Electronic supplementary information

Plastics to Fertilizers: Chemical Recycling of a Bio-based Polycarbonate to a Fertilizer Source

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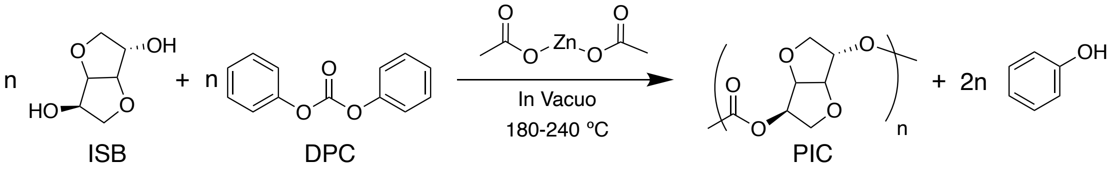
1. Experimental procedure

1.1. Synthesis of PIC



Scheme S-1. Synthesis of PIC.

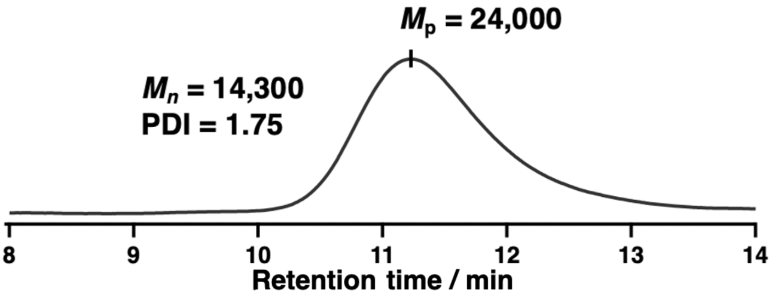


Figure S-1. GPC profile of PIC (eluent: DMF, detector: RI, polystyrene standard).

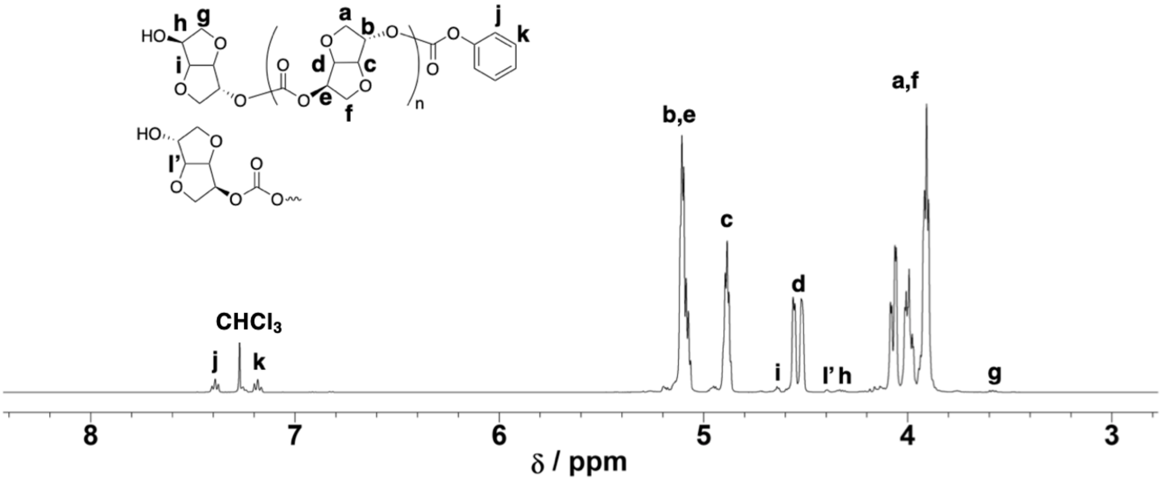


Figure S-2. ^{1}H NMR spectrum of PIC (500 MHz, 25 °C, CDCl$_3$).

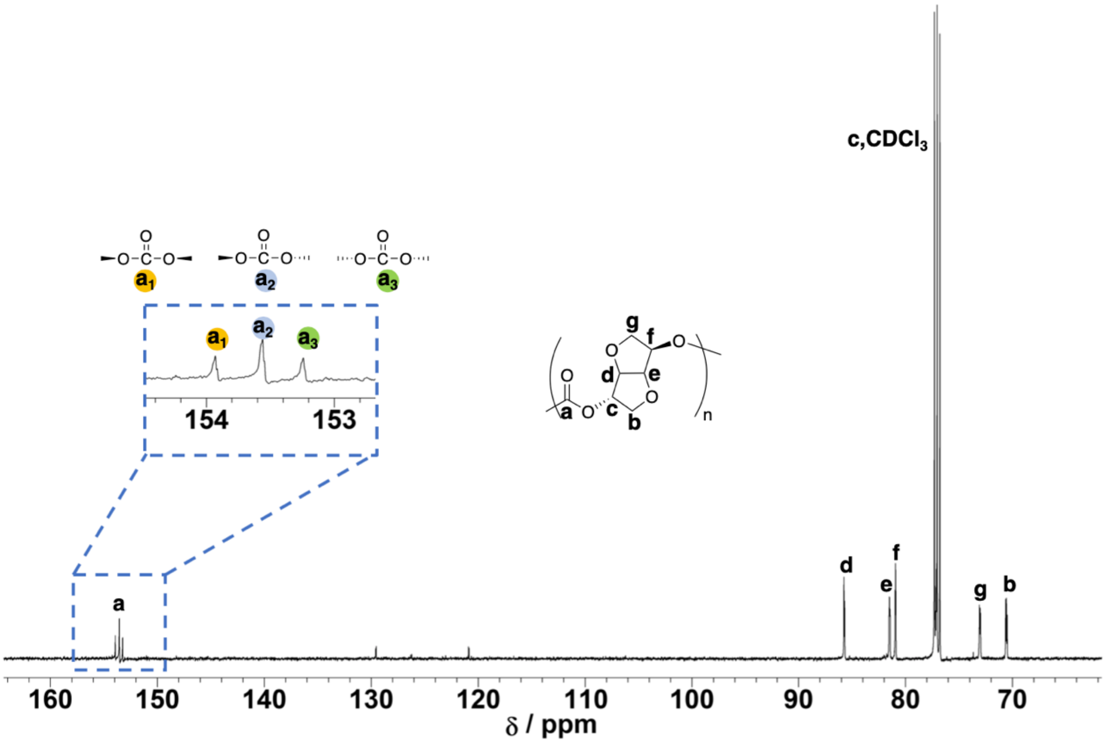
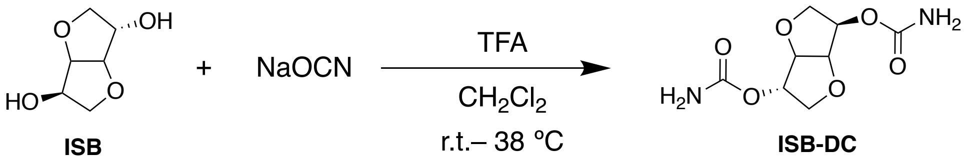


Figure S-3. ^{13}C NMR spectrum of PIC (125 MHz, 25 °C, $CDCl_3$).

