

Supporting information for

Towards high-performance polyurethanes: A mechanism of amine catalyzed aromatic imide formation from the reaction of isocyanates with anhydrides

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1. General

1.1 Materials and methods

Phthalic anhydride ($\geq 99\%$), phthalic acid ($\geq 99.5\%$), phenyl isocyanate ($\geq 98\%$), 1,3-diphenylurea (98%), triethylamine (99.5%), pyromellitic dianhydride (97%), hexyl isocyanate (97%), triethyl phosphate ($\geq 99.8\%$), *N*-butylamine ($\geq 99.5\%$), dibutylamine ($\geq 99.5\%$), *N,N*-diisopropylethylamine ($\geq 99\%$), tributylamine ($\geq 99.5\%$), *N,N*-dimethylcyclohexylamine (99%), 4-methylmorpholine ($\geq 99.5\%$), 4-(dimethylamino)pyridine ($\geq 99\%$), 1,4-diazabicyclo[2.2.2]octane (DABCO) ($\geq 99\%$), 1,5,7-triazabicyclo[4.4.0]dec-5-en (TBD) (98%), *N*-methylaniline (98%), 4-methoxy-*N*-methylaniline (98%), *N*-methyl-*o*-toluidine ($\geq 95\%$), imidazole (99%), diphenylamine (99%), ϵ -caprolactam (for synthesis), phthalimide ($\geq 99\%$), *p*-tolyl isocyanate (99%) were purchased from Sigma-Aldrich and all the reagents were used directly without treatment. Polymeric MDI, Lupranate® M20 (NCO content=31.5%, $f_n=2.7$, calculated average molecular weight $M_n=360$ g/mol) was kindly provided by BASF Polyurethanes GmbH. Dimethylformamide (DMF) and tetrahydrofuran (THF, without stabilizer BHT) was directly obtained from the dry solvent system. Triethyl phosphate ($\geq 99.8\%$) was purchased from Sigma-Aldrich and dried with mol-sieves before use.

Liquid chromatography-mass spectrometry (LC-MS) measurement for identification of intermediates was carried out on a LCQ Fleet ESI-MS (Thermo Fisher Scientific) with H₂O containing 0.1% formic acid as eluents. Sample was diluted in water/acetonitrile (1:1) solution with a concentration of 1 mg/mL for LC-MS measurement.

¹H nuclear magnetic resonance (NMR) spectroscopy measurement was performed using either Bruker UltraShield 400 MHz or Varian Mercury 400 MHz spectrometer at room temperature using acetone-*d*₆ or DMSO-*d*₆ as solvent with 32 scans per spectrum.

¹³C NMR spectroscopy for monitoring the reactions was performed using either Bruker UltraShield 400 MHz or Varian Mercury 400 MHz spectrometer at room temperature using acetone-*d*₆ or DMSO-*d*₆ as solvent with 256 scans per spectrum. For characterization of compounds, a number of 1024 scans were used.

1.2 Synthesis procedures

1.2.1 Study of reaction between phthalic anhydride and phenyl isocyanate (2)

Phthalic anhydride (28.0 mg, 0.19 mmol) and phenyl isocyanate (22.6 mg, 0.19 mmol) were dissolved by DMSO-*d*₆ (ampule) in an NMR tube. The reaction was monitored with ¹H and ¹³C NMR spectroscopy.

1.2.2 Study of reaction between phthalic anhydride and 1,3-diphenyl urea (3a)

Phthalic anhydride (0.6 g, 4.07 mmol) and 1,3-diphenyl urea (0.43 g, 2.03 mmol) were dissolved in 5.3 mL DMF in a dry 2-neck flask equipped with a condenser. The reaction was carried out at 140 °C in an oil bath under an Ar atmosphere overnight and monitored with ¹³C NMR spectroscopy.

1.2.3 Study of reaction between phthalic acid and phenyl isocyanate (3b)

Phthalic acid (0.9 g, 5.23 mmol) and phenyl isocyanate (0.6 g, 5.23 mmol) were dissolved in 7.5 mL THF in a dry 2-neck flask equipped with a condenser. The reaction was carried out at 80 °C in an oil bath in THF reflux under an Ar atmosphere for 5 h and then triethylamine (5 mg, 0.05 mmol) was added in the solution. The solution was stirred overnight and the reaction was monitored with ¹³C NMR spectroscopy.

1.2.4 Study of reaction between pyromellitic dianhydride and hexyl isocyanate (4)

Pyromellitic dianhydride (1.6 g, 7.45 mmol) and hexyl isocyanate (1.9 g, 14.90 mmol) were dissolved in 18 mL THF in a dry 2-neck flask equipped with a condenser. Then water (2.7 mg, 0.15 mmol) was added in the solution and the reaction was carried out at 80 °C in an oil bath in THF reflux under an Ar atmosphere overnight. After that, most of the solvent was blown by an Ar flow. The reaction was monitored with ¹H NMR spectroscopy and obtained product was analyzed using LC-MS.

