

Supporting information

**Facile Synthesis of a Linear Porous Organic Polymer via Schiff-base
chemistry for Propyne/Propylene Separation**

Shengtai Hou, Xian Suo, Nanqing Chen, Pengfei Zhang*, and Sheng Dai

Email: chemistryzpf@sjtu.edu.cn

Table of content

1. General remarks.....	S2
2. Experimental Section.....	S2
3. Analytical Data of polymers.....	S7
4. References.....	S11

1. General remarks

1.1 Chemicals:

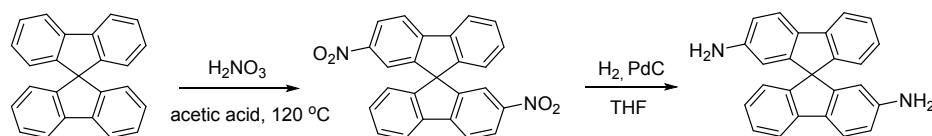
Chemicals involved in the material synthesis are used directly without further purification if no specification. 4,4'-(9-Fluorenylidene)dianiline (>98%, TCI Chemicals), Benzaldehyde (>98%, MERYER Chemicals), 1,4-Benzenedialdehyde (>98%, Macklin Chemicals)

1.2 General Methods:

The materials were characterized by N₂ adsorption (TriStar, Micromeritics) at 77 K, powder XRD (Panalytical Empyrean diffractometer with Cu K α radiation operating at 45 kV and 40 mA), thermogravimetric analysis (TGA 2950, TA Instruments), Fourier-transform infrared spectrum (PerkinElmer Frontier FTIR spectrometer), Elemental Analysis (Vario EL Cube). Scanning electron microscopy (SEM) was carried out on a field emission scanning electron microscope (FESEM, Zeiss Gemini 500). Differential scanning calorimetry (DSC) was performed on a DSC2A-01130 at a heating rate 10 °C/min.