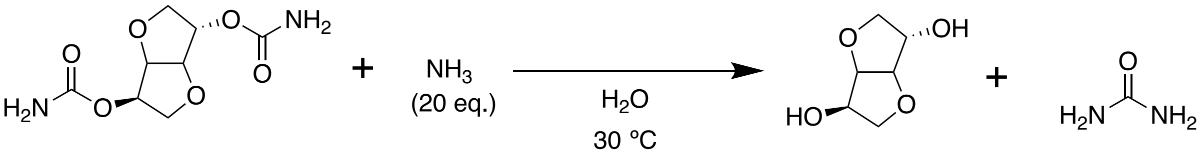
1.2. Synthesis of ISB-DC[1]



Scheme S-2. Synthesis of ISB-DC.

ISB (5.00 g, 34.2 mmol), sodium cyanate (8.91 g, 137 mmol), and 20 mL of dichloromethane were placed in a round-bottomed flask (50 mL). While stirring slowly at room temperature, trifluoroacetic acid (TFA, 12 mL) was added dropwise over a period of 10 min. The temperature was increased to 38 °C and maintained for 30 min, and the mixture was then cooled down to room temperature and continued to stir slowly for 2 h. After this time, a pasty white precipitate was observed, which was washed with methylene chloride and water, filtered, and dried under vacuum. ISB-DC was obtained as a white solid (yield: 1.98 g, 25.9%). ^{1}H NMR (500 MHz, DMSO-d_6): δ/ppm = 6.83–6.36 (br, 4H), 4.93 (dd, J = 10.8, 5.4 Hz, 1H), 4.90–4.86 (m, 1H), 4.66 (t, J = 5.1 Hz, 1H), 4.39–4.35 (m, 1H), 3.39–3.76 (m, 3H), 3.64–3.59 (m, 1H).

1.3. Ammonolysis of ISB-DC



Scheme S-3. Ammonolysis of ISB-DC.

ISB-DC (50.0 mg) was placed in a round-bottomed flask (20 mL). Then, water (3.72 mL) and aqueous ammonia (14.8 mol/L, 1.24 mL) were added to the flask. The reaction mixture was stirred for 24 h, and the rection mixture was then freeze-dried to remove the ammonia and water. The dried degradation product was used for ^{1}H NMR measurement.

2. Ammonolysis evaluation

2.1. Ammonolysis under initial reaction condition

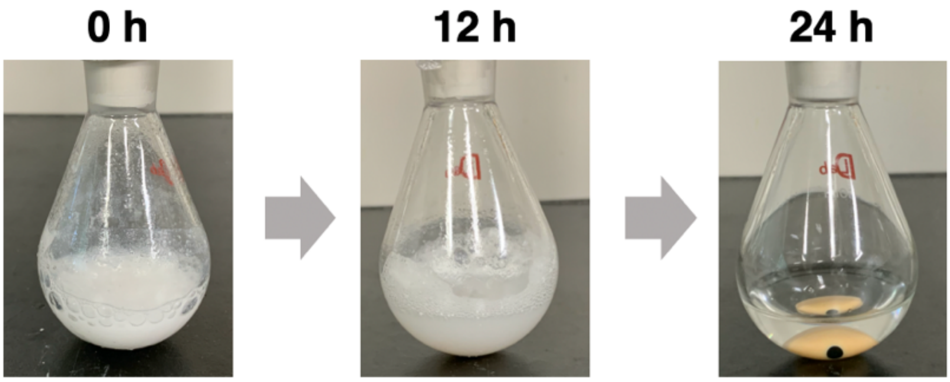


Figure S-4. Photographs of the reaction mixture during ammonolysis.

2.2. Analysis of the degradation products

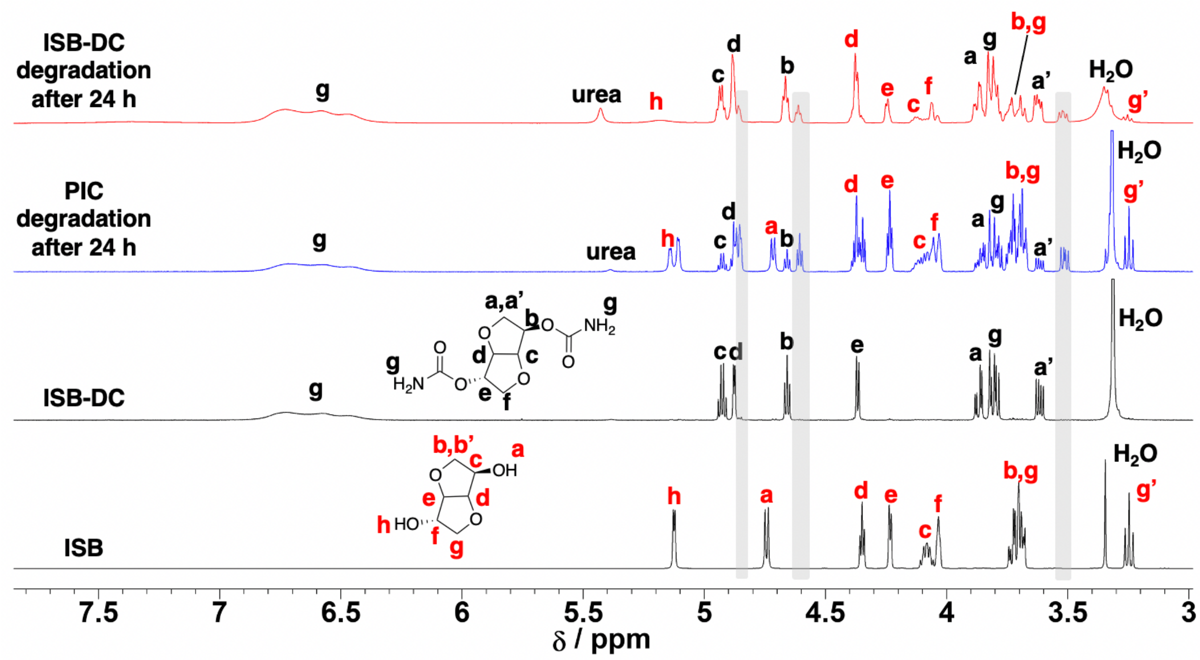


Figure S-5. ^{1}H NMR spectrum of the degradation product of **ISB-DC** after 24 h ammonolysis (red) compared with the degradation product of PIC after 24 h ammonolysis (blue) and raw materials (ISB and **ISB-DC**) (500 MHz, 25 °C, DMSO-*d*$_6$).

