

Supporting Information

A Facile Synthetic Route to Poly(p-phenylene terephthalamide) with Dual Functional Groups

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Experimental Section

Instruments and Measurements

¹H- and ¹³C-NMR (400 MHz) measurements were run on a Bruker AVANCE III 400 spectrometer at ambient temperature. Mass spectra were obtained on a Bruker APEX IV Fourier Transform Ion Cyclotron Resonance Mass Spectrometer. The element analysis was made on an Elemental Vario EL Analyzer. Infrared spectra were recorded on a Bio-Rad FTS-65A Fourier transform infrared spectrometer. Thermogravimetric analysis(TGA) was performed on a TAQ600 instrument at a heating rate of 10°C min⁻¹ under a nitrogen atmosphere. Number average molecular weight (*M_n*) and molecular weight polydispersity index ($PDI=M_w/M_n$) of the polymer were estimated by gel permeation chromatography with a Waters 1515 HPLC pump and a Waters 2410 refractive-index detector. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 mL min⁻¹ at 35 °C. Calibration was made against a series of monodispersed polystyrene standards. One-dimensional powder wide-angle X-ray diffraction experiments were performed on a Philips X'Pert Pro diffractometer with a 3-kW ceramic tube as the X-ray source (CuK α) and an X'celerator detector. The sample stage was set horizontally. The reflection peak positions were calibrated against silicon powder ($2\theta>15^\circ$) and silver behenate ($2\theta<10^\circ$). Background scattering was recorded and subtracted from the sample patterns. The contact angle was tested on an OCA20 Contact Angle Measuring System produced by Dataphysics.

The milling of rubber and carbon black was carried out on a rubber mixer machine (Shanghai

rubber machinery works, X(S)K-160). Vulcanization of rubber was operated on a plate vulcanizer (Huzhou East Machinery Co., Ltd., XLB-D350×350). The single fibre pull-out test was run on a Micro Computer Controlled Electronic Universal Testing Machine (Shenzhen Sans metering technology companies, CMT4104).

Materials

2,5-Dihydroxyterephthalic acid (99%; Beijing HWRK Chem. Co.), allyl bromide (analytical reagent; Beijing Chemical Co.), and other reagents and solvents were used as received unless otherwise specified. *N*-Methyl-2-pyrrolidone (analytical reagent; Beijing Chemical Co.) and dimethyl sulfoxide (analytical reagent; Beijing Chemical Co.) were dried by stirring with CaH₂ and distilled under reduced pressure. Pyridine (analytical reagent; Beijing Chemical Co.) was dried by stirring with KOH pellets and then distilled. *p*-Phenylenediamine (analytical reagent; Beijing Chemical Co.) was sublimated twice under vacuum before use. Calcium chloride (analytical reagent; Beijing Chemical Co.) was finely ground and dried at 300 °C in muffle furnace for 6 h before use. 2,5-Bis(allyloxy)terephthaloyl dichloride (**V**) was synthesized according to the literature method¹⁻⁴.

Rubber (SBR-1502) was purchased from Jilin Chemical Industrial Co., Ltd.. Carbon black (N234) was purchased from Cabot Chemical (Tianjin) Co., Ltd.. Aramid fiber (Tapanan, 600D) was purchased from Yantai Tayho Advanced materials Co., Ltd..

Synthesis of diethyl 2,5-dihydroxyterephthalate. Into a 150 ml round bottomed flask were placed 10.0 g (50.4 mmol) of 2,5-dihydroxyterephthalate acid, 100 ml of ethanol and 15 ml of concentrated sulfuric acid. The mixture was refluxed for 8 h. After cooling to room temperature, plenty of needle crystals precipitated and were collected by filtration. After recrystallization from ethanol, 10.8 g of light green crystals were obtained with a yield of 87%. ¹H NMR (CDCl₃, ppm) 10.14 (s, 2H), 7.47 (s, 2H), 4.34-4.45 (q, 4H), 1.40 (t, 6H, J = 7.5 Hz).

Synthesis of diethyl 2,5-bis(allyloxy)terephthalate. Into a 250 ml round bottomed flask were added 7.8 g (30.6 mmol) of diethyl 2,5-dihydroxyterephthalate, 8.59 g (62.2 mmol) of K₂CO₃, 12.6 g (104.1 mmol) of allyl bromide and 150 ml of THF. The mixture was refluxed for 96 h. After cooling to room temperature, the mixture was filtered and the filtrate was evaporated under vacuum. The solids were recrystallized from petroleum ether and 9.0 g of white needle crystals

were obtained with a yield of 96%. ¹H NMR (CDCl₃, ppm) 7.39 (s, 2H), 6.01-6.10 (m, 2H), 5.44-5.52 (dd, 2H), 5.27-5.32 (dd, 2H), 4.59-4.61 (d, 4H), 4.34-4.41 (q, 4H), 1.36-1.41 (t, 6H); ¹³C NMR (CDCl₃, ppm) 14.26, 61.35, 70.60, 117.37, 117.58, 125.01, 132.77, 151.53, 165.63; FT-MS (M+H⁺)335.1488; Elem. Anal. Cal. C,64.66, H, 6.63; Found C,64.75, H,6.62.