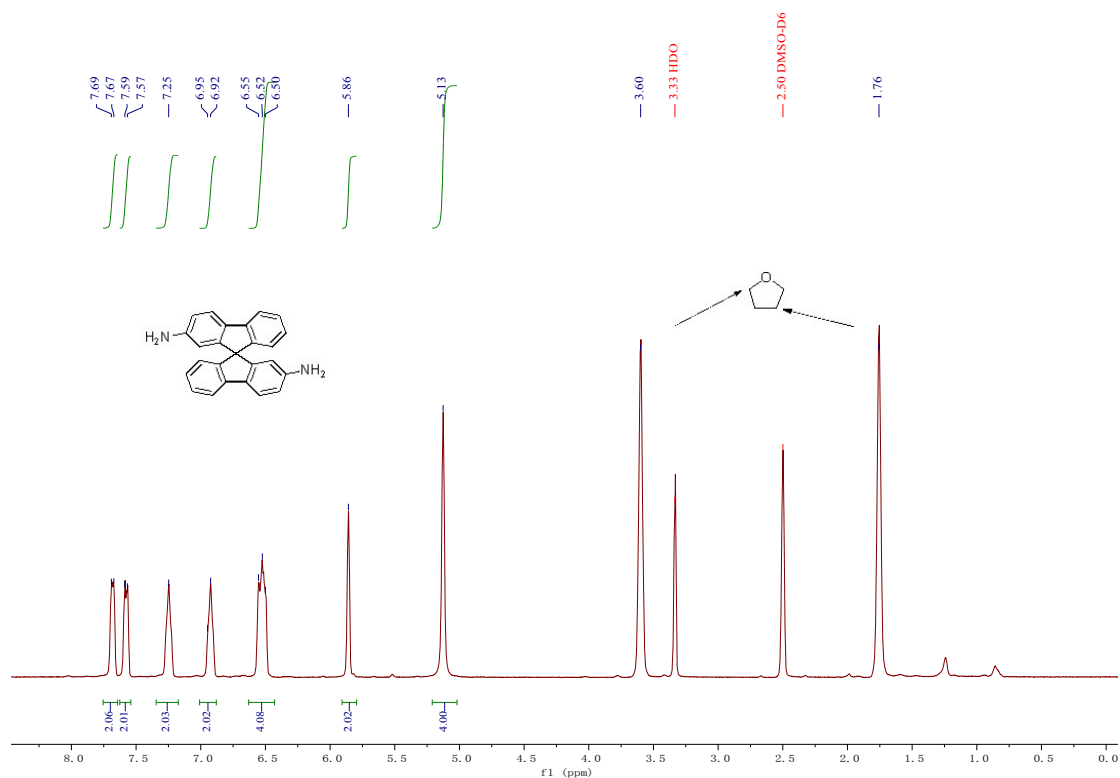
2. Experimental Section

2.1 The synthesis of 9,9'-spirobi[fluorene]-2,2'-diamine^[1]



The mixed solution of 70 % HNO₃ (2.0 mL) and acetic acid (2.0 mL) was added dropwise to the solution of 9,9'-spirobifluorene (0.2 g, 6.32×10⁻⁴ mol) in acetic acid (6.6 mL) heated at 120 °C. The resulting mixture was stirred at 120 °C for 90 minutes and cooled down to room temperature. After the reaction finished, the mixture was poured into iced water. The pure 3,3'-dinitro-9,9'-spirobifluorene was obtained through extraction with dichloromethane and flash chromatography of silica gel. Then, a suspension of 3,3'-dinitro-9,9'-spirobifluorene (830 mg) and 10% Pd/C (100 mg) in THF (4 mL) was stirred for 24 h in a reactor at 25 °C under H₂ (160 psi). The resulting mixture was filtered through Celite using THF as eluent, and the filtrate was

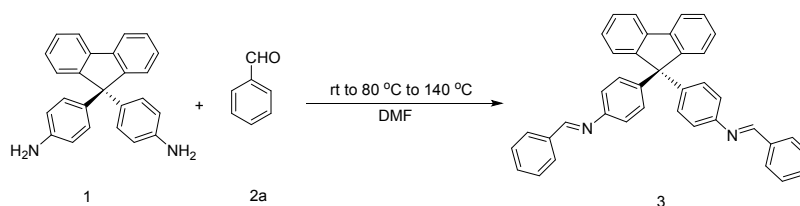
concentrated under reduced pressure. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.68 (d, $J = 7.5$ Hz, 2H), 7.58 (d, $J = 8.1$ Hz, 2H), 7.25 (s, 2H), 6.94 (d, $J = 9.4$ Hz, 2H), 6.53 (t, $J = 10.6$ Hz, 4H), 5.86 (s, 2H), 5.13 (s, 4H).



^1H NMR was recorded on Bruker 400 MHz; Solvent: $\text{DMSO-}D_6$

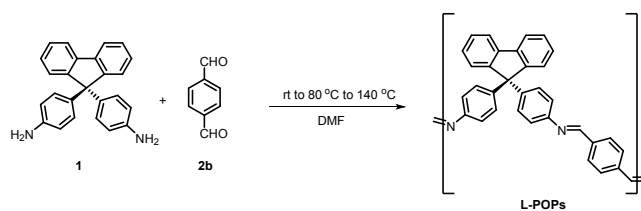
The ^1H NMR spectrum of 9,9'-spirobi[fluorene]-2,2'-diamine in $\text{DMSO-}D_6$ at ambient temperature

2.2 Synthesis of compound 3



DMF (8 mL) was added to a flask containing 4,4'-(9H-fluorene-9,9-diyl)dianiline (**1**) (1 mmol, 1 eq.) and benzaldehyde (**2a**) (2 mmol, 2 eq.). The reaction mixture was stirred at room temperature for 2 h then heated at 80 °C for 24 h under nitrogen.

