Supplementary Information (SI) for Polymer Chemistry.
This journal is © The Royal Society of Chemistry 2025

Supporting Information

Ugi Five-component Polymerizations of CO_2 and 5-hydroxymethylfurfural Derivatives toward Functional Polyfurans

Ziliang Wang,† Chang Liu,† Li Xu, Baixue Li, Jie Liu, Xue Wang, Yusheng Qin**

School of Chemistry and Chemical Engineering, Yantai University, Yantai 264005, PR China

† Both authors have made equal contributions.

** E-mail for X.W.: wangxue@ytu.edu.cn*

** E-mail for Y.Q.: ysqin@ytu.edu.cn*

Table of Contents

Experimental Section

Materials

2,5-diformylfurane, glutaraldehyde, 1,8-diaminooctane, 1,10-diaminodecane, 1,12-diaminododecane, furfural, *n*-butylamine, and *tert*-butyl isocyanide were purchased from Energy Chemical. 2,5-bis (aminomethyl) furan was obtained from Macklin reagent. The purity of carbon dioxide (CO_2) was 99.999%. Dichloromethane (CH_2Cl_2) and methanol (MeOH) was purchased from Tianjin Fuyu Fine Chemical Co., Ltd. Deuterated chloroform ($CDCl_3$) was provided by Energy Chemical. Other solvents like *n*-hexane, ethyl acetate, and petroleum ether were used without further purification.

Ugi five-component model reaction (Ugi-5CR)

n-butylamine (87.8 mg, 1.2 mmol) and furfural (115.3 mg, 1.2 mmol) were dissolved in a mixed solution of 2.4 mL of MeOH and 2.4 mL of CH_2Cl_2. The reaction mixture was stirred at room temperature for 1 h. Then, *tert*-butyl isocyanide (99.8 mg, 1.2 mmol) was added. The reaction was carried out in a high-pressure reactor under a carbon dioxide pressure of 1.5 MPa at room temperature for 24 h. After evaporation of the solvent, the crude product was purified through silica-gel chromatography using petroleum ether/ethyl acetate ($v/v = 5/1$) as the eluent.

Ugi five-component polymerization (Ugi-5CP)

1,10-diaminodecane (206.8 mg, 1.2 mmol) and 2,5-diformylfurane (148.9 mg, 1.2 mmol) were dissolved in a mixed solution of 2.4 mL of MeOH and 2.4 mL of CH_2Cl_2. The reaction mixture was stirred at room temperature for 1 h. Then, *tert*-butyl isocyanide (299.3 mg, 3.6 mmol) was added. The reaction was carried out in a high-pressure reactor under a carbon dioxide pressure of 1.5 MPa at room temperature for 48 h. Subsequently, the polymerization product remained soluble in the MeOH/CH_2Cl_2 mixture. The reaction mixture was concentrated in vacuum and dissolved in CH_2Cl_2, and precipitated in *n*-hexane, yielding a sticky brown polymer. The reaction conditions were optimized by varying the diamine, dialdehyde, solvent, and pressure of carbon dioxide.

Characterization

The structure of Ugi-5CP products was analyzed by FT-IR spectroscopy (IRAffinity-1S, Shimadzu, Japan). ^{1}H NMR and ^{13}C NMR spectra were collected by JEOL 400 MHz spectrometer using $CDCl_3$ as solvent. Differential scanning calorimetry (DSC) was characterized by a TA Instruments, DSC 250 system in a nitrogen atmosphere with heating/cooling rates of 10 °C min^{-1} from -25 to 150°C. Thermogravimetric analysis (TGA) was recorded on a Germany NETZSCH TG 209 F3 Tarsus at a heating rate of 10 °C min^{-1} under nitrogen.

The average molecular weights and polydispersities were recorded on a Waters GPC system equipped with a Waters 1515 HPLC solvent pump and a Waters 2414 refractive index detector. Chloroform was utilized as eluent at a flow rate of 1 mL/min at 35°C. ESI High resolution mass spectroscopic (HRMS) were measured using Thermo Q Exactive Focus mass spectrometer. Matrix-assisted laser desorption/ionization-time of flight mass spectroscopy (MALDI-TOF-MS) analysis was carried out in positive ion mode using a Bruker Autoflex Speed TOF/TOF mass spectrometer with a 337 nm nitrogen laser. Trans-2-[3-(4-tert-butylphenyl) -2-methyl-2-propenylidene] malononitrile (DCTB) was used as the matrix and chloroform as the solvent. X-ray diffraction patterns were measured by A Rigaku SmartLab III X-ray diffractometer (German). The mechanical properties were tested by SUNS UTM4103 universal test machine, which was carried out at room temperature with a tensile rate of 5 mm min^{-1}. Photoluminescence (PL) spectra were measured with a Shimadzu RF-6000 fluorescence spectrophotometer at room temperature. All calculations were carried out using the Gaussian 16 software.[1] The B3LYP functional[2] was adopted for all calculations in combination with the D3BJ dispersion correction.[3] For geometry optimization and frequency calculations, 6-31G (d, p) basis set was used for all atmos.[4,5]

