Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information

Terpolymerizations of cyclohexene oxide, CO_2, and isocyanates or isothiocyanates for the synthesis of poly(carbonate–urethane)s or poly(carbonate–thioimidocarbonate)s

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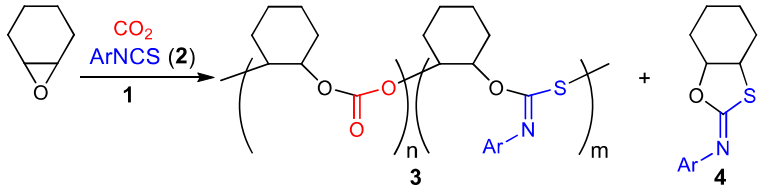
[A] General methods.

Instrumentation. NMR spectra were measured on a JEOL ECS400 or ECZ600 spectrometer, and chemical shifts are reported as the delta scale in ppm using an internal reference (δ = 7.26 ppm ($CDCl_3$) or 2.50 ppm (DMSO-d_6) for ^{1}H NMR and δ = 77.16 ppm ($CDCl_3$) for ^{13}C NMR). DOSY was measured with 16 gradient increments using a ledbpgp2s sequence. Size-exclusion chromatography (SEC) was carried out with Shodex KF-804L columns (ϕ 8 mm × 30 cm × 2) using THF as an eluent at 1 mL/min at 40 °C, and molecular weights were calibrated with standard polystyrene samples. IR spectra were recorded on a Shimadzu IRAffinity-1 spectrophotometer. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry was measured on a Shimadzu MALDI-8020, while atmospheric pressure chemical ionization (APCI) mass spectrometry was measured on a Thermo Fisher Scientific LTQ Orbitrap XL Hybrid Ion Trap-Orbitrap Mass Spectrometer. High-resolution double-focusing mass spectrometry was measured on a JEOL JMS-700N. The stainless steel autoclave reactors were heated on a EYELA ChemiStation PPV-CTRL1. UV irradiation experiments were done in a quartz cell under N_2 atmosphere with an Asahi Spectra REX-250 fitted with a Hg lamp (250 W).

Materials. Catalysts **1** were prepared according to the reported procedures.[S1] Cyclohexene oxide (CHO) was distilled from CaH_2. Aryl isothiocyanates **2** were dried over CaH_2 and distilled under vacuum, while aryl isocyanates **5** were distilled under vacuum. Other reagents were purchased and used without further purification unless otherwise specified. THF containing BHT (250 ppm) as a stabilizer was used as an eluent in SEC, while THF containing no stabilizers was used as solvent in the experiments to test the degradability of polymers upon acid treatment or UV irradiation. Column chromatography on silica gel was performed with BW-127 ZH (Fuji Silysia, 100–270 mesh), while column chromatography on alumina was done with alumina 019-08295 (FUJIFILM Wako Pure Chemical Corporation, 200 mesh).

[B] Terpolymerization of CHO, CO_2, and aryl isothiocyanates.



General procedure. Catalyst **1** (amount indicated in the Tables) and a magnetic stirring bar were put in a glass test tube, which was then put in a 50-mL stainless steel autoclave (preheated at 150 °C for a few hours and cooled down), and the reactor was dried under vacuum at 80 °C overnight. The autoclave was put in a glovebox (purge type) under N_2 atmosphere, and aryl isothiocyanate **2** (amount indicated in the Tables) and CHO (amount indicated in the Tables) were added via syringes. The autoclave was closed, and it was taken out from the glovebox and pressurized with CO_2 (2.0 MPa). The mixture was stirred at a constant temperature for a reaction time. The reactor was then cooled in a water bath for 10 min, and excess CO_2 was released carefully in a draft chamber. The reaction mixture was diluted with $CDCl_3$ for ^1H NMR analysis, and dimethyl sulfoxide (DMSO, 50 mg, 0.64 mmol) was added as an internal standard to determine the conversion of CHO, the TON of catalyst **1**, and the amount of byproduct **4**. Aryl isothiocyanate **2** remaining in the reaction mixture was quantified by the ^1H NMR analysis of the $CDCl_3$ solution to which cyclohexylamine was added to convert **2** into the corresponding thiourea in the NMR tube. Terpolymer **3** was isolated by adding the reaction mixture diluted with chloroform (ca. 5 mL) dropwise to methanol (ca. 200 mL) followed by filtration and vacuum drying. The ratio of the PCHC to PTIC units and molecular weights were determined by ^1H NMR and SEC analysis, respectively.

The ratio of the PCHC to PTIC units. The ratio of the PCHC to PTIC units was determined by the ^{1}H NMR spectrum of a crude reaction mixture or a purified polymer. In the case of the crude reaction mixture, the PTIC unit was quantified by the integration of the signals for the aromatic protons (6.5–7.8 ppm) subtracted by that for the aromatic protons of **2** and **4**; the amount of **2** was estimated from the corresponding thiourea formed in the same NMR tube upon addition of cyclohexylamine, while that of **4** was determined by the integration of the signal for methine proton **e** (for example, Fig. S1). The PCHC unit was quantified by the integration of the signals at 3.2–5.6 ppm subtracted by that estimated for the PTIC unit and that for **4**. PCHC : PTIC (n : m) = (the integration of the signals for the PCHC unit divided by 2) : (the integration of the signals for the PTIC unit divided by the number of the aromatic protons). In the case of the purified polymer, the PTIC unit was quantified simply by the integration of the signals for the aromatic protons (for example, Fig. S6a), while the PCHC unit was quantified by the integration of the signals at 3.2–5.6 ppm subtracted by that estimated for the PTIC unit. The ratio of the PCHC to PTIC units (n : m) was calculated as described for the crude reaction mixture.

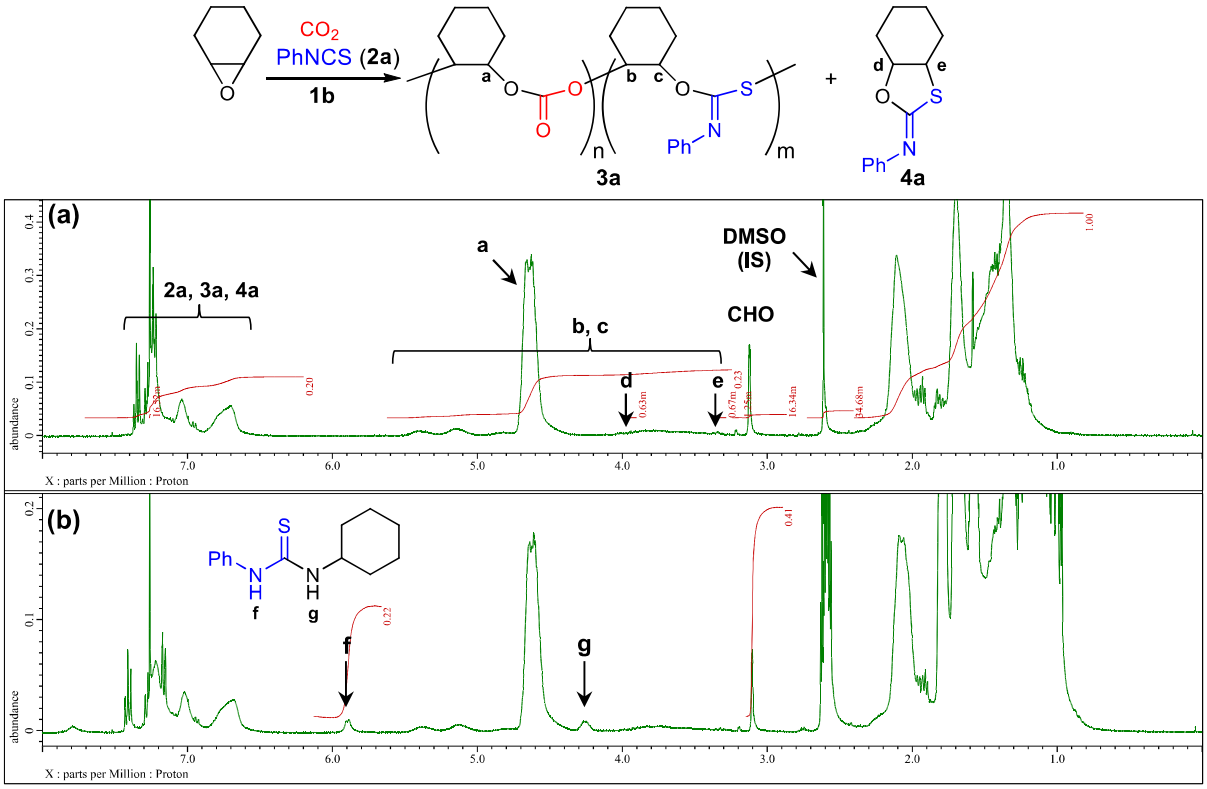


Fig. S1. ^{1}H NMR spectra ($CDCl_3$) of crude reaction mixtures (a) after terpolymerization and (b) after the addition of cyclohexylamine (Table 1, entry 1).

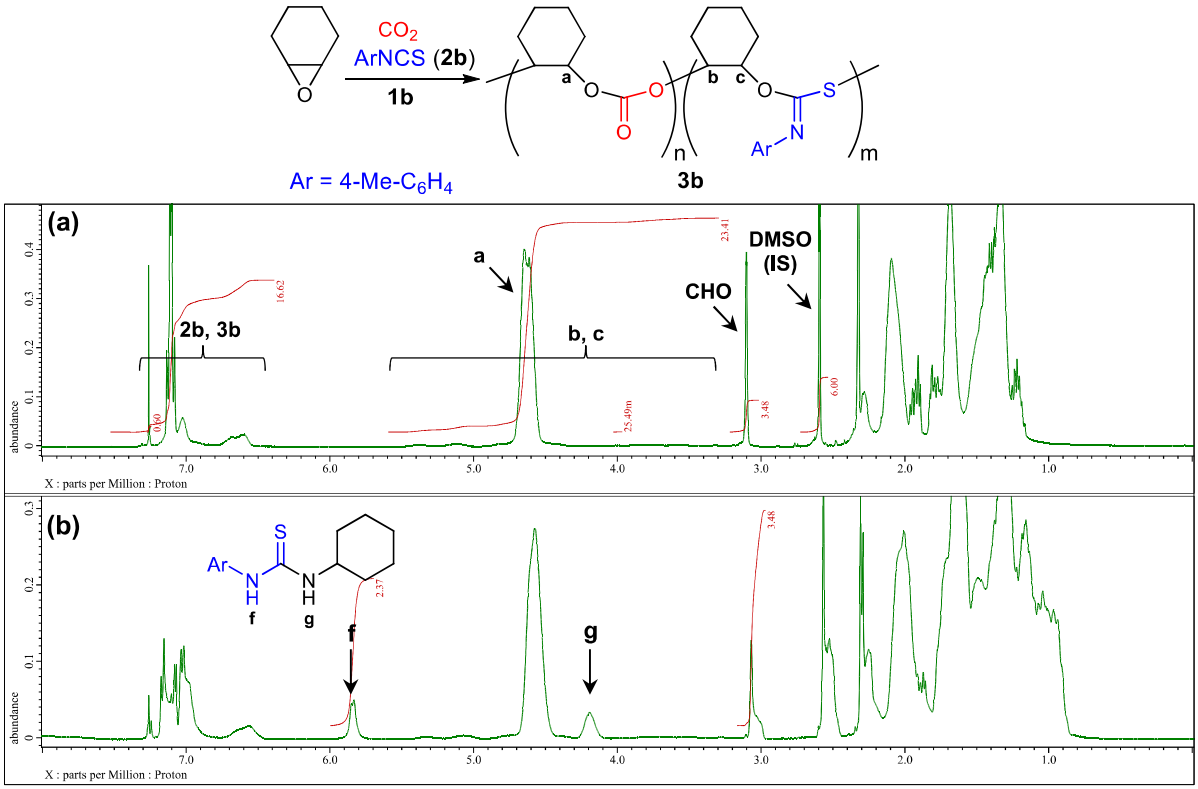


Fig. S2. ^{1}H NMR spectra ($CDCl_3$) of the crude reaction mixtures (a) after terpolymerization and (b) after the addition of cyclohexylamine (Table 1, entry 6).

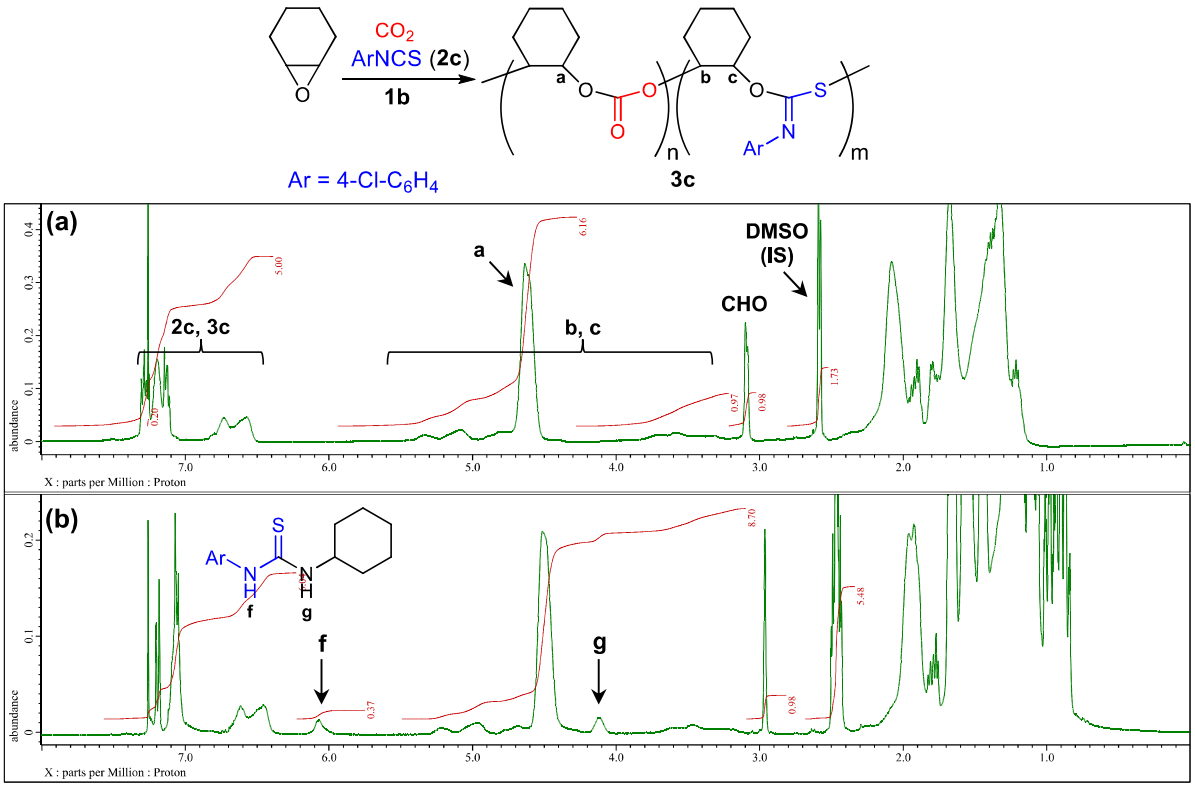


Fig. S3. ^{1}H NMR spectra ($CDCl_3$) of the crude reaction mixtures (a) after terpolymerization and (b) after the addition of cyclohexylamine (Table 1, entry 7).

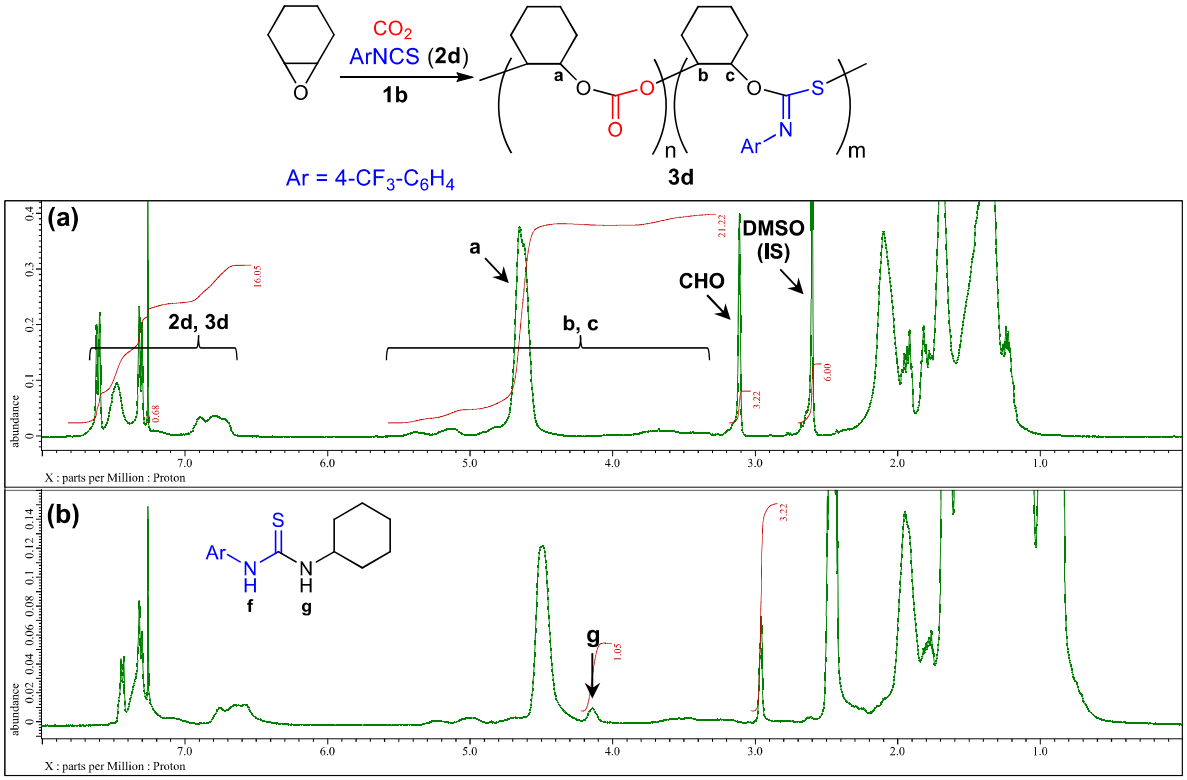


Fig. S4. ^{1}H NMR spectra ($CDCl_3$) of the crude reaction mixtures (a) after terpolymerization and (b) after the addition of cyclohexylamine (Table 1, entry 8).

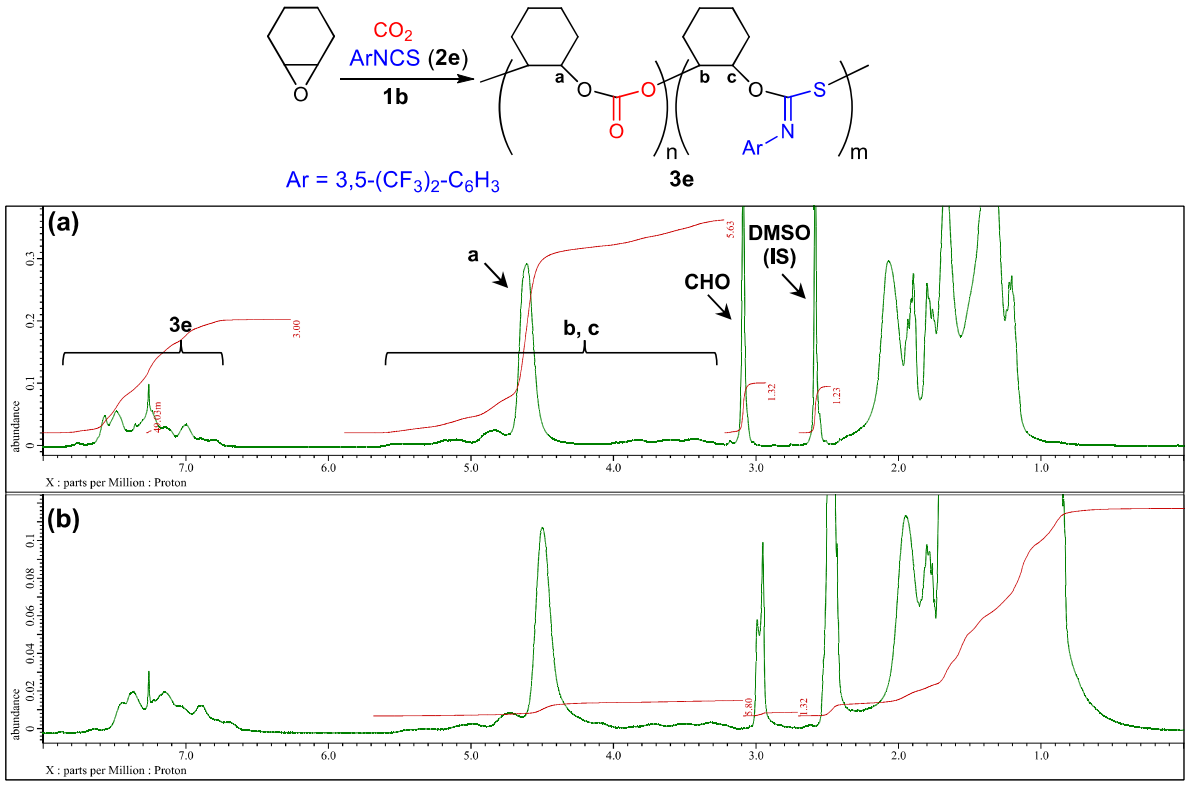


Fig. S5. ^{1}H NMR spectra ($CDCl_3$) of the crude reaction mixtures (a) after terpolymerization and (b) after the addition of cyclohexylamine (Table 1, entry 9).

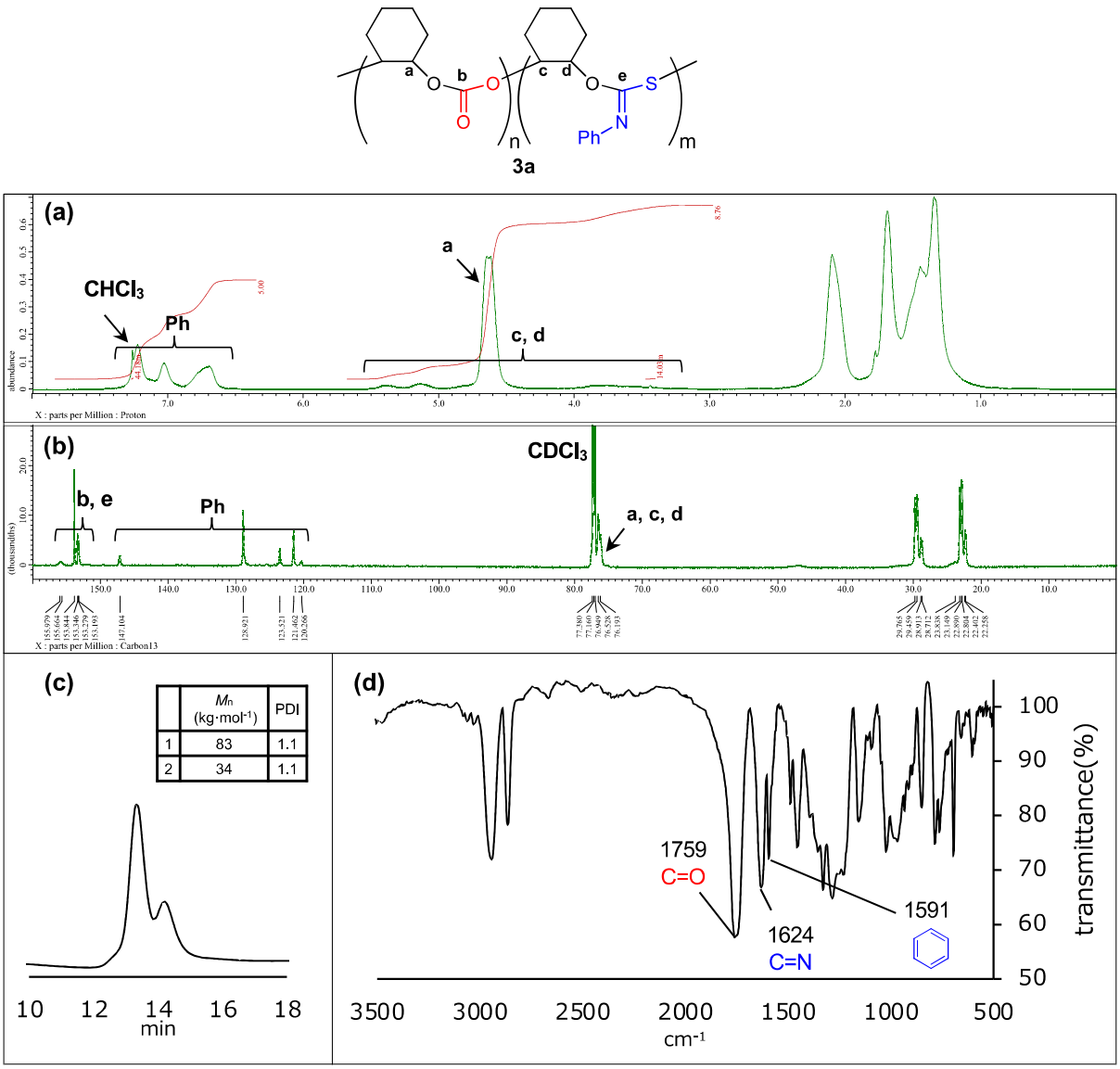


Fig. S6. (a) ^{1}H NMR spectrum ($CDCl_3$), (b) ^{13}C NMR spectrum ($CDCl_3$), (c) SEC chart, and (d) IR spectrum of purified polymer **3a** (Table 1, entry 1).

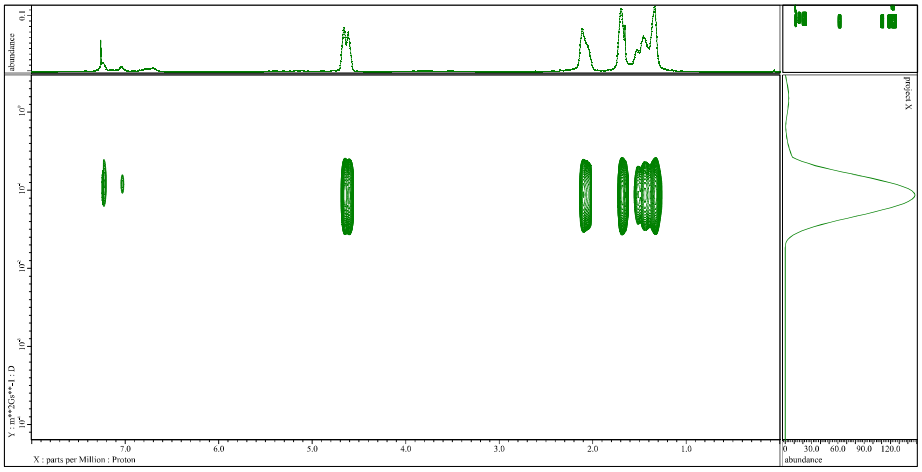


Fig. S7. DOSY spectrum ($CDCl_3$) of purified polymer **3a**.

MALDI-TOF mass spectrum of terpolymer 3a. Terpolymer **3a** for the measurement of MALDI-TOF mass spectrometry was obtained according to the following procedure. Catalyst **1b** (2.07 mg, 1.00 μmol, 0.016 mol%), CHO (606 mg, 6.17 mmol), and **2a** (170 mg, 1.26 mmol) were put in a glass test tube, which was then put in a 50-mL stainless steel autoclave. The autoclave was pressurized with CO_2 (0.5 MPa), and the mixture was stirred at 90 °C for 20 h. The reactor was then cooled in a water bath for 10 min, and excess CO_2 was released carefully. The terpolymer was isolated by adding the reaction mixture diluted with chloroform dropwise to methanol followed by filtration and vacuum drying.

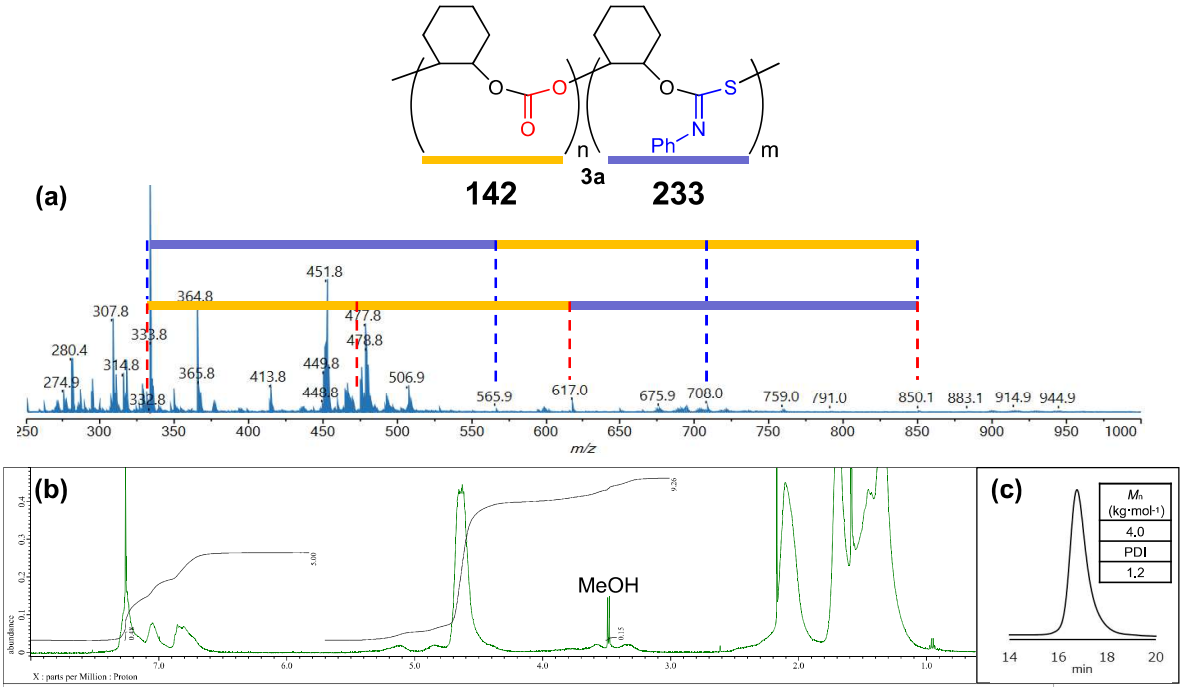


Fig. S8. (a) MALDI-TOF mass spectrum, (b) ^1H NMR spectrum ($CDCl_3$), and (c) SEC chart of terpolymer **3a**.