1.2.5 Study of reaction between pyromellitic dianhydride and polymeric MDI (5)

The reaction between pyromellitic dianhydride and polymeric MDI using *N*-methylaniline as a pre-catalyst and *N,N*-dimethylcyclohexylamine as a co-catalyst is used as an example to illustrate the general synthetic route:

A mixture of pyromellitic dianhydride (1.1 g, 4.83 mmol) and Lupranate® M20 (20.0 g, 55.6 mmol) in a dry 2-neck flask and was heated to 100 °C under an Ar atmosphere. A pre-catalyst solution was prepared by dissolving *N*-methylaniline (0.1 g, 1.11 mmol) and *N,N*-dimethylcyclohexylamine (28.5 mg, 0.22 mmol) in 2 mL triethyl phosphate. Then the pre-catalyst solution was added into the flask and the reaction was carried out at 140 °C in an oil bath. The reaction was monitored with ¹³C NMR spectroscopy and the time when carbonyl peaks of anhydride and mono-imides could no longer be observed was defined as reaction time. Dark brown liquid was obtained at 140 °C, which solidified over the time at room temperature.

1.3. Computational details

DFT calculations were employed to compute the reaction free energies of the investigated species to decipher the underlying reaction mechanism and to rationalize the experimental observations. For the protocol, the input structures of all molecules were generated by applying the conformer-rotamer ensemble sampling tool (CREST)^[1] at the GFN2-xTB^[2] and GFN-FF^[3] level of theory with the implicit GBSA(THF) solvation model.^[4] The energetically lowest-lying conformers were then determined out of both runs. These conformers (up to 200 structures) were further optimized using the DFT method

TPSS with a def2-TZVP basis set.^[5] The D3 dispersion correction and the implicit COSMO solvation model ($\epsilon = \infty$) were applied throughout.^[6,7] Free energies were calculated based on the optimized geometries by utilizing a multilevel approach. High level single-point energies were calculated with the hybrid density functional M06-2x^[8] with a large def2-QZVP basis set. Solvation contributions to the free energy were calculated with COSMO-RS,^[9,10] also including the volume work to convert an ideal gas at 1 bar to a solution of 1 mol L⁻¹. All quantum mechanical calculations were performed with the TURBOMOLE 7.5.1 (DFT) and xtb 6.4.1 (GFN2-xTB, and GFN-FF) program packages.^[11,12]

For the COSMO-RS free energy, two single-point calculations with BP86/TZ, one in the gas phase and one in an ideal conductor, were performed. The output of these calculations was then processed by the COSMOtherm program. For the COSMO-RS free energy, the BP_TZVP_C30_1601 parameterization was used. Bulk phenyl isocyanate with 10 vol% of TEP was chosen as solvent. Thermostatistical contributions to the free energy were calculated at the same level of theory as the geometry optimization (TPSS-D3/def2-TZVP) applying the rigid-rotor-harmonic-oscillator scheme (RRHO). The temperature was set to 413.15 K.

In the computational approach, total free energies were calculated as sum of the electronic gas phase binding energy ΔE (single-point energy), including the London dispersion contribution, thermostatistical (ΔG_{RRHO}) and solvation ($\Delta\delta G_{solv}$) contribution according to Equation below. The prefix Δ refers to the differences regarding the reaction from reactants to products.

$$\Delta G = \Delta E + \Delta G_{RRHO} + \Delta\delta G_{solv}$$

2. Hydrolysis product in aromatic isocyanate-dianhydride reaction

Formation of the 7-member ring intermediate proposed by Meyer et al. was investigated first. The model reaction between phthalic anhydride and phenyl isocyanate was monitored by ^1H and ^{13}C NMR spectroscopy in $\text{DMSO-}d_6$ (ampule) at room temperature in order to capture the intermediate (Fig. S1). The multiple peaks between 8.14-7.99, 7.99-7.88, 7.58-7.42 and 7.41-7.19 ppm in ^1H NMR spectra are assigned to the aromatic protons of phthalic anhydride, *N*-phenylphthalimide (phthalimide part), *N*-phenylphthalimide (phenyl part) and phenyl isocyanate, respectively. The peaks at 167.0 and 163.2 ppm in ^{13}C NMR spectra are assigned to the carbonyl peaks of phthalic anhydride and *N*-phenylphthalimide, respectively. No evidence of 7-member ring was found. The formation of *N*-phenylphthalimide may be due to the presence of catalytic amount of water in $\text{DMSO-}d_6$.