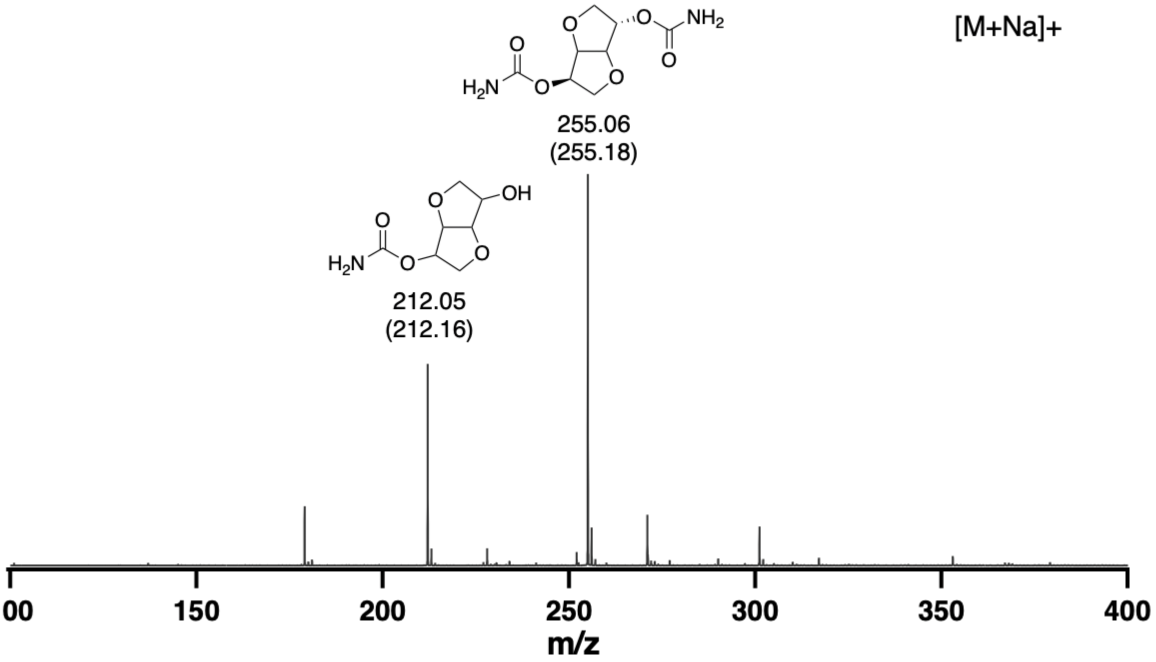


Figure S-6. ESI-TOF MS spectrum for the degradation products (all peaks were detected as [M+Na]+).

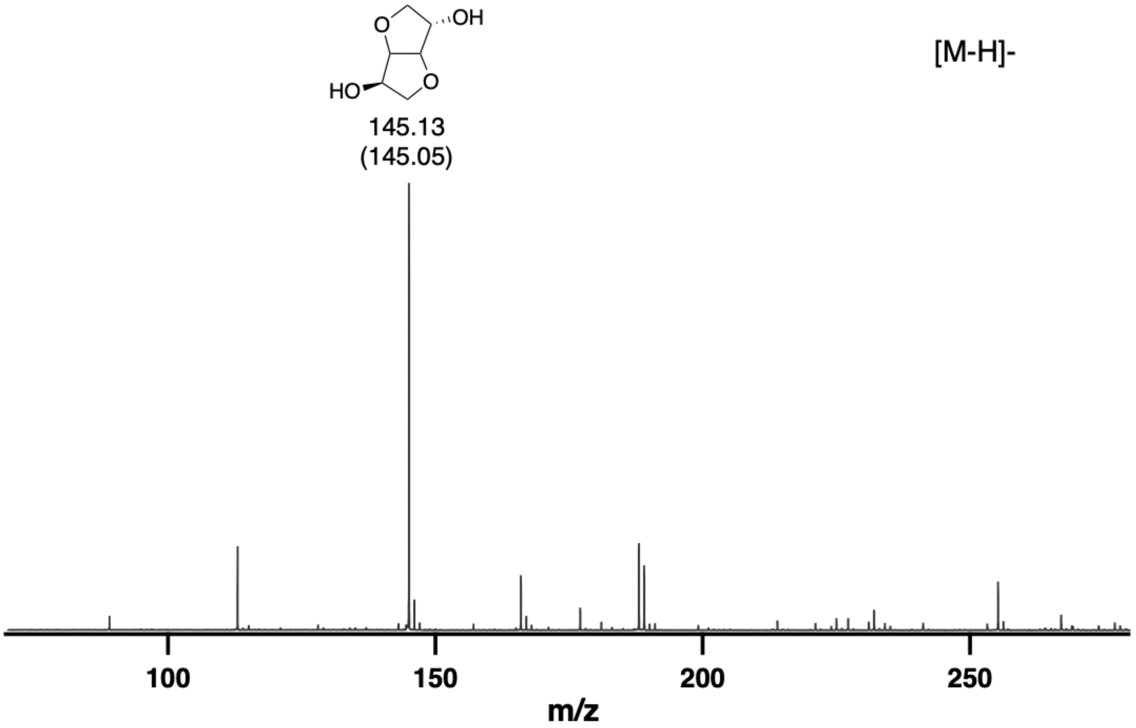


Figure S-7. ESI-TOF MS spectrum for the degradation products (all peaks were detected as [M-H]-).

2.3. Preparation of Calibration curve for ammonolysis of PIC

The samples whose stoichiometric ratios of carbonate bond in PIC to ISB and urea were 10/0/0, 7/3/3, 5/5/5, 3/7/7, 1/9/9 and 0/10/10, were mixed in mortar to prepare degradation standard samples. Each sample was regarded as virtual depolymerized product (for example, the sample which was mixed at the ratio of 7/3/3 stated above was regarded as 30% degradation product; note that all degradation products were assumed to have been completely converted to urea and ISB). Then, the standard samples were analyzed by FT-IR. From the FT-IR spectra, the ratio of transmittance of C=O stretching derived from PIC to the sum of transmittance of C–H stretching derived from PIC and ISB were calculated and plotted against the mixing ratio.

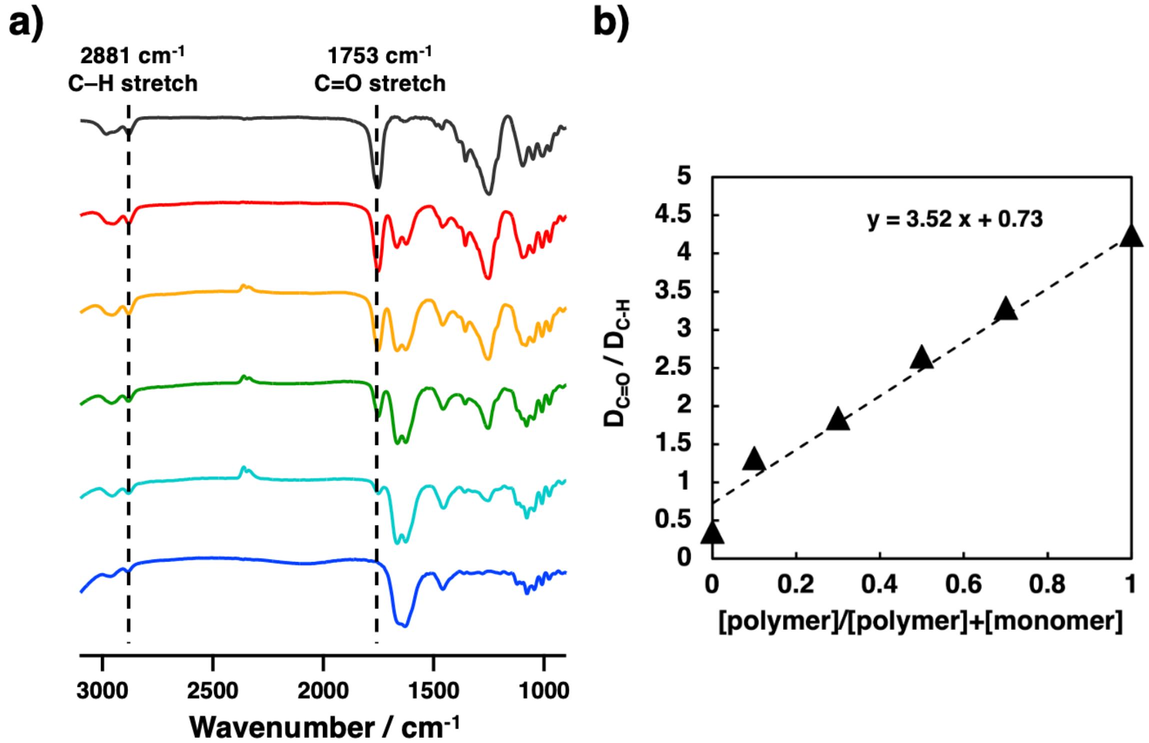


Figure S-8. (a) FT-IR spectra of the standard samples for preparation of the calibration curve (KBr) and (b) Calibration curve for estimation of the remaining carbonate bonds in the degradation products.