2.3 Synthesis of L-POPs



2.3.1 Synthesis of L-POP-1

THF (5 mL) was added to a flask containing 4,4'-(9H-fluorene-9,9-diyl) dianiline (**1a**) (1 mmol) and benzaldehyde (**2b**) (1 mmol). The reaction mixture was stirred at room temperature for 2 h, 60 °C for 4 days under nitrogen. After the reaction finished, the reaction temperature was lowered to room temperature. The production was washed by DMF, deionized water, alcohol and L-POP-1 (yellow solid) was purified by centrifugation.

2.3.2 Synthesis of L-POP-2

DMSO (5 mL) was added to a flask containing 4,4'-(9H-fluorene-9,9-diyl) dianiline (**1a**) (1 mmol) and benzaldehyde (**2b**) (1 mmol). The reaction mixture was stirred at room temperature for 2 h, 80 °C for 1 day and 120 °C for 3 days under nitrogen. After the reaction finished, the reaction temperature was lowered to room temperature. The production was washed by DMF, deionized water, alcohol and L-POP-2 (yellow solid) was purified by centrifugation.

2.3.3 Synthesis of L-POP-3

DMF (5 mL) was added to a flask containing 4,4'-(9H-fluorene-9,9-diyl) dianiline (**1a**) (1 mmol) and benzaldehyde (**2b**) (1 mmol). The reaction mixture was stirred at room temperature for 2 h, 80 °C for 1 day and 120 °C for 3 days under nitrogen. After the reaction finished, the reaction temperature was lowered to room temperature. The production was washed by DMF, deionized water, alcohol and L-POP-3 (yellow solid) was purified by centrifugation.

2.3.4 Synthesis of L-POP-4

DMF (5 mL) was added to a flask containing 4,4'-(9H-fluorene-9,9-diyl) dianiline (**1a**) (1 mmol) and benzaldehyde (**2b**) (1 mmol). The reaction mixture was stirred at room temperature for 2 h, 80 °C for 1 day and 140 °C for 3 days under nitrogen. After

the reaction finished, the reaction temperature was lowered to room temperature. The production was washed by DMF, deionized water, alcohol and L-POP-6 (yellow solid) was purified by centrifugation.

2.3.5 Synthesis of L-POP-5

DMF (5 mL) was added to a flask containing 4,4'-(9H-fluorene-9,9-diyl) dianiline (**1**) (1 mmol) and benzaldehyde (**2b**) (1 mmol). AcOH (32 mmol) was added to the solution. The reaction mixture was stirred at room temperature for 2 h, 80 °C for 1 day and 120 °C for 3 days under nitrogen. After the reaction finished, the reaction temperature was lowered to room temperature. The production was washed by DMF, deionized water, alcohol and L-POP-7 (yellow solid) was purified by centrifugation.

2.3.6 Synthesis of L-POP-6

DMF (8 mL) was added to a flask containing 4,4'-(9H-fluorene-9,9-diyl) dianiline (**1a**) (1 mmol) and benzaldehyde (**2b**) (1 mmol). The reaction mixture was stirred at room temperature for 2 h, 80 °C for 1 day and 120 °C for 3 days under nitrogen. After the reaction finished, the reaction temperature was lowered to room temperature. The production was washed by DMF, deionized water, alcohol and L-POP-6 (yellow solid) was purified by centrifugation.

2.3.7 Synthesis of L-POP-7

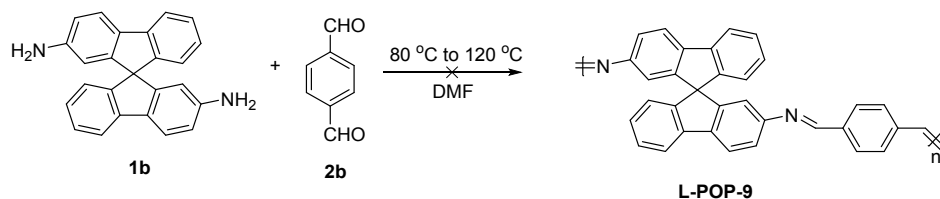
DMF (10 mL) was added to a flask containing 4,4'-(9H-fluorene-9,9-diyl) dianiline (**1a**) (1 mmol) and benzaldehyde (**2b**) (1 mmol). The reaction mixture was stirred at room temperature for 2 h, 80 °C for 1 day and 120 °C for 3 days under nitrogen. After the reaction finished, the reaction temperature was lowered to room temperature. L-POP-7 was purified by repeated precipitation from the DMF solution into methanol for three times. Then it was collected by centrifugation giving the yellow solid.