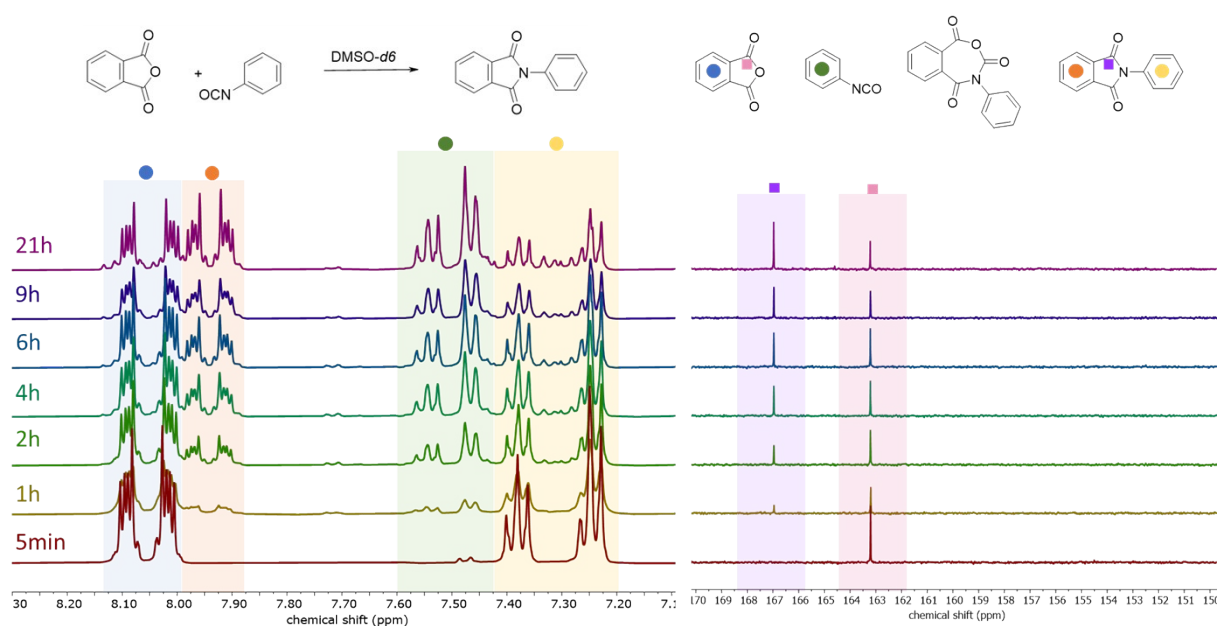
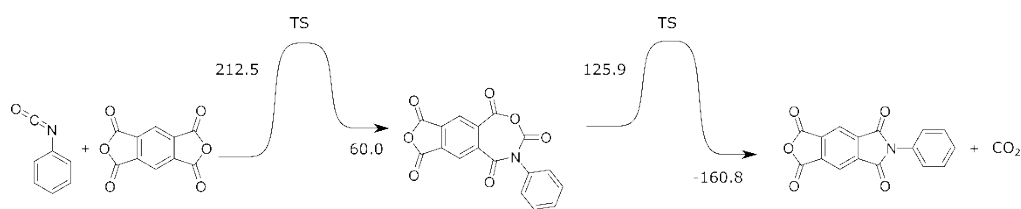
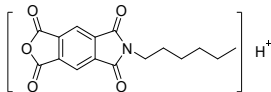
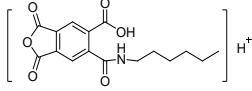
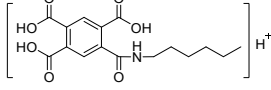
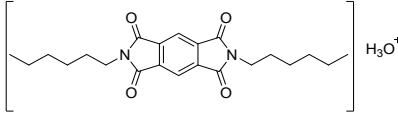
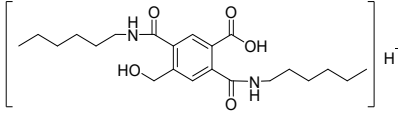
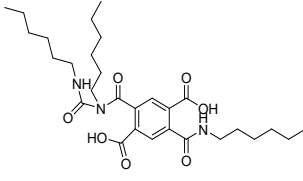
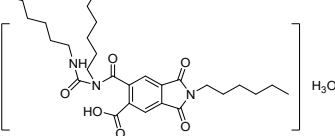
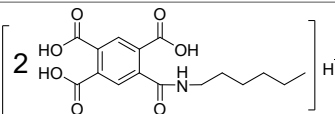
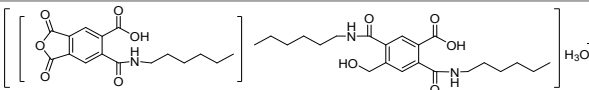
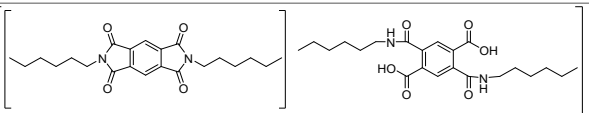
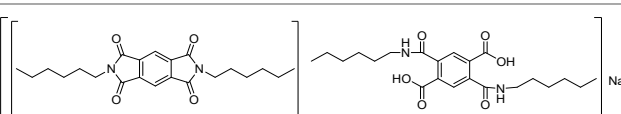
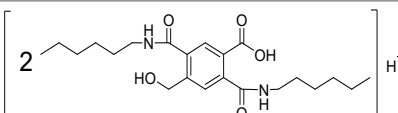