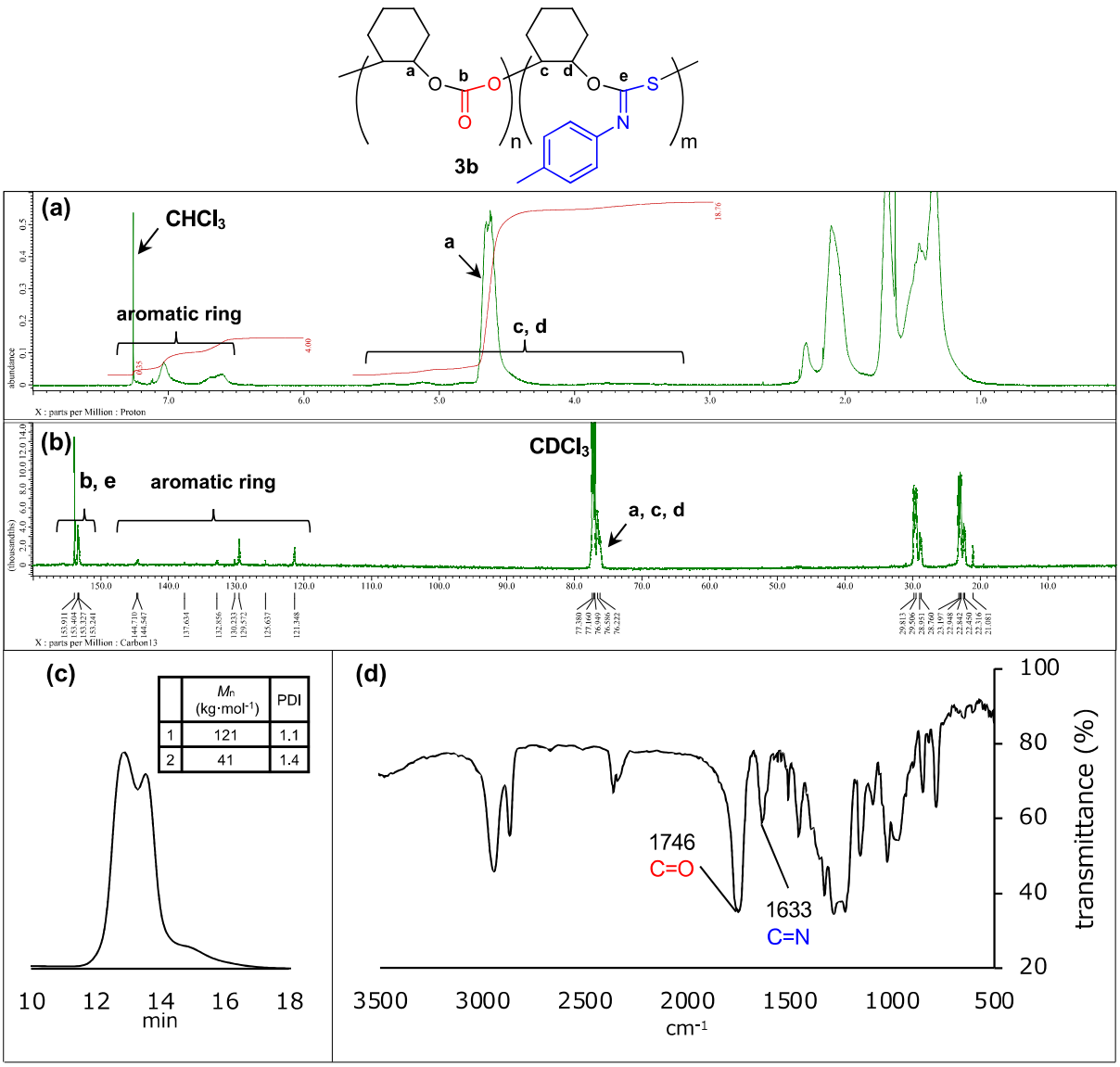


Fig. S9. (a) ^{1}H NMR spectrum ($CDCl_3$), (b) ^{13}C NMR spectrum ($CDCl_3$), (c) SEC chart, and (d) IR spectrum of purified polymer **3b** (Table 1, entry 6).

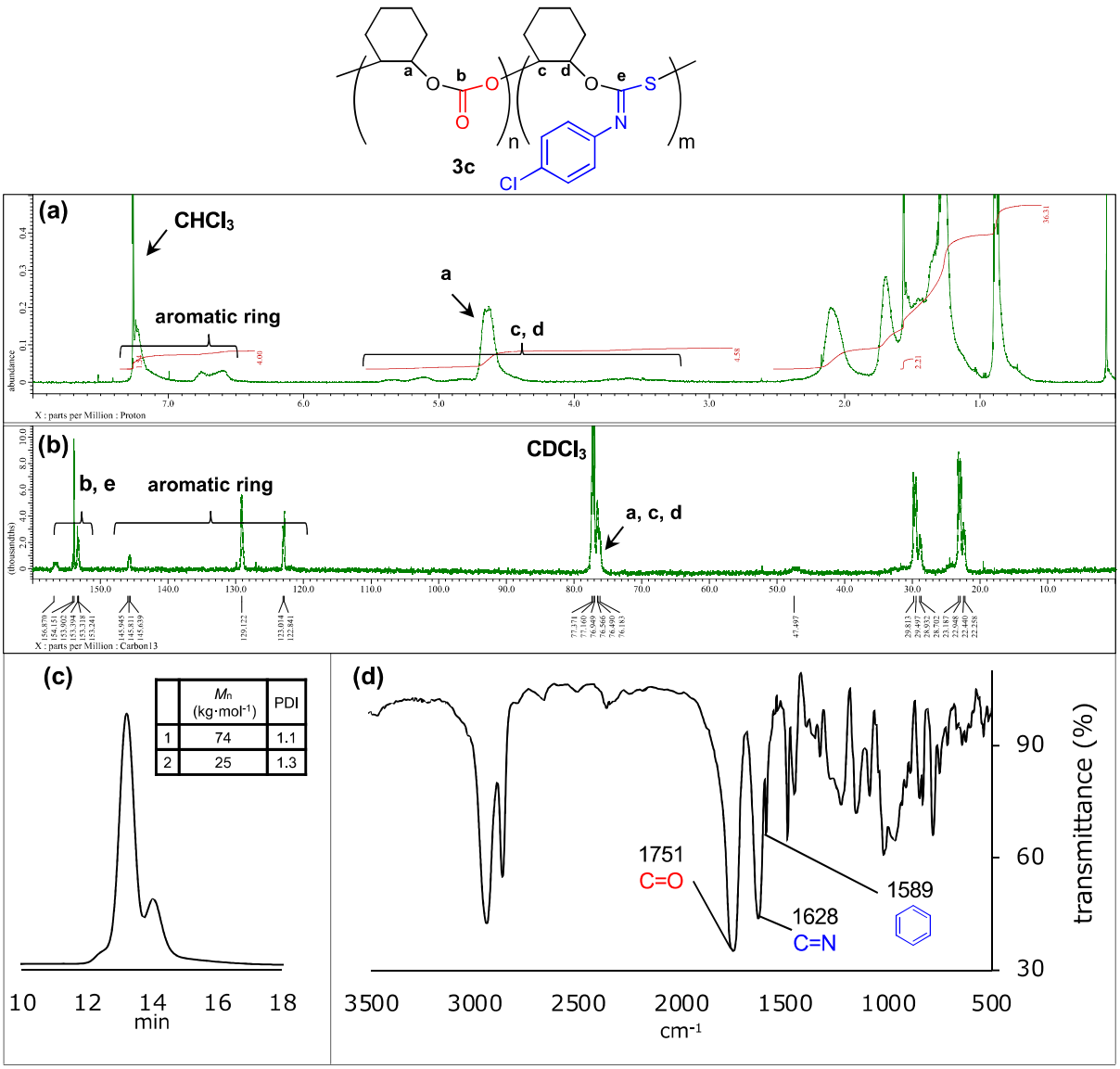


Fig. S10. (a) ^{1}H NMR spectrum ($CDCl_3$), (b) ^{13}C NMR spectrum ($CDCl_3$), (c) SEC chart, and (d) IR spectrum of purified polymer **3c** (Table 1, entry 7).

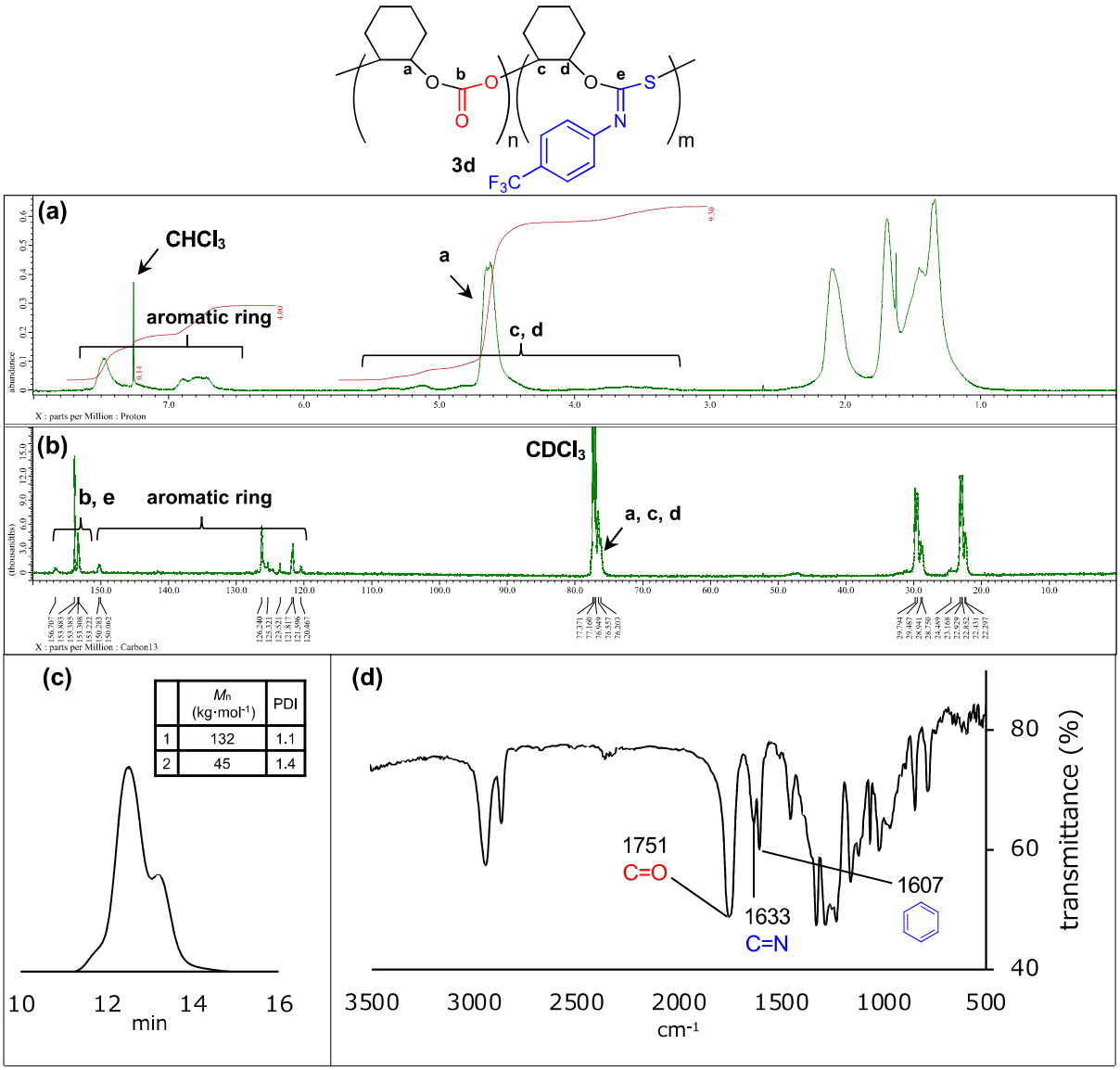


Fig. S11. (a) ^{1}H NMR spectrum ($CDCl_3$), (b) ^{13}C NMR spectrum ($CDCl_3$), (c) SEC chart, and (d) IR spectrum of purified polymer **3d** (Table 1, entry 8).

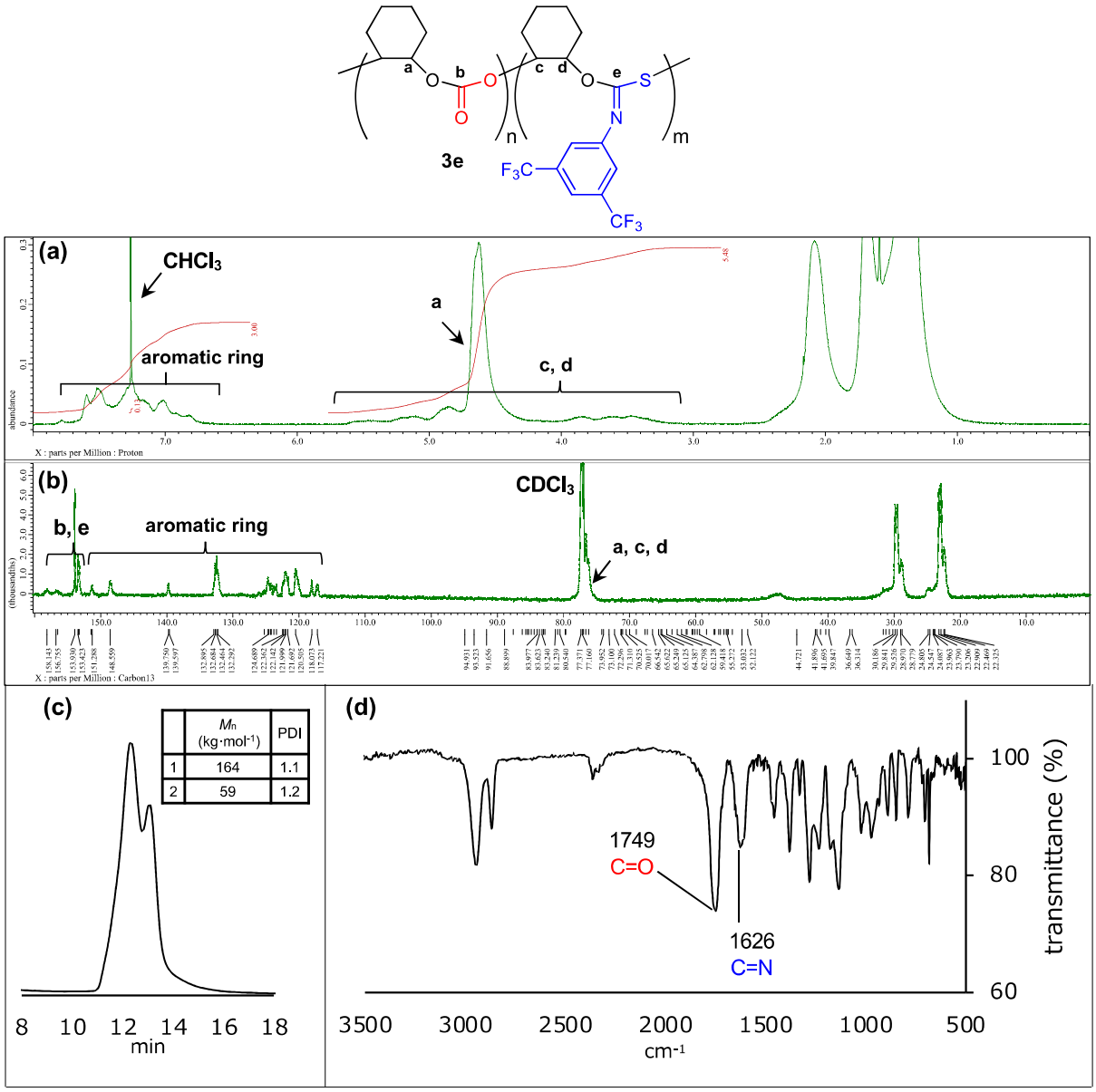
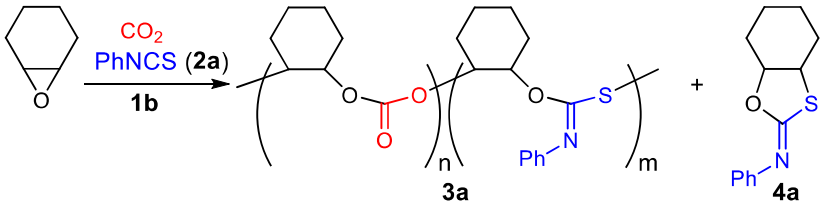


Fig. S12. (a) ^{1}H NMR spectrum ($CDCl_3$), (b) ^{13}C NMR spectrum ($CDCl_3$), (c) SEC chart, and (d) IR spectrum of purified polymer **3e** (Table 1, entry 9).

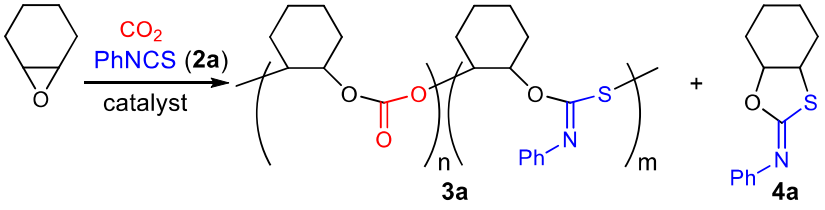
Table S1. Optimization of reaction conditions for the terpolymerization of CHO, CO_2, and **2a** with **1b**.



			conv.[b] (%)			**3a**			**4a**
entry[a]	T (°C)	CHO/**2a**	CHO	**2a**	TON[b]	n:m[b]	M_n[c] (kg mol^{-1})	PDI[c]	yield[b] (%)
1	80	5	91	61	5700	5:1	71/28	1.1/1.2	0
2	90	5	79	87	4600	3:1	45/16	1.1/1.3	5
3	100	5	92	85	5700	4:1	38	1.5	9
4	90	4	94	75	5400	3:1	73/26	1.1/1.3	6
5	90	3	98	67	5400	3:1	80/29	1.1/1.3	3
6	90	2	99	40	5800	4:1	109/39	1.1/1.3	2

[a] Reaction conditions: CHO (12.5 mmol), **2a** (quantity indicated above), **1b** (S/C = 6250 for CHO), CO_2 (2.0 MPa), 24 h, in an autoclave. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. TON for the formation of **3a**. The yields of **4a** were calculated based on **2a**. [c] Determined by SEC analysis of the crude reaction mixture using THF as an eluent and polystyrene as a molecular-weight standard.

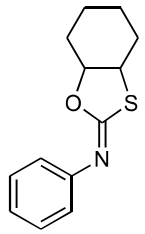
Table S2. Screening of catalysts for the terpolymerization of CHO, CO_2, and **2a**.



		conv.[b] (%)			**3a**			**4a**
entry[a]	catalyst	CHO	**2a**	TON[b]	n:m[c]	M_n[d] (kg mol^{-1})	PDI[d]	yield[b] (%)
1	**1a**	82	5	17100	>20:1	121/59	1.0/1.1	0
2	**1b**	87	30	31600	8:1	183/57	1.1/1.5	3
3	**1c**	90	5	23600	20:1	104/44	1.1/1.2	0
4	**1d**	82	11	28000	10:1	78	1.5	0
5[e]	Al(TPP)Br	30	0	600	N.D.	<1.0[f]	–[f]	0

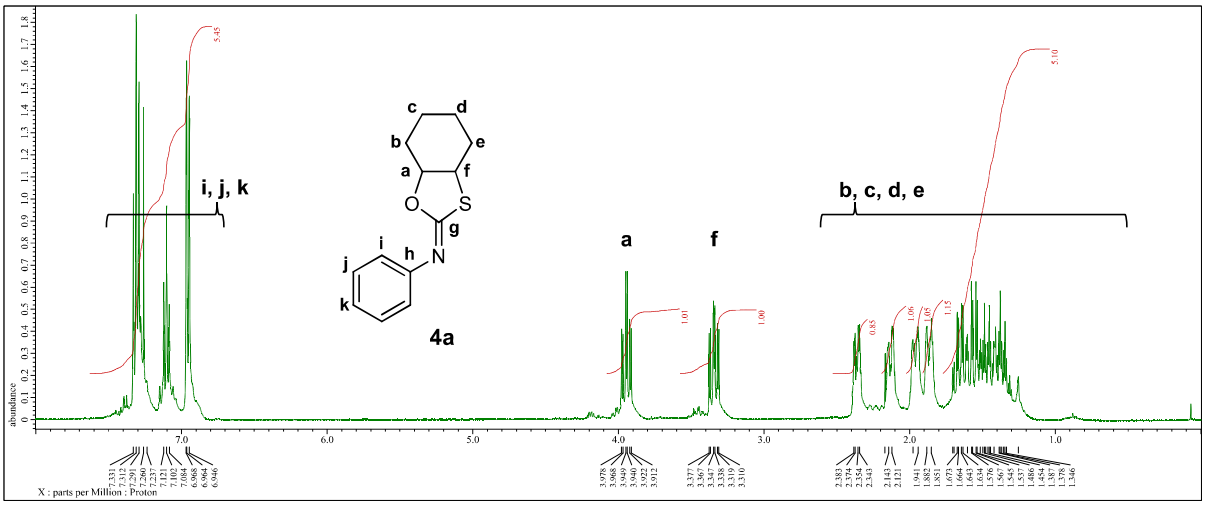
[a] Reaction conditions: CHO (12.5 mmol), **2a** (3.1 mmol), catalyst (S/C = 40000 for CHO), CO_2 (2.0 MPa), 90 °C, 24 h, in an autoclave. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. TON for the formation of **3a**. The yields of **4a** were calculated based on **2a**. [c] Determined by ^{1}H NMR analysis of the purified polymer. [d] Determined by SEC analysis of the purified polymer using THF as an eluent and polystyrene as a molecular-weight standard. [e] Tetrabutylammonium bromide (4 equiv relative to Al(TPP)Br) was added. [f] Crude reaction mixtures were analyzed.

Characterization of 4a. Byproduct **4a** was isolated from the reaction mixture of the terpolymerization of CHO, CO_2, and **2a** by means of silica gel column chromatography (hexane/EtOAc = 7/3).

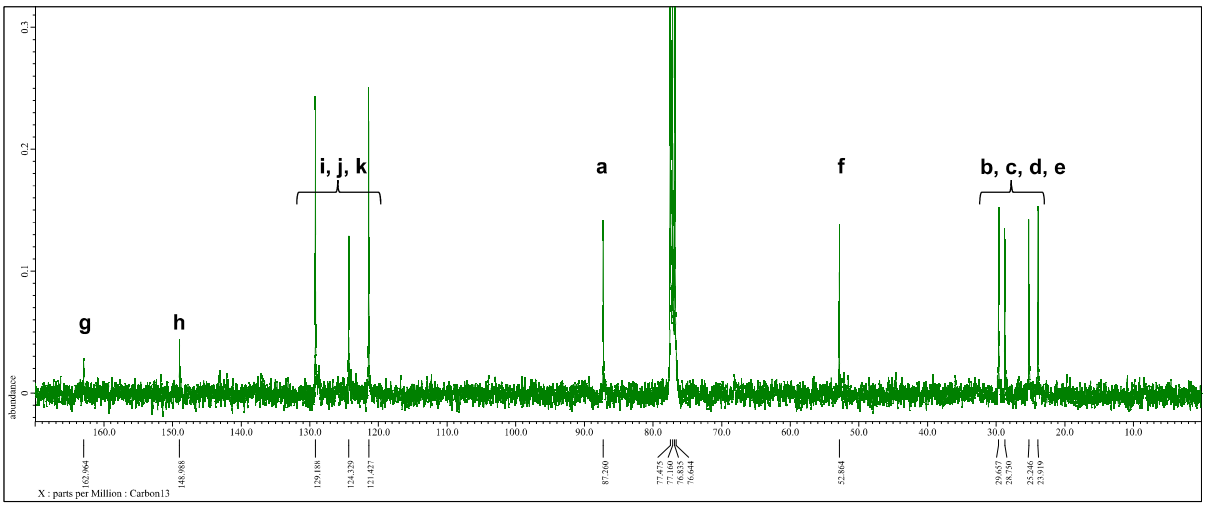


4a

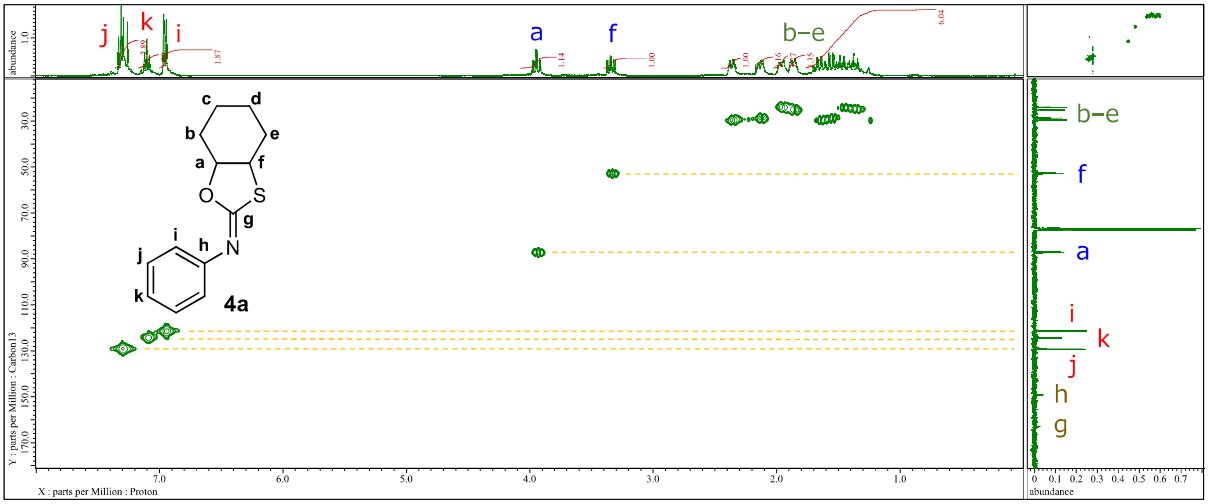
White solid; mp 88–92 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.34–1.70 (m, 4H), 1.87 (d, J = 12.3 Hz, 1H), 1.96 (d, J = 14.6 Hz, 1H), 2.13 (d, J = 8.7 Hz, 1H), 2.36 (dd, J = 3.9, 12.1 Hz, 1H), 3.34 (dt, J = 3.7, 11.4 Hz, 1H), 3.94 (dt, J = 4.0, 11.2 Hz, 1H), 6.96 (d, J = 7.3 Hz, 2H), 7.10 (t, J = 7.3 Hz, 1H), 7.31 (t, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 23.9, 25.2, 28.8, 29.7, 52.9, 87.3, 121.4, 124.3, 129.2, 149.0, 163.0; IR (KBr) 2938, 2864, 1645, 1589, 1483, 1447, 1362, 1265, 1213, 1206, 1150, 1103, 1087, 1042, 1026, 972, 881, 766, 692, 675, 637, 600, 579 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{15}NOS$ 233.0874, found 233.0874 (M^+).