2.3.8 Synthesis of L-POP-8

DMF (12 mL) was added to a flask containing 4,4'-(9H-fluorene-9,9-diyl) dianiline (**1a**) (1 mmol) and benzaldehyde (**2b**) (1 mmol). The reaction mixture was stirred at

room temperature for 2 h, 80 °C for 1 day and 120 °C for 3 days under nitrogen. After the reaction finished, the reaction temperature was lowered to room temperature. L-POP-8 was purified by repeated precipitation from the DMF solution into methanol for three times. Then it was collected by centrifugation giving the yellow solid.

2.3.9 The Synthesis of L-POP-9



DMF (10 mL) was added to a flask containing 9,9'-spirobi[fluorene]-2,2'-diamine (1b) (1 mmol) and benzaldehyde (2b) (1 mmol). The reaction mixture was stirred at room temperature for 2 h, 80 °C for 1 day and 120 °C for 3 days under nitrogen. After the reaction finished, the reaction temperature was lowered to room temperature. No precipitation can be obtained by directly adding the reaction solution to methanol (40 mL).

2.3.10 The procedure of refluxed experiments.

The L-POP-6 was refluxed in MeOH, CH₂Cl₂, EtOAc, and acetone for 24 h. Then, the polymer was obtained by centrifugation and drying at 50 °C.

3. Analytical Data of the polymers

3.1

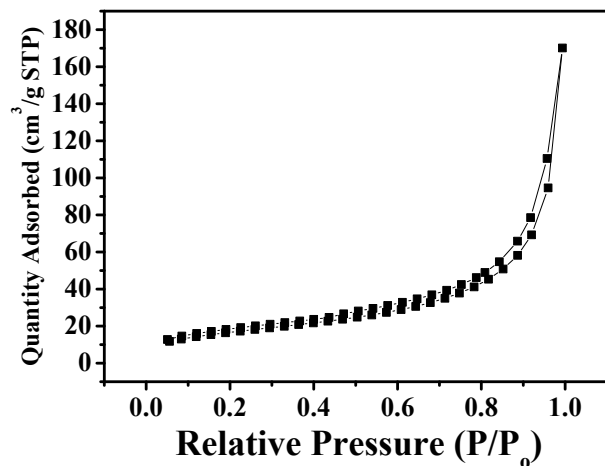


Fig. S1 The nitrogen adsorption isotherms (77 K) of L-POP-6 (recovery of polymer dissolved in DMF)