Fig. S1 ^1H NMR spectra (400 MHz, $\text{DMSO-}d_6$) and ^{13}C NMR spectra (400 MHz, $\text{DMSO-}d_6$) of reaction between phthalic anhydride and phenyl isocyanate.



Scheme. S1 QM studies on the proposed seven-member ring reaction mechanism of aromatic isocyanate-anhydride reaction. All values are given in kJ mol^{-1} .

Table S1 LC-MS analysis of the intermediates obtained in the model reaction 4.

	m/z	Abundance (%)	Assignment
I	302.33	11	
II	320.25	12	
III	338.17	100	
IV	403.25	31	
V	421.25	35	
VI	548.25	21	
VII	548.25	21	
VIII	674.75	41	
IX	757.83	27	
X	804.92	18	
XI	826.92	10	
XII	841.00	28	

3. Optimization of the aromatic isocyanate-dianhydride reaction

3.1 Model reaction 5 with H₂O or dibutylamine as a pre-catalyst

The reaction between polymeric MDI (PMDI) and pyromellitic dianhydride in 19:1 weight ratio using 2mol% water or dibutylamine as a pre-catalyst was carried out at 140 °C with 10 vol% TEP (Entry 5-1 and 5-3). The reaction was monitored by ¹³C NMR spectroscopy at the carbonyl carbon region (Fig. S2). During the reaction, the pyromellitic dianhydride carbonyl carbon peak at 162.0 ppm disappeared and the two carbonyl peaks of one-sided imide structure were found at 162.5 and 165.8 ppm, respectively. Further, when pyromellitic dianhydride was fully converted to diimide structure, only one carbonyl carbon peak at 166.3 ppm was observed.

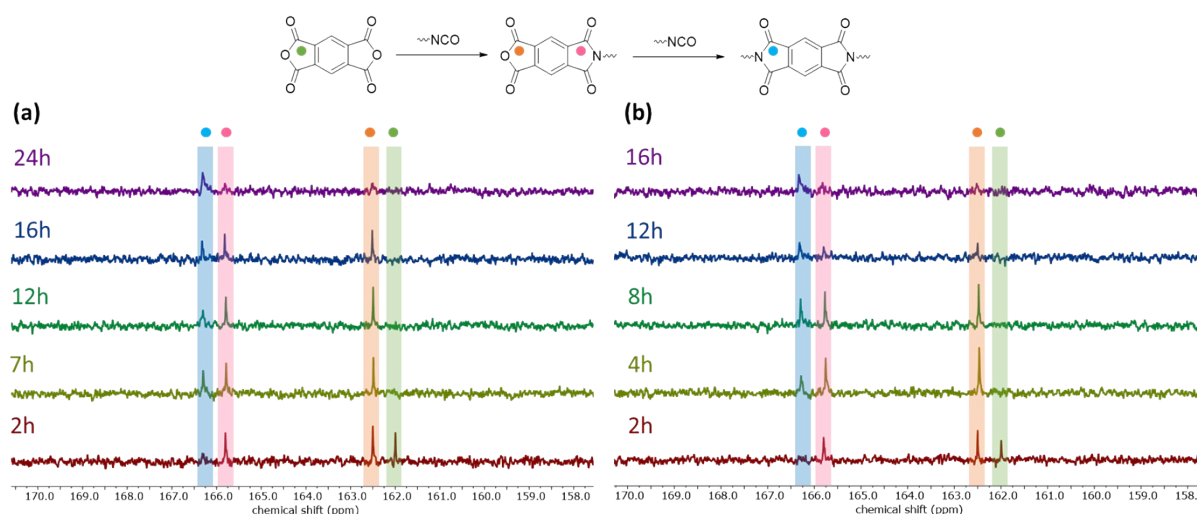


Fig. S2 ¹³C NMR spectra (400 MHz, acetone-*d*₆) of model reaction 5 using (a) water or (b) dibutylamine as a catalyst.