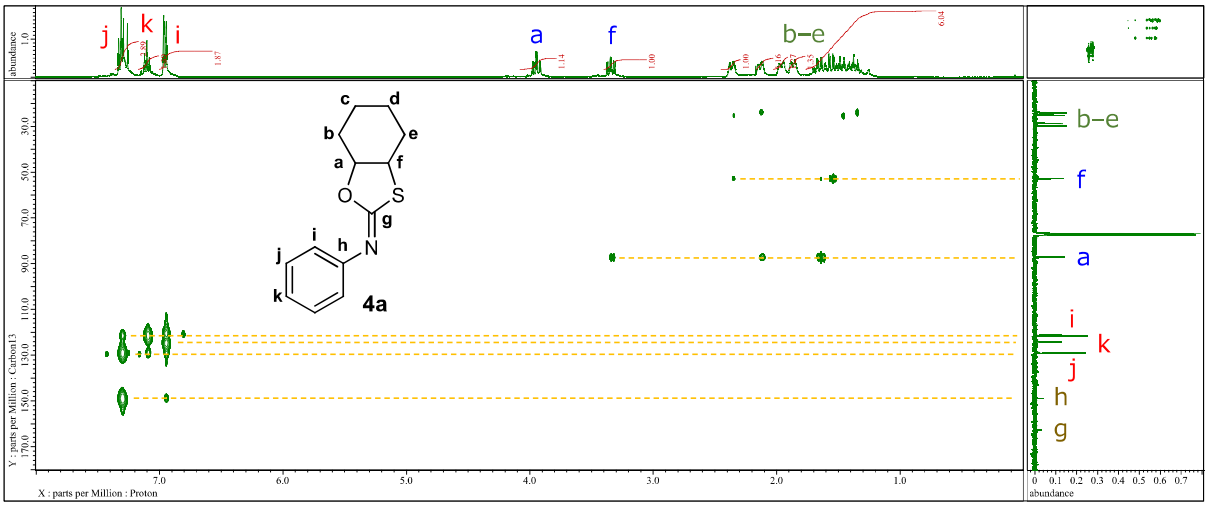
400 MHz ^{1}H NMR spectrum of **4a** in $CDCl_3$



100 MHz ^{13}C NMR spectrum of **4a** in $CDCl_3$

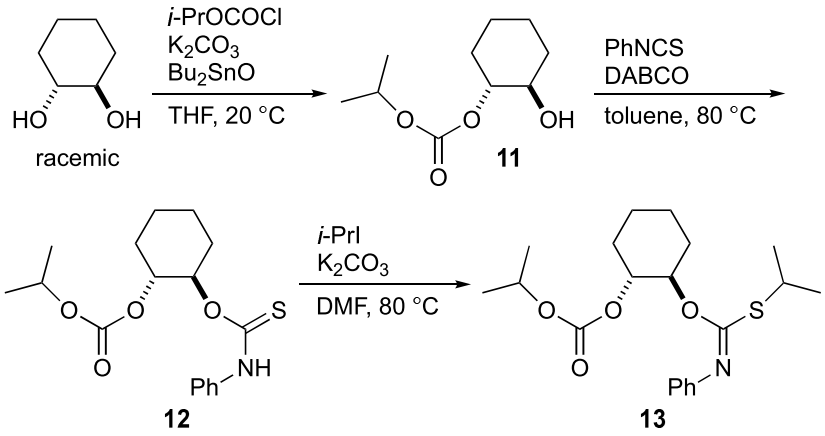


^{1}H–^{13}C HMQC spectrum of **4a** in $CDCl_3$



^{1}H–^{13}C HMBC spectrum of **4a** in $CDCl_3$

[C] Synthesis and characterization of a model compound for terpolymer 3a.

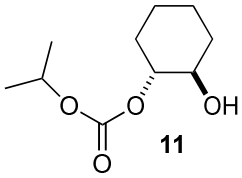


Synthesis of 11. *trans*-1,2-Cyclohexanediol (234 mg, 2.01 mmol), K_2CO_3 (336 mg, 2.43 mmol), and Bu_2SnO (5.2 mg, 0.021 mmol) were put in a flask (25 mL), and the mixture was dried under vacuum at room temperature for 2 h. Dry THF (4.0 mL) and isopropyl chloroformate (468 μL, 4.12 mmol) were added at 20 °C under N_2, and the mixture was stirred at 20 °C for 20 h. The mixture was diluted with EtOAc, washed with water, and dried over Na_2SO_4. Purification by silica gel column chromatography (hexane/EtOAc = 3/1) followed by alumina column chromatography (hexane/EtOAc = 3/1) gave **11** as a colorless oil (382 mg, 1.89 mmol, 94%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.14–1.40 (m, 10H), 1.67–1.73 (m, 2H), 1.99–2.14 (m, 2H), 2.49 (s, 1H), 3.50–3.60 (m, 1H), 4.35–4.43 (m, 1H), 4.82–4.90 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.9, 23.8, 23.9, 30.0, 32.9, 72.1, 72.6, 81.8, 154.7; IR (neat) 3445, 2982, 2940, 2864, 1740, 1456, 1375, 1261, 1094, 995, 916, 831, 791 cm^{-1}; HRMS (FAB) calcd for $C_{10}H_{19}O_4$ 203.1283, found 203.1283 ([M + H]$^+$).

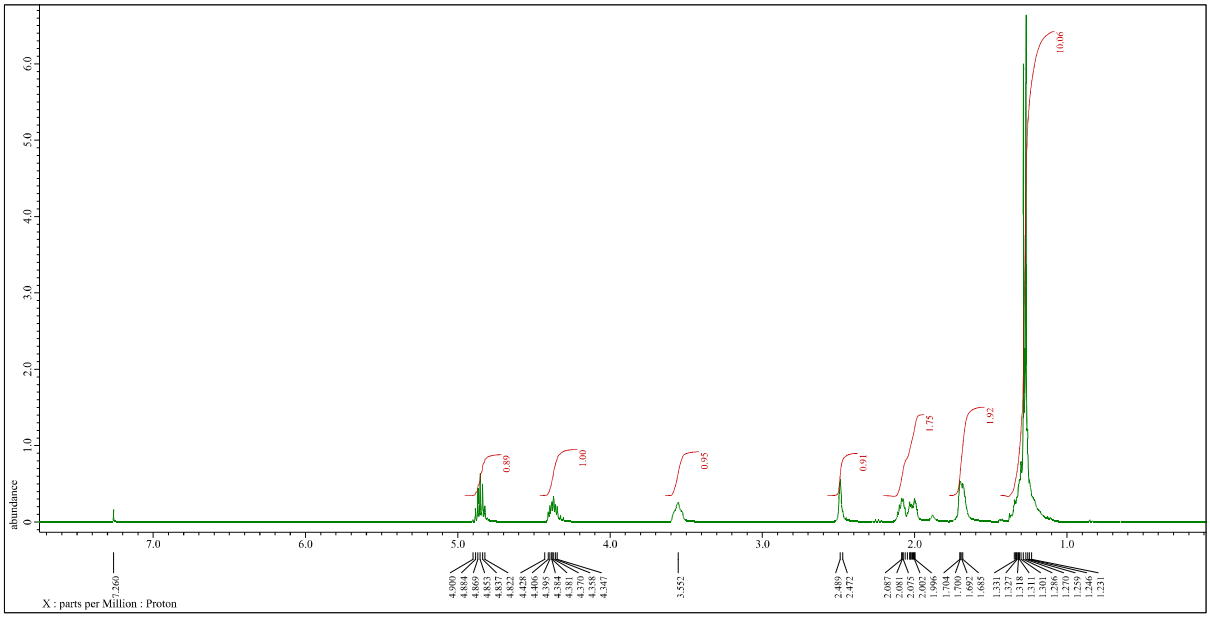
Synthesis of 12. To a solution of **11** (818 mg, 4.04 mmol) and DABCO (456 mg, 4.07 mmol) in dry toluene (4.0 mL) was added phenyl isothiocyanate (1.46 mL, 12.3 mmol) under N_2, and the mixture was stirred at 80 °C for 48 h. The mixture was diluted with EtOAc, washed with water, and dried over Na_2SO_4. Purification by silica gel column chromatography (hexane/EtOAc = 8/1) gave **12** as a white solid (625 mg, 1.85 mmol, 46%). mp 137–142 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, 40 °C) δ 1.20–1.58 (m, 10H), 1.72–1.78 (m, 2H), 2.09–2.16 (m, 1H), 2.40 (s, 1H), 4.68–4.89 (m, 2H), 5.42–5.48 (m, 1H), 7.14–7.37 (m, 5H), 8.16 (s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz, 40 °C) δ 21.8, 21.9, 23.2, 23.4, 29.8, 30.2, 72.1, 76.7, 82.1, 122.0, 125.7, 129.1, 137.2, 154.3, 187.9; IR (KBr) 3231, 3075, 2945, 1732, 1597, 1553, 1495, 1414, 1360, 1302, 1267, 1213, 1188, 1094, 1034, 1001, 793, 748 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{23}NO_4S$ 337.1348, found 337.1344 (M$^+$).

Synthesis of 13. Compound **12** (339 mg, 1.01 mmol) and K_2CO_3 (280 mg, 2.03 mmol) were put in a flask (25 mL), and the mixture was dried under vacuum at room temperature for 2 h. Dry DMF (1.0 mL) and 2-iodopropane (312 μL, 3.14 mmol) were added under N_2, and the mixture was stirred at 80 °C for 4 h. The mixture was diluted with EtOAc, washed with water, and dried over Na_2SO_4. Purification by silica gel column chromatography (hexane/EtOAc = 12/1) gave **13** as a slightly yellow solid (360 mg, 0.950 mmol, 94%). mp 50–52 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.25–1.33 (m, 12H), 1.35–1.62 (m, 4H), 1.74–1.78 (m, 2H), 2.12–2.15 (m, 1H), 2.49–2.51 (m, 1H), 3.59–3.65 (m, 1H), 4.83–4.92 (m, 2H), 5.12–5.16 (m, 1H), 6.85–6.86 (m, 2H), 7.05 (t, J = 7.6 Hz, 1H), 7.28 (t, J = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 21.90, 21.93, 23.4, 23.6, 23.8, 24.0, 29.6, 30.4, 36.2, 72.0, 77.3, 121.6, 123.6, 129.0, 147.5, 154.4, 157.2; IR (KBr) 2980, 2941, 2866, 1740, 1626, 1595, 1489, 1454, 1385, 1366, 1267, 1163, 1094, 1024, 982, 912, 766, 696 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{29}NO_4S$ 379.1817, found 379.1817 (M^+).

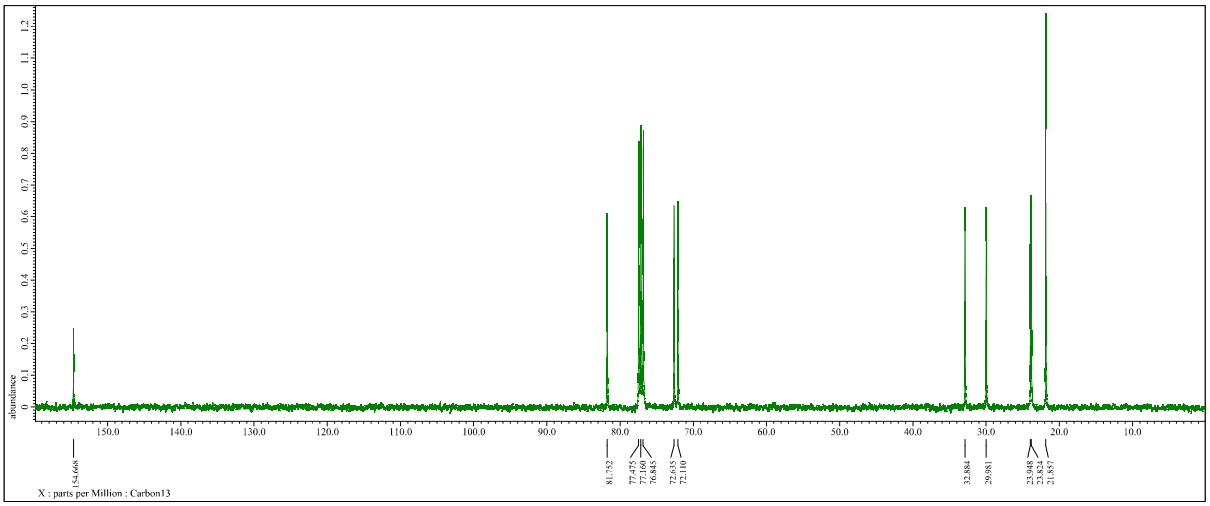
NMR spectra.



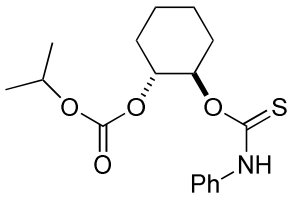
11



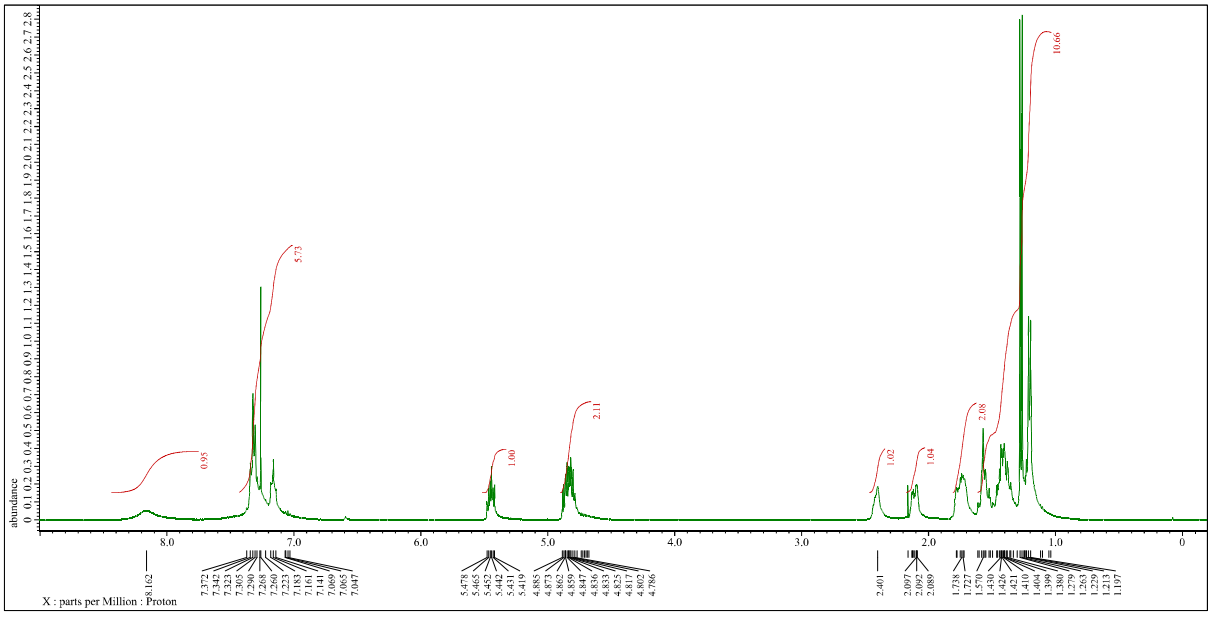
400 MHz ^{1}H NMR spectrum of **11** in $CDCl_3$



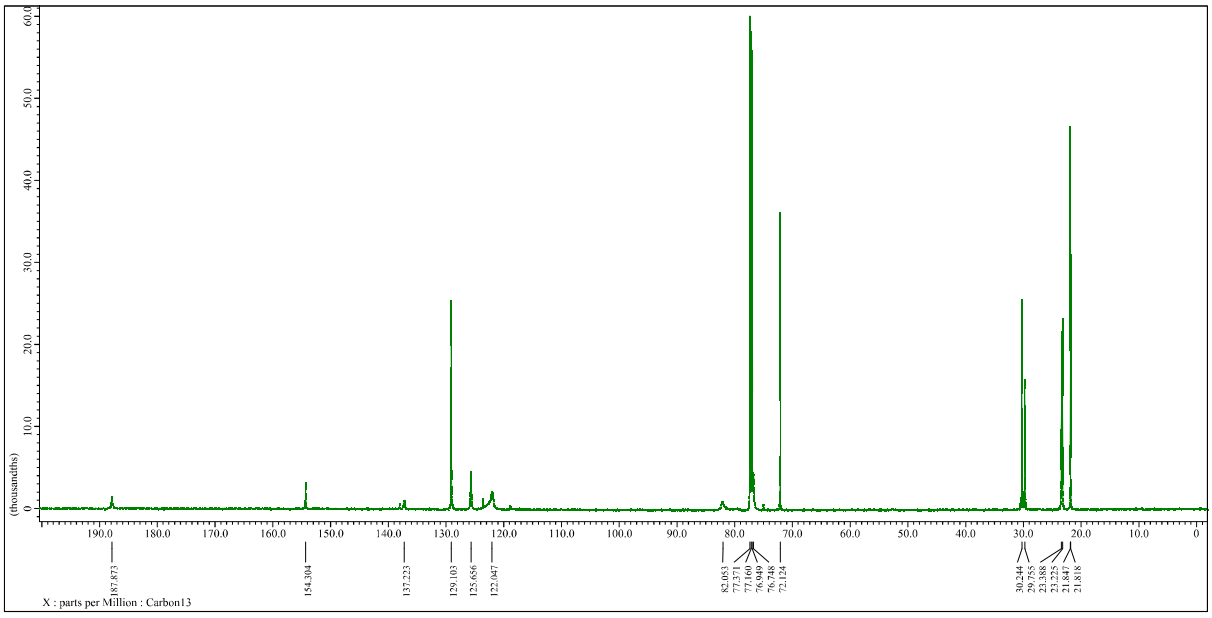
100 MHz ^{13}C NMR spectrum of **11** in $CDCl_3$



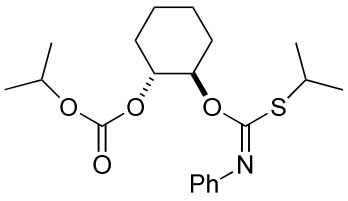
12



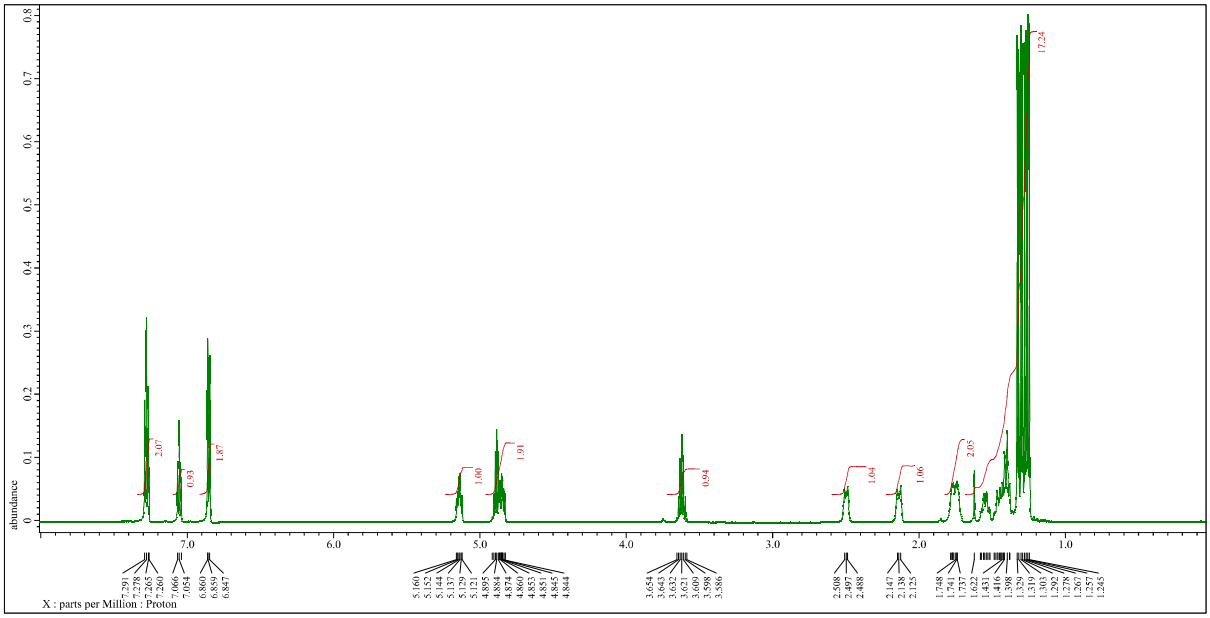
400 MHz ^{1}H NMR spectrum of **12** in $CDCl_3$ (40 °C)



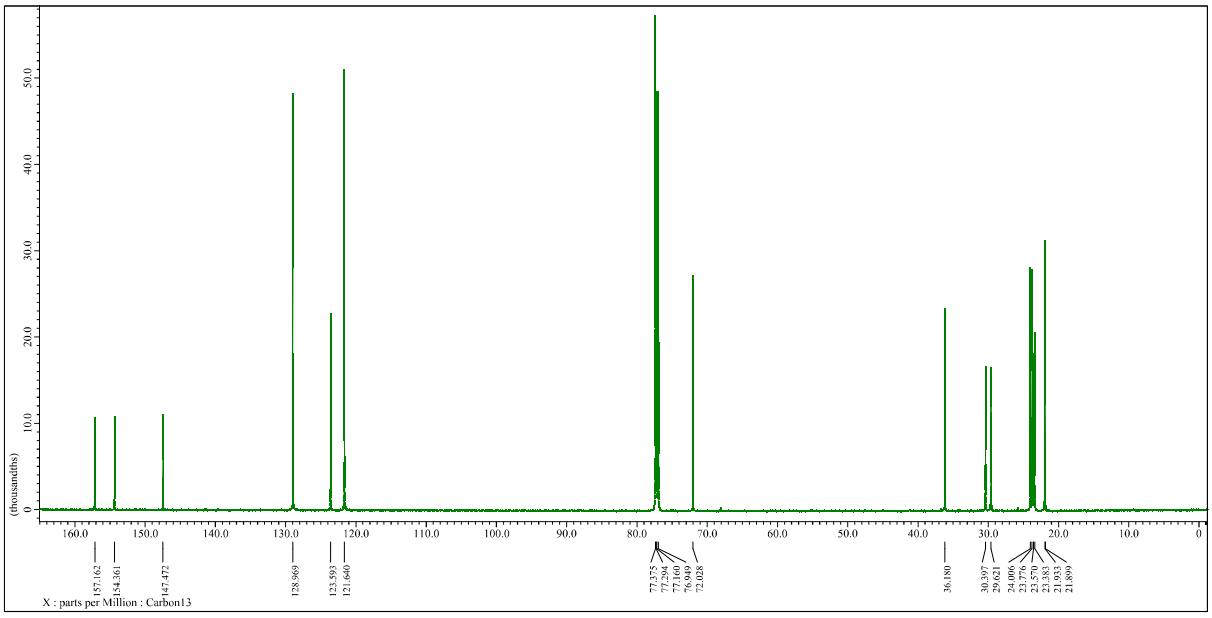
150 MHz ^{13}C NMR spectrum of **12** in $CDCl_3$ (40 °C)



13



600 MHz ^{1}H NMR spectrum of model compound **13** in $CDCl_3$



150 MHz ^{13}C NMR spectrum of model compound **13** in $CDCl_3$

Comparison of ^{1}H NMR spectra of 3a and model compound 13.

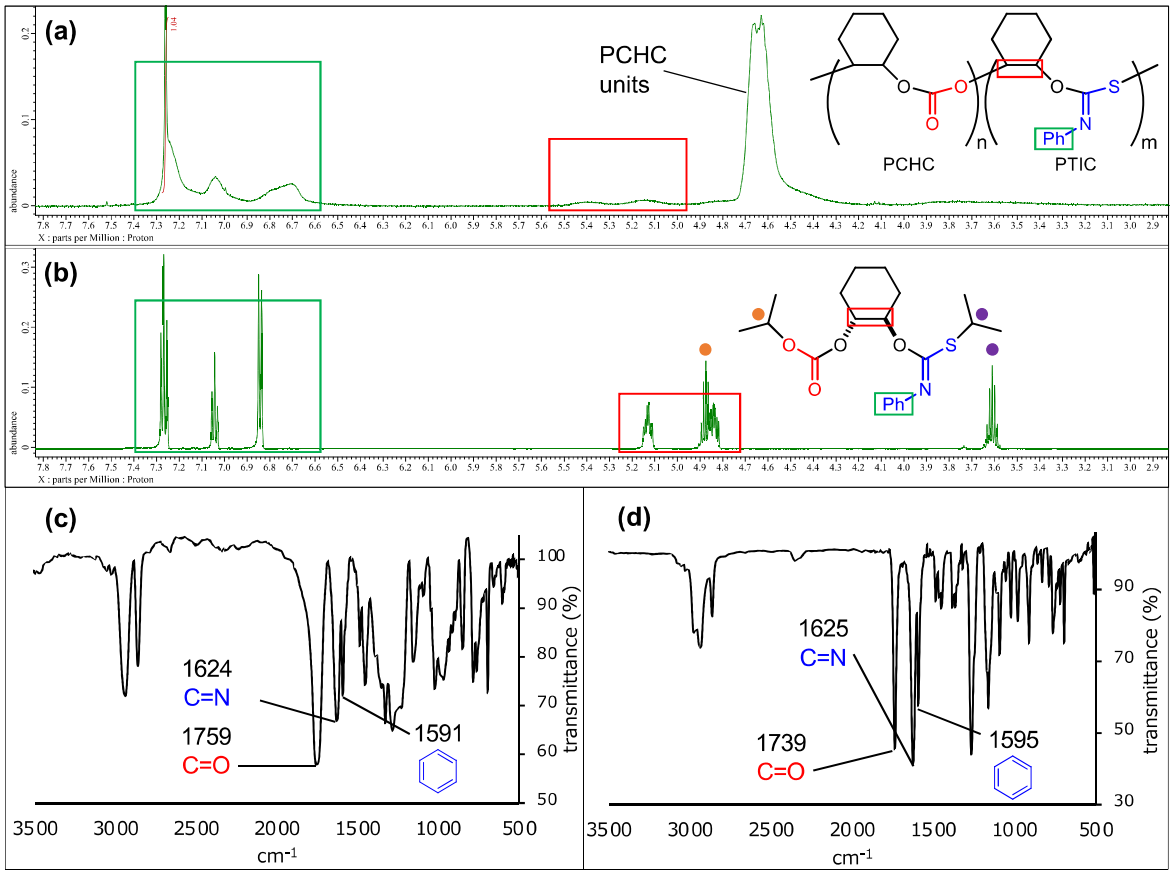


Fig. S13. ^{1}H NMR spectra ($CDCl_3$) of (a) purified terpolymer **3a** and (b) model compound **13**. IR spectra of (c) purified terpolymer **3a** and (d) model compound **13**.

[D] Kinetic studies.

The time courses of the terpolymerizations of CHO (12.5 mmol), CO_2 (2.0 MPa), and **2a** or **2d** (3.1 mmol) with **1b** (S/C = 40000 for CHO) were monitored. The reaction mixture was diluted with $CDCl_3$, and the conversion of CHO and the amount of polymers were determined by ^1H NMR analysis. The conversion of **2** was determined by the ^1H NMR analysis of the $CDCl_3$ solution that was treated with cyclohexylamine to convert **2** into the corresponding thiourea in the NMR tube.

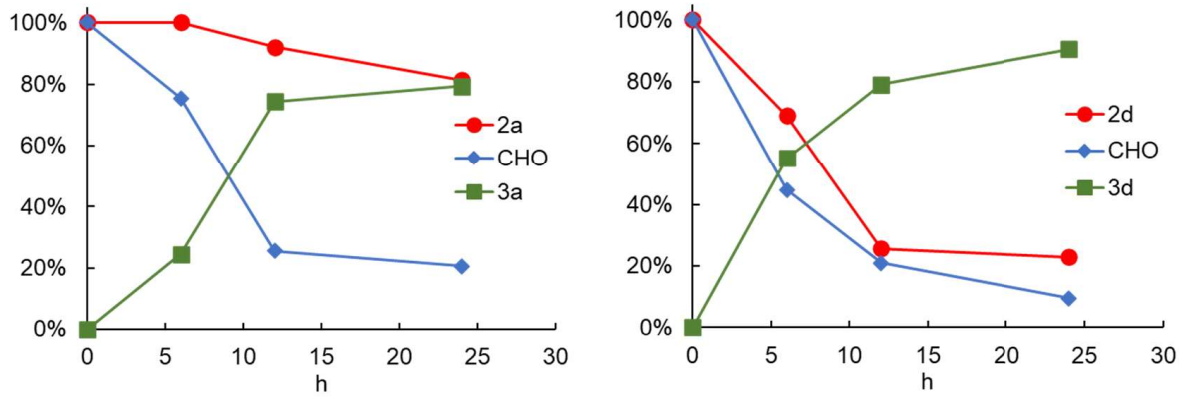
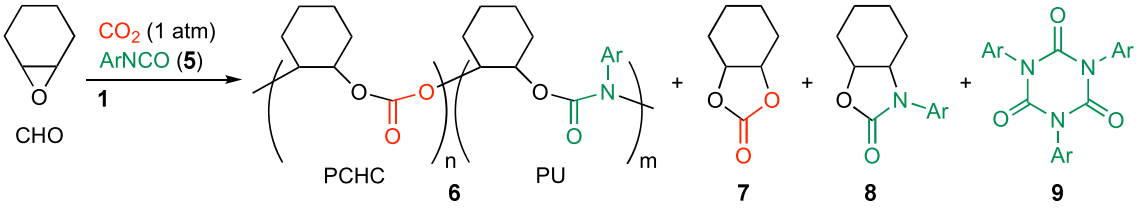


Fig. S14. Plots of the conversions and the yields in the terpolymerizations of CHO, CO_2, and **2a** or **2d**.

[E] Terpolymerization of CHO, CO_2, and aryl isocyanates.