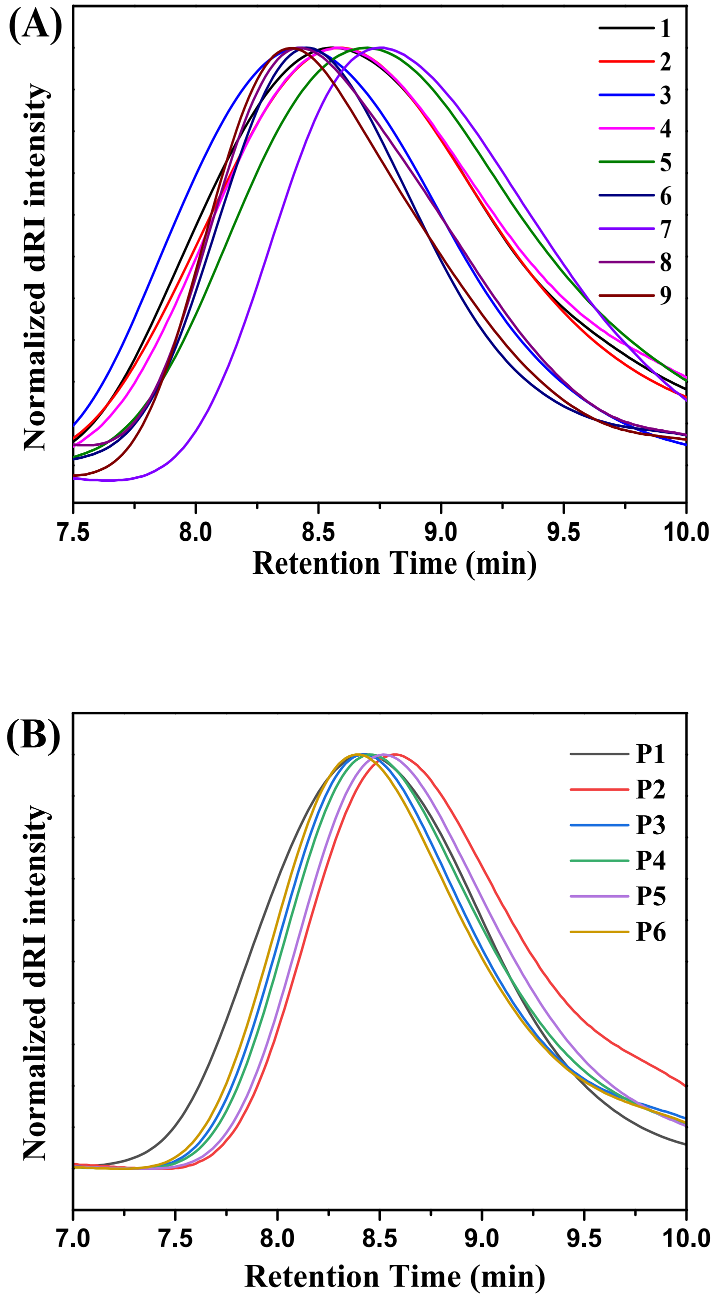


Figure S1. GPC spectrum of Ugi-5CPs products.

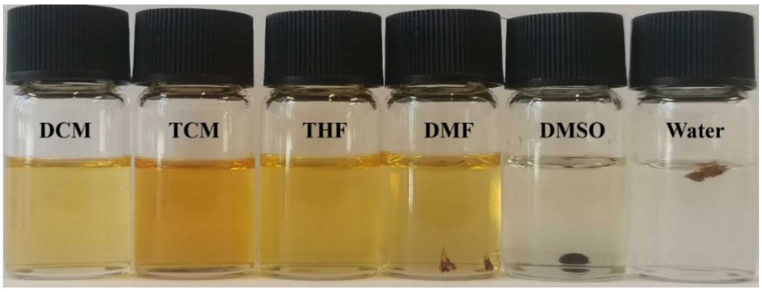
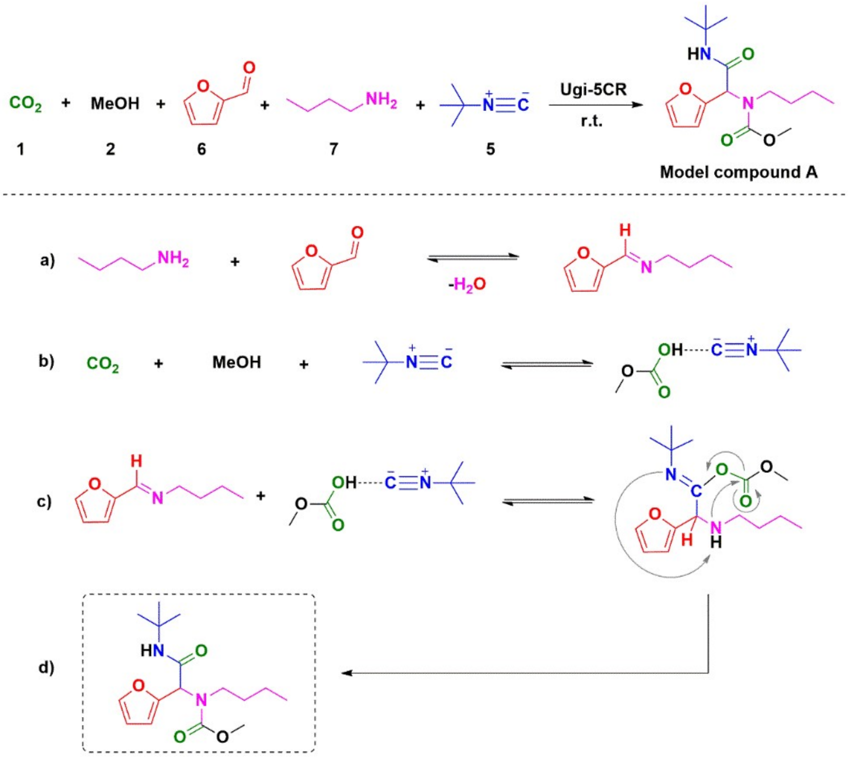


Figure S2. The solubility of polymer **P1** (1 mg/mL) after being dissolved at room temperature for 24 h.



Scheme S1. Model reaction of Ugi-5CR (CO_2, MeOH, furfural, *n*-butylamine, and *tert*-butyl isocyanide).