3.2 Hydrolysis product in model reaction 5

In order to confirm that urea is the only hydrolysis product in model reaction 5, pyromellitic acid was used to react with polymeric methylene diphenyl diisocyanate instead of pyromellitic dianhydride in a 1:19 weight ratio. With excess of isocyanates, pyromellitic acid loses one H₂O molecule and forms PMDA. Due to the bad solubility of pyromellitic dianhydride in isocyanate, the carbonyl peak of pyromellitic dianhydride was not shown in the ¹³C NMR spectra, but the urea formed from the reaction between isocyanate and H₂O was found (Fig. S3).

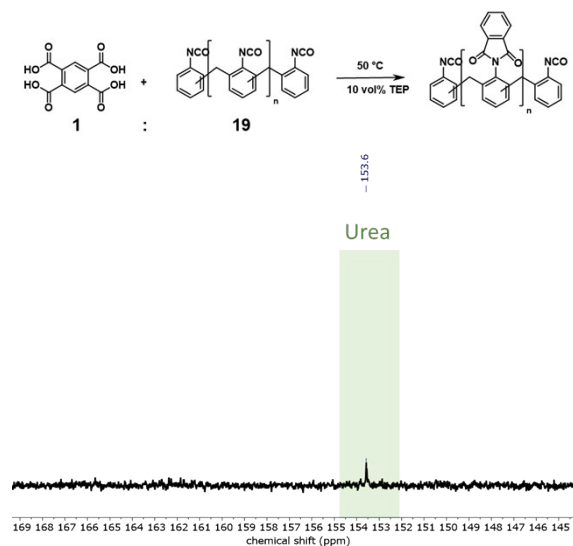


Fig. S3 ^{13}C NMR spectrum (400 MHz, acetone- d_6) of the reaction between pyromellitic acid and polymeric methylene diphenyl diisocyanate in 1:19 weight ratio at 50 $^\circ\text{C}$ with 10 vol% triethyl phosphate. Strong bubbling was observed after 15 min and only carbonyl peak for urea was found.

Similar result was also observed by reacting phthalic acid with polymeric methylene diphenyl diisocyanate in a 1:19 weight ratio. With excess of isocyanates, phthalic acid loses one H_2O molecule and forms phthalic anhydride (Fig. S4).

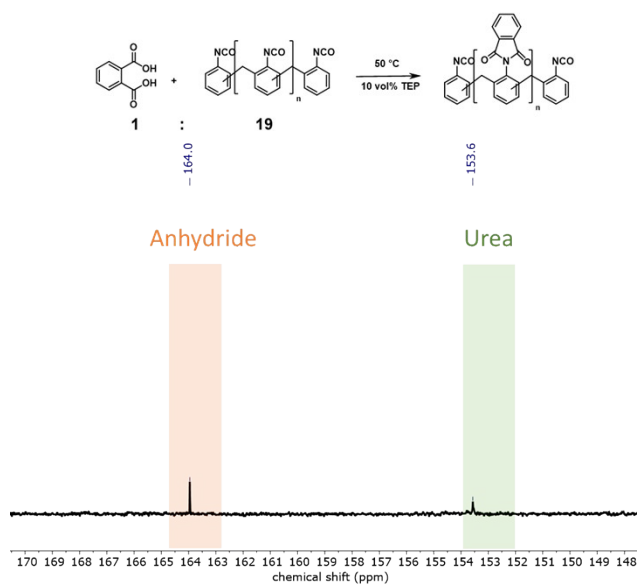


Fig. S4 ^{13}C NMR spectrum (400 MHz, acetone- d_6) of the reaction between phthalic acid and polymeric methylene diphenyl diisocyanate in a 1:19 weight ratio at 50 $^\circ\text{C}$ with 10 vol% triethyl phosphate. Strong bubbling was observed after 15 min and only carbonyl peak for urea was found.

Thus, if an excess of isocyanates reacts with pyromellitic dianhydride in the presence of water, the hydrolysis product can only be urea. This also supports our proposal that water only acts as a pre-catalyst for the formation of urea, which then is the real catalyst of the reaction.