General procedure. Catalyst **1** (amount indicated in the Tables) and a magnetic stirring bar were put in a Schlenk flask (30 mL), and the flask was dried under vacuum at 80 °C overnight. The flask was put in a glovebox (purge type) under N_2 atmosphere, and CHO (amount indicated in the Tables) was added via syringe. The flask was taken out from the glovebox. A CO_2 balloon (1 atm, approximately 2.8 L) was attached to the flask, and the flask was quickly evacuated and filled with CO_2. A mixture of **5** (amount indicated in the Tables) and CHO (amount indicated in the Tables) was added dropwise via syringe at a constant rate with a syringe-pump to the mixture of CHO and **1** at a constant temperature under CO_2, and the mixture was further stirred for 2 h. The reaction mixture was cooled to room temperature and diluted with $CDCl_3$ for ^1H NMR analysis, and mesitylene (50 mg, 0.42 mmol) was added as an internal standard to determine the conversion of CHO, TON, and the amounts of byproducts **7**,[S2] **8**,[S3] and **9**[S4]. The conversion of **5** was determined by the ^1H NMR analysis of the $CDCl_3$ solution that was treated with cyclohexylamine at room temperature to convert **5** into the corresponding urea in the NMR tube. Terpolymer **6** was isolated by adding the reaction mixture diluted with chloroform (ca. 2.5 mL) dropwise to methanol (ca. 150 mL) followed by filtration and vacuum drying. The ratio of the PCHC to PU units and the molecular weight were determined by ^1H NMR and SEC analysis of the isolated terpolymer, respectively.

The ratio of the PCHC to PU units. The ratio of the PCHC to PU units was determined by the ^{1}H NMR spectrum of a purified polymer. The PU unit was quantified simply by the integration of the signals for the aromatic protons (for example, Fig. S20a), while the PCHC unit was quantified by the integration of the signals at 3.2–5.2 ppm subtracted by that for the PU unit. The ratio of the PCHC to PTIC units (n : m) was calculated as follows: PCHC : PU (n : m) = (the integration of the signals for the PCHC units divided by 2) : (the integration of the signals for the PU units divided by the number of aromatic protons).

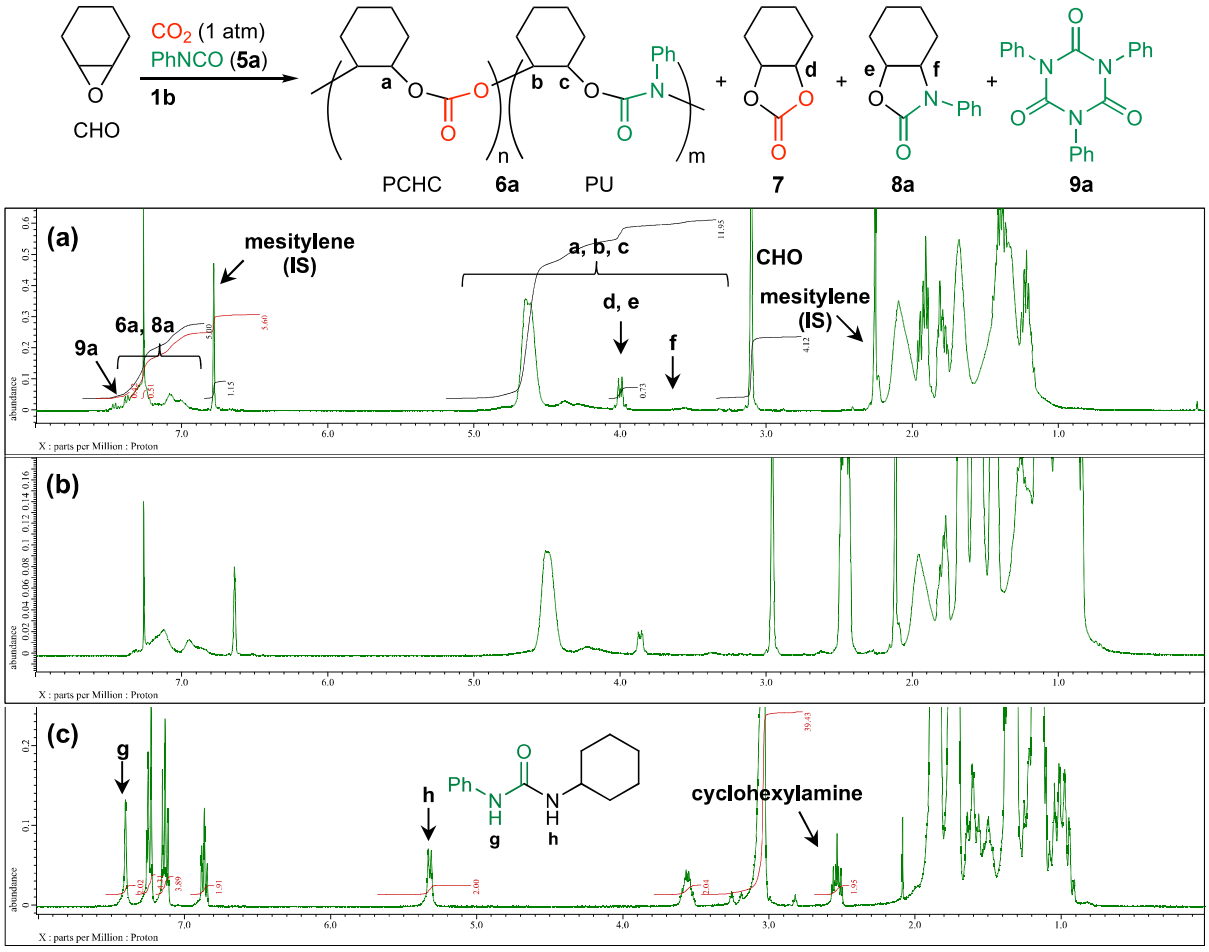


Fig. S15. ^{1}H NMR spectra ($CDCl_3$) of the crude reaction mixture (a) after terpolymerization and (b) after the addition of cyclohexylamine (Table 2, entry 1). (c) An example of the ^{1}H NMR spectrum of a mixture of CHO, **5a**, and cyclohexylamine in $CDCl_3$.

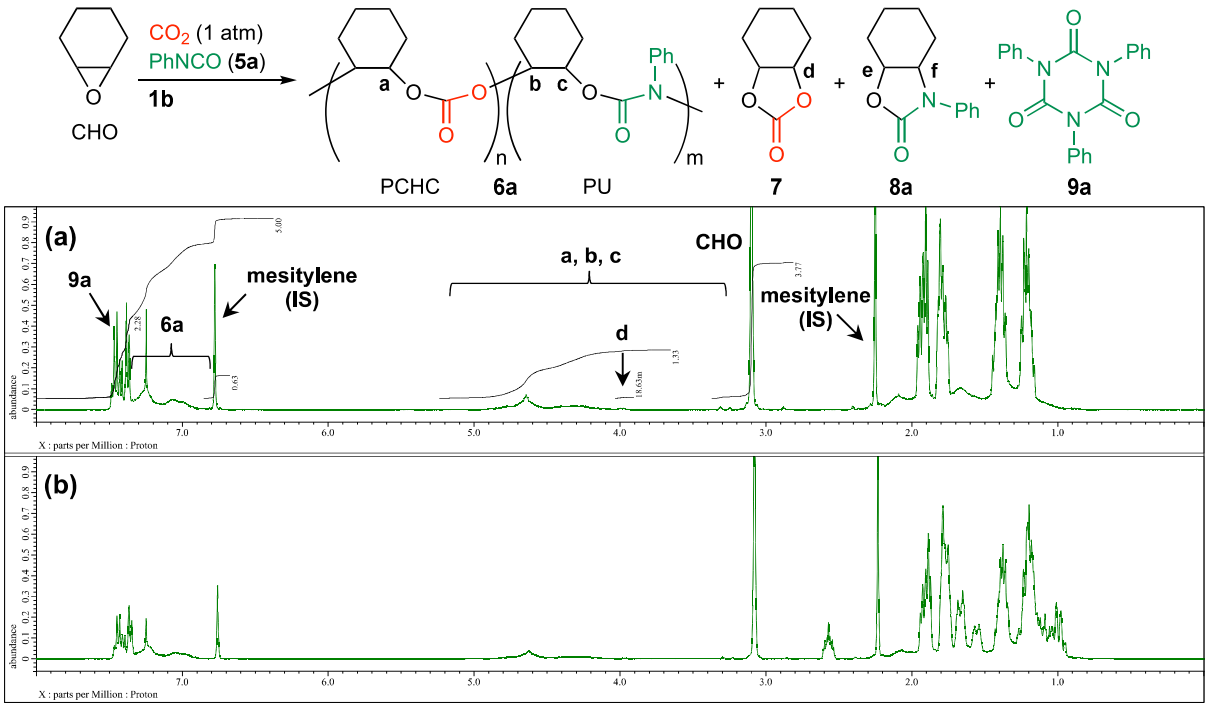


Fig. S16. ^{1}H NMR spectra ($CDCl_3$) of the crude reaction mixture (a) after terpolymerization and (b) after the addition of cyclohexylamine (Table S3, entry 7).

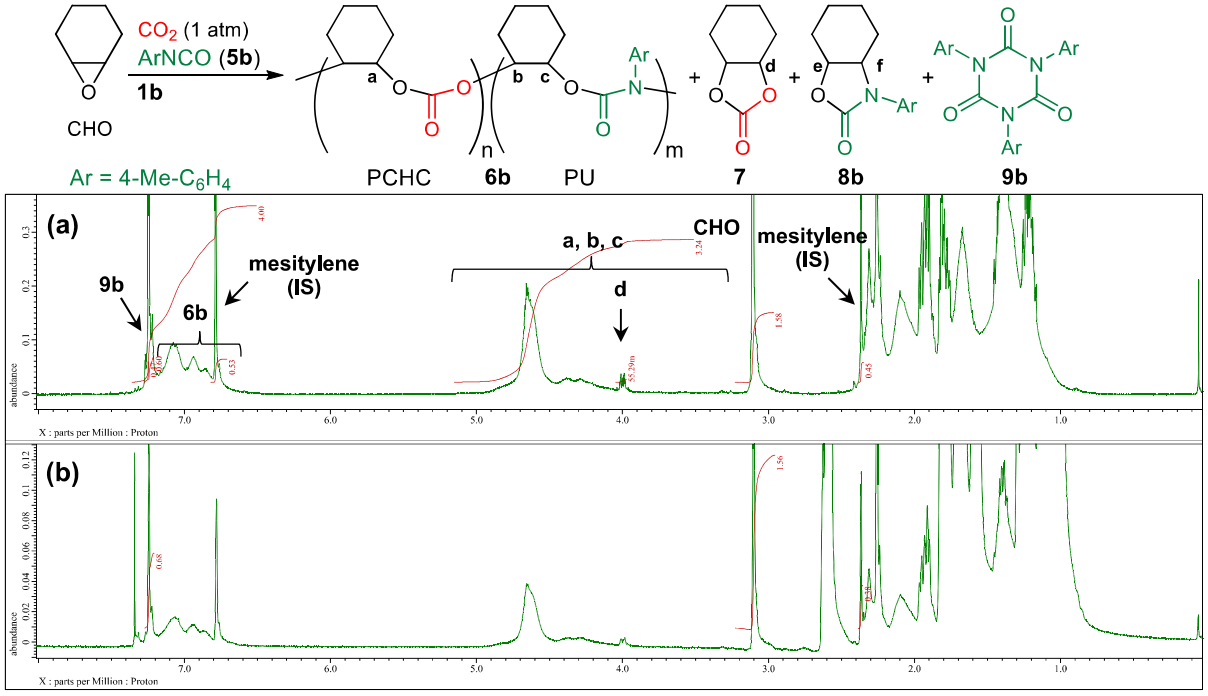


Fig. S17. ^{1}H NMR spectra ($CDCl_3$) of the crude reaction mixture (a) after terpolymerization and (b) after the addition of cyclohexylamine (Table 2, entry 2).

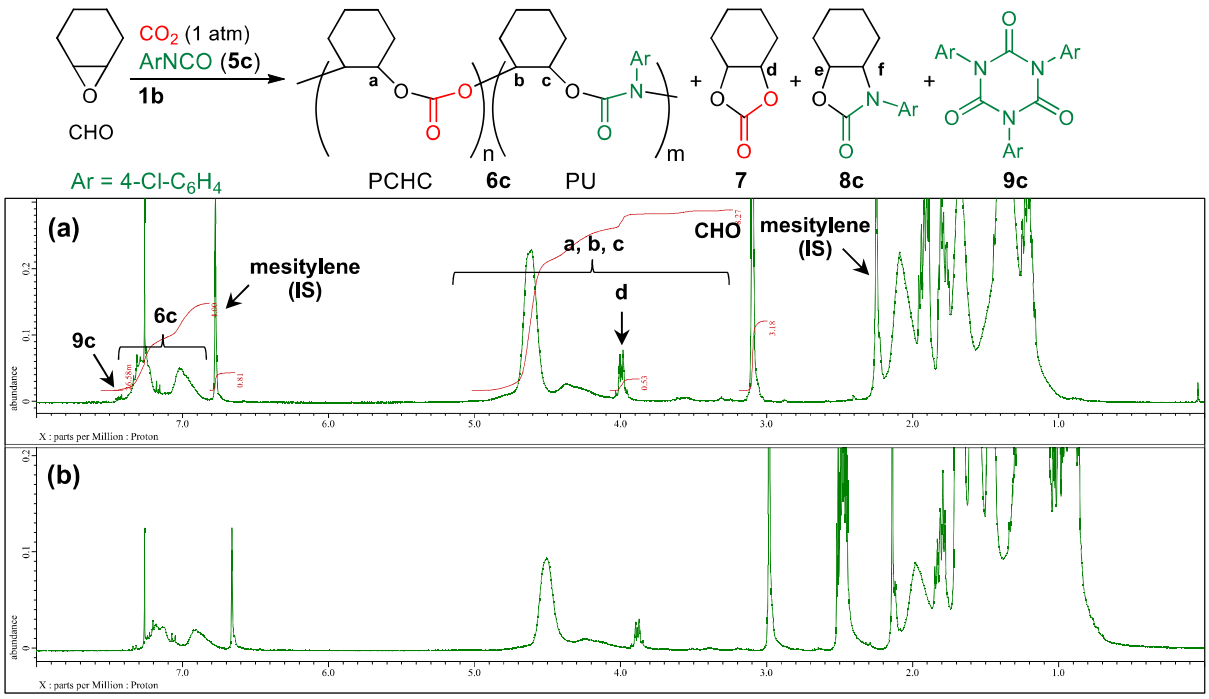


Fig. S18. ^{1}H NMR spectra ($CDCl_3$) of the crude reaction mixture (a) after terpolymerization and (b) after the addition of cyclohexylamine (Table 2, entry 3).

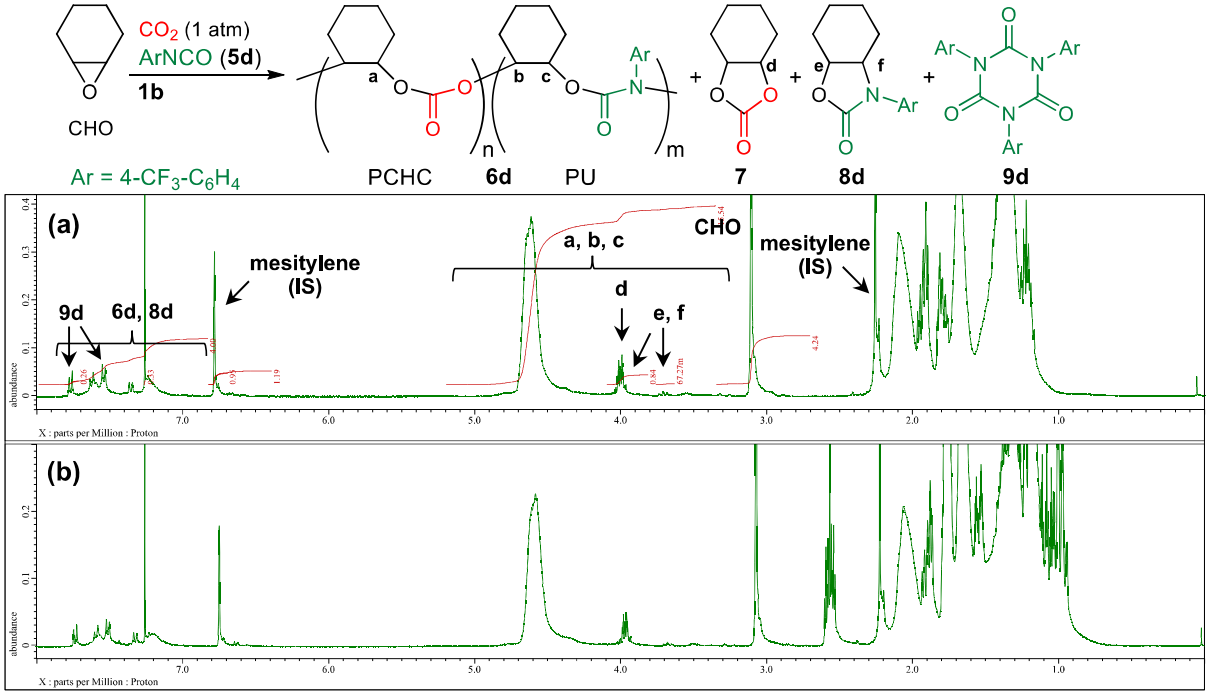


Fig. S19. ^{1}H NMR spectra ($CDCl_3$) of the crude reaction mixture (a) after terpolymerization and (b) after the addition of cyclohexylamine (Table 2, entry 4).

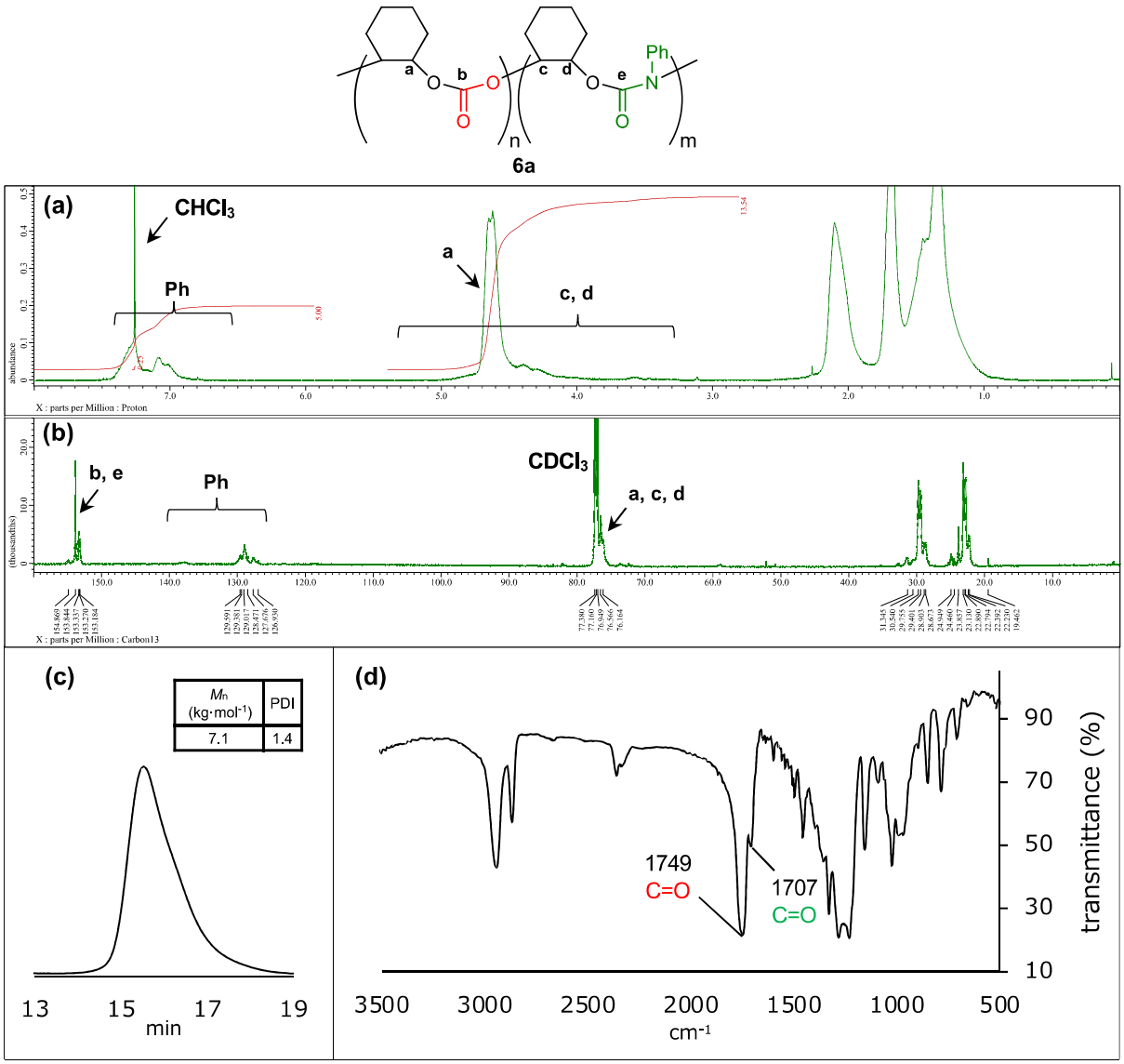


Fig. S20. (a) ^{1}H NMR spectrum ($CDCl_3$), (b) ^{13}C NMR spectrum ($CDCl_3$), (c) SEC chart, and (d) IR spectrum of purified polymer **6a** (Table 2, entry 1).

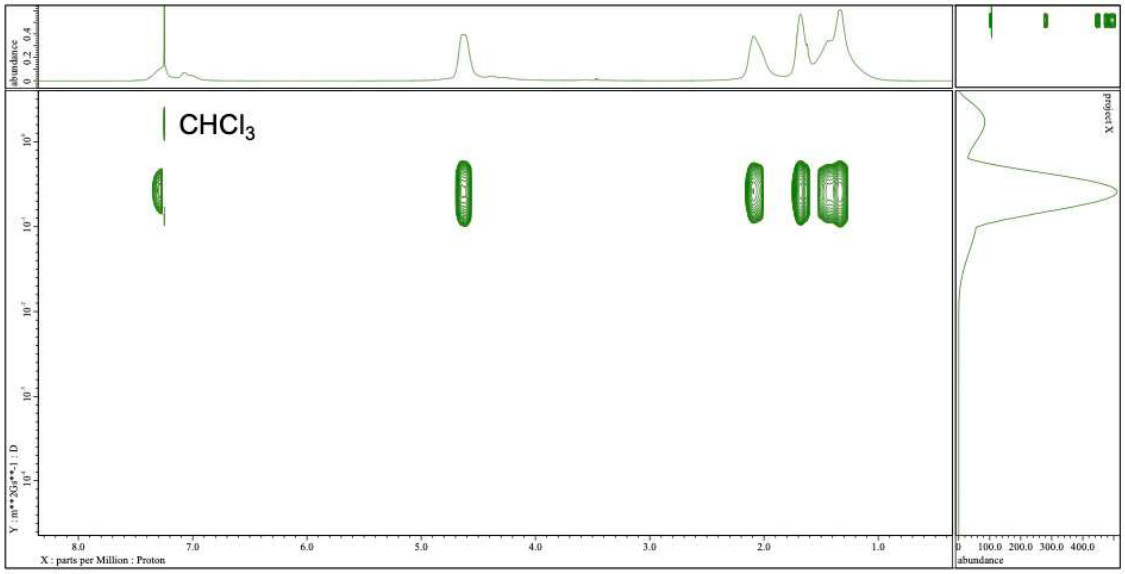


Fig. S21. DOSY spectrum ($CDCl_3$) of purified polymer **6a**.

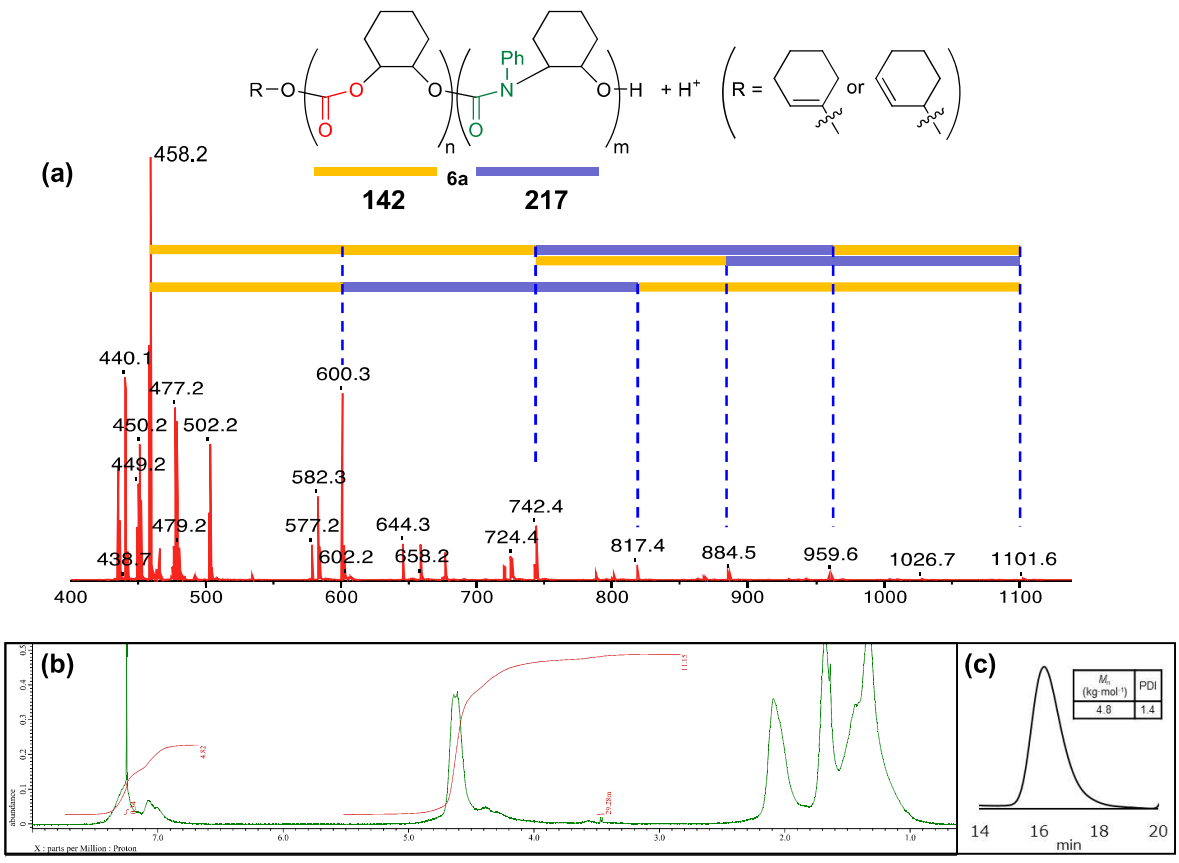


Fig. S22. (a) MALDI-TOF mass spectrum, (b) ^{1}H NMR spectrum ($CDCl_3$), and (c) SEC chart of terpolymer **6a**.

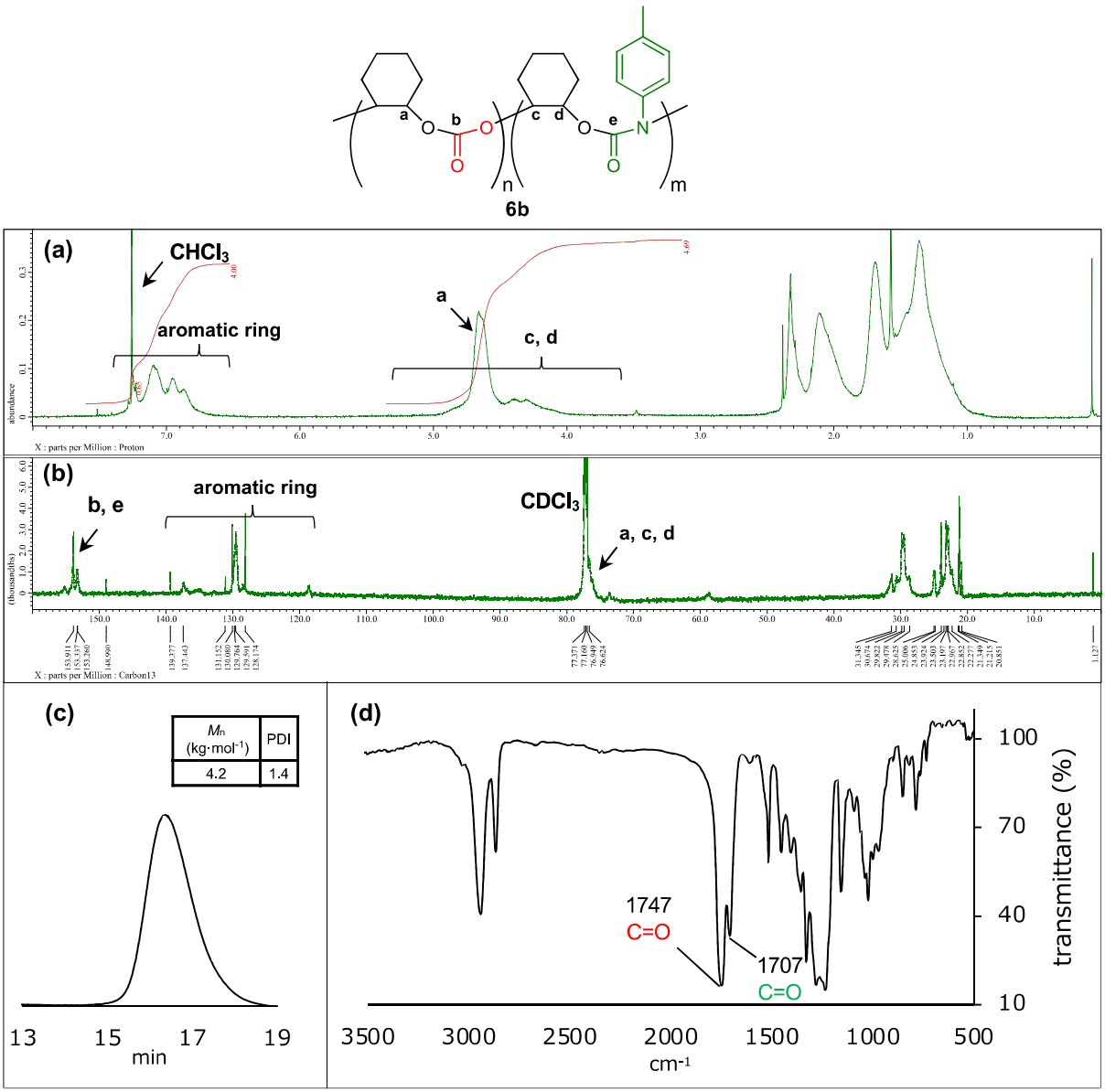


Fig. S23. (a) ^{1}H NMR spectrum ($CDCl_3$), (b) ^{13}C NMR spectrum ($CDCl_3$), (c) SEC chart, and (d) IR spectrum of purified polymer **6b** (Table 2, entry 2).