2.4. Ammonolysis under different $[NH_3]_0/[PIC]_0$ condition

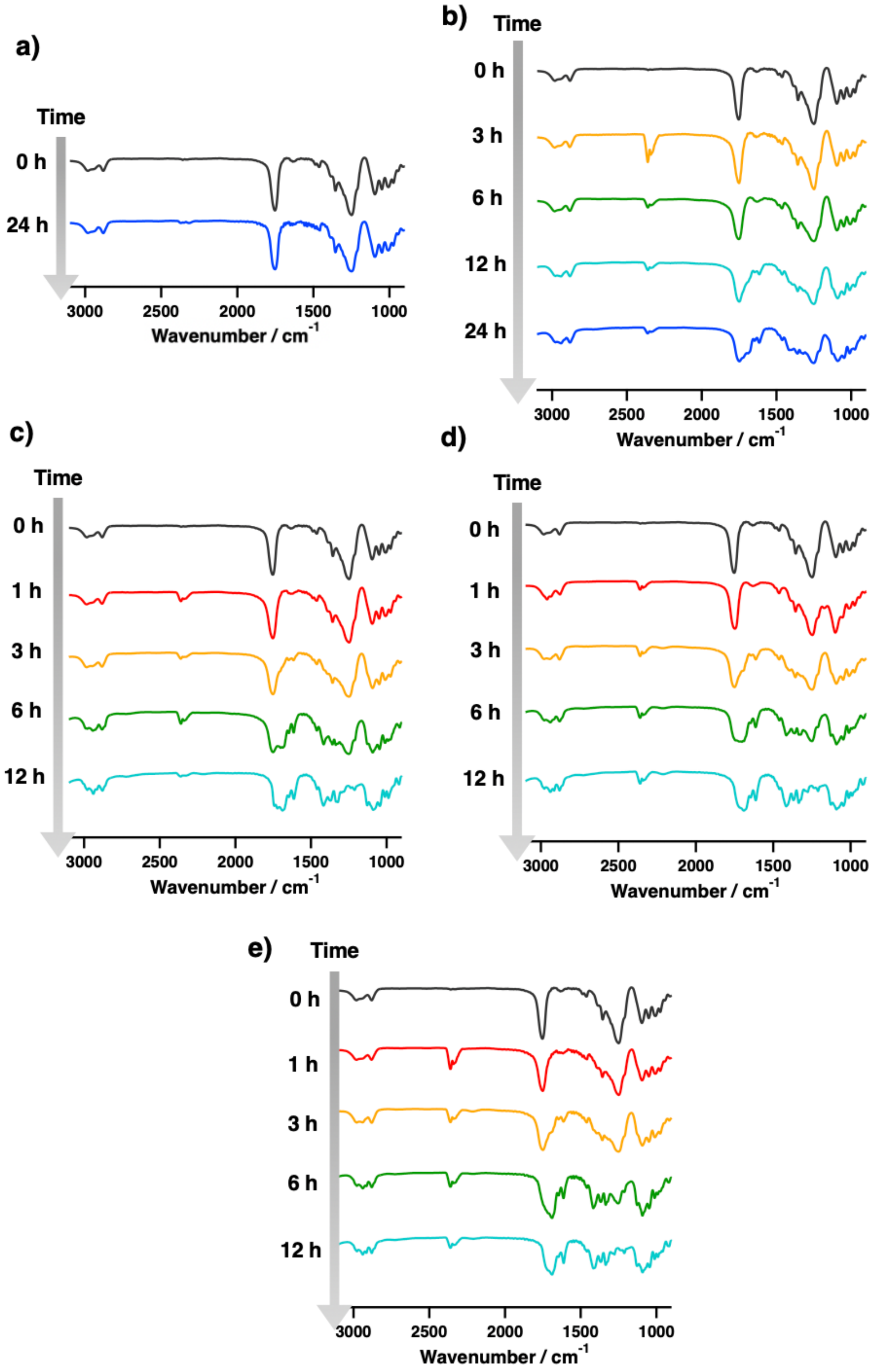


Figure S-9. FT-IR spectra of the degradation products during ammonolysis under the reaction condition of (a) $[NH_3]_0/[PIC]_0 = 0$, (b) $[NH_3]_0/[PIC]_0 =10$, (c) $[NH_3]_0/[PIC]_0 = 30$, (d) $[NH_3]_0/[PIC]_0 = 40$ and (e) $[NH_3]_0/[PIC]_0 = 50$. (KBr)

