carbonate. As shown in Table 3, further increasing the **TBD** content has no obvious effect on the molecular weight of **PHU**. Compared to the previous reports, which need high reaction temperature (100 °C)[26] and long reaction time (40 days)[27], with **TBD** as catalyst and NMP as solvent, the aminolysis of **B5CC** can be accomplished at room temperature in less than 4 hours to reach a higher 95% conversion of monomer and obtain the **PHU** with a moderate molecular weight.

Conclusion

A series of organic amines, including the aliphatic- (**TEA** and **DABCO**) and aromatic- (**DMAP**), monocyclic (**Mim**) and bicyclic amidine- (**DBU**), thiourea- and bicyclic guanidine-type (**TBD**) have been investigated systemically on catalyzing the aminolysis of five-membered cyclic carbonate (**5CC**) in NMP as the reaction solvent at room temperature. It has been found that NMP acts as both solvent and promoter for the aminolysis of **5CC** and the bicyclic guanidine **TBD** exhibits an excellent catalytic behavior, compared to the other types of amines. The reaction rate constant of the guanidine-type **TBD** is 100 times higher than those of the aliphatic and aromatic amines (**TEA**, **DABCO**, **Mim** and **DMAP**), which reveals the potential of the guanidine-type structure for developments of catalysts in the future. In addition, the polymerization of **B5CC** and *1, 6*-diaminohexane in NMP with **TBD** as catalyst can complete in less than 4 hours at room temperature to obtain **PHU**s with M_n of about 7500 g mol^{-1}.

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References

1. M. S. Kathalewar, P. B. Joshi, A. S. Sabnis, V. C. Malshe, *RSC Adv.* **2013**, 3, 4110-4129.

2. B. Nohra, L. Candy, J. -F. Blanco, C. Guerin, Y. Raoul, Z. Mouloungui, *Macromolecules* **2013**, 46, 3771-3792.
3. H. Sardon, A. C. Engler, J. M. W. Chan, J. M. García, D. J. Coady, A. Pascual, D. Mecerreyes,; G. O. Jones, J. E. Rice, H. W. Horn, J. L. Hedrick, *J. Am. Chem. Soc.* **2013**, 135, 16235-16241.
4. S. -H. Pyo, P. Persson, M. A. Mollaahmad, K. Sörensen, S. Lundmark, R. Hatti-Kaul, *Pure Appl. Chem.* **2012**, *84*, 637-661.
5. A. Cornille, M. Blain, R. Auvergne, B. Andrioletti, B. Boutevin, S. Caillol, *Polym. Chem.* **2017**, 8, 592-604.
6. M. Helou, J. -F. Carpentier, S. M. Guillaume *Green Chem.* **2011**, 13, 266-271.
7. H. Tomita, F. Sanda, T. Endo, *J. Polym. Sci., Part A: Polym. Chem.* **2001**, 39, 162-168.
8. H. Tomita, F. Sanda, T. Endo, *J. Polym. Sci., Part A: Polym. Chem.* **2001**, 39, 4091-4100.
9. D. C. Webster, *Prog. Org. Coat.* **2003**, 47, 77-86.
10. M. North, R. Pasquale, C. Young, *Green Chem.* **2010**, 12, 1514-1539.
11. L. Maisonneuve, O. Lamarzelle, E. Rix, E. Grau, H. Cramail, *Chem. Rev.* **2015**, 115, 12407-12439.
12. H. Tomita, F. Sanda, T. Endo, *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 3678-3685.
13. Y. He, V. Goel, H. Keul, M. Möller, *Macromol. Chem. Phys.* **2010**, 211, 2366-2381.
14. A. Bossion, K. V. Heifferon, L. Meabe, N. Zivic, D. Taton, J. L. Hedrick, T. E. Long, H. Sardon, *Prog. Polym. Sci.* **2019**, 90, 164-210.
15. J. Sun, W. Cheng, Z. Yang, J. Wang, T. Xu, J. Xin, S. Zhang, *Green Chem.* **2014**, 16, 3071-3078.
16. M. Blain, L. Jean-Gérard, R. Auvergne, D. Benazet, S. Caillol, B. Andrioletti, *Green Chem.* **2014**, 16, 4286-4291.
17. C. D. Diakoumakos, D. L. Kotzev, *Macromol. Symp.* **2004**, 216, 37-46.
18. M. Fleischer, H. Blattmann, R. Mülhaupt, *Green Chem.* **2013**, 15, 934-942.
19. S. W. Ng, P. Naumov, S. Chantrapromma, S. S. S. Raj, H. -K. Fun, A. R.Ibrahimd, G. Wojciechowski, B. Brzezinski, *J. Mol. Struct.* **2001**, 562, 185-196.
20. L. R. Snyder, *J. Chromatogr.* **1974**, 92, 223-230.
21. M. P. Coles, M. S. Khalaf, R. M. Claramunt, M. A. García, I. Alkorta, J. Elguero, *J. Phys. Org. Chem.* **2010**, 6, 526-535.
22. V. Besse, F. Camara, F. Méchin, E. Fleury, S. Caillol, J. -P. Pascault, B. Boutevin *Eur. Polym. J.* **2015**, 71, 1-11.
23. A. Bossion, R. H. Aguirresarobe, L. Irusta, D. Taton, H. Cramail, E. Grau, D. Mecerreyes, C. Su, G. Liu, A. J. Müller, H. Sardon *Macromolecules* **2018**, 51, 5556-5566.
24. W. Guo, J. Gýnzalez-Fabra, N. A. G. Bandeira, C. Bo, A. W. Kleij Angew. Chem. **2015**, 127, 11852-11856.
25. https://sdbs.db.aist.go.jp/sdbs/cgi-bin/landingpage?spcode=HSP-42-916
26. C. Wulf, M. Reckers, A. Perechodjuk, T. Werner, *ACS Sustainable Chem. Eng.* **2020**, 8, 1651-1658.
27. H. Tomita, F. Sanda, T. Endo, *J. Polym. Sci., Part A: Polym. Chem.* **2001**, 39, 851-859.