Synthesis of 2,5-bis(allyloxy)terephthalate acid. A mixture of 9.0 g (26.8 mmol) of diethyl 2,5-bis(allyloxy)terephthalate, 9.0 g (225.0 mmol) of NaOH, 30 ml of methanol and 60 ml of water was stirred overnight at 30 °C. Then hydrochloric acid was added to the mixture until pH = 1 and a large amount of white solids were obtained. After filtration, the solids were recrystallized from ethanol and 7.0 g of yellowish needle crystals were obtained with a yield of 93%. ¹H NMR (DMSO-*d*₆, ppm) 13.02 (s, 2H), 7.34 (s, 2H), 5.95-6.08 (m, 2H), 5.39-5.47 (dd, 2H), 5.21-5.26 (dd, 2H), 4.58-4.61 (d, 4H). ¹³C NMR ((DMSO-*d*₆, ppm) δ 166.67, 150.09, 133.39, 125.36, 116.92, 115.89, 69.42, 40.00, 39.79, 39.58, 39.37, 39.16, 38.95, 38.74. FT-MS (M+Na⁺) 301.0677. Elem. Anal. Cal. C, 60.43, H,5.07; Found C, 60.58, H, 5.13.

Synthesis of 2,5-bis(allyloxy)terephthaloyl dichloride (V). A mixture of 7.0 g (23.2 mmol) of 2,5-bis(allyloxy)terephthalate acid, 15 ml of oxalyl chloride, 40 ml of dichloromethane and two drops of *N,N*-dimethylformamide was stirred overnight at 30 °C. After the solids totally dissolved, the solvent was removed by evaporation under vacuum. The solids were recrystallized from *n*-heptane and 6.3 g of yellowish needle crystals were obtained with a yield of 80%. ¹H NMR (CDCl₃, ppm) 7.55 (s, 2H), 5.99-6.08 (m, 2H), 5.49-5.54 (dd, 2H), 5.35-5.38 (dd, 2H), 4.66-4.68 (d, 4H); ¹³C NMR (CDCl₃, ppm) 70.55, 117.95, 118. 70, 128.55, 131.59, 150.81, 163.46. Elem. Anal. Cal. C, 53.36, H, 3.84. Found C, 54.08, H, 4.25.

Synthesis of 2,5-bis(allyloxy)-*N,N'*-diphenylterephthalamide (IV). A solution of 2.0 g (6.3 mmol) of 2,5-bis(allyloxy)terephthaloyl dichloride in 10 ml of dry THF was added dropwise into the mixture of 4 ml of aniline and 30 ml of dry THF and then the mixture was stirred for 4 h. After filtration, the filtrate was concentrated and precipitated in 500 ml of water with 10 ml of concentrated hydrochloric acid. The precipitates formed were collected by filtration and recrystallized from ethanol, yielding 2.53 g white needle crystals with a yield of 93%. ¹H NMR (DMSO-*d*₆, ppm) 10.27 (s, 2H), 7.68-7.78 (d, 4H), 7.47 (s, 2H), 7.32-7.42 (t, 4H), 7.06-7.16 (t, 2H), 6.04-6.18 (m, 2H), 5.35-5.50 (dd, 2H), 5.20-5.35 (dd, 2H), 4.66-4.80 (d, 4H); ¹³C NMR (DMSO-*d*₆, ppm) 163.27, 149.31, 138.78, 133.24, 128.80, 127.67, 123.72, 119.57, 117.78, 114.92,

69.76. FT-MS (M+H⁺) 429.1799. Elem. Anal. Cal. C,72.88, H,5.65, N6.54; Found C,72.38, H, 5.65, N, 6.56.

Claisen rearrangement reaction of model compound. A Schlenk tube containing 0.30 g (0.70 mmol) of **IV** was heated to 170 °C under nitrogen for various time. In a typical run that the reaction was continued for 6 h, the product was recrystallized from toluene, yielding 0.275 g of yellow needle crystals with a yield of 92%. ¹H NMR (DMSO-*d*₆, ppm) 10.16 (s, 2H), 8.25 (s, 2H), 7.68-7.78 (d, 4H), 7.28-7.38 (t, 4H), 7.02-7.10 (t, 2H), 5.80-5.95 (m, 2H), 4.93-5.03 (dd, 2H), 5.85-5.92 (dd, 2H), 3.32-3.42 (d, 4H). ¹³C NMR (DMSO-*d*₆, ppm) 165.73, 144.21, 139.34, 136.17, 129.37, 128.52, 123.65, 123.21, 119.53, 115.26, 31.39.