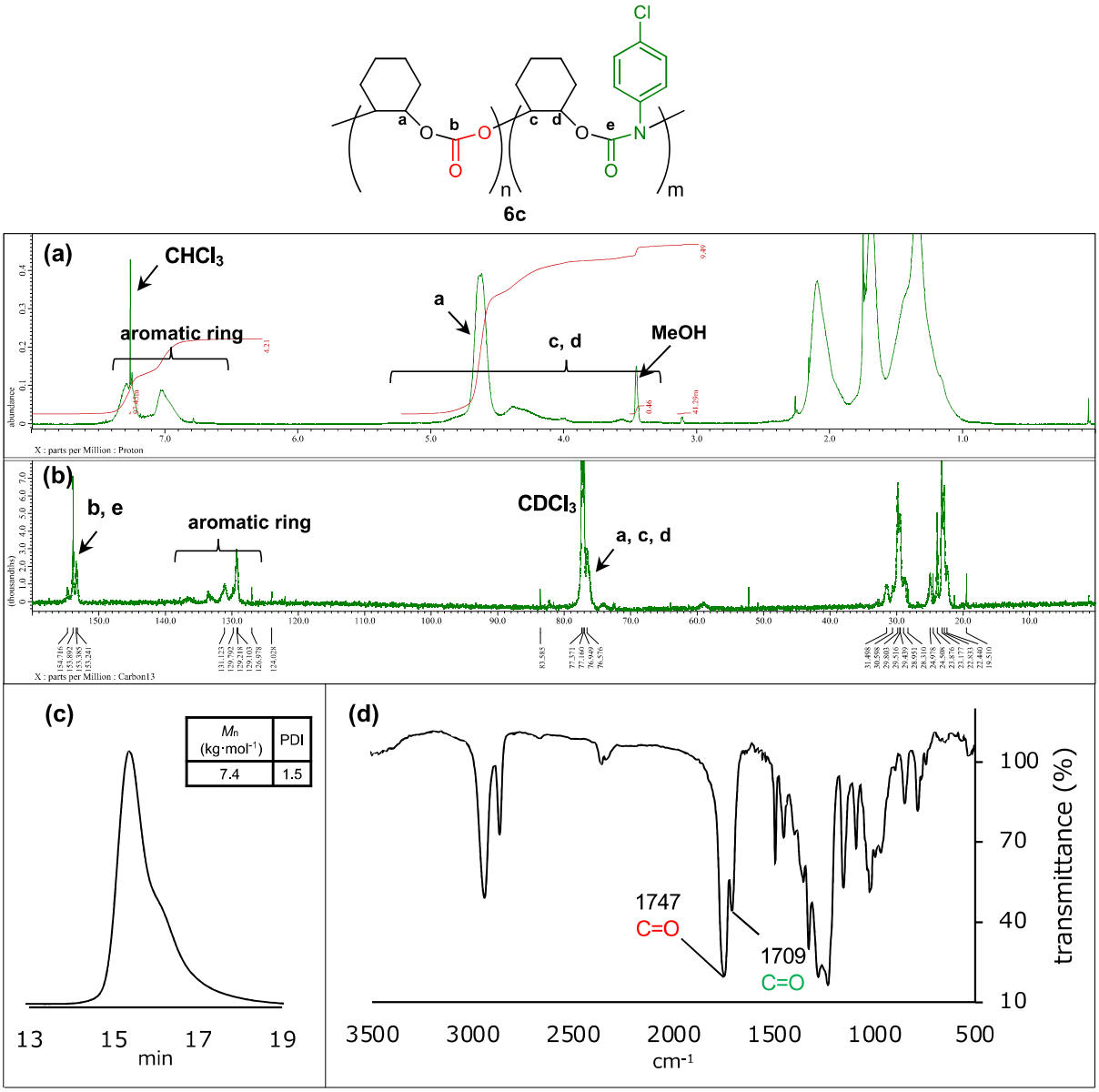


Fig. S24. (a) ^{1}H NMR spectrum ($CDCl_3$), (b) ^{13}C NMR spectrum ($CDCl_3$), (c) SEC chart, and (d) IR spectrum of purified polymer **6c** (Table 2, entry 3).

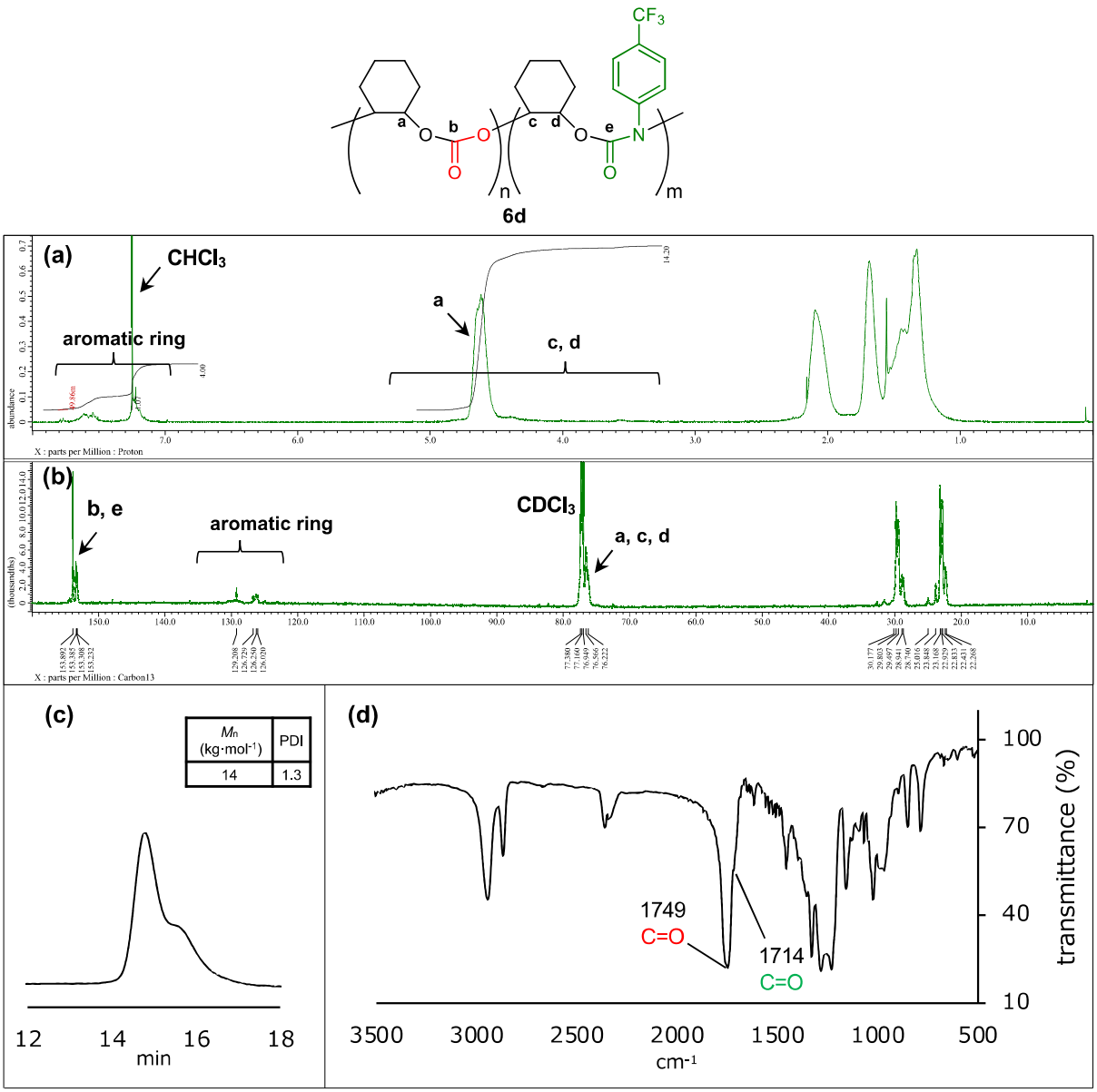


Fig. S25. (a) ^{1}H NMR spectrum ($CDCl_3$), (b) ^{13}C NMR spectrum ($CDCl_3$), (c) SEC chart, and (d) IR spectrum of purified polymer **6d** (Table 2, entry 4).

Hydrolysis experiments. To confirm the existence of the PU unit, hydrolysis experiments were conducted according to the procedure reported by Adriaenssens.[S5] A solution of purified terpolymer **6a** (approximately 10 mg) and 2.0 M KOH in D_2O (0.1 g) in DMSO-d_6 in an NMR tube was heated at 90 °C for 15 h in an oil bath. ^{1}H NMR spectrum is shown in Fig. S26. It is reported in the above reference that the hydrolysis of the polyallophanate linkage gives amino alcohol **B**, aniline (**C**), and cyclic urea **D**. In the present case, **C** and **D** were not detected at all, which revealed the absence of the polyallophanate linkage.

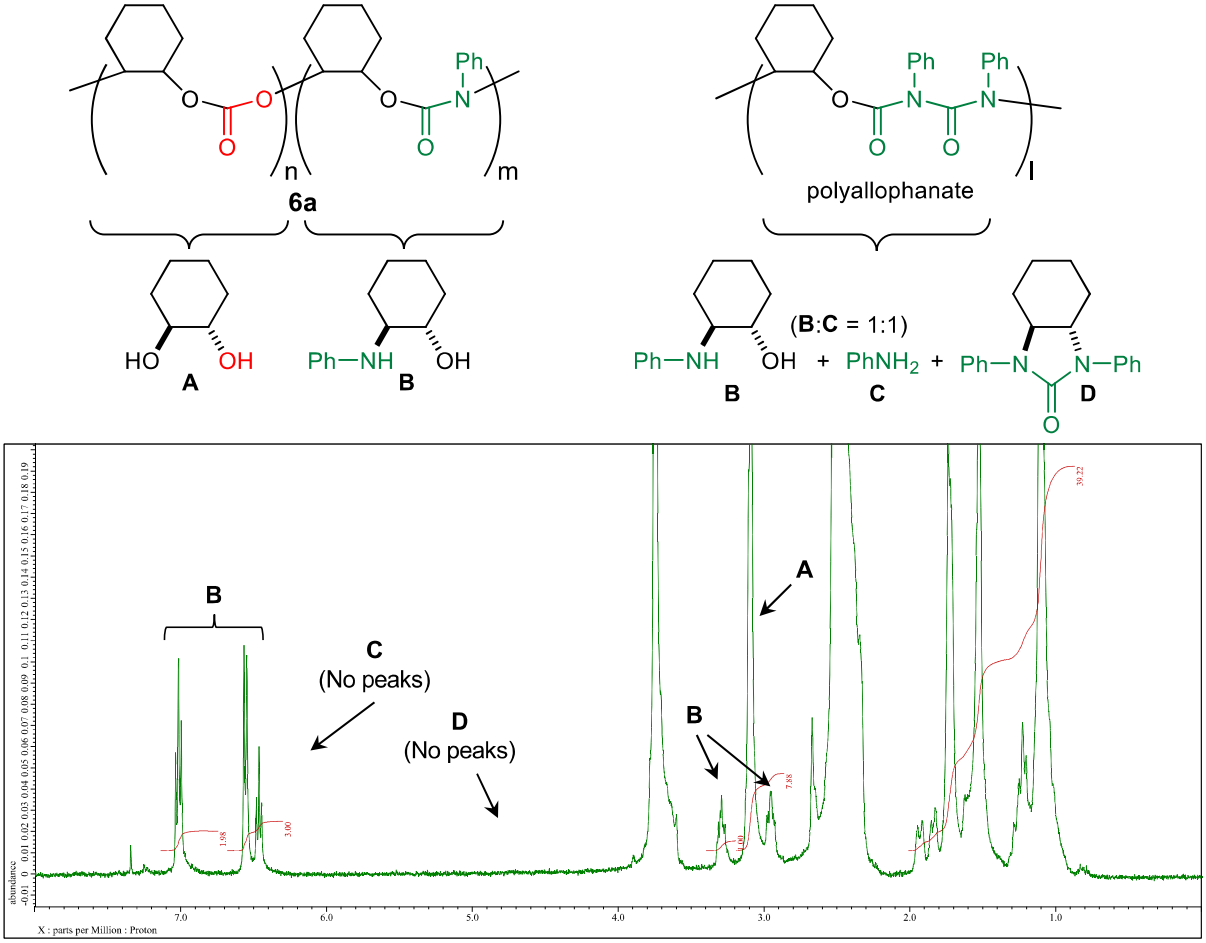
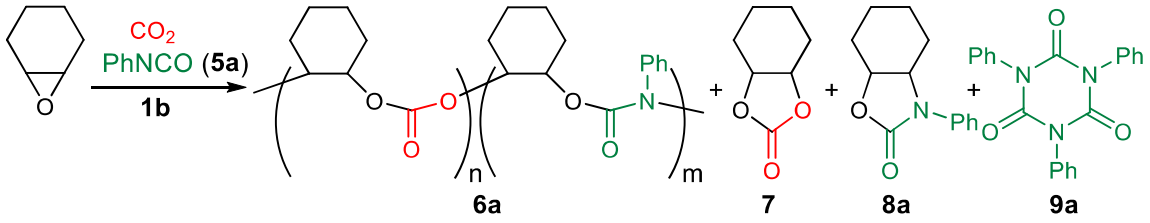


Fig. S26. ^{1}H NMR spectrum after the hydrolysis of purified polymer **6a**.

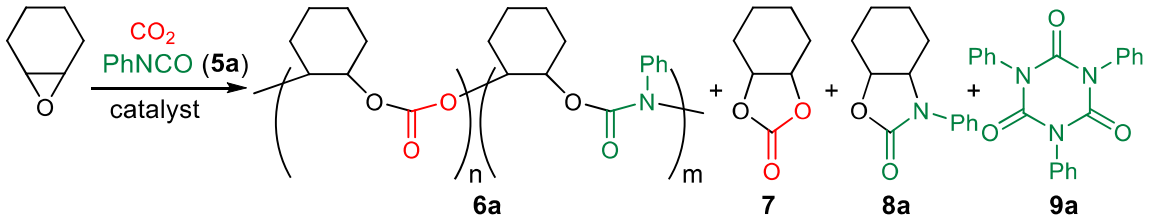
Table S3. Optimization of reaction conditions for the terpolymerization of CHO, CO_2, and **5a** with **1b**.



			conv.[c] (%)			**6a**			byproduct[c] (%)		
entry[a]	S/C[b]	*T* (°C)	CHO	**5a**	TON[c]	n:m[d]	M_n[e] (kg mol^{-1})	PDI[e]	**7**	**8a**	**9a**
1	10000	90	53	>99	1500	N.D.[f]	1.4[g]	1.4[g]	1	0	52
2	6250	90	81	>99	3200	6:1	7.1	1.4	3	0	8
3	3000	90	85	>99	1900	6:1	7.3	1.3	4	0	7
4	6250	80	79	>99	3600	5:1	6.0	1.3	3	0	14
5	6250	100	85	>99	3400	6:1	6.4	1.2	4	0	15
6[h]	6250	90	35	>99	1100	N.D.[f]	1.1[g]	1.5[g]	0	0	75
7[i]	6250	90	46	>99	1200	N.D.[f]	2.6[g]	1.3[g]	0	0	66
8[j]	6250	90	79	>99	3300	8:1	7.2	1.5	3	0	18

[a] A mixture of CHO (1.2 mmol) and **5a** (1.2 mmol) was added dropwise to a mixture of CHO (11.2 mmol) and **1b** (quantity indicated above) at 15 μL/h with a syringe-pump under CO_2 (1 atm, balloon) at 90 °C, and the mixture was stirred at 90 °C for 2 h. [b] Ratio of CHO to **1b**. [c] Determined by ^{1}H NMR analysis of the crude reaction mixture. TON for the formation of **6a**. The yields of **7** were calculated based on CHO, and those of **8a** and **9a** were calculated based on **5a**. [d] Determined by ^{1}H NMR analysis of the purified polymer. [e] Determined by SEC analysis of the purified polymer using THF as an eluent and polystyrene as a molecular-weight standard. [f] The PCHC/PU ratio was not determined due to the low molecular weight of polymers or the considerable formation of byproduct **9a**. [g] The crude reaction mixture was analyzed. [h] Addition at 24 μL/h. [i] CHO = 4.8 mmol instead of 11.2 mmol. [j] CHO = 16.8 mmol instead of 11.2 mmol.

Table S4. Screening of catalysts for the terpolymerization of CHO, CO_2, and **5a**.

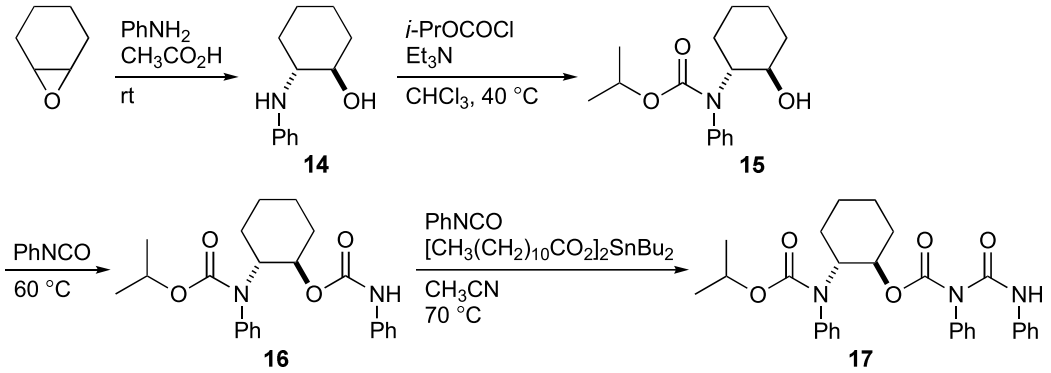


		conv.[b] (%)			**6a**			byproduct[b] (%)		
entry[a]	catalyst	CHO	**5a**	TON[b]	n:m[c]	M_n[d] (kg mol^{-1})	PDI[d]	**7**	**8a**	**9a**
1	**1a**	57	>99	1400	N.D.[e]	3.7	1.3	0	2	82
2	**1b**	81	>99	3200	6:1	7.1[f]	1.4[f]	3	0	8
3	**1c**	63	>99	2600	N.D.[e]	2.5	1.5	2	1	21
4	**1d**	50	>99	1500	N.D.[e]	1.0	1.4	2	0	48
5[g]	Al(TPP)Br	35	>99	100	N.D.[e]	<1.0	–	0	0	91

[a] A mixture of CHO (1.2 mmol) and **5a** (1.2 mmol) was added dropwise to a mixture of CHO (11.2 mmol) and catalyst (S/C = 6250 for CHO) at 15 μL/h with a syringe-pump under CO_2 (1 atm, balloon) at 90 °C, and the mixture was stirred at 90 °C for 2 h. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. TON for the formation of **6a**. The yields of **7** were calculated based on CHO, and those of **8a** and **9a** were calculated based on **5a**. [c] Determined by ^{1}H NMR analysis of the purified polymer. [d] Determined by SEC analysis of crude reaction mixtures using THF as an eluent and polystyrene as a molecular-weight standard. [e] The PCHC/PU ratio was not determined due to the low molecular weight of polymers or the formation of a large amount of byproduct **9a**. [f] The purified polymer was analyzed. [g] TBAB (4 equiv of Al(TPP)Br) was added.

[F] Synthesis and characterization of model compounds for terpolymer 6a.

Amino alcohol **14** was prepared and characterized according to the literature.[S6]

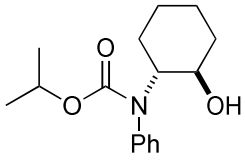


Synthesis of 15. Amino alcohol **14** (500 mg, 2.62 mmol) was put in a flask (25 mL), and it was dried under vacuum at room temperature for 3 h. After the addition of Et_3N (0.35 mL, 2.6 mmol) and dry $CHCl_3$ (2.0 mL) under N_2, isopropyl chloroformate (1.0 mL, 8.8 mmol) was added dropwise at 40 °C, and the reaction mixture was stirred at 40 °C for 4 h. The mixture was diluted with EtOAc, washed with water, and dried over Na_2SO_4. Purification by silica gel column chromatography (hexane/EtOAc = 5/1) gave **15** as a white solid (436 mg, 1.57 mmol, 60%). mp 84–87 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, 50 °C) δ 1.00–1.41 (m, 10H), 1.60–1.69 (m, 2H), 1.83–1.90 (m, 1H), 2.04–2.11 (m, 1H), 2.28 (d, J = 6.0 Hz, 1H), 3.38–3.46 (m, 1H), 4.03–4.09 (m, 1H), 4.87–4.96 (m, 1H), 7.10–7.36 (m, 5H); ^{13}C NMR ($CDCl_3$, 150 MHz, 40 °C) δ 21.96, 22.01, 24.4, 25.4, 30.5, 35.5, 63.0, 69.1, 71.6, 127.4, 128.6, 130.0, 139.0, 157.1; IR (KBr) 3443, 2988, 2951, 2934, 2859, 1690, 1655, 1597, 1495, 1452, 1408, 1364, 1308, 1261, 1184, 1148, 1109, 1072, 1053, 1034, 1016, 999, 957, 866, 785, 768 cm^{-1}; HRMS (FAB) calcd for $C_{16}H_{24}NO_3$ 278.1756, found 278.1756 ([M + H]$^+$).

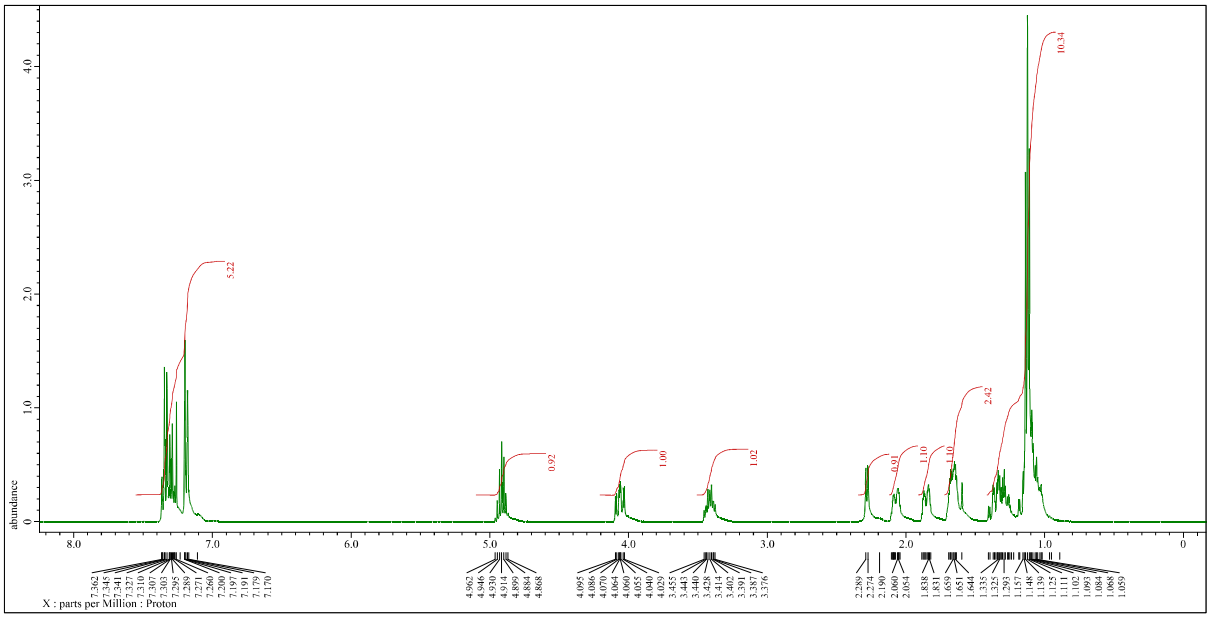
Synthesis of 16. Alcohol **15** (525 mg, 1.90 mmol) was put in a Schlenk flask (25 mL), and it was dried under vacuum at 40 °C for 2 h. To the flask under N_2 was added phenyl isocyanate (1.16 g, 9.74 mmol) via syringe, and the mixture was stirred at 60 °C for 2 h. Residual phenyl isocyanate was removed by vacuum distillation at 100 °C, and purification by silica gel column chromatography (hexane/EtOAc = 3/1) gave **16** as a white solid (324 mg, 0.817 mmol, 43%). mp 121–125 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, 60 °C) δ 1.07–1.45 (m, 10H), 1.67–1.75 (m, 2H), 1.95 (br s, 1H), 2.23 (d, J = 10.5 Hz, 1H), 4.34 (br s, 1H), 4.65–4.69 (m, 1H), 4.87–4.94 (m, 1H), 6.61 (br s, 1H), 7.03–7.39 (m, 10H); ^{13}C NMR ($CDCl_3$, 150 MHz, 50 °C) δ 22.1, 24.1, 25.3, 29.9, 31.0, 32.2, 59.9, 69.1, 74.4, 118.9, 123.5, 127.5, 128.9, 129.2, 129.8, 138.3, 139.1, 153.1, 156.1; IR (KBr) 3298, 3063, 2980, 2934, 2860, 1732, 1699, 1682, 1601, 1541, 1501, 1445, 1404, 1373, 1312, 1223, 1109, 1082, 1061, 1042, 1030, 756, 706, 692 cm^{-1}; HRMS (FAB) calcd for $C_{23}H_{29}N_2O_4$ 397.2127, found 397.2127 ([M + H]$^+$).

Synthesis of 17. Compound **16** (130 mg, 0.327 mmol) was put in a Schlenk flask (25 mL), and it was dried under vacuum at 60 °C for 2 h. To the flask under N_2 was added phenyl isocyanate (408 mg, 3.43 mmol), dibutyltin dilaurate (216 mg, 0.342 mmol), and CH_3CN (1.0 mL) via syringes. The mixture was stirred at 70 °C for 4 h. Residual phenyl isocyanate and CH_3CN were removed by vacuum distillation at 100 °C, and purification by alumina column chromatography (hexane/EtOAc = 6/1) gave **17** as a white solid (42.9 mg, 0.083 mmol, 25%). mp 57–61 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, 50 °C) δ 1.12–1.33 (m, 10H), 1.69 (d, J = 7.3 Hz, 2H), 1.91–1.94 (m, 1H), 2.21–2.23 (m, 1H), 3.67 (br s, 1H), 4.85–4.94 (m, 1H), 5.08 (br s, 1H), 6.84 (d, J = 6.4 Hz, 2H), 7.06–7.10 (m, 1H), 7.17–7.33 (m, 7H), 7.36–7.46 (m, 3H), 7.48–7.57 (m, 2H), 10.9 (s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz, 50 °C) δ 22.0, 22.1, 24.0, 25.0, 30.1, 31.8, 62.3, 68.9, 76.6, 120.2, 124.1, 127.0, 128.3, 128.7, 128.9, 129.0, 129.1, 129.2, 137.3, 138.1, 141.0, 151.7, 154.8, 155.5; IR (KBr) 3285, 2978, 2938, 2862, 1732, 1697, 1593, 1545, 1493, 1449, 1375, 1329, 1304, 1269, 1234, 1179, 1155, 1109, 1078, 1007, 989, 756, 737, 694, 669 cm^{-1}; HRMS (FAB) calcd for $C_{30}H_{34}N_3O_5$ 516.2498, found 516.2498 ($[M + H]^+$).