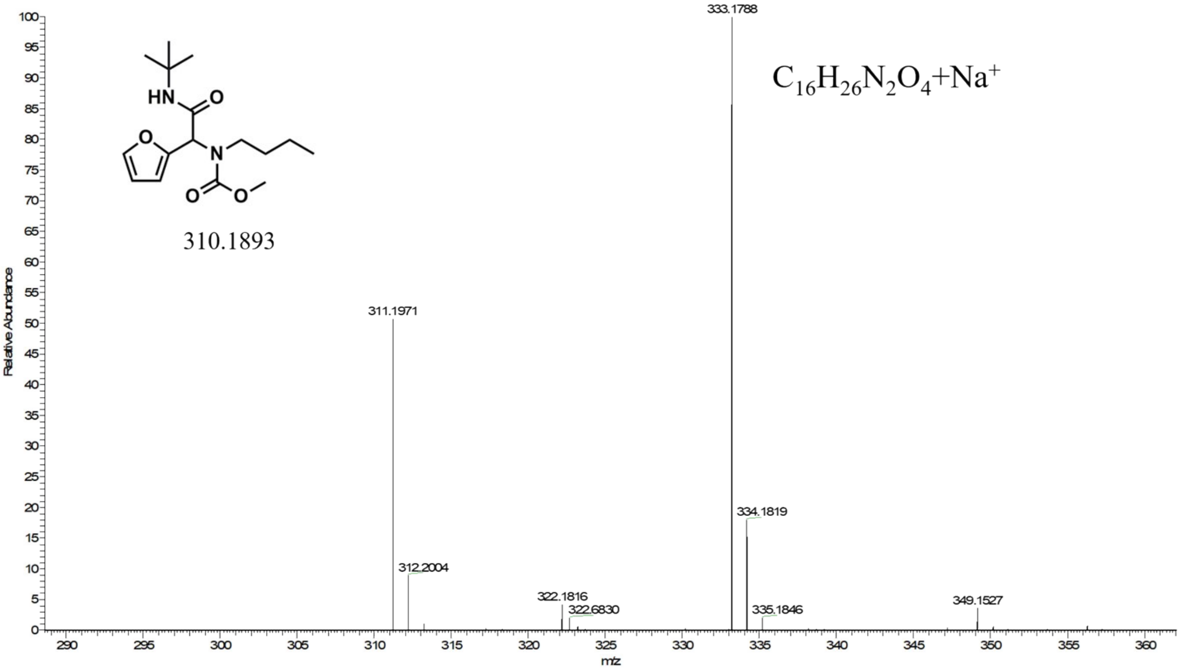


Figure S3. ESI-MS mass spectrometry of model compound **A**.

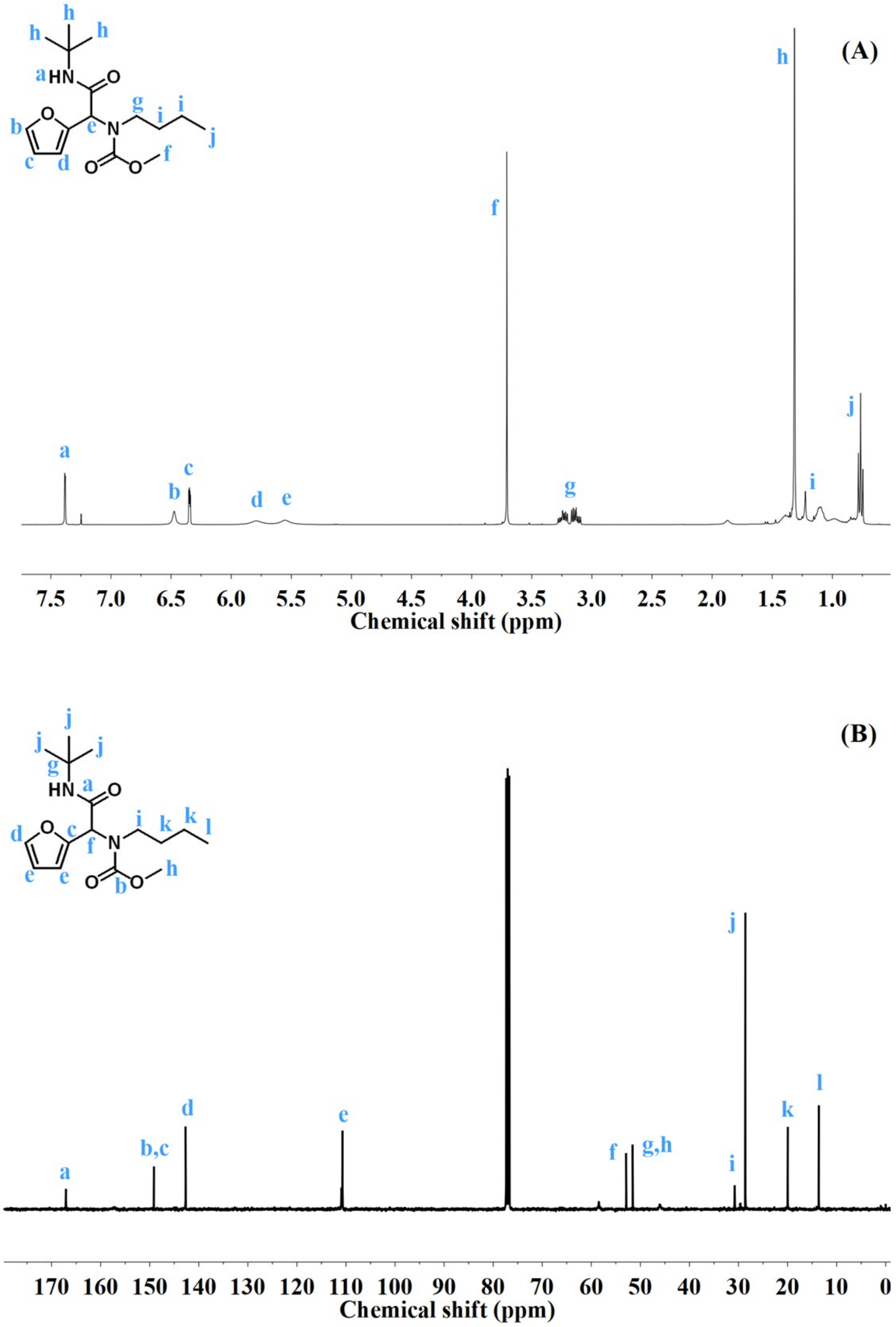


Figure S4. (A) ^{1}H and (B) ^{13}C NMR spectra of model compound **A**.