4. Computational studies of aromatic isocyanate-anhydride reaction with secondary amines as catalysts

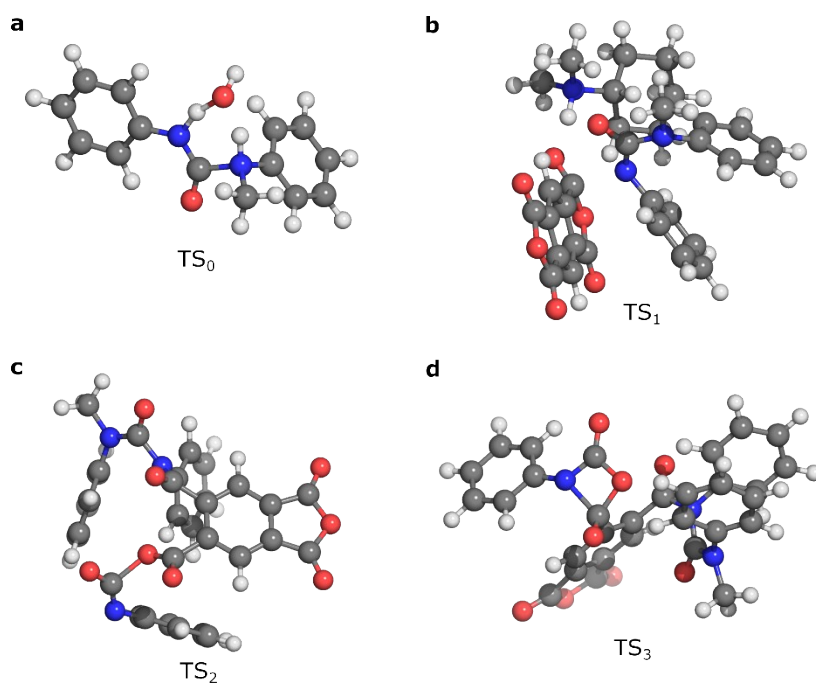


Fig. S5 Refined transition state structures at the TPSS-D3/def2-TZVP level of theory within the reaction of pyromellitic dianhydride and phenyl isocyanate to form the imide.

5. Experimental verification of urea obtained from reaction between secondary amine and isocyanate as the real catalyst

5.1 Results

To verify that the urea is the real catalyst, *N*-methylaniline was reacted with *p*-tolyl isocyanate in 1:1 molar ratio to obtain 1-methyl-1-phenyl-3-(*p*-tolyl) urea (Fig. S6). After that, the 1-methyl-1-phenyl-3-(*p*-tolyl) urea was used as catalyst instead of *N*-methylaniline in model reaction 5, Entry 5-11. The reaction was completed in 8 h, which was slower than that using *N*-methylaniline as a catalyst, which may be due to different solubility of urea's that are obtained from *N*-methylaniline reacted with different isocyanates (Fig. S7).

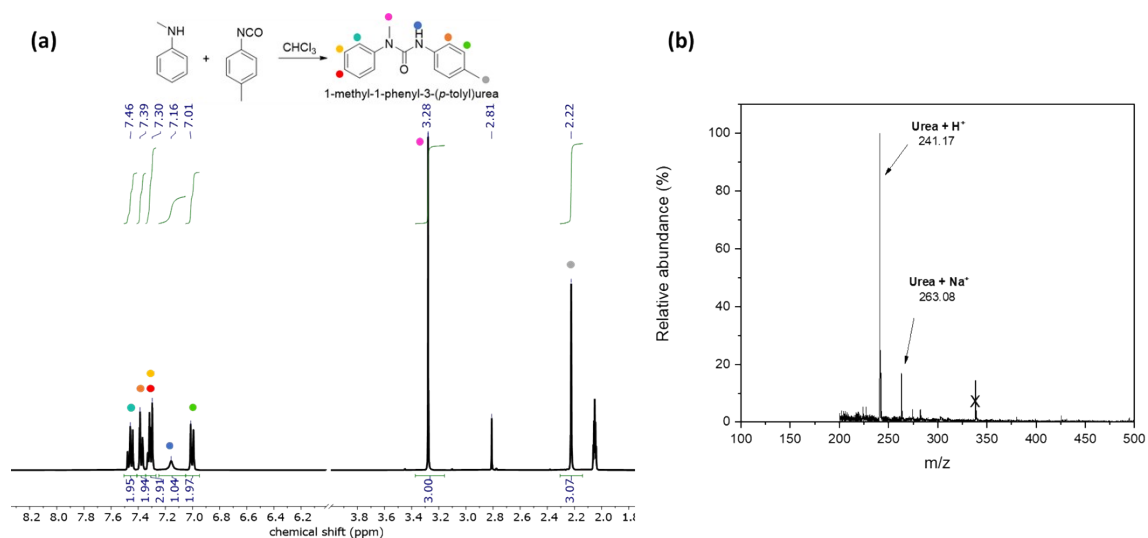


Fig. S6 (a) ^1H NMR spectrum (400MHz, $\text{acetone-}d_6$) and (b) LC-MS spectrum of the 1-methyl-1-phenyl-3-(*p*-tolyl) urea obtained from the reaction between *N*-methylaniline and *p*-tolyl isocyanate.