3.2

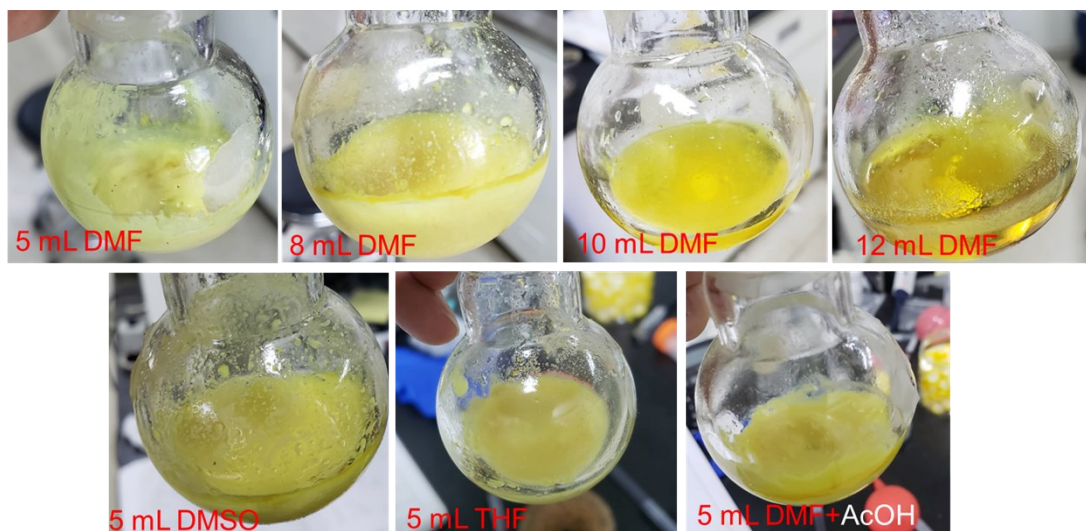


Fig S2. The images of different reaction systems.

3.3

Table S1 a list of solubility chart for the L-POP-6 and L-POP-7

<div style="display: inline-block; border-left: 1px solid black; border-bottom: 1px solid black; padding: 2px;"> Solvents Solubility Entry </div>	THF	acetone	CHCl ₃	DMF	DMSO	EtOAc	CH ₂ Cl ₂	NMP
L-POP-6	NO	NO	NO	NO	NO	NO	NO	NO
L-POP-7	YES	NO	YES	YES	NO	NO	YES	YES

3.4 The FTIR data

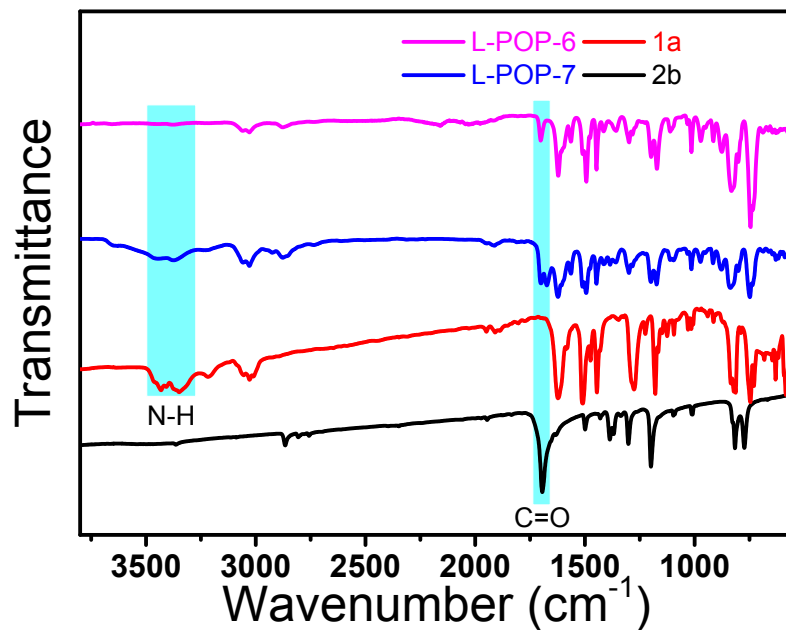
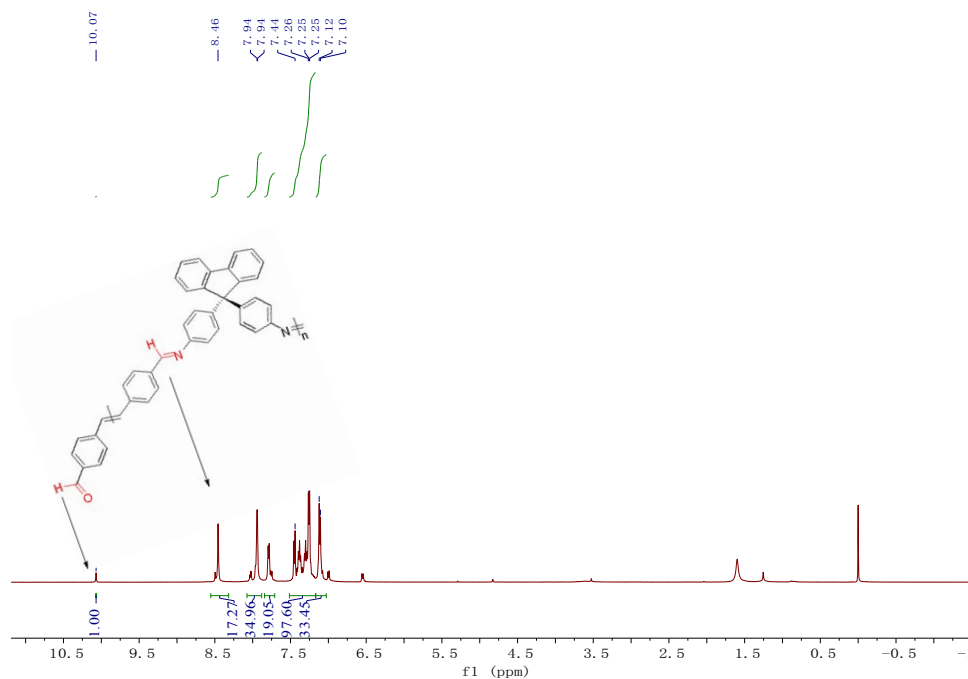