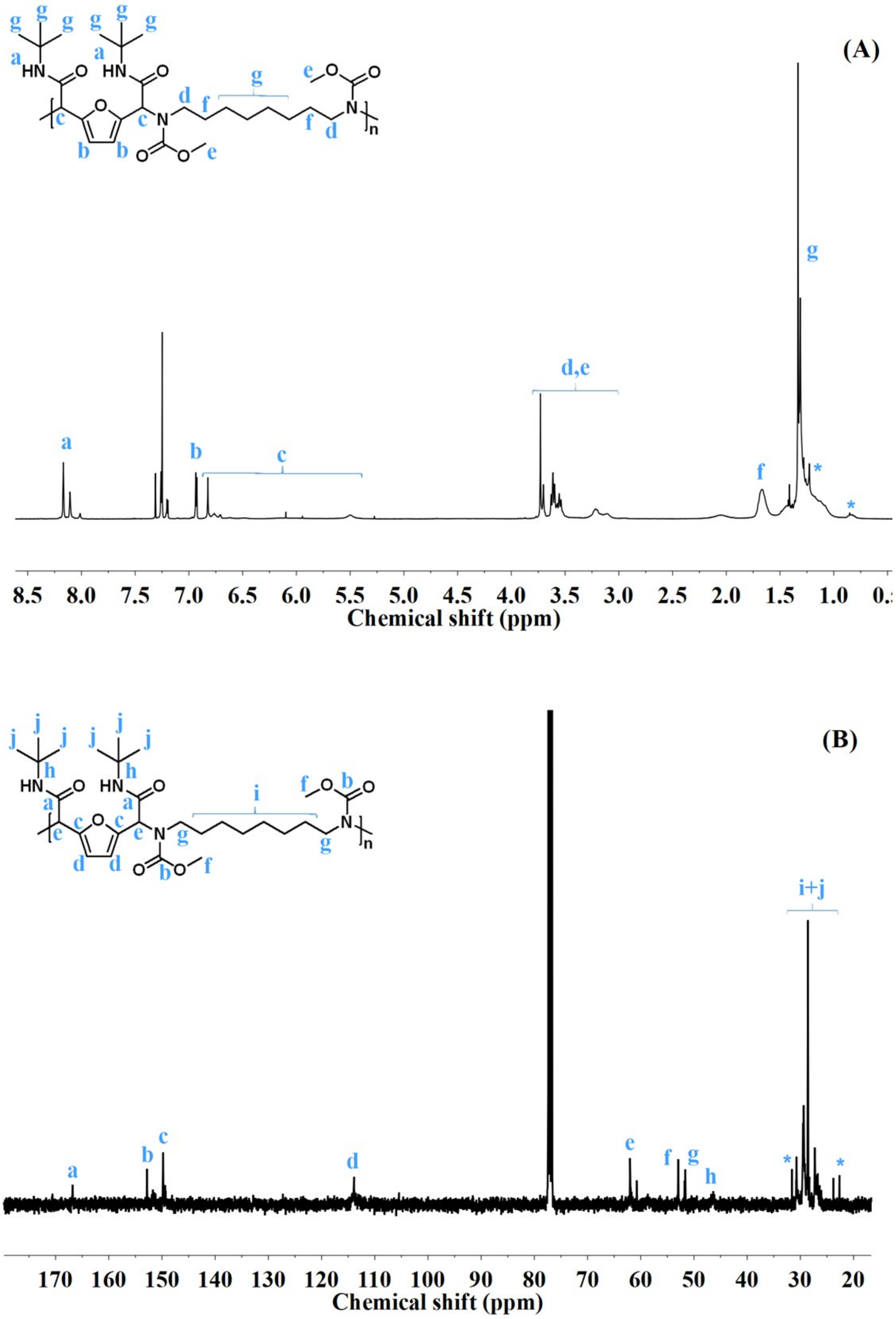


Figure S5. (A) ^{1}H and (B) ^{13}C NMR spectra of **P2**.

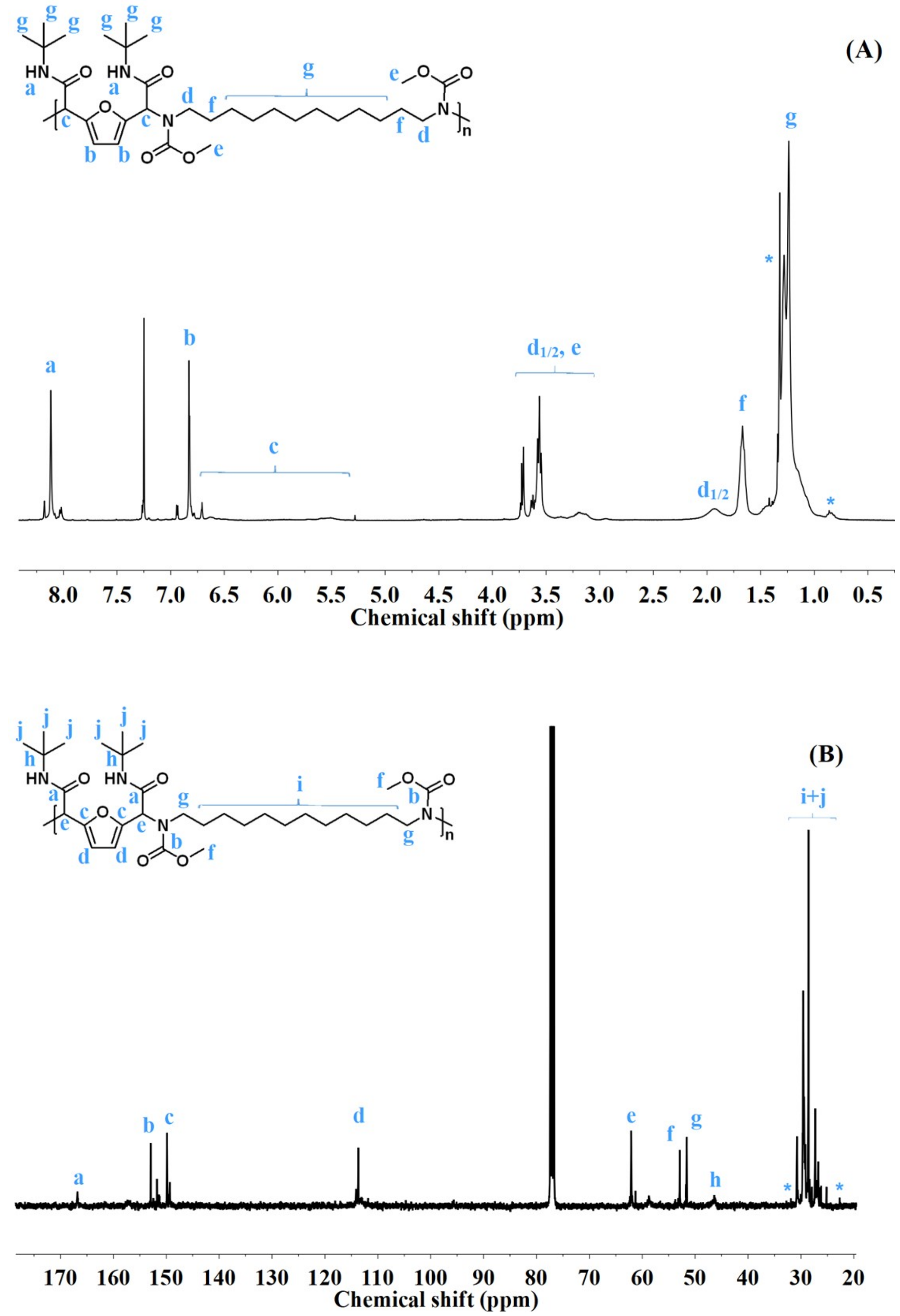


Figure S6. (A) ^{1}H and (B) ^{13}C NMR spectra of **P3**.