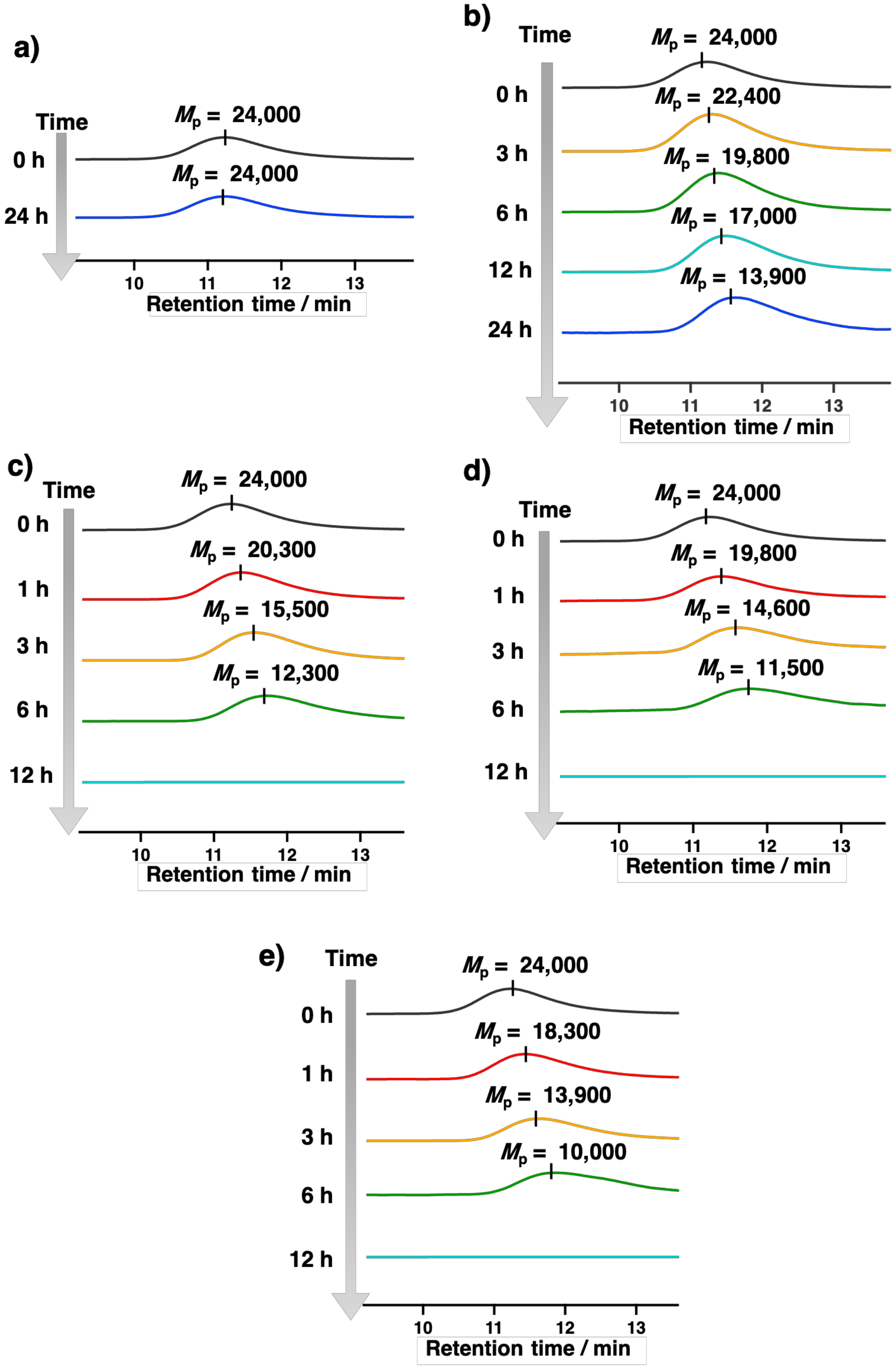


Figure S-10. GPC profiles of the degradation products during ammonolysis under the reaction condition of (a) [NH$_3$]$_0$/[PIC]$_0$ = 0, (b) [NH$_3$]$_0$/[PIC]$_0$ =10, (c) [NH$_3$]$_0$/[PIC]$_0$ = 30, (d) [NH$_3$]$_0$/[PIC]$_0$ = 40, (e) [NH$_3$]$_0$/[PIC]$_0$ = 50 (eluent: DMF, detector: RI, polystyrene standard).

2.5. Ammonolysis at different reaction temperature

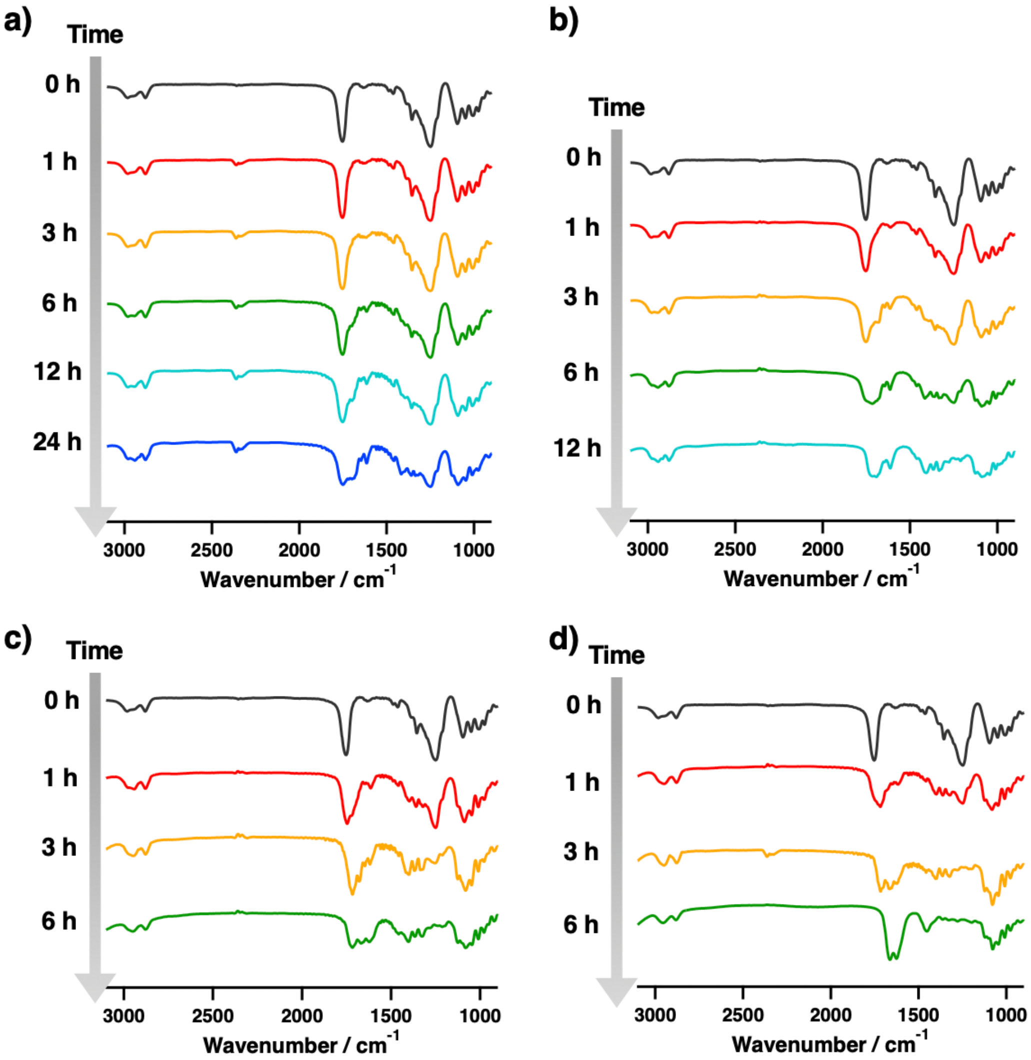


Figure S-11. FT-IR spectra of the degradation products during ammonolysis at (a) 10 °C, (b) 50 °C, (c) 70 °C, and (d) 90 °C (KBr).