Fig. S3 The FTIR data of 4'-(9H-fluorene-9,9-diyl) dianiline (1a), 1,4-benzenedialdehyde (2b), L-POP-6, and L-POP-7

3.5



¹H NMR was recorded on Bruker 500 MHz; Solvent: CDCl₃

Fig. S4 the ¹H NMR spectrum of L-POP-7 in CDCl₃ at ambient temperature

3.6 The GPC data

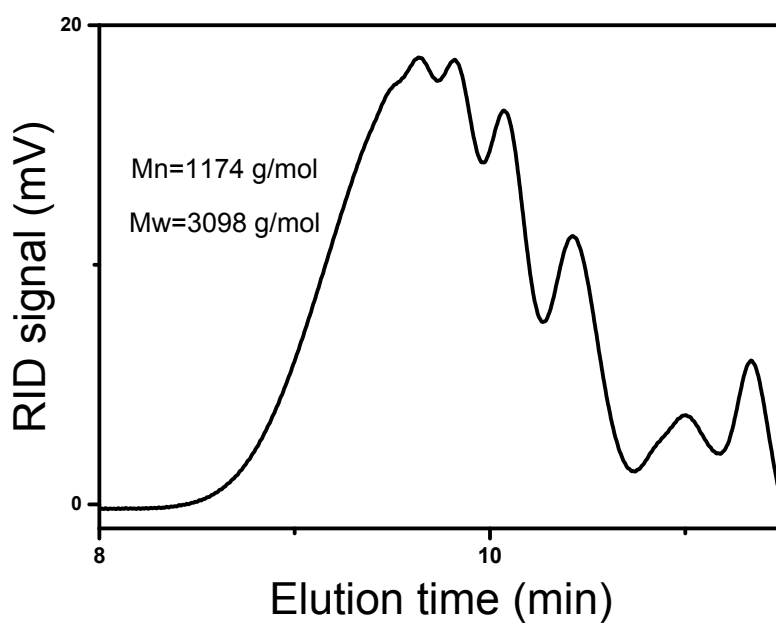


Fig. S5 The GPC chromatogram of L-POP-7