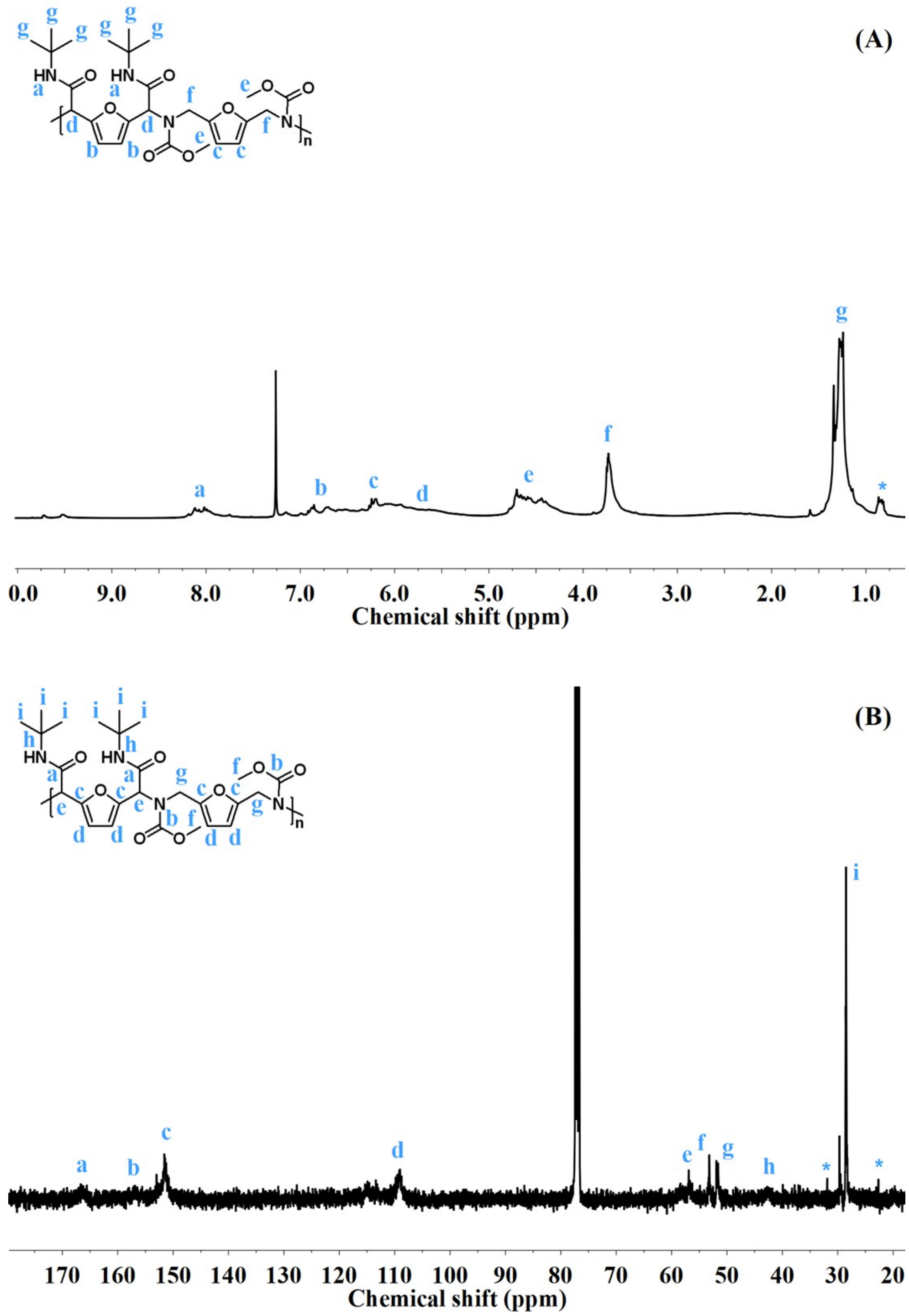


Figure S7. (A) ^{1}H and (B) ^{13}C NMR spectra of **P4**.