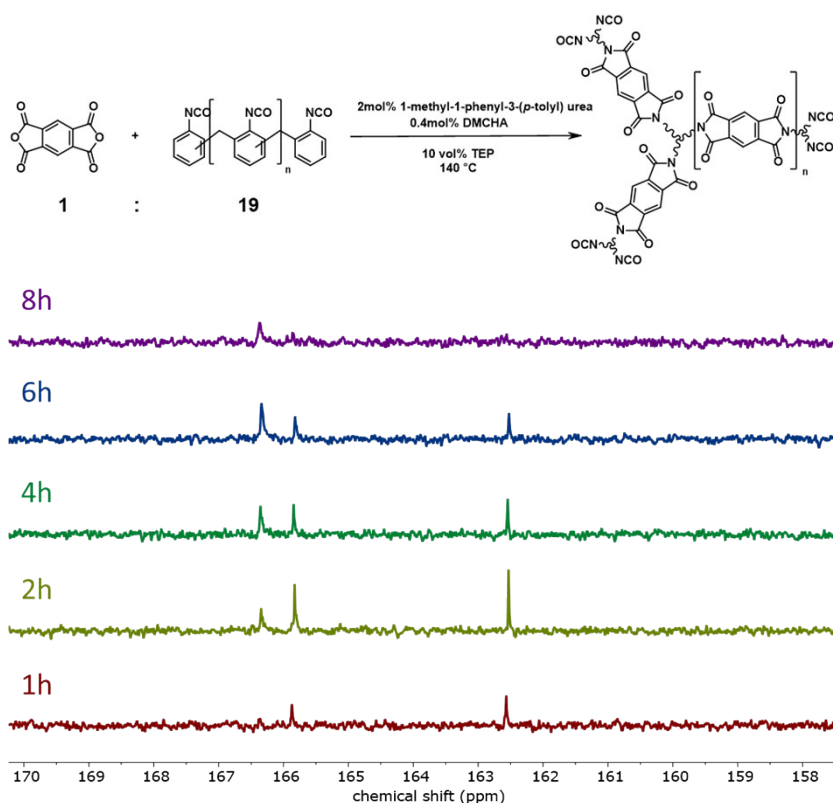


Fig. S7 ¹³C NMR spectra (400 MHz, acetone-*d*₆) of model reaction 5 using 1-methyl-1-phenyl-3-(*p*-tolyl) urea as a catalyst.

Similarly, dibutylamine was reacted with *p*-tolyl isocyanate in 1:1 molar ratio to obtain 1,1-dibutyl-3-(*p*-tolyl) urea (Fig. S8). After that, the 1,1-dibutyl-3-(*p*-tolyl) urea was used as catalyst instead of dibutylamine in model reaction 5, Entry 5-6. The reaction was completed in 14 h (Fig. S9).

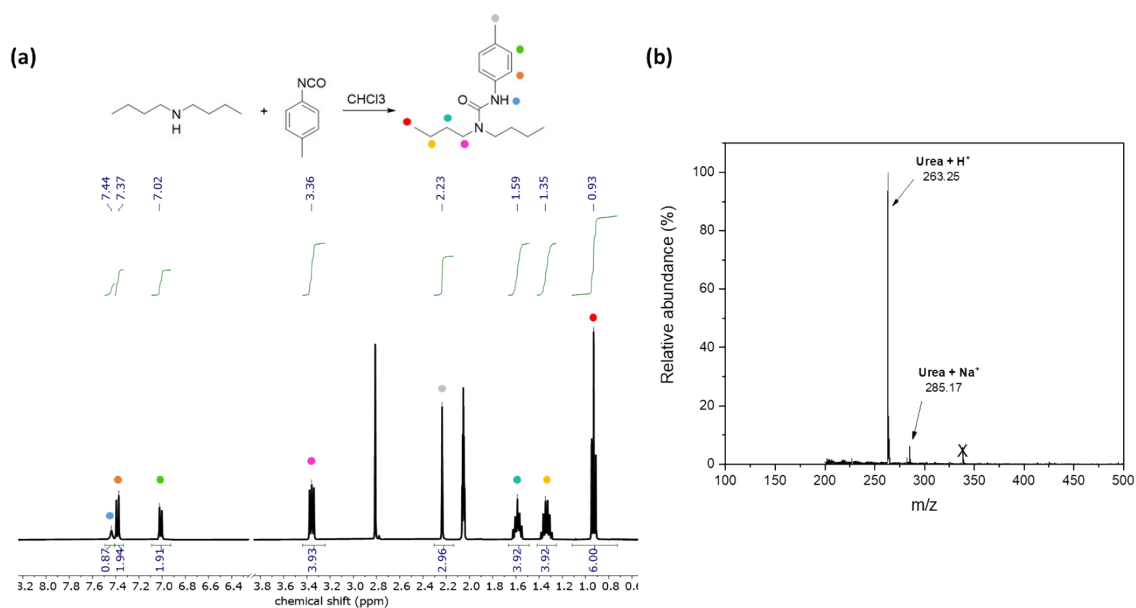


Fig. S8 (a) ¹H NMR spectrum (400MHz, acetone-*d*₆) and (b) LC-MS spectrum of the 1,1-dibutyl-3-(*p*-tolyl) urea obtained from the reaction between dibutylamine and *p*-tolyl isocyanate.