3.7 The PXRD patterns

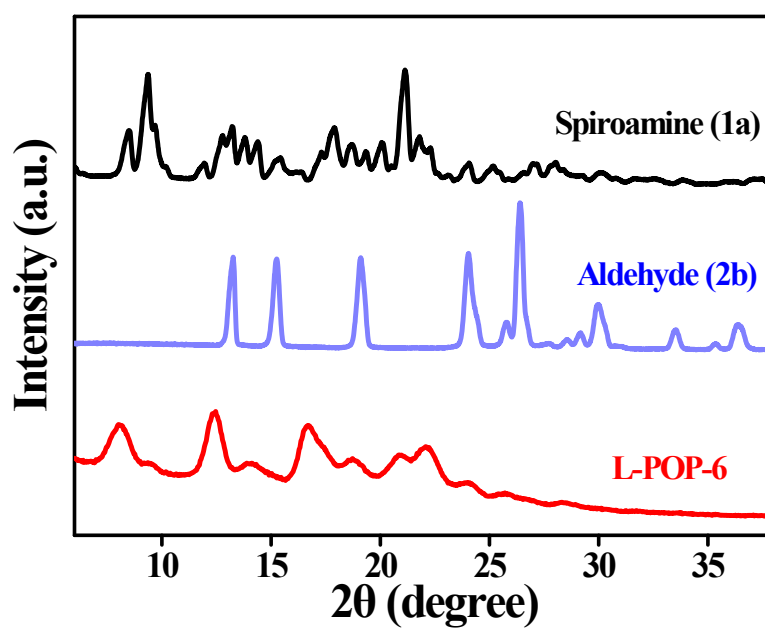


Fig. S6 The PXRD patterns of 4'-(9H-fluorene-9,9-diyl) dianiline (**1a**), 1,4-benzenedialdehyde (**2b**), and L-POP-6

3.8

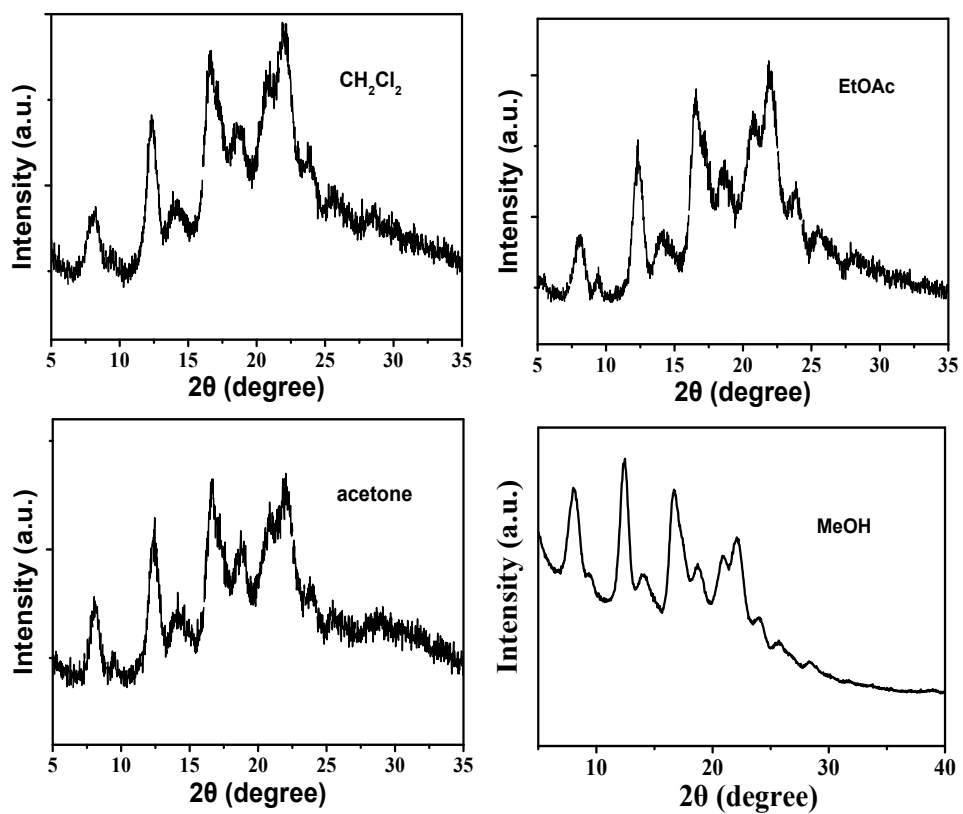


Fig. S7 The PXRD patterns of L-POP-6 (the polymers were refluxed in various solvents: CH₂Cl₂, EtOAc, acetone, MeOH)