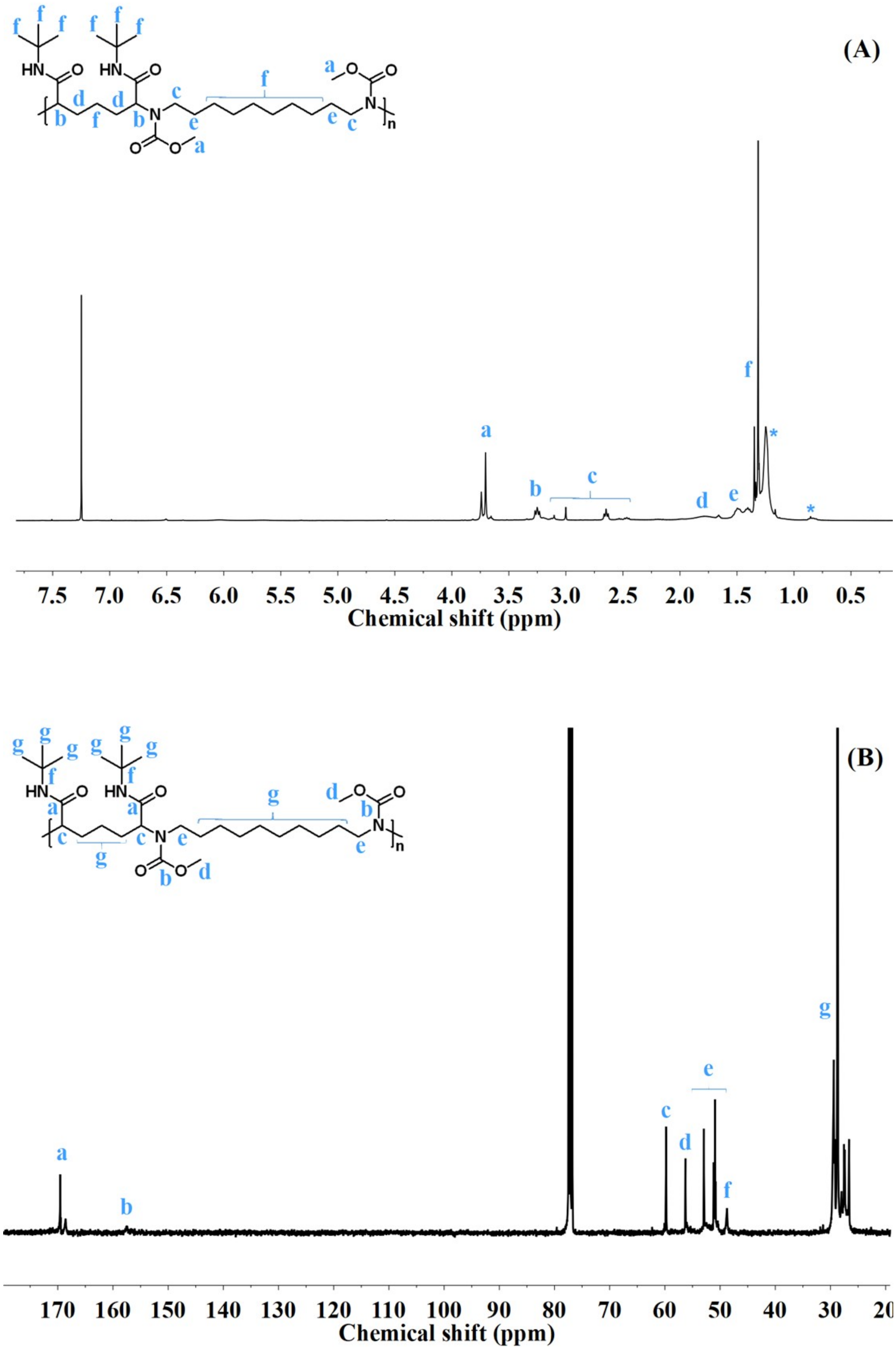


Figure S8. (A) ^{1}H and (B) ^{13}C NMR spectra of **P5**.

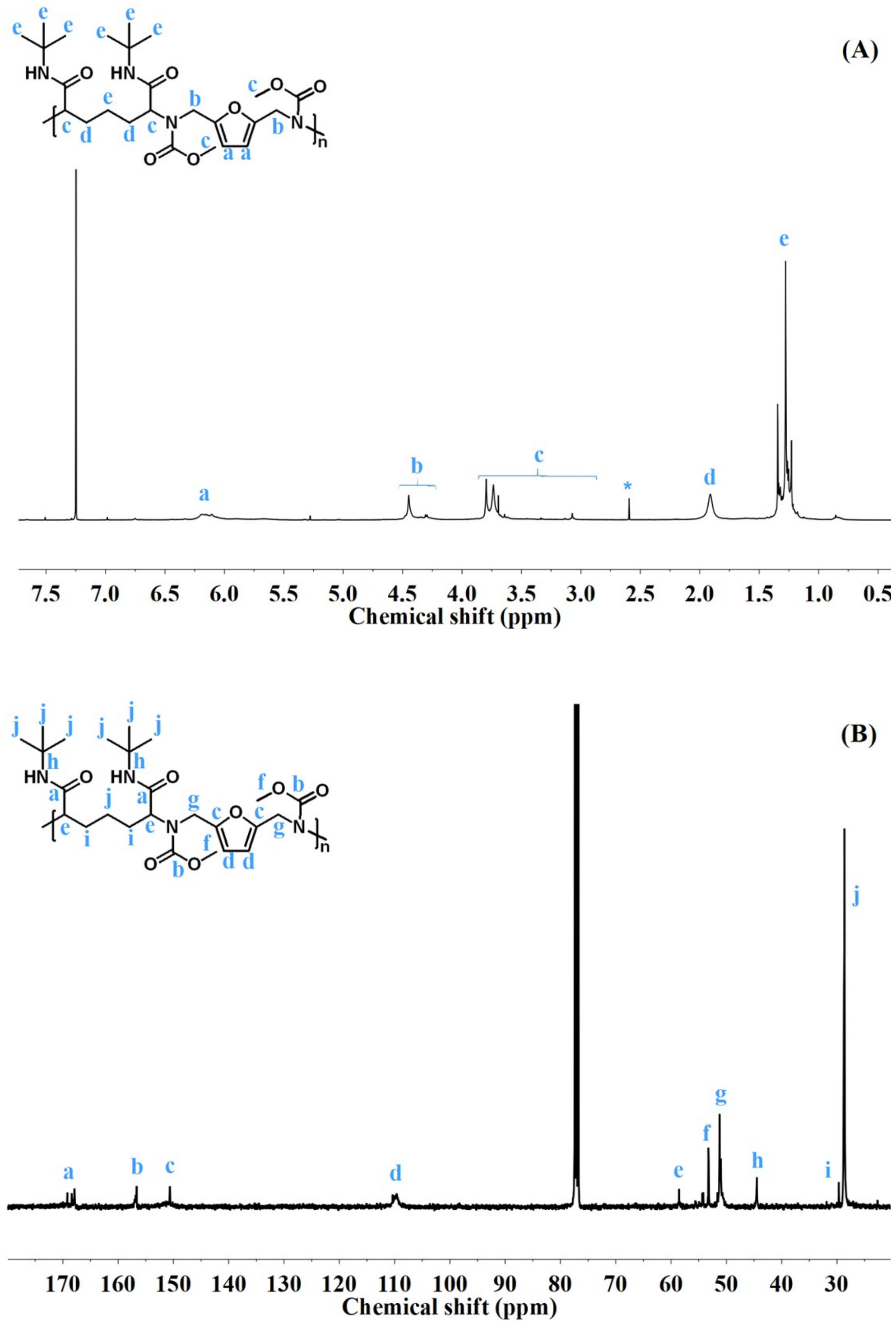


Figure S9. (A) ^{1}H and (B) ^{13}C NMR spectra of **P6**.