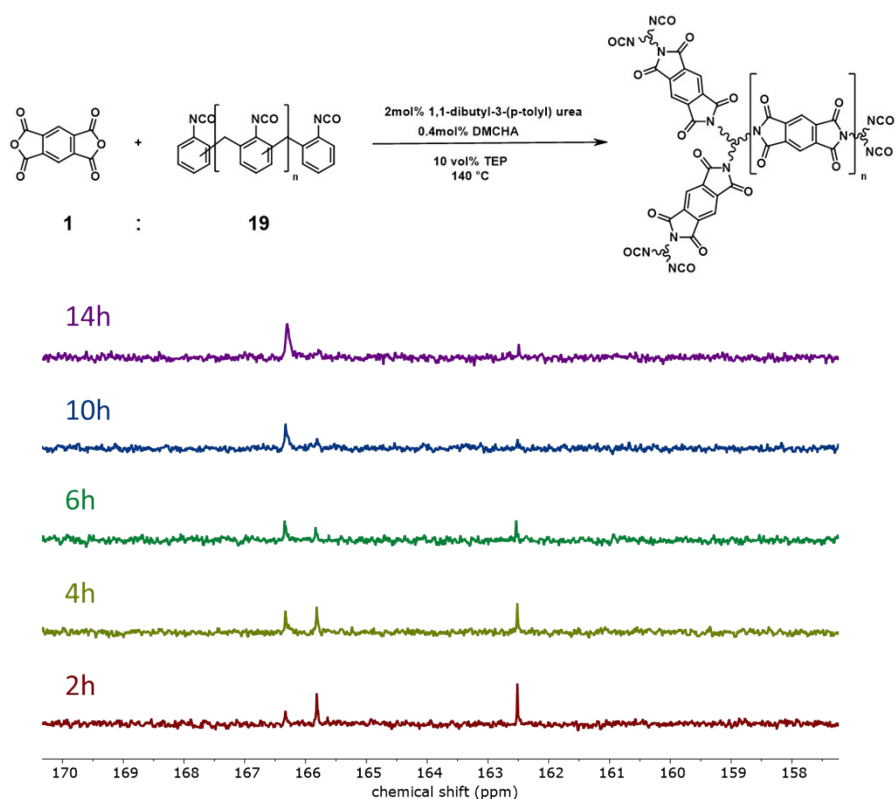


Fig. S9 ^{13}C NMR spectra (400 MHz, acetone- d_6) of model reaction 5 using 1,1-dibutyl-3-(*p*-tolyl) urea as a catalyst.

5.2. Synthesis procedures

Synthesis of 1-methyl-1-phenyl-3-(*p*-tolyl) urea:

N-Methylaniline (1.8 g, 17.12 mmol) and *p*-tolyl isocyanate (2.3 g, 17.12 mmol) were dissolved in 10 mL CHCl_3 and the reaction was carried out at room temperature for 2 h. After that, CHCl_3 was removed by vacuum and the obtained solid was dried at 80 °C oven overnight. Slightly yellow solid was obtained (4.0 g, 97% yield).

Synthesis of 1,1-dibutyl-3-(*p*-tolyl) urea:

Dibutylamine (1.9 g, 14.70 mmol) and *p*-tolyl isocyanate (2.0 g, 14.70 mmol) were dissolved in 10 mL CHCl_3 and the reaction was carried out at room temperature for 1 h. After that, CHCl_3 was removed by vacuum and the obtained solid was dried at 80 °C oven overnight. White solid was obtained (3.7 g, 95% yield).

6. Aliphatic isocyanate-dianhydride reaction when secondary amine is used as a pre-catalyst

A mixture of pyromellitic dianhydride (1.1 g, 4.83 mmol) and hexamethylene diisocyanate (20.0 g, 118.9 mmol) in a dry 2-neck flask was heated to 100 °C under an Ar atmosphere. A catalyst solution was prepared by dissolving *N*-methylaniline (0.1 g, 1.11 mmol) and *N,N*-dimethylcyclohexylamine (28.2 mg, 0.22 mmol) in 2 mL triethyl phosphate. Then the catalyst solution was added to the flask and the solution was heated to 140 °C. The reaction was monitored with ¹³C NMR spectroscopy and the time when carbonyl peaks of anhydride and mono-imides could no longer be observed was defined as reaction time.

It was found that the reaction was finished after 4 h and dark brown liquid was obtained.

7. References

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