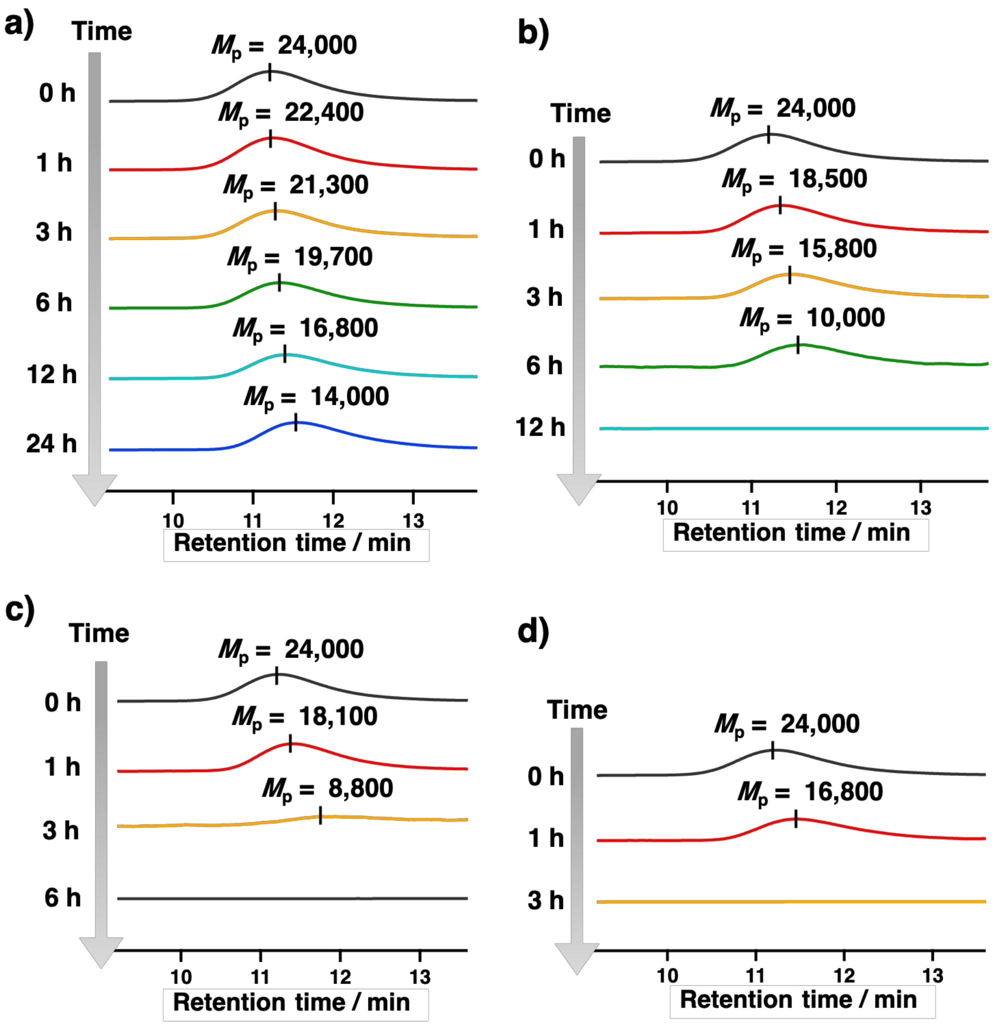


Figure S-12. GPC profiles of the degradation products during ammonolysis at (a) 10 °C, (b) 50 °C, (c) 70 °C, and (d) 90 °C (eluent: DMF, detector: RI, polystyrene standard).

2.6. Calculation of yield of the degradation products

Yield of ISB under the ammonolysis reaction condition at the reaction condition of 30 °C and $[NH_3]_0/[PIC]_0 = 30$ was calculated in the similar manner in the case of the reaction condition at the reaction condition of 90 °C and $[NH_3]_0/[PIC]_0 = 30$. PIC (50 mg) was placed in round-bottomed flask (30 mL), and water (1.80 mL) and aqueous ammonia (0.600 mL) were added. The reaction mixture was stirred for 24 h, and was freeze-dried to remove water and ammonia. Here, DMSO-*d*$_6$ (2.00 mL) and toluene (50.0 µL, internal standard) were added to the dried sample to prepare a solution for ^{1}H NMR measurement (sample: 1.00 mL).

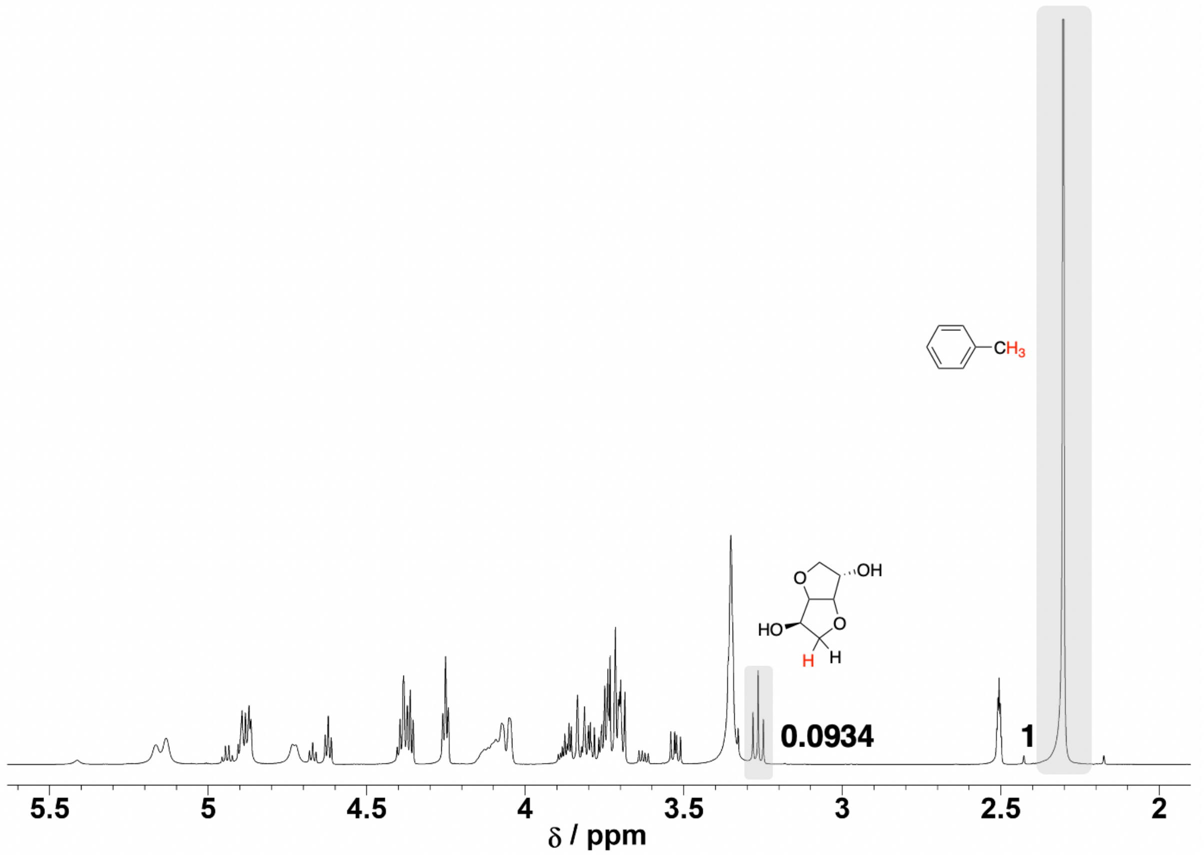


Figure S-13. ^{1}H NMR spectrum of the degradation products after 24 h with the reaction condition of 30 °C and $[NH_3]_0/[PIC]_0 = 30$ (500 MHz, 25 °C, DMSO-*d*$_6$). The number next to the signal of ISB (around 3.27 ppm) is the integration ratio of the signal of toluene (around 2.30 ppm).