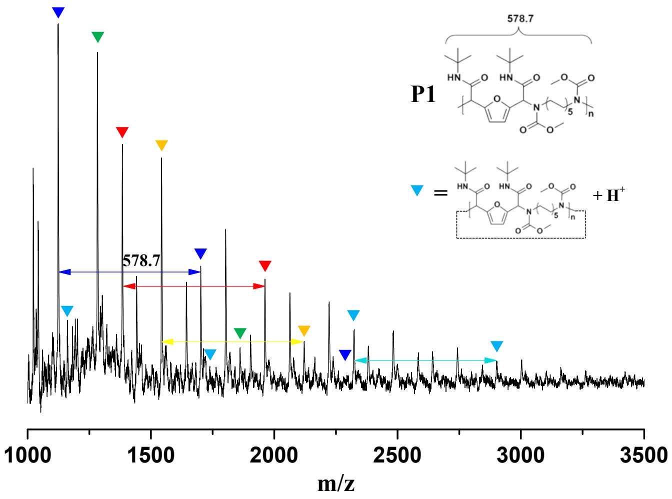
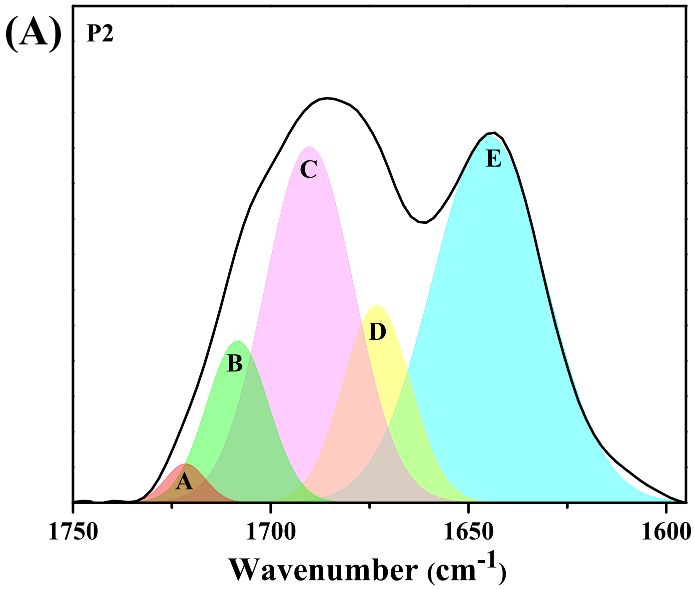
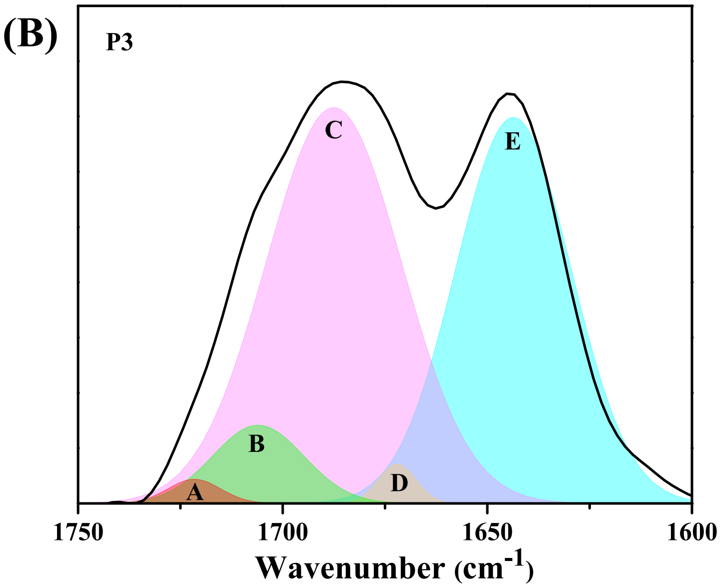
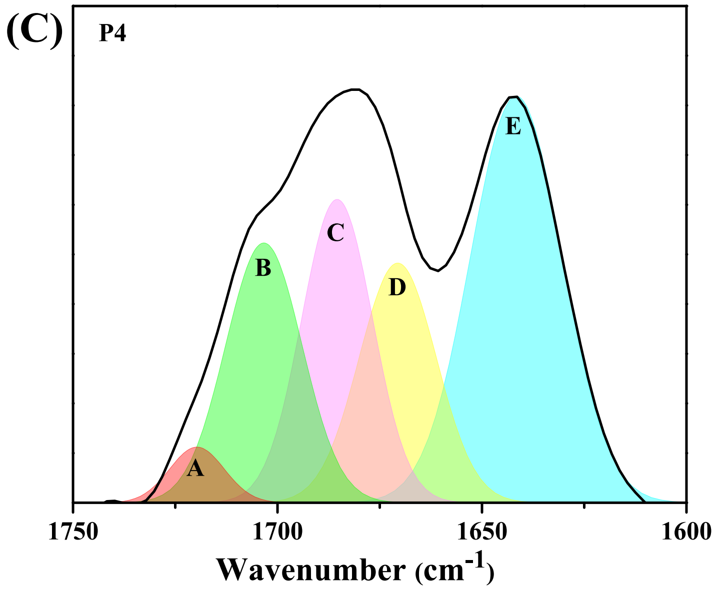
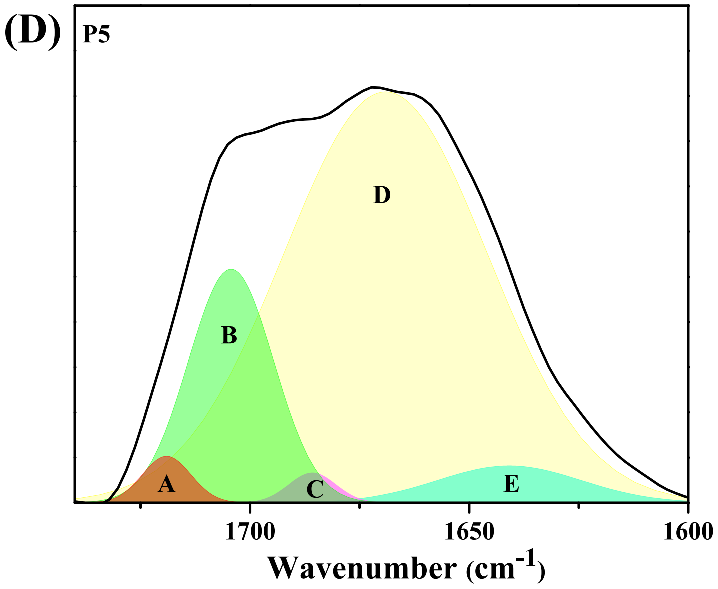


Figure S10. MALDI-TOF-MS spectrum of **P1**; the spacing between the peaks corresponds to the molar masses of the repeating unit.