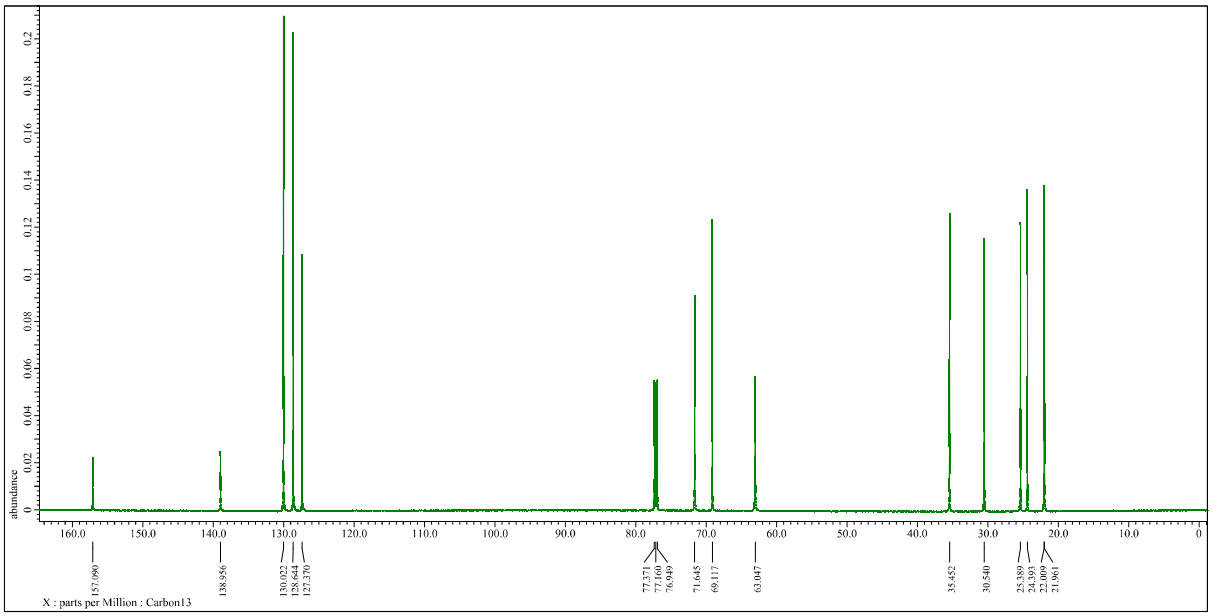
NMR spectra.



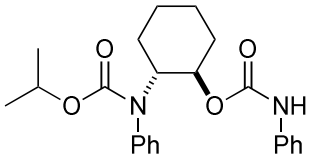
15



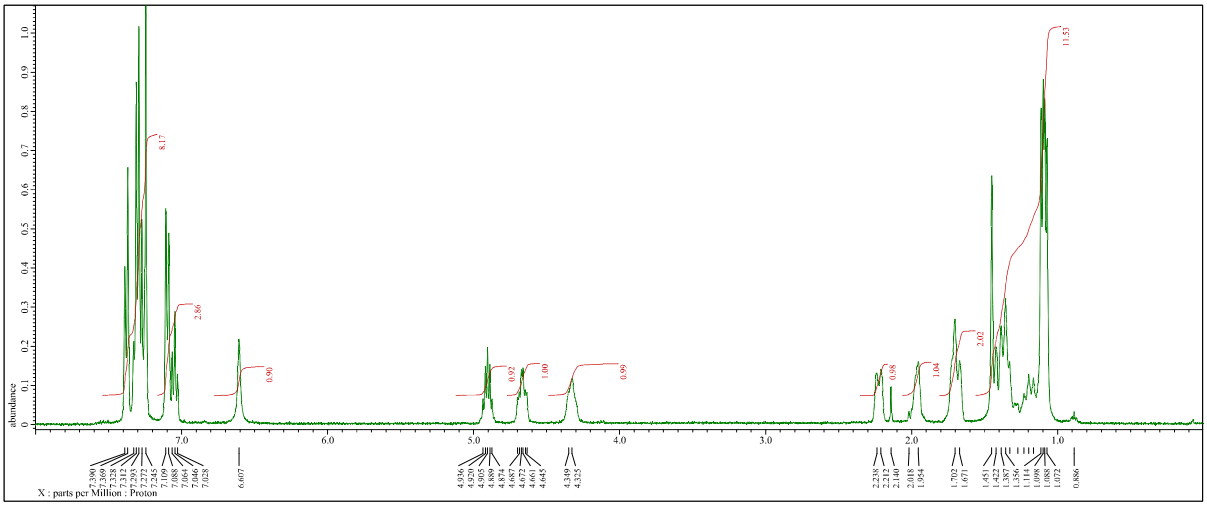
400 MHz ^{1}H NMR spectrum of **15** in $CDCl_3$ (50 °C)



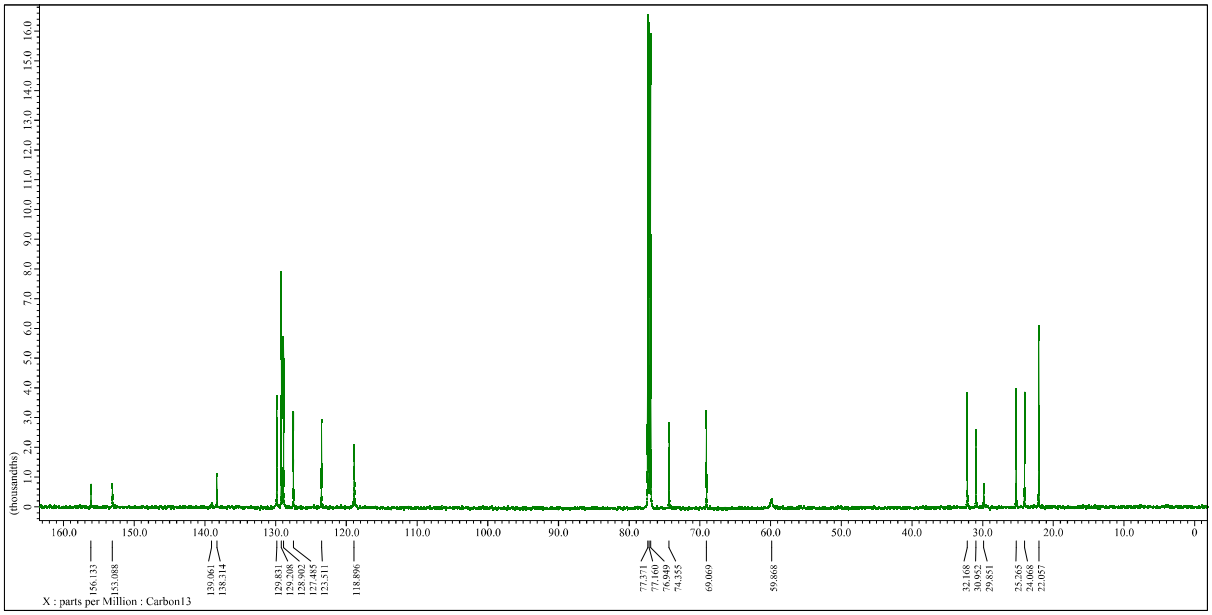
150 MHz ^{13}C NMR spectrum of **15** in $CDCl_3$ (40 °C)



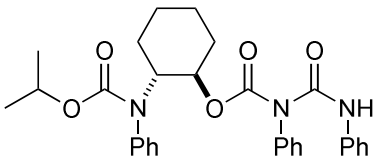
16



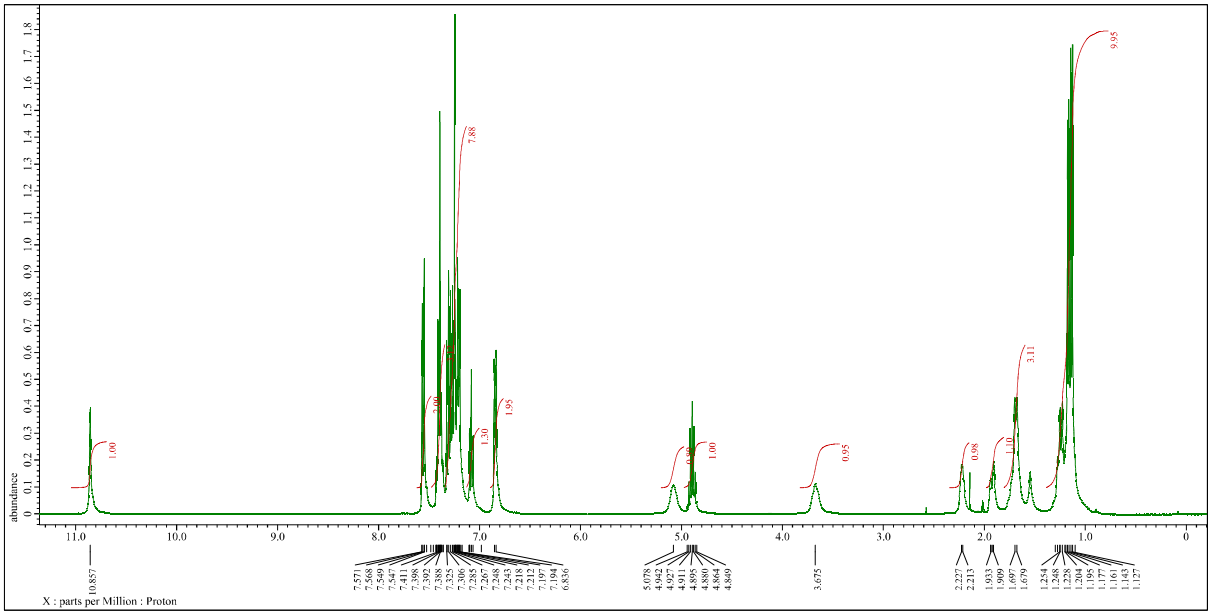
400 MHz ^{1}H NMR spectrum of model compound **16** in $CDCl_3$ (60 °C)



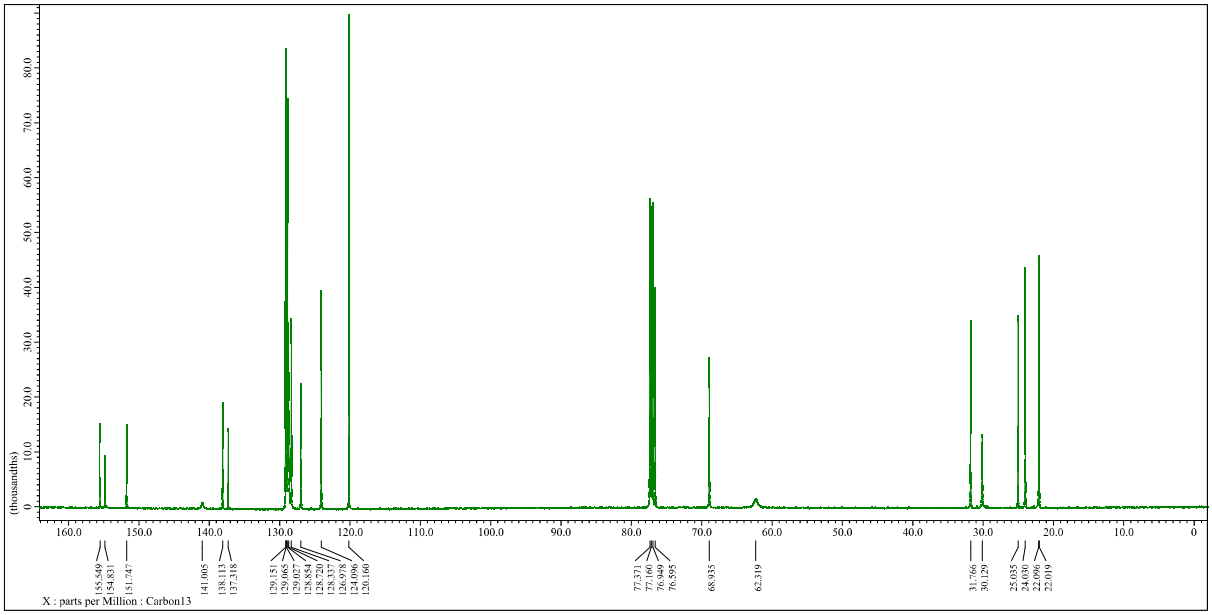
150 MHz ^{13}C NMR spectrum of model compound **16** in $CDCl_3$ (50 °C)



17



400 MHz ^{1}H NMR spectrum of model compound **17** in $CDCl_3$ (50 °C)



150 MHz ^{13}C NMR spectrum of model compound **17** in $CDCl_3$ (50 °C)

Comparison of the ^{1}H NMR spectrum of terpolymer 6a and those of model compounds 16 and 17.

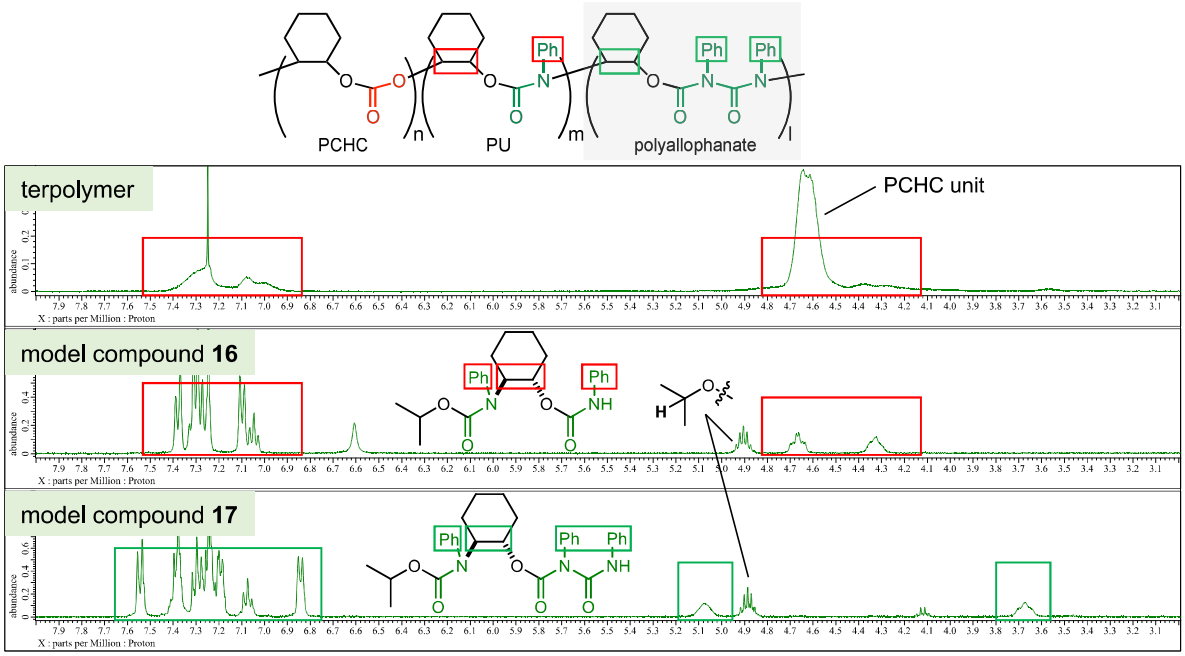
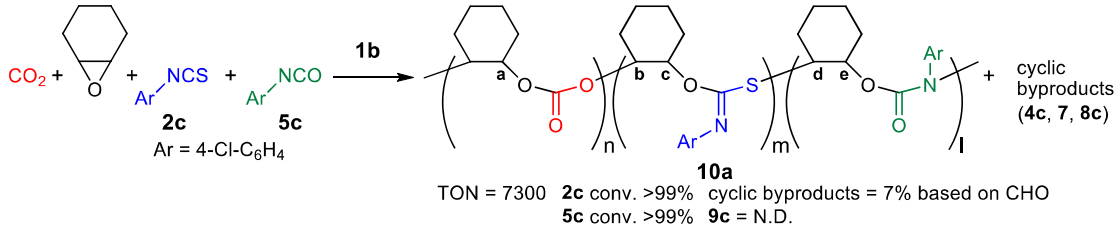


Fig. S27. ^{1}H NMR spectra ($CDCl_3$) of purified terpolymer **6a** and model compounds **16** and **17**.

[G] Quaterpolymerization of CHO, CO_2, aryl isothiocyanates, and aryl isocyanates.

(a) Quaterpolymerization of CHO, CO_2, 2c, and 5c.

Catalyst **1b** (2.09 mg, 1.01 μmol, S/C = 12000 for CHO) was put in a Schlenk flask (30 mL) equipped with a magnetic stirrer, and it was dried at 80 °C under vacuum overnight. The flask was put in a glovebox (purge type) under N_2 atmosphere, and CHO (1.10 g, 11.2 mmol) and **2c** (0.42 g, 2.4 mmol) were added. The flask was taken out from the glovebox. A CO_2 balloon (1 atm) was attached to the flask, and the flask was quickly evacuated and filled with CO_2. A mixture of **5c** (0.19 g, 1.2 mmol) and CHO (0.12 g, 1.2 mmol) was added dropwise via syringe with a syringe-pump over 13 h to the mixture of CHO, **2c**, and **1b** at 90 °C under CO_2 (1 atm, balloon). The reaction mixture was cooled to room temperature and diluted with $CDCl_3$ for ^1H NMR analysis. The conversion of CHO, TON, and the amounts of cyclic byproducts were determined by using DMSO (41 mg, 0.53 mmol) as an internal standard. The conversions of **2c** and **5c** were determined by the ^1H NMR analysis of the $CDCl_3$ solution that was treated with cyclohexylamine at room temperature to convert **2c** and **5c** into the corresponding thiourea and urea, respectively, in the NMR tube. The quaterpolymer **10a** was isolated by adding the reaction mixture diluted with chloroform dropwise to methanol followed by filtration and vacuum drying.



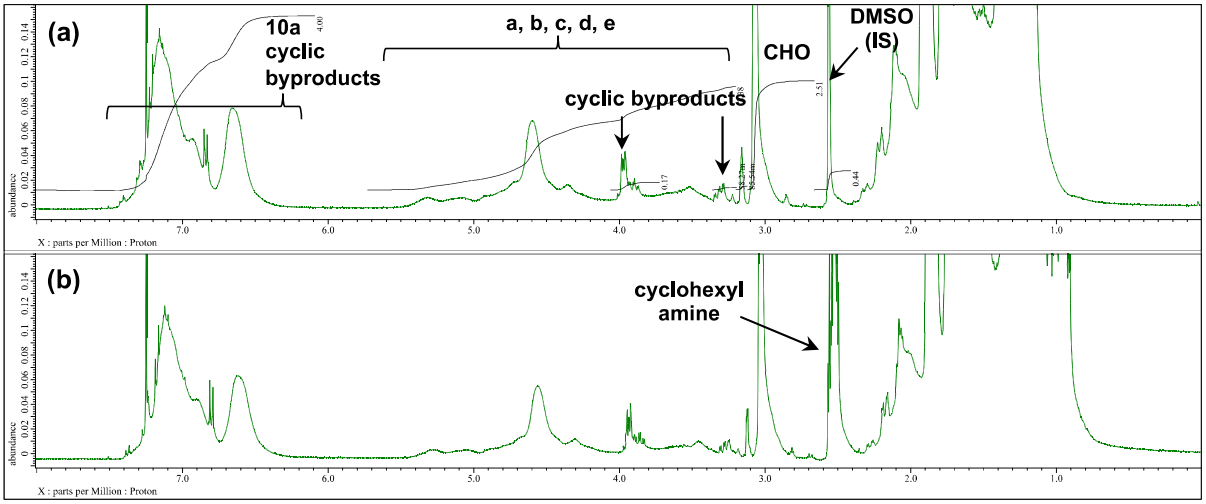


Fig. S28. ^1H NMR spectra ($CDCl_3$) of the crude reaction mixture (a) after quaterpolymerization and (b) after the addition of cyclohexylamine.

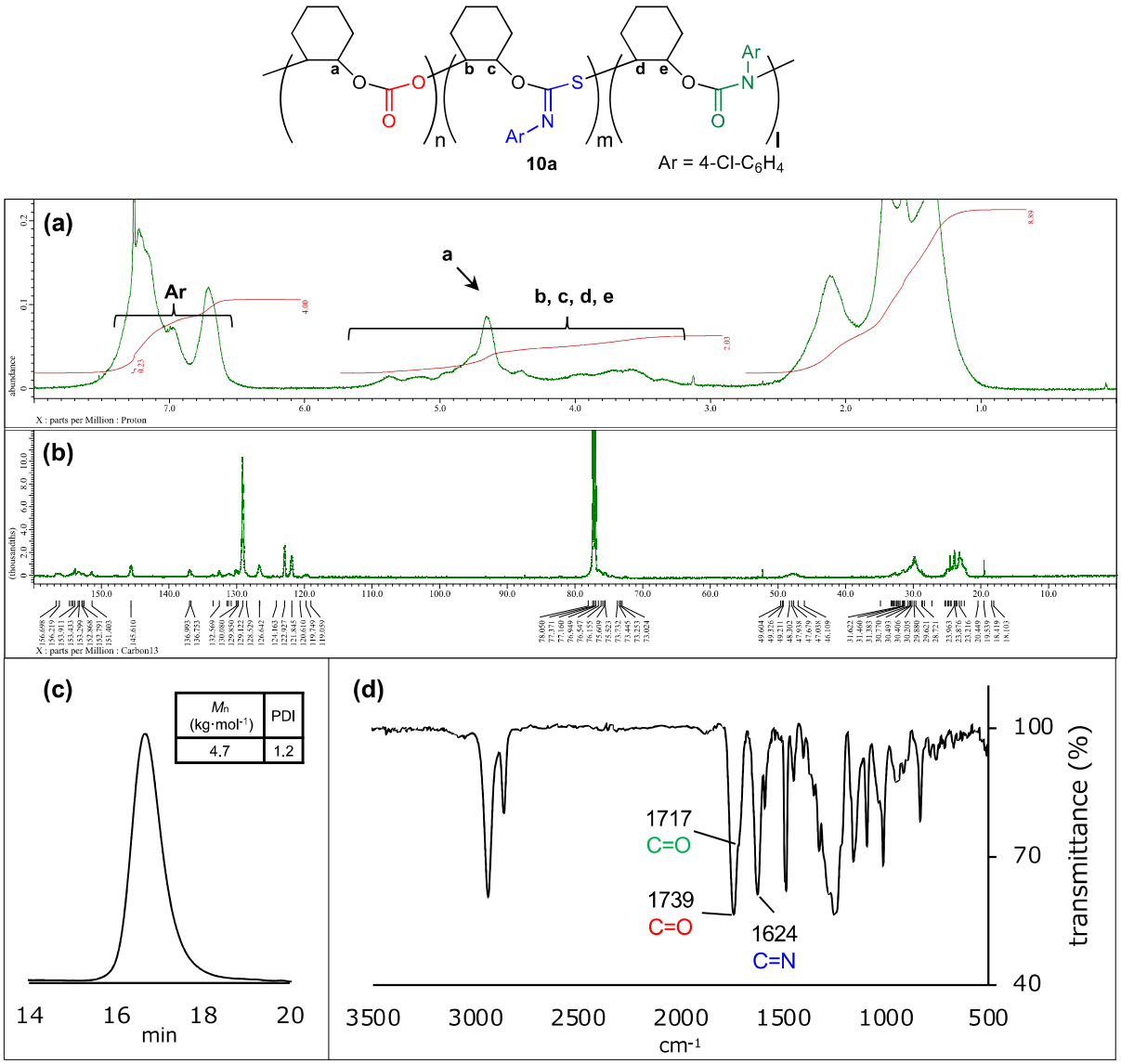


Fig. S29. (a) ^{1}H NMR spectra ($CDCl_3$), (b) ^{13}C NMR spectra ($CDCl_3$), (c) SEC chart, and (d) IR spectrum of purified polymer **10a**.

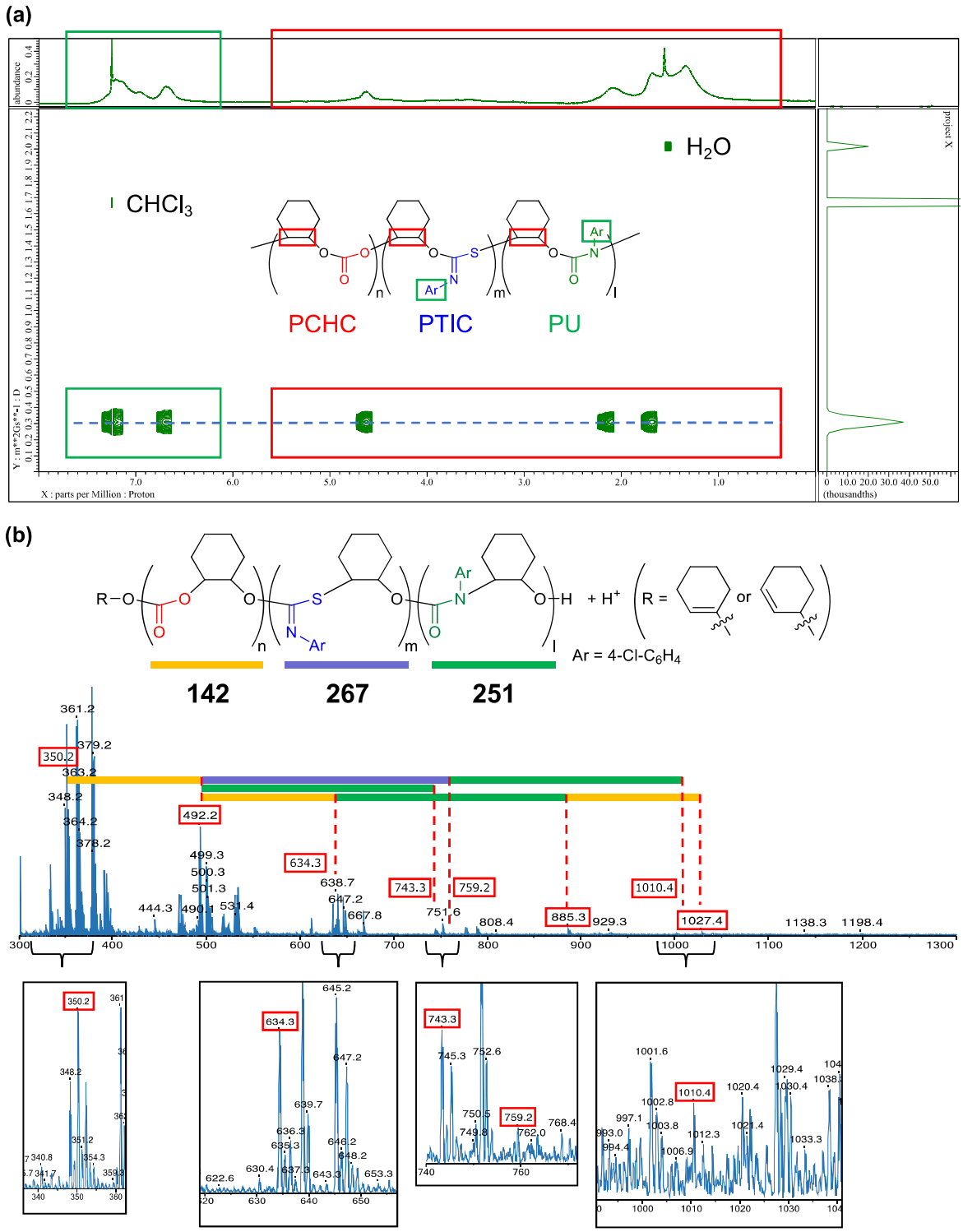
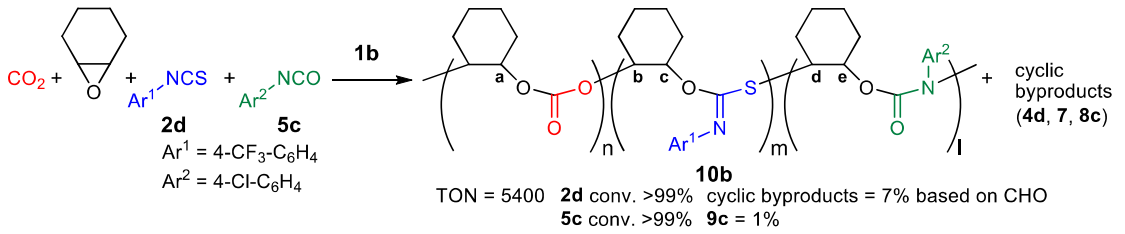


Fig. S30. (a) DOSY spectrum ($CDCl_3$) of purified polymer **10a**. (b) MALDI-TOF mass spectrum of polymer **10a**.

(b) Quaterpolymerization of CHO, CO_2, 2d, and 5c.

Catalyst **1b** (2.09 mg, 1.01 μmol, S/C = 12000 for CHO) was put in a Schlenk flask (30 mL) equipped with a magnetic stirrer, and it was dried at 90 °C under vacuum overnight. The flask was put in a glovebox (purge type) under N_2 atmosphere, and CHO (1.09 g, 11.2 mmol) and **2d** (0.50 g, 2.5 mmol) were added. The flask was taken out from the glovebox. A CO_2 balloon (1 atm) was attached to the flask, and the flask was quickly evacuated and filled with CO_2. A mixture of **5c** (0.20 g, 1.3 mmol) and CHO (0.12 g, 1.2 mmol) was added dropwise via syringe with a syringe-pump over 21 h to the mixture of CHO, **2d**, and **1b** at 90 °C under CO_2 (1 atm, balloon). The reaction mixture was cooled to room temperature and diluted with $CDCl_3$ for ^1H NMR analysis. The conversion of CHO, TON, and the amounts of cyclic byproducts were determined by using DMSO (56 mg, 0.72 mmol) as an internal standard. The conversions of **2d** and **5c** were determined by the ^1H NMR analysis of the $CDCl_3$ solution that was treated with cyclohexylamine at room temperature to convert **2d** and **5c** into the corresponding thiourea and urea, respectively, in the NMR tube. The quaterpolymer **10b** was isolated by adding the reaction mixture diluted with chloroform dropwise to methanol followed by filtration and vacuum drying.