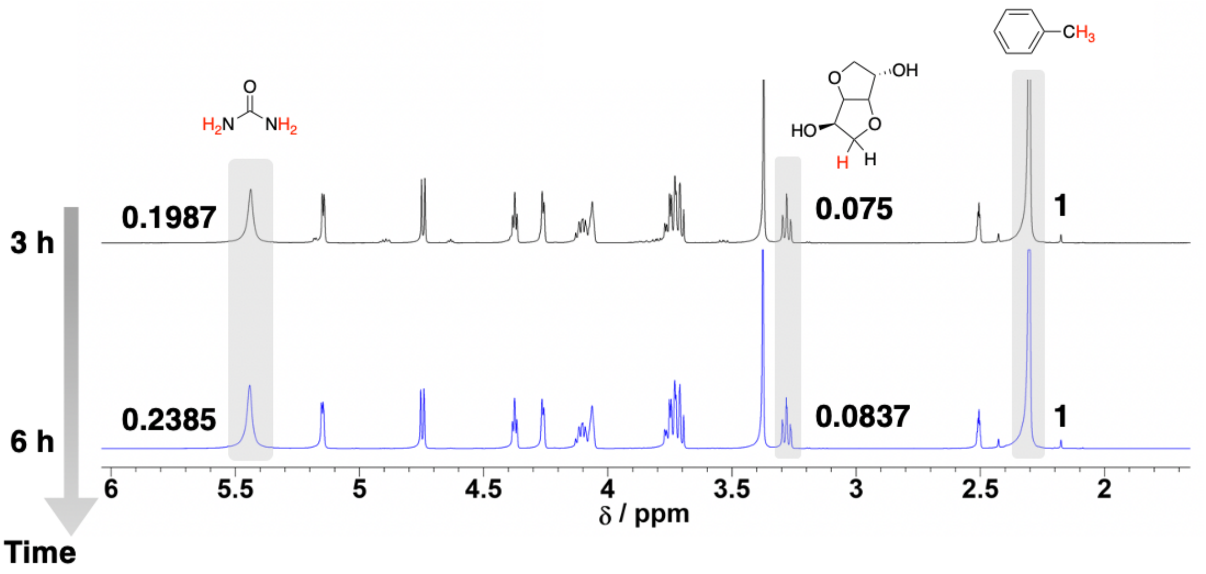


Figure S-14. ^{1}H NMR spectra of the degradation products during the ammonolysis with the reaction condition of 90 °C and $[NH_3]_0/[PIC]_0 = 30$ (500 MHz, 25 °C, DMSO-d_6). The yield of ISB and urea was calculated by the integration ratio written next to gray square against the methyl proton of toluene (2.3 ppm).

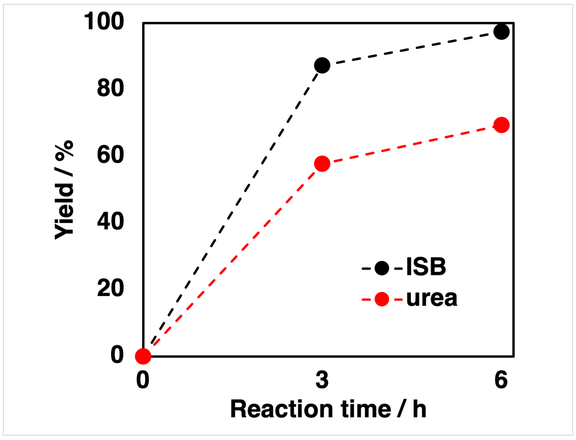
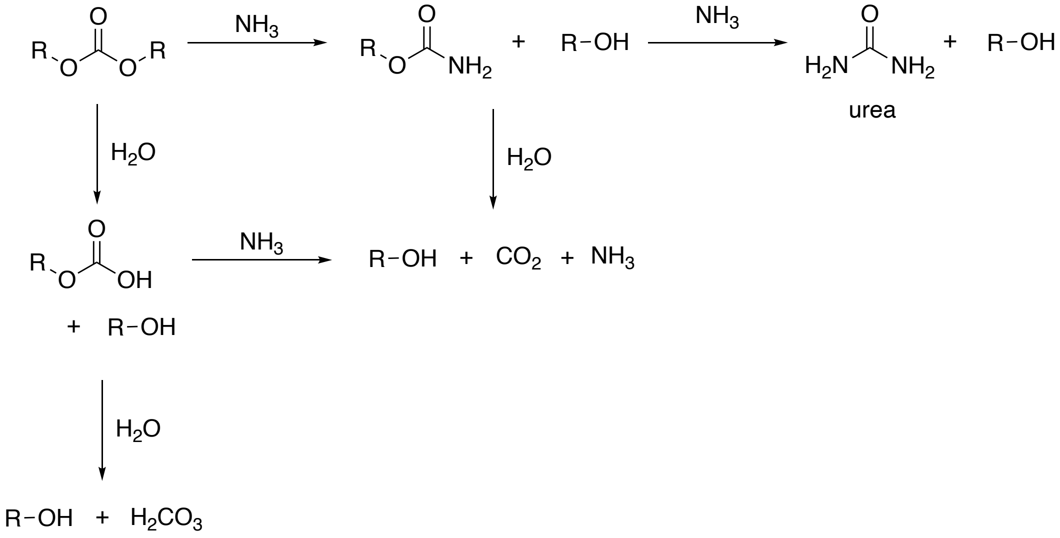


Figure S-15. Yield of ISB and urea during ammonolysis with the reaction condition of 90 °C and $[NH_3]_0/[PIC]_0 = 30$.



Scheme S-4. Considerable reaction during the ammonolysis of PIC.

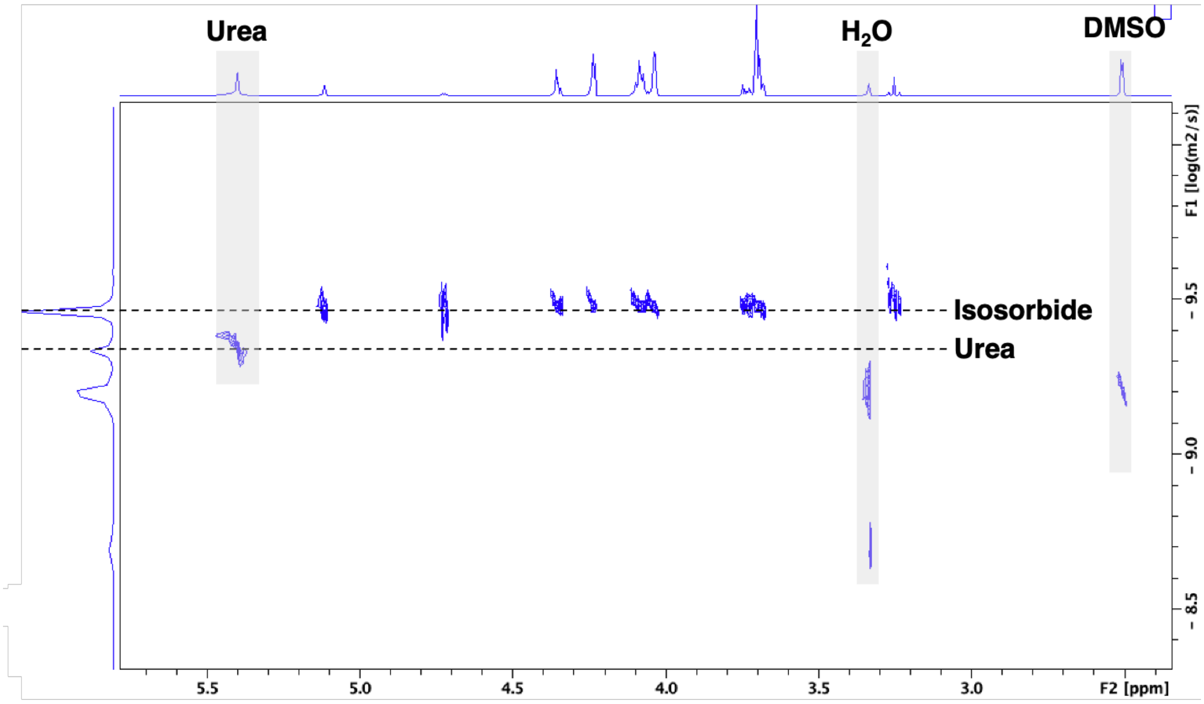


Figure S-16. ^{1}H DOSY NMR spectrum of the degradation product after 6 h under the reaction condition of 90 °C and $[NH_3]_0/[PIC]_0 = 30$ (500 MHz, 25 °C, DMSO-*d*$_6$).