(A)
P2
A
B
C
D
E
1750
1700
1650
1600
Wavenumber (cm^{-1})


(B)
P3
A
B
C
D
E
1750
1700
1650
1600
Wavenumber (cm^{-1})


(C)
P4
E
C
B
D
A
1750
1700
1650
1600
Wavenumber (cm-1)


(D)
P5
D
B
A
C
E
1700
1650
1600
Wavenumber (cm-1)

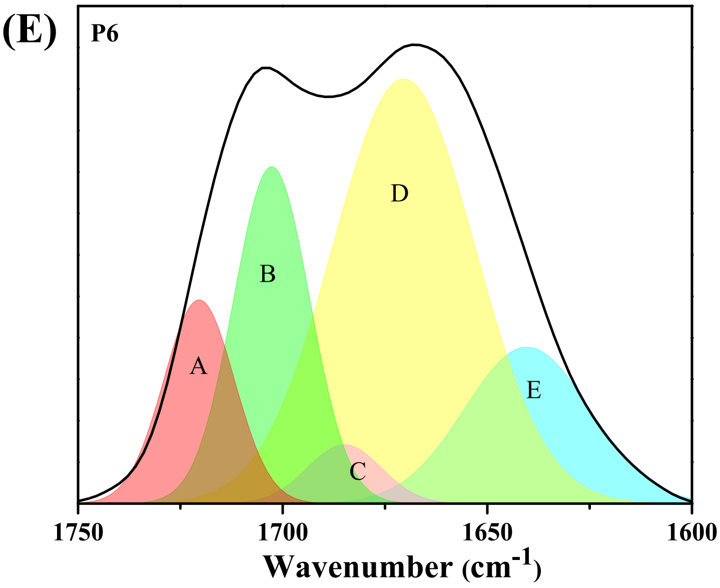


Figure S11. FT-IR spectra of the **P2-P6** in the C=O stretching vibration region.

Table S1 Summary of the assignment of the deconvoluted subpeaks in the FTIR C=O absorption bands for **P1-P6**.

Assignment		υ (C=O) urethane			υ (C=O) amide	
		Free	H-bonded (disordered)	H-bonded (ordered)	Free	H-bonded
P1	Wavenumber (cm^{-1})	1720	1702	1683	1670	1641
P2	Wavenumber (cm^{-1})	1721	1708	1690	1670	1644
P3	Wavenumber (cm^{-1})	1721	1706	1687	1672	1643
P4	Wavenumber (cm^{-1})	1719	1703	1690	1670	1641
P5	Wavenumber (cm^{-1})	1719	1704	1686	1669	1641
P6	Wavenumber (cm^{-1})	1720	1703	1685	1670	1640

Table S2 TGA data of **P1-P6** at a heating rate of 10 °C/min in nitrogen.

Samples	**P1**	**P2**	**P3**	**P4**	**P5**	**P6**
$T_{5\%}$ (°C)	176.7	131.0	234.7	146.6	121.7	193.9
$T_{50\%}$ (°C)	452.6	448.2	458.7	623.9	388.3	328.2
Char yield (%)	12.5	15.1	19.5	47.4	4.5	13.3

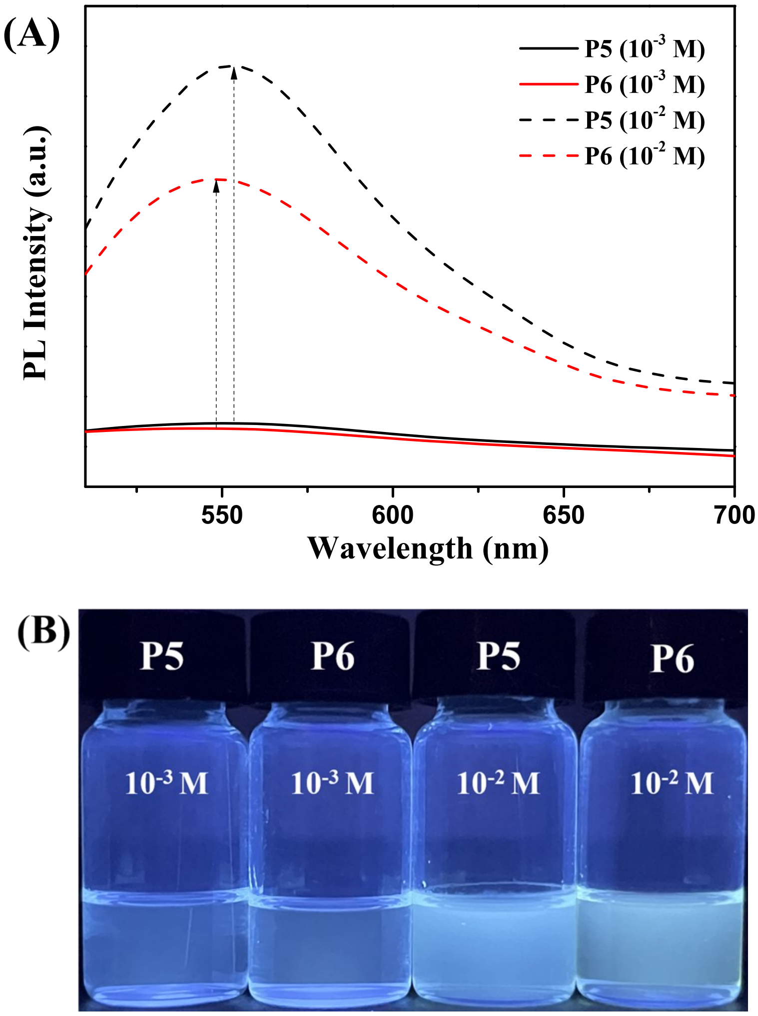


Figure S12. (A) Fluorescence spectra of **P5** and **P6** (10^{-3} and 10^{-2} M) in chloroform (λ_{ex} = 496 nm), (B) Fluorescence images of **P5** and **P6** (10^{-3} and 10^{-2} M) in chloroform under a 365 nm UV lamp.

References:

1. Gaussian 16, Revision A.01, M. J. Frisch, G. W. Trucks, et al, Gaussian, Inc., Wallingford CT, 2016. https://gaussian.com
2. P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623.
3. S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
4. P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213.
5. W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257.