3.9

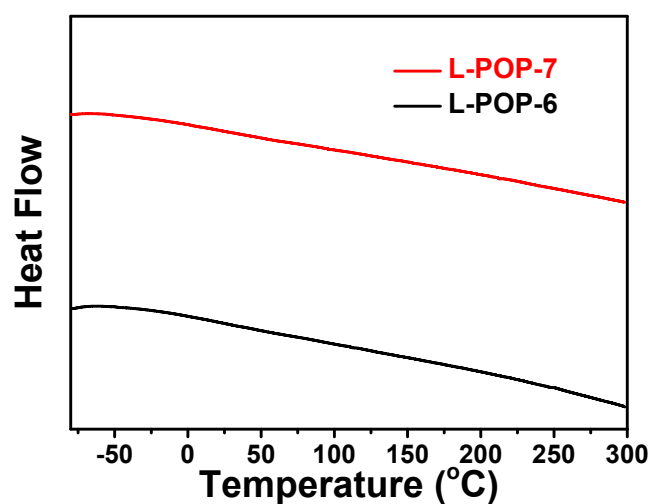


Fig. S8 the DSC curves of L-POP-6 and L-POP-7.

3.10 The TGA pattern

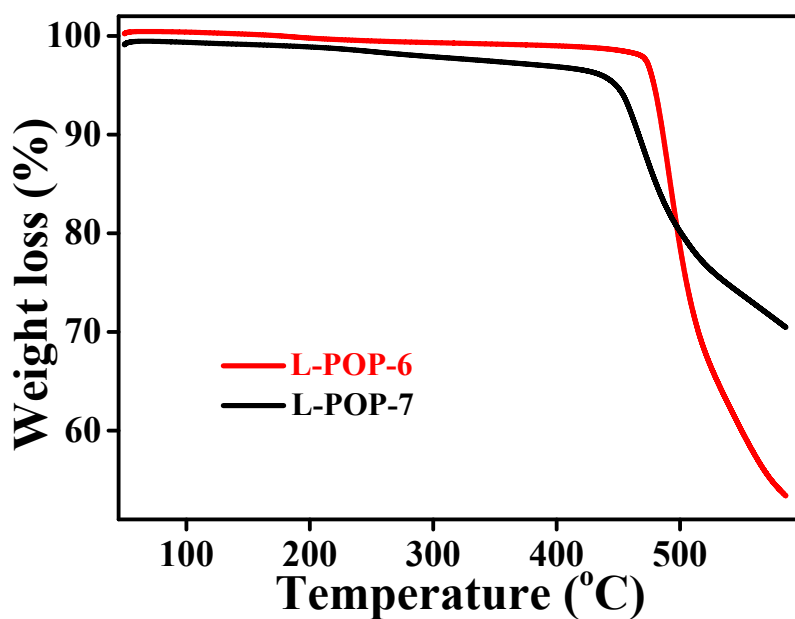


Fig. S9 The TGA data of L-POP-6 and L-POP-7

3.11 The elemental analysis of L-POP-6 and L-POP-7

Table S2. The EA of L-POP-6 and L-POP-7

Formula	Elemental Analysis (%)		
	N	C	H
L-POP-7	6.18	86.31	4.51
L-POP-6	6.16	87.26	4.39

Table S3. The theoretical values of L-POPs

Formula	Theoretical Values (%)		
	N	C	H
L-POPs	6.27	88.76	4.97

4. References

1. J.-H. Fournier, T. Maris, J. D. Wuest, *J. Org. Chem.* **2004**, *69*, 1762-1775.