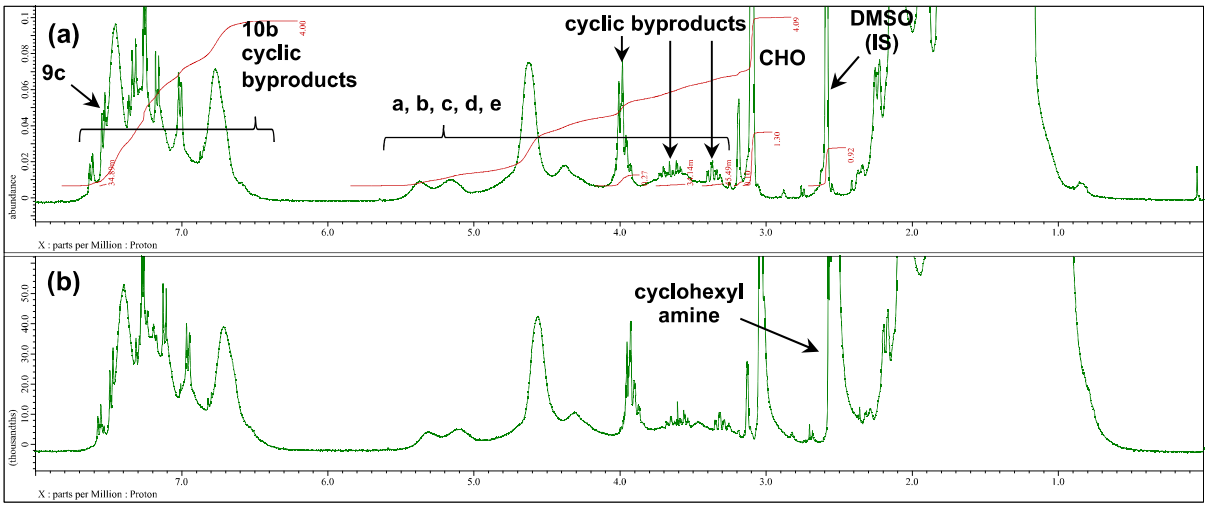


Fig. S31. ^1H NMR spectra ($CDCl_3$) of the crude reaction mixture (a) after quaterpolymerization and (b) after the addition of cyclohexylamine.

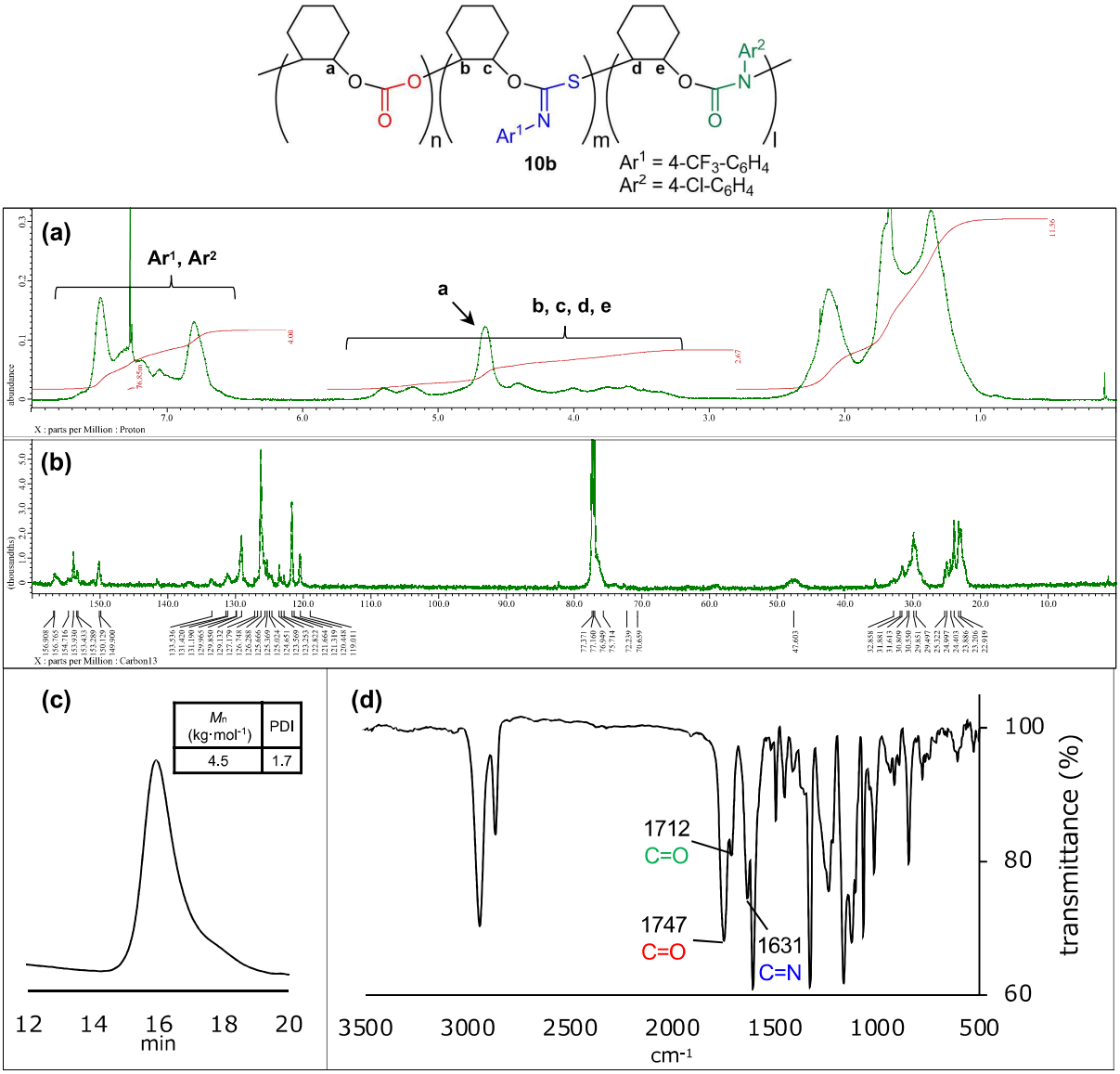


Fig. S32. (a) ^{1}H NMR spectra ($CDCl_3$), (b) ^{13}C NMR spectra ($CDCl_3$), (c) SEC chart, and (d) IR spectrum of purified polymer **10b**.

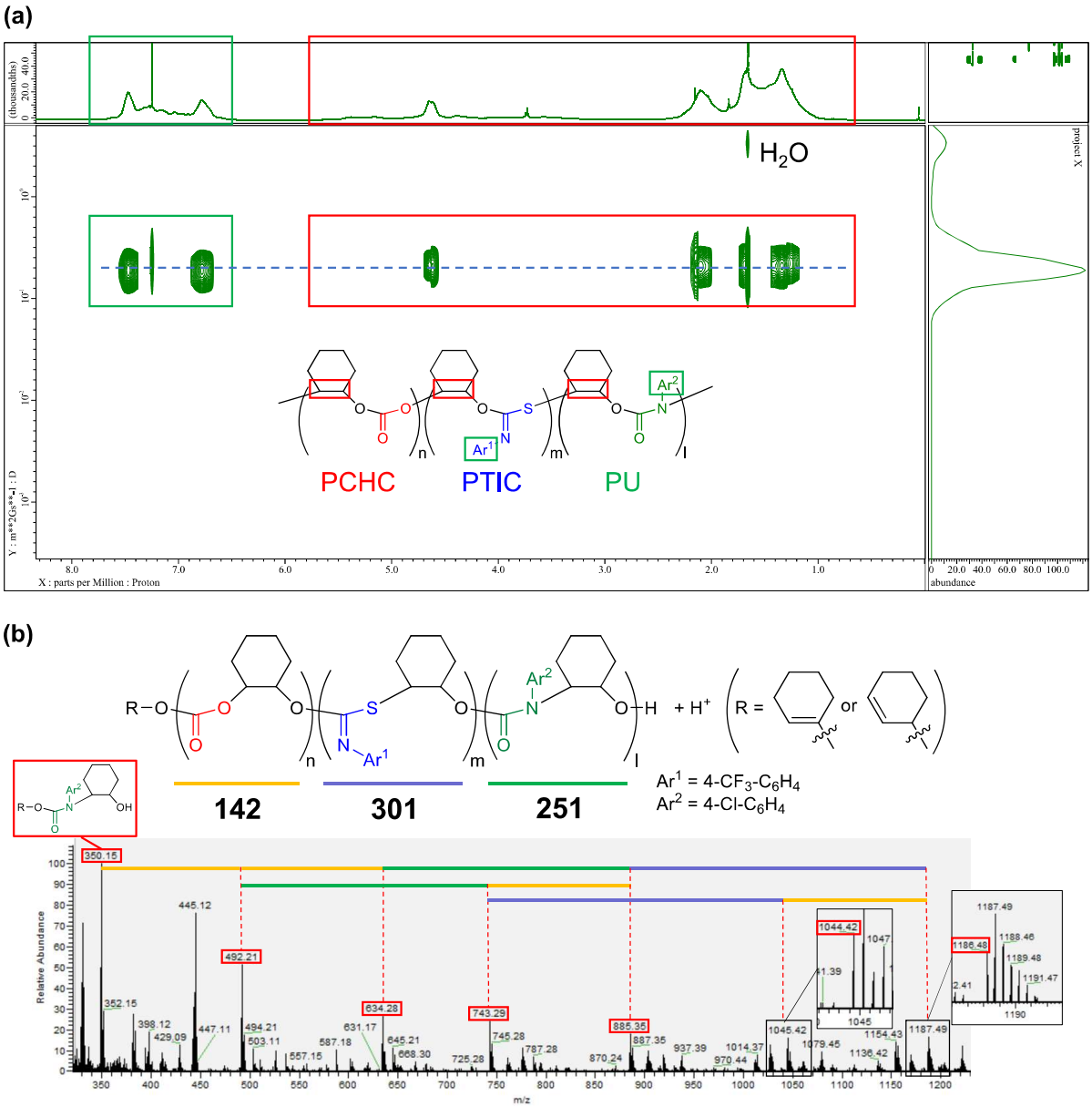


Fig. S33. (a) DOSY spectrum ($CDCl_3$) of purified polymer **10b**. (b) APCI mass spectrum of polymer **10b**.

[H] Degradation of polymers by acid treatment or UV irradiation.

General procedure for acid treatment. Purified polymer (30 mg), THF (1 mL), and conc. HCl (35%, five drops, 0.15 g) were put in a flask (10 mL), and the mixture was stirred at room temperature for reaction time indicated in Fig. 1b. The mixture was evaporated and diluted with $CDCl_3$ for ^1H NMR analysis or with THF for SEC analysis (Fig. S34, S36, and S37). The residual polymer was isolated by adding the reaction mixture diluted with chloroform dropwise to methanol followed by filtration and vacuum drying. The purified polymer was analyzed by ^1H NMR spectroscopy and SEC, which indicated that the purified polymer consisted of only the PCHC unit (Fig. S35).

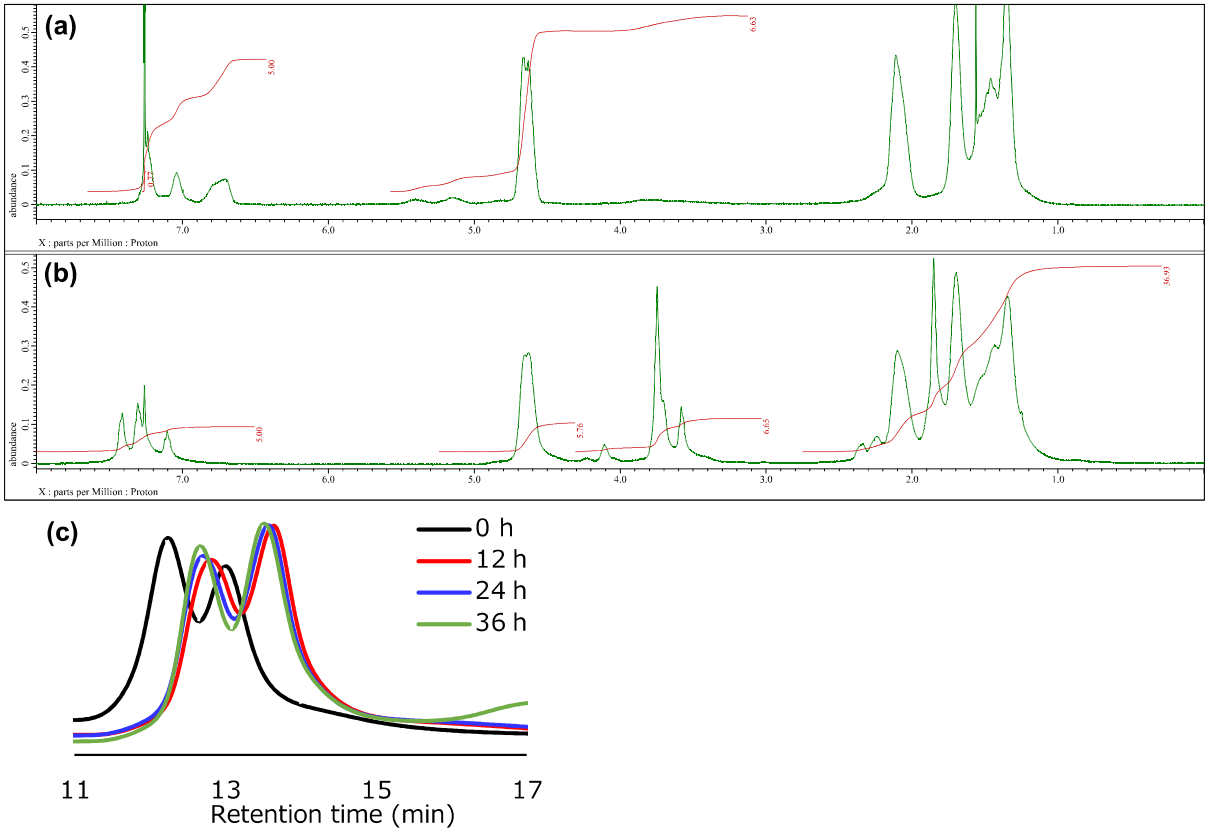


Fig. S34. ^1H NMR spectra ($CDCl_3$) of (a) terpolymer **3a** and (b) the reaction mixture after acid treatment of **3a**. (c) SEC charts during the acid treatment of **3a**.

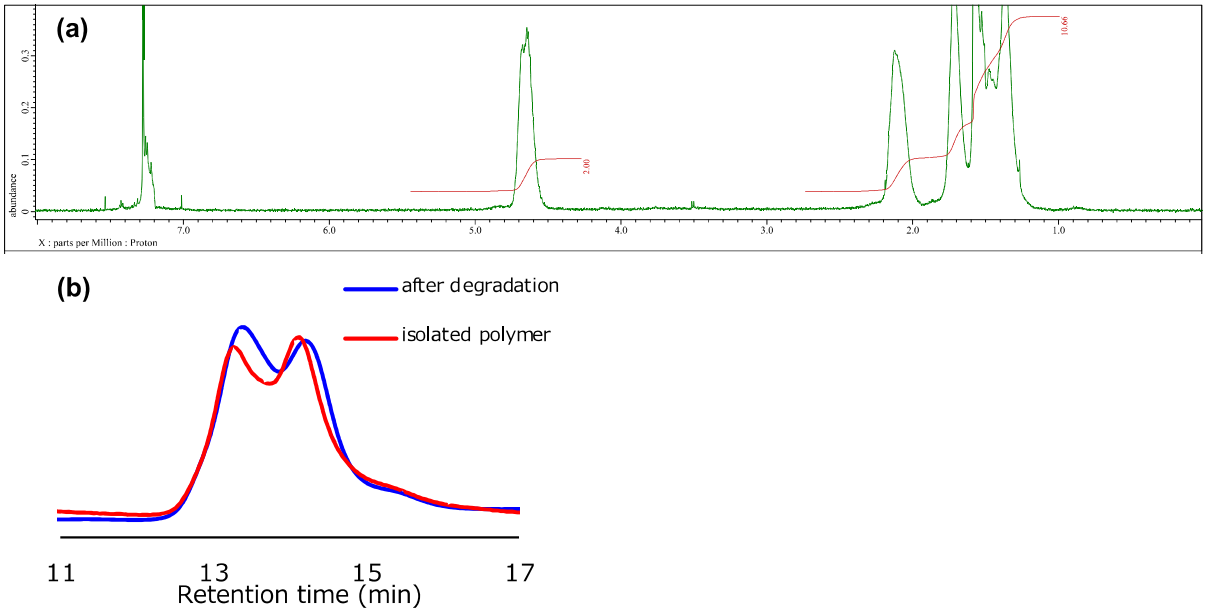


Fig. S35. (a) ^{1}H NMR spectrum ($CDCl_3$) of the polymer isolated from the mixture after the acid treatment of **3a**. (b) SEC charts of the mixture after the acid treatment of **3a** and the polymer isolated from the mixture after the acid treatment of **3a**.

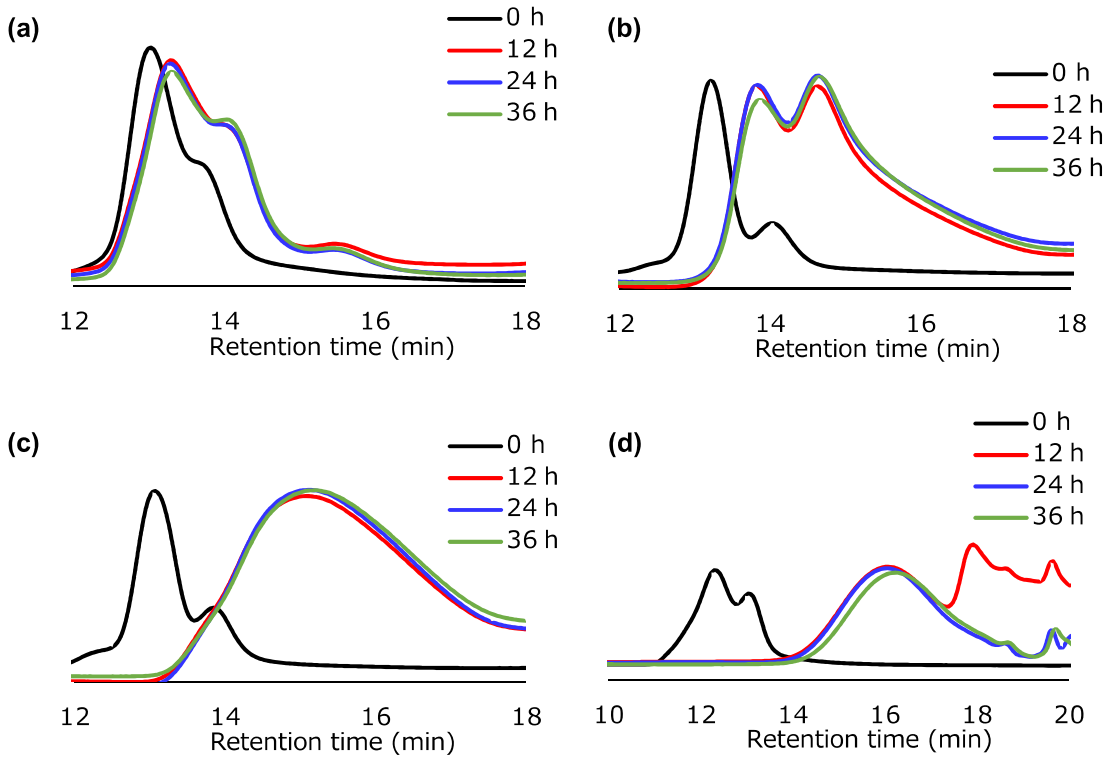


Fig. S36. SEC charts during the acid treatment of (a) **3b**, (b) **3c**, (c) **3d**, and (d) **3e**.

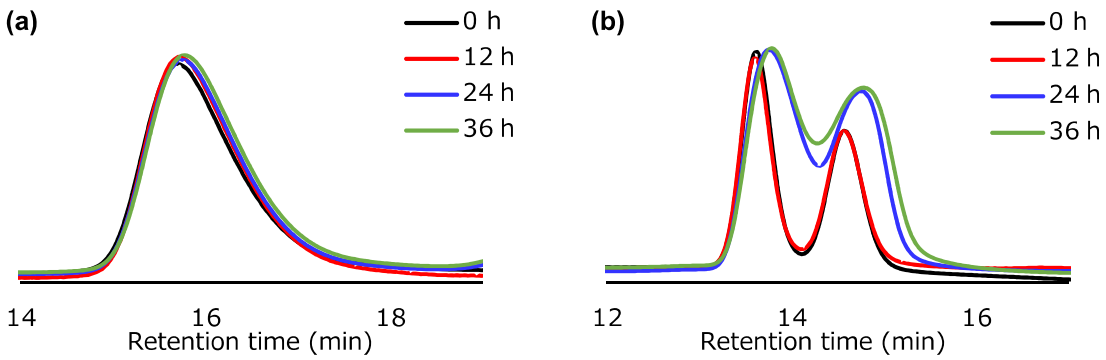


Fig. S37. SEC charts during the acid treatment of (a) **6a** and (b) PCHC.

General procedure for UV irradiation. Purified polymer (30 mg) was dissolved in THF (1 mL) and irradiated with UV light for reaction time shown in Fig. 1c. The reaction mixture was evaporated and diluted with $CDCl_3$ for ^1H NMR analysis or with THF for SEC analysis (Fig. S38, S40, and S41). The residual polymer was isolated by adding the reaction mixture diluted with chloroform dropwise to methanol followed by filtration and vacuum drying. The purified polymer was analyzed by ^1H NMR spectroscopy and SEC, which indicated that the purified polymer consisted of only the PCHC unit (Fig. S39).

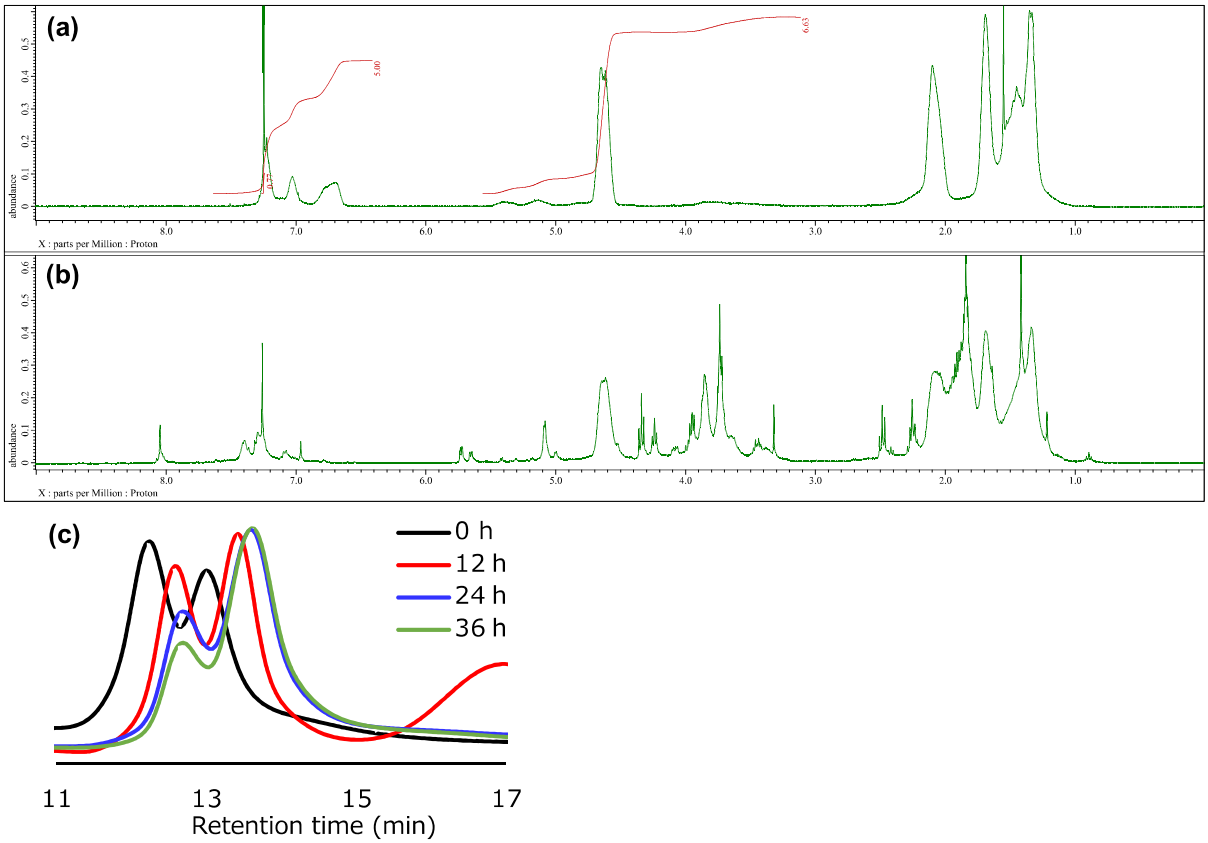


Fig. S38. ^1H NMR spectra ($CDCl_3$) of (a) terpolymer **3a** and (b) the reaction mixture after UV irradiation of **3a**. (c) SEC charts during the UV irradiation of **3a**.

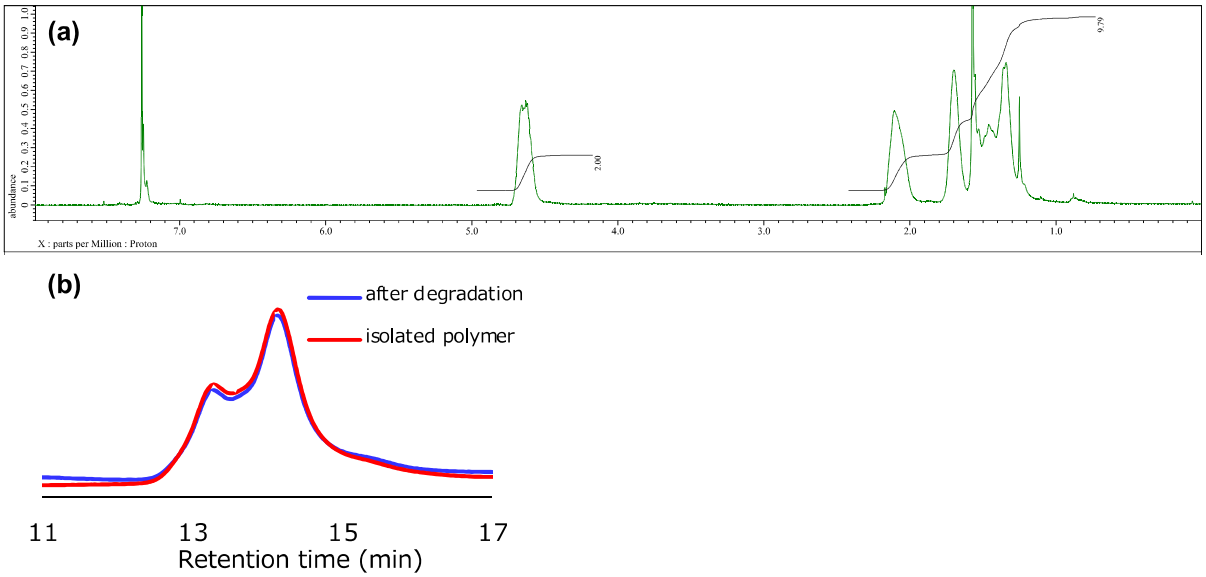


Fig. S39. (a) ^{1}H NMR spectrum ($CDCl_3$) of the polymer isolated after the UV irradiation of **3a**. (b) SEC charts of the mixture after the UV irradiation of **3a** and the polymer isolated after the UV irradiation of **3a**.

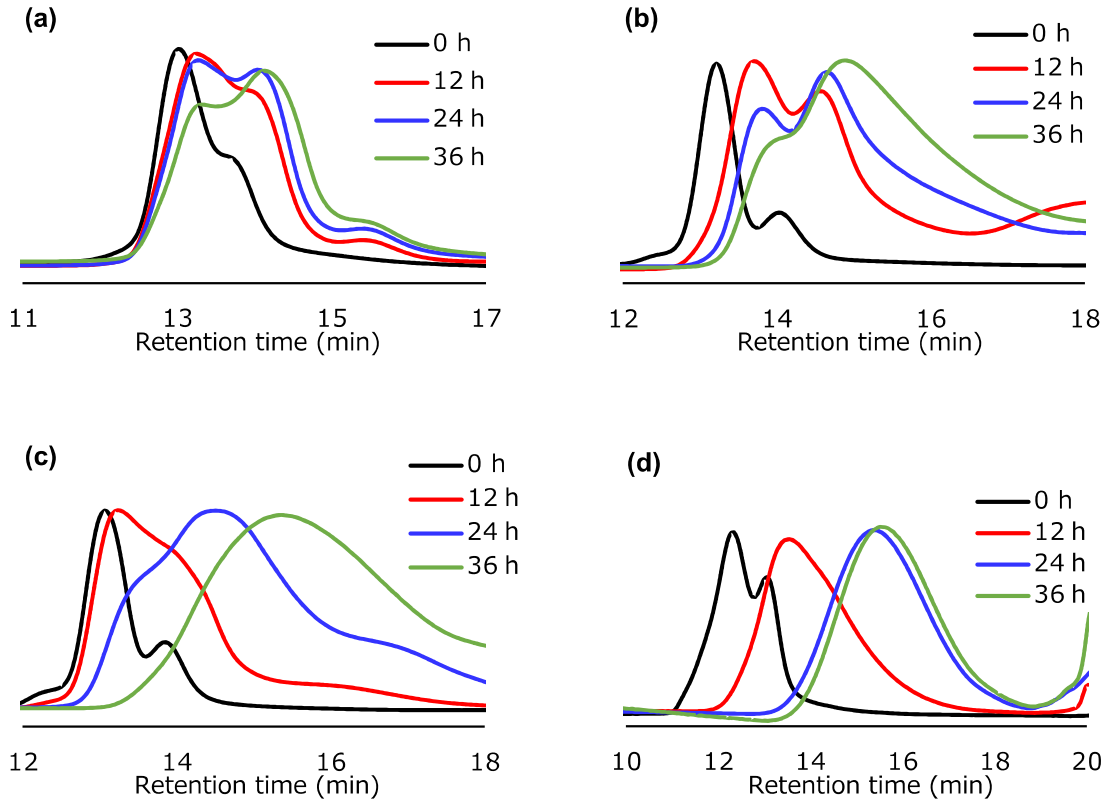


Fig. S40. SEC charts during the UV irradiation of (a) **3b**, (b) **3c**, (c) **3d**, and (d) **3e**.