2.7. Mass balance of the ammonolysis of PIC at the optimized reaction condition

Table S-1. Mass balance of the ammonolysis of PIC at optimized reaction condition

	PIC	NH_3	ISB	Urea	Total
Input	250 mg	756 mg	0 mg	0 mg	1.01 g
Output (theoretical)	0 mg	706 mg	212 mg	87.2 mg	1.01 g
Output (experimental)	0 mg	648 mg[a]	207 mg[b]	60.5 mg[b]	916 mg
Ratio to theoretical value	100%	91.7%	97.4%	69.4%	90.7%

a) Calculated from titration experiment. The water solution containing the degradation product was acidified with 50 mL of 1 M nitric acid, which was titrated with 0.1 M NaOH. b) Calculated from ^1H NMR spectrum.

2.8. Ammonia reusing test

First ammonolysis reaction was conducted in the same manner as the optimized condition (90 °C, 30eq. of ammonia). The ammonia aqueous solution of the degradation products in the flask was then stored at 5 °C for 17 h, followed by addition of further PIC (250 mg). The reaction mixture was heated again to 90 °C and stirred for another 6 h, the part of which was collected, freeze-dried and analyzed by ^{1}H NMR. Furthermore, the titration measurement of the residual ammonia after second ammonolysis experiment was performed to show the effective use of ammonia in this study.

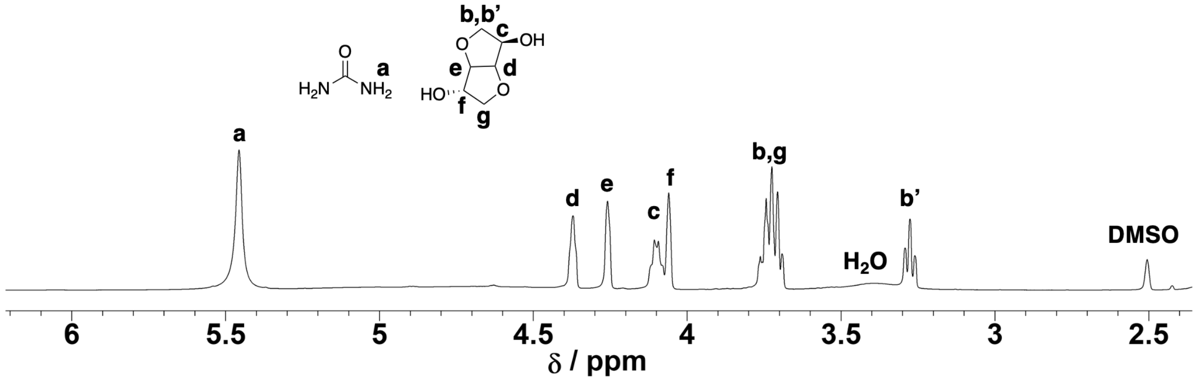


Figure S17. ^{1}H NMR spectrum of the degradation product after 6 h in second time ammonolysis of PIC.

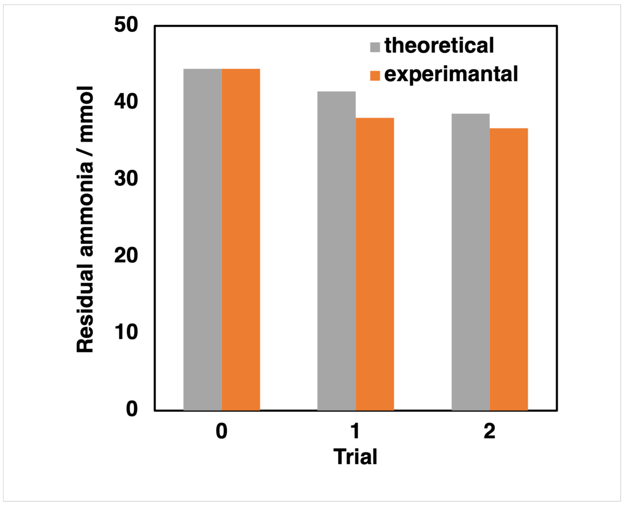


Figure S18. Residual ammonia amount after each ammonolysis experiment of PIC. The data of trial 1 was calculated from the mass balance (**Table S1**) of the ammonolysis experiment.

3. plant-growth test

Table S-2. Adjustment condition of fertilizer solution

Entry	1	2	3	4	5	6
200×Pi	1.25 mL	1.25 mL	1.25 mL	1.25 mL	1.25 mL	1.25 mL
200×Mg	1.25 mL	1.25 mL	1.25 mL	1.25 mL	1.25 mL	1.25 mL
200×micro	1.25 mL	1.25 mL	1.25 mL	1.25 mL	1.25 mL	1.25 mL
1M $CaCl_2$	500 µL	500 µL	500 µL	500 µL	500 µL	500 µL
200×K_2SO_4 (300 mM)	1.25 mL	1.25 mL	1.25 mL	1.25 mL	1.25 mL	1.25 mL
300 mM urea	2.50 mL	0 mL	0 mL	0 mL	0 mL	0 mL
300 mM ISB	0 mL	0 mL	0 mL	2.5 mL	0.25 mL	0 mL
300 mM urea & ISB	0 mL	2.50 mL	0 mL	0 mL	0 mL	0 mL
300 mM degradation products	0 mL	0 mL	2.50 mL	0 mL	0 mL	0 mL

200 x Pi: 350 mM NaH_2PO_4, 350 mM Na_2HPO_4

200 x Mg: 300 mM $MgSO_4$

200 x micro: 200 µM $CuSO_4$, 6 mM H_3BO_3, 34 µM $(NH_4)_6Mo_7O_{24}$, 26 µM $CoCl_2$, 13.4 mM Na_2-EDTA, 1.72 mM $FeSO_4$, 2.06 mM $MnSO_4$, 200 µM $ZnSO_4$

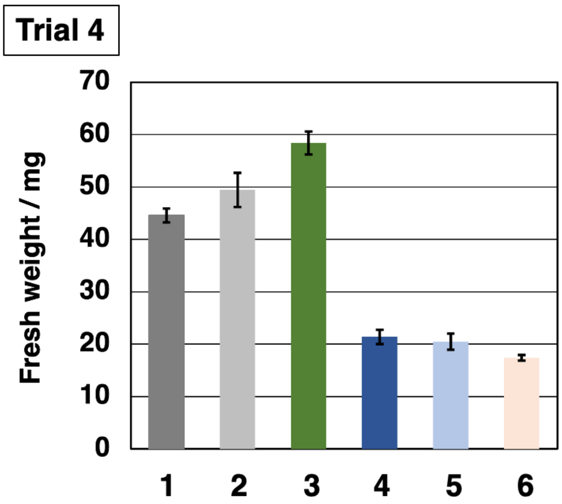


Figure S19. Fresh weight of *Arabidopsis thaliana* grown by using different additive.