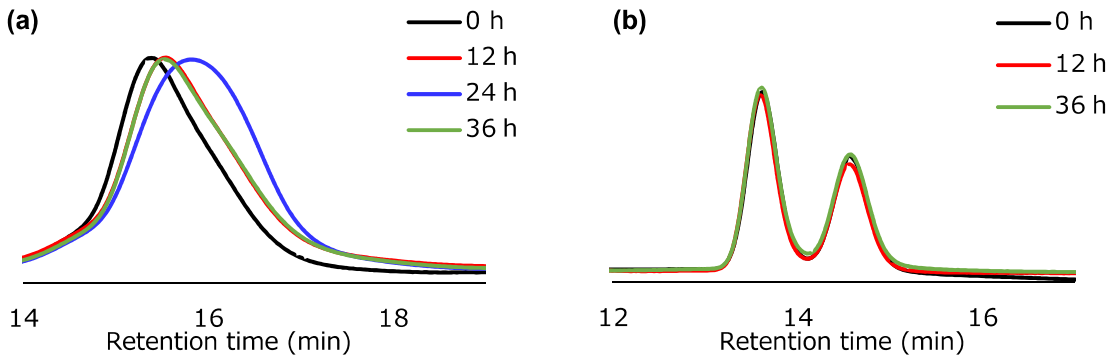
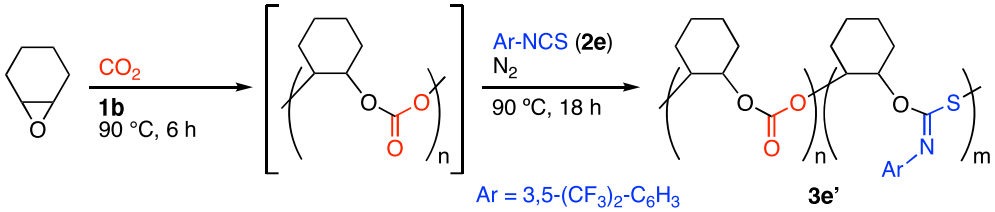


Fig. S41. SEC charts during the UV irradiation of (a) **6a** and (b) PCHC.

[I] Synthesis and degradation of PCHC-*b*-PTIC and PTIC.

Two-step synthesis of block polymer PCHC-*b*-PTIC (3e').



Catalyst **1b** (1.30 mg, 0.63 μmol, S/C = 20000 for CHO) and a magnetic stirring bar were put in a Schlenk flask (30 mL), and the flask was dried under vacuum at 90 °C overnight. The flask was put in a glovebox (purge type) under N_2 atmosphere, and CHO (1.22 g, 12.4 mmol) was added via syringe. The flask was taken out from the glovebox. A CO_2 balloon (1 atm, approximately 2.8 L) was attached to the flask, and the flask was quickly evacuated and filled with CO_2. The mixture was stirred at 90 °C for 6 h. After release of CO_2, a N_2 balloon was attached to the flask, and the flask was quickly evacuated and filled with N_2. Aryl isothiocyanate **2e** (839 mg, 3.1 mmol) was added via syringe. The mixture was stirred at 90 °C for 18 h. A small amount of reaction mixture was withdrawn by syringe at a time interval. After cooling to room temperature, the reaction mixture was diluted with $CDCl_3$, and DMSO (56.9 mg, 0.73 mmol) was added as an internal standard. The conversion of CHO was determined by ^{1}H NMR spectroscopy. Block polymer **3e'** was isolated by adding the reaction mixture diluted with chloroform dropwise to methanol followed by filtration and vacuum drying.

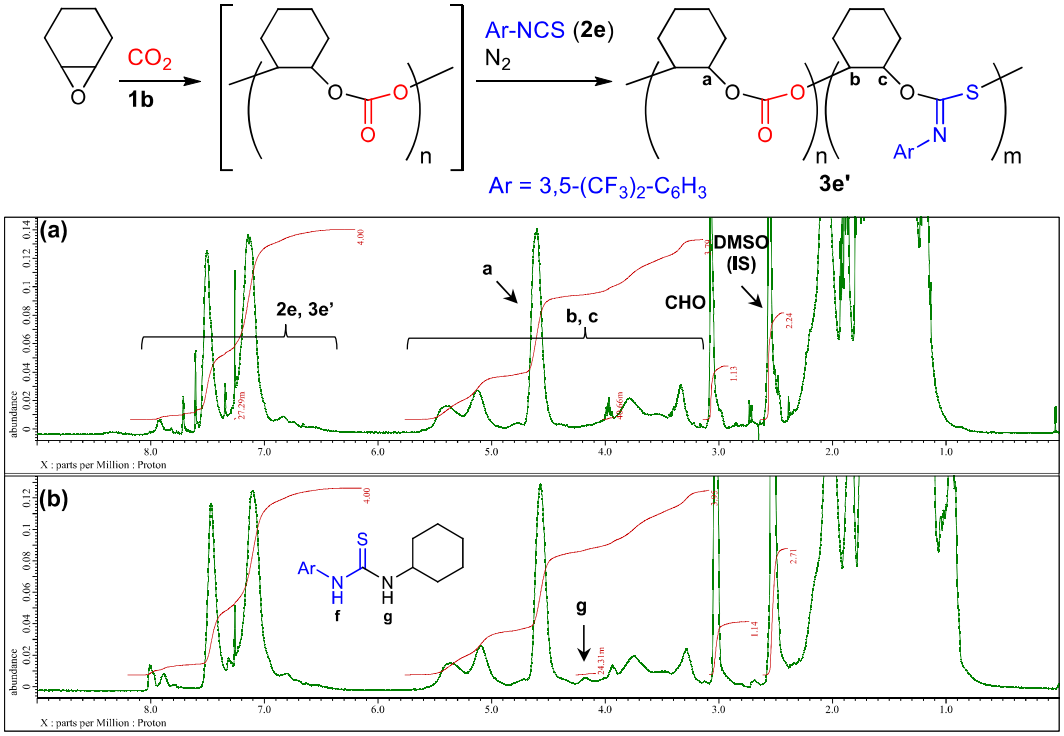


Fig. S42. ^{1}H NMR spectra ($CDCl_3$) of the crude reaction mixtures (a) after block polymerization and (b) after the addition of cyclohexylamine (Fig. 1d).

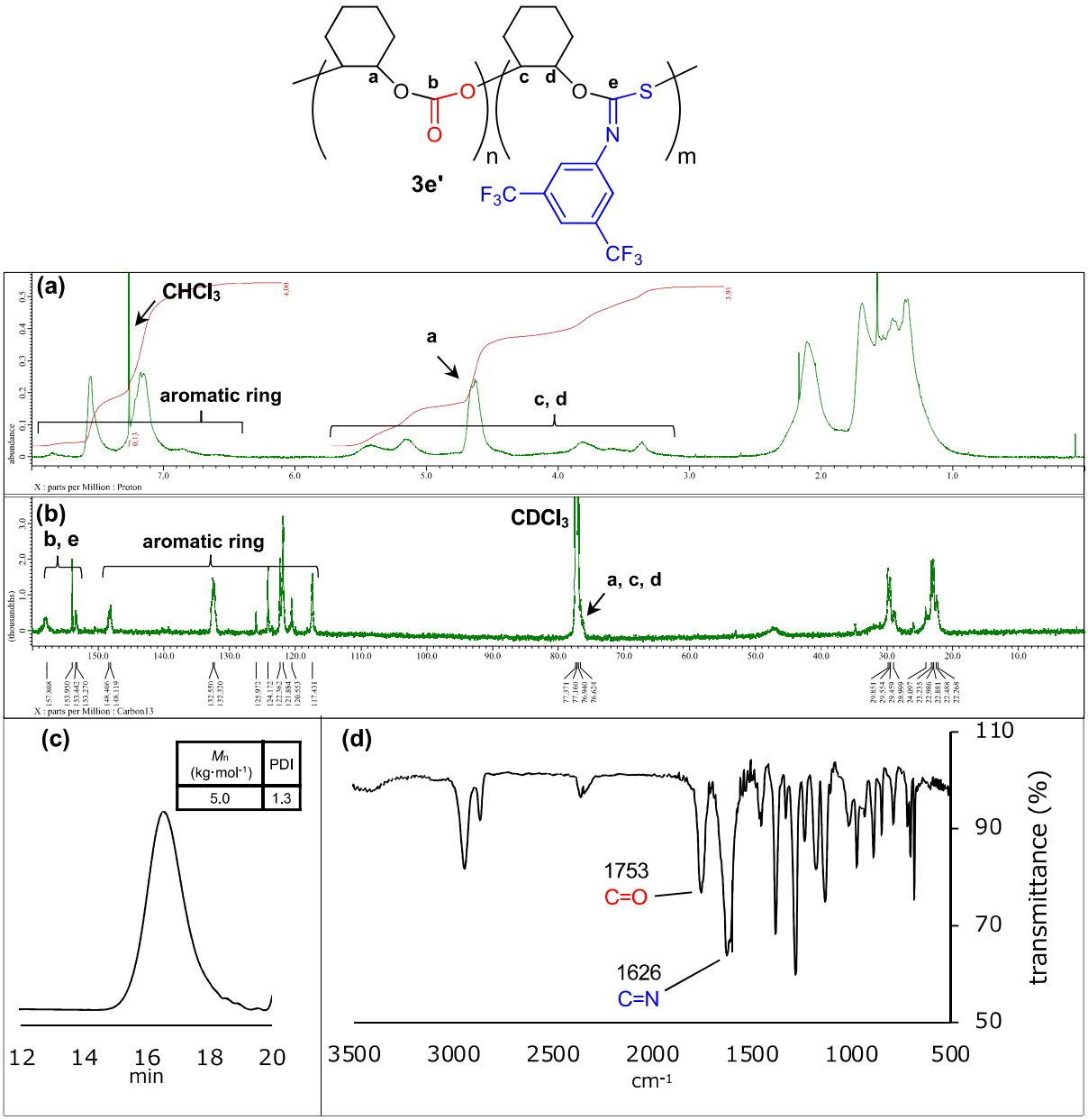


Fig. S43. (a) ^{1}H NMR spectrum ($CDCl_3$), (b) ^{13}C NMR spectrum ($CDCl_3$), (c) SEC chart, and (d) IR spectrum of purified polymer **3e'** (Fig. 1d).

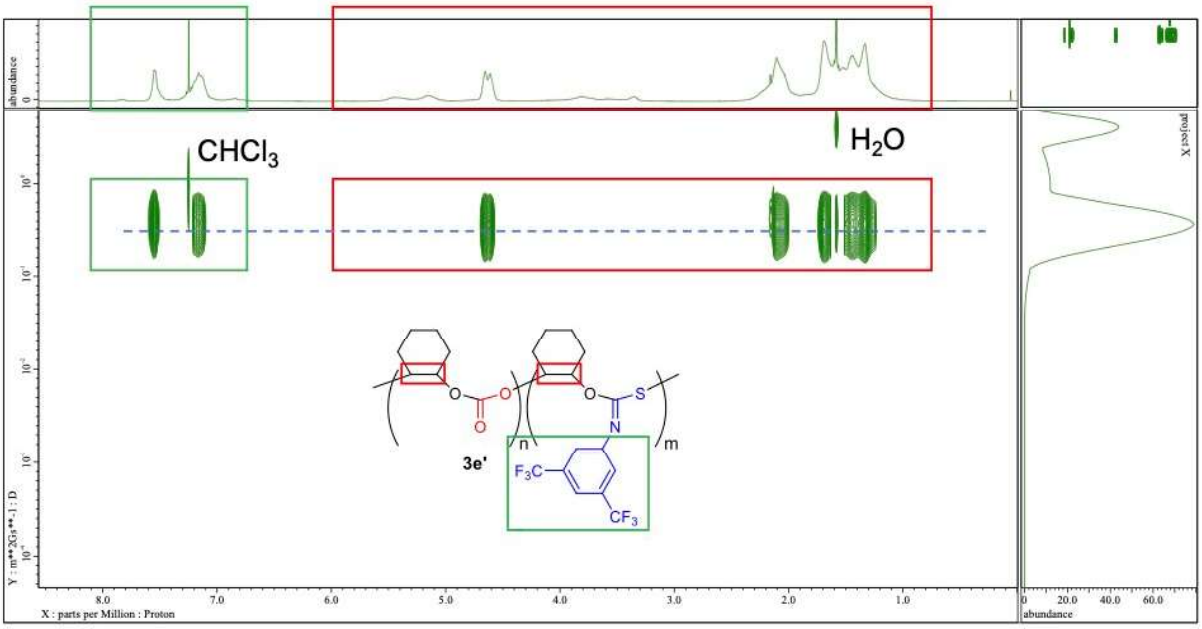
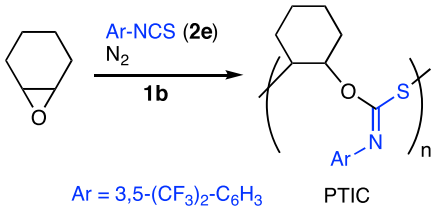
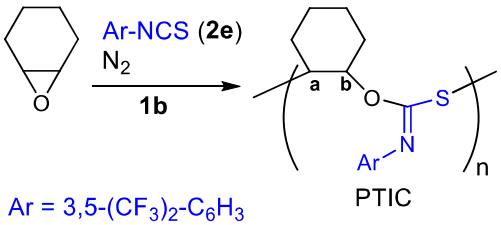


Fig. S44. DOSY spectrum ($CDCl_3$) of purified polymer **3e'** (Fig. 1d).

Synthesis of PTIC from CHO and isothiocyanate.



Catalyst **1b** (1.30 mg, 0.63 μmol, S/C = 20000 for CHO) and a magnetic stirring bar were put in a Schlenk flask (30 mL), and the flask was dried under vacuum at 90 °C overnight. The flask was put in a glovebox (purge type) under N_2 atmosphere, and CHO (1.22 g, 12.5 mmol) and aryl isothiocyanate **2e** (842 mg, 3.1 mmol) were added via syringes. A N_2 balloon (1 atm) was attached to the flask, and the flask was quickly evacuated and filled with N_2. The mixture was stirred at 90 °C for 24 h. The reaction mixture was cooled to room temperature and diluted with $CDCl_3$ for ^1H NMR analysis. The conversion of CHO and the TON of catalyst **1b** were determined by adding DMSO (54 mg, 0.69 mmol) as an internal standard. Aryl isothiocyanate **2e** remaining in the reaction mixture was quantified by the ^1H NMR analysis of the $CDCl_3$ solution to which cyclohexylamine was added to convert **2e** into the corresponding thiourea in the NMR tube. PTIC was isolated by adding the reaction mixture diluted with chloroform dropwise to methanol followed by filtration and vacuum drying.



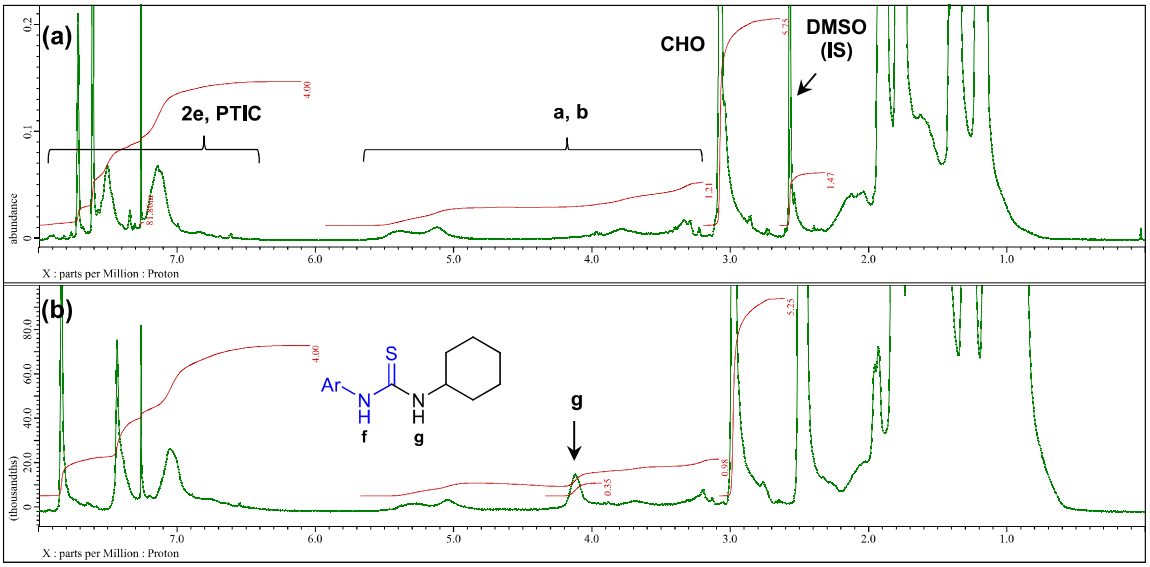


Fig. S45. ^1H NMR spectra ($CDCl_3$) of the crude reaction mixtures (a) after polymerization and (b) after the addition of cyclohexylamine.

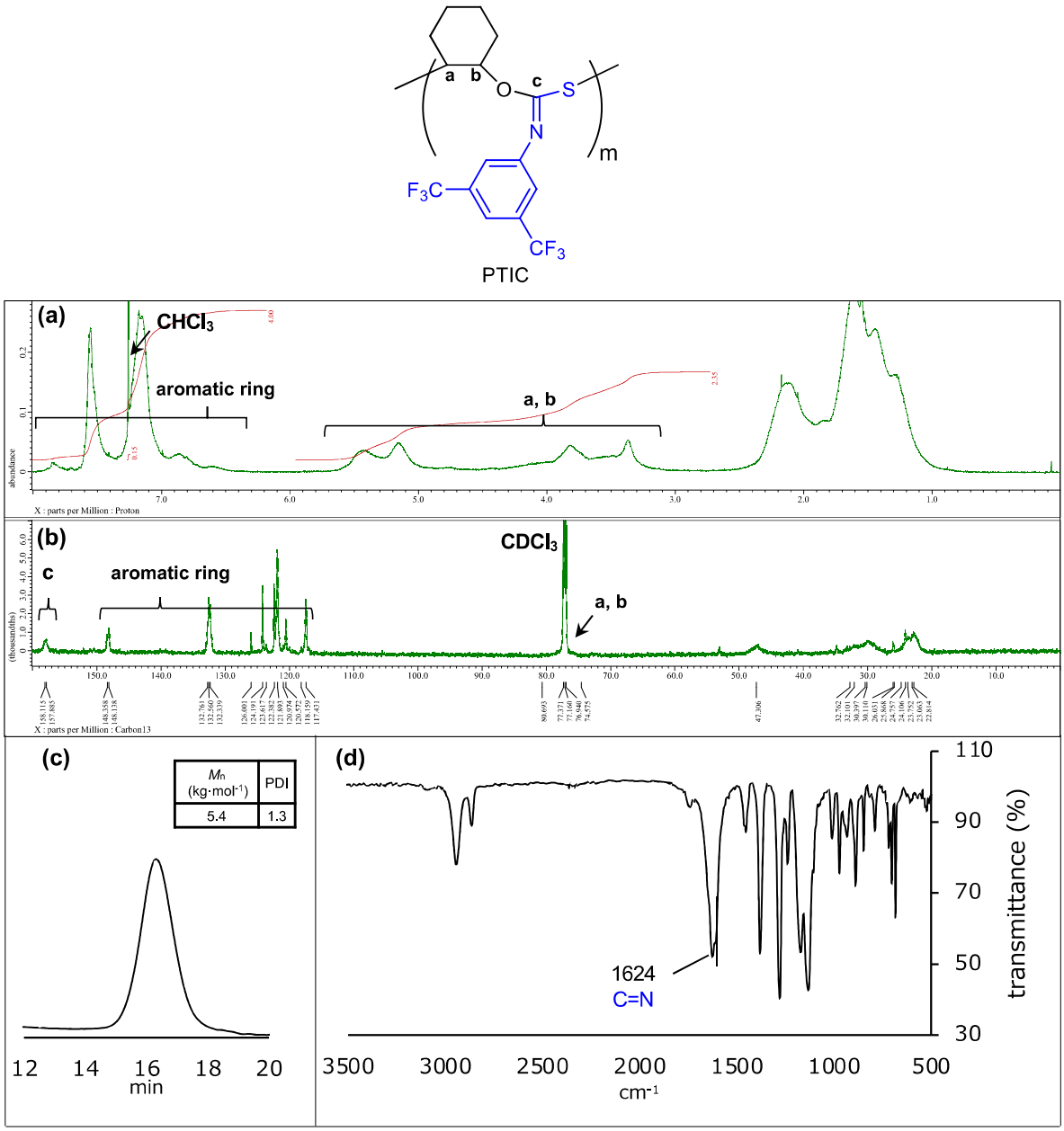


Fig. S46. (a) ^{1}H NMR spectrum ($CDCl_3$), (b) ^{13}C NMR spectrum ($CDCl_3$), (c) SEC chart, and (d) IR spectrum of purified PTIC.

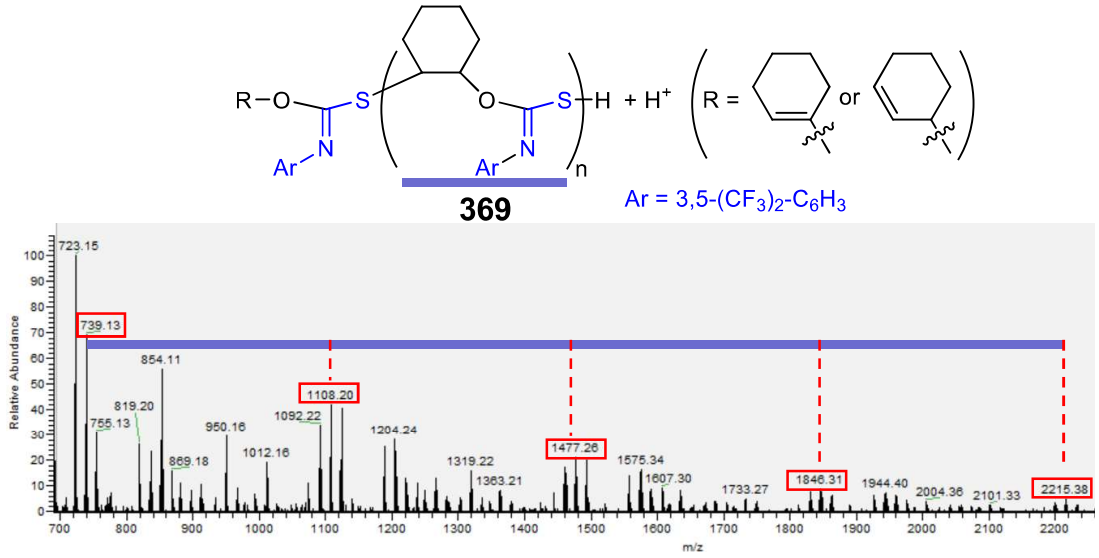


Fig. S47. APCI mass spectrum of PTIC.

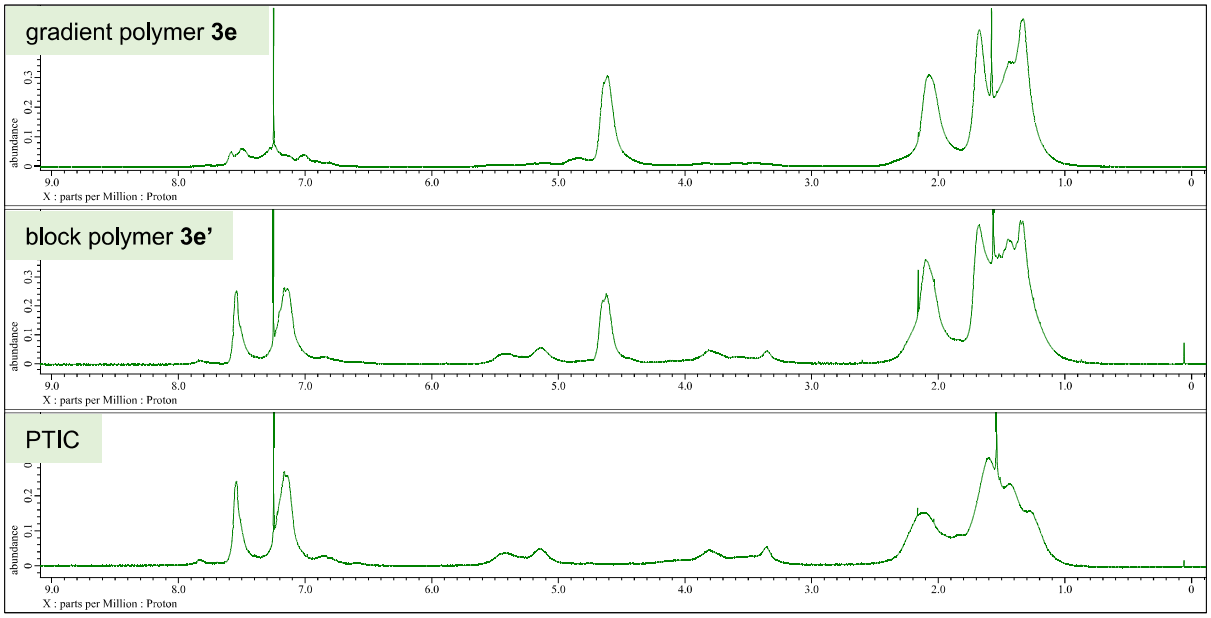


Fig. S48. ^{1}H NMR spectra ($CDCl_3$) of purified gradient polymer **3e**, block polymer **3e'**, and PTIC.

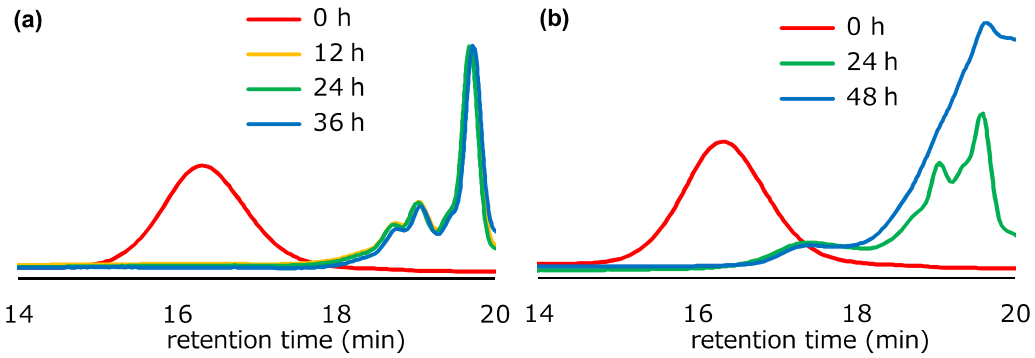


Fig. S49. SEC charts during (a) the acid treatment and (b) the UV irradiation of purified PTIC.

[J] Photograph of typical samples of catalysts and polymers.

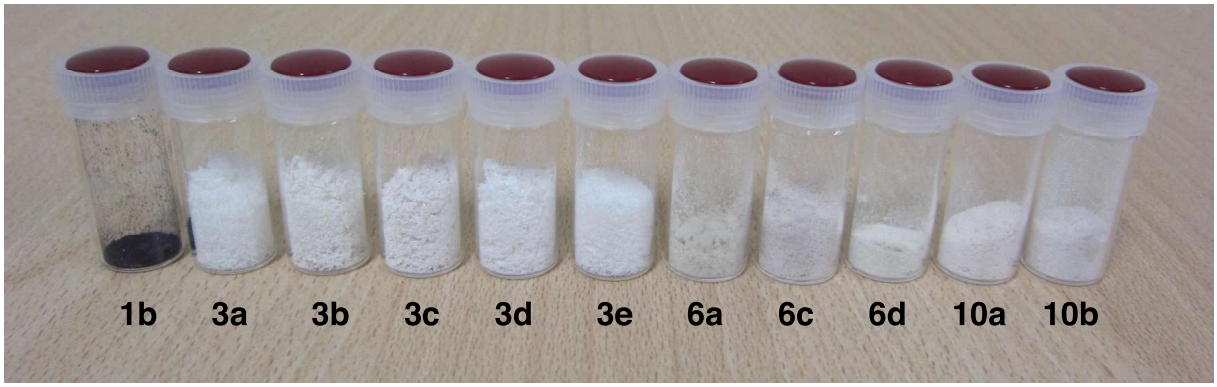


Fig. S50. Photograph of typical samples of catalysts and polymers.

[K] References.

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