Synthesis of allyloxy substituted PPTA (II). In a round-bottomed flask equipped with a drying tube and nitrogen inlet and outlet, a mixture of CaCl₂ (4.10 g), PPD (1.53 g, 14.1 mmol), and *N*-methylpyrrolidone (50 mL) was introduced and stirred until the suspension was converted into a clear solution. The resulting solution was cooled to -10 °C. Subsequently, with continued cooling and vigorous stirring, the compound **V** (4.48 g, 14.2 mmol) was quickly added into the reaction system. Then pyridine (2.2 mL) was injected quickly via syringe. Stirring was continued for 30 min, the temperature rose to room temperature and the reaction was stirred for another 6 h. The reaction mixture was poured into water (500 mL) and the precipitated polymer was collected by filtration, washed thoroughly with boiling water and dried at 80 °C for 24 h under vacuum to afford 4.75 g of polymer **II** as yellow solids. Yield: 96 %.

Claisen rearrangement reaction of allyloxy substituted PPTA. A Schlenk tube containing 0.15 g of **II** and 3 ml of NMP was heated to 190 °C for 6 h under nitrogen atmosphere and a red solution was obtained. After precipitation in methanol, the solids was collected by filtration and dried under vacuum for 24 h, yielding 0.14 g of final products as brown powder. Yield: 97 %.

Test of single fibre pull-out force. Raw rubber was milled with carbon black. Kevlar fibers were immersed into NMP solutions of polymer **I** with concentrations of 0.1~2wt% using a dip tank for 2 min. After drying at 130°C for 5 minutes, they were sandwiched by two sheets of milled rubber. Vulcanization of rubber was carried out on a plate vulcanizer at 140 °C under a press of 24.5 MPa. The single fibre pull-out test was operated on at a moving speed of 50mm/min according to method GB13022-91.

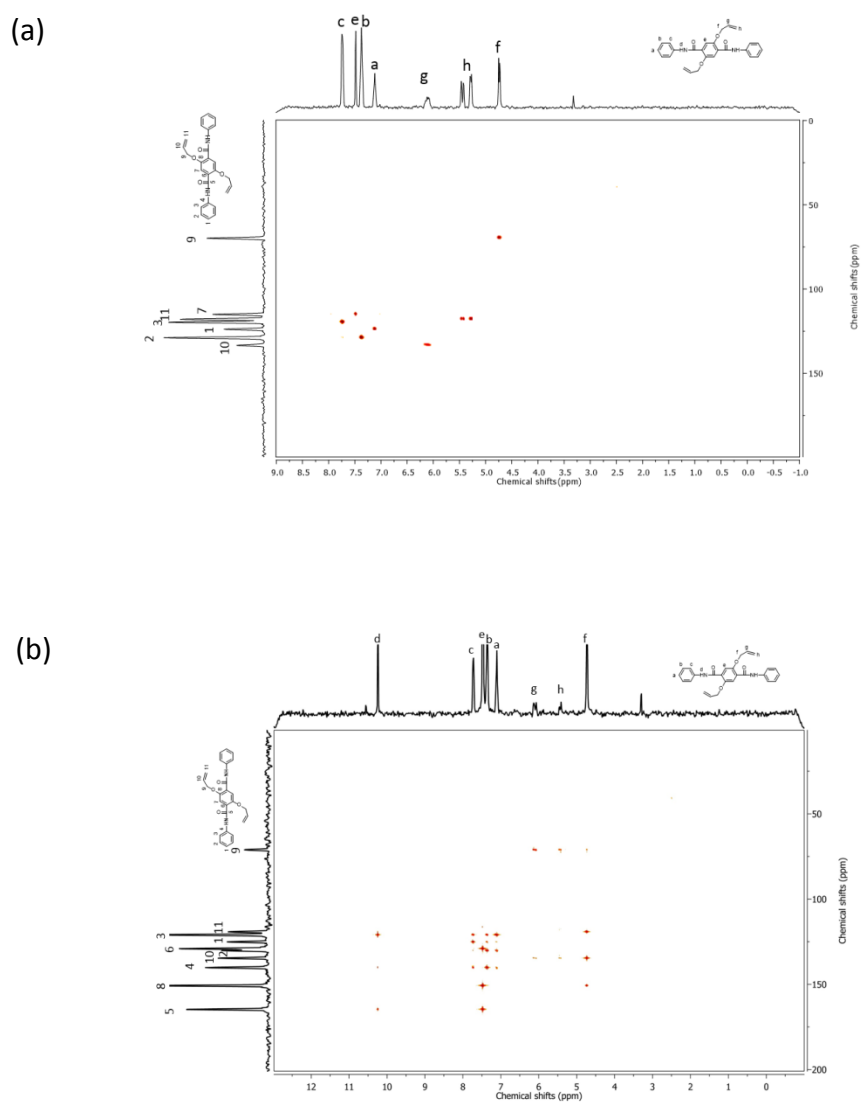


Fig. S1 HMQC (a) and HMBC (b) NMR spectra of 2,5-diallyloxy-*N,N'*-diphenylterephthalamide measured in d_6 -DMSO at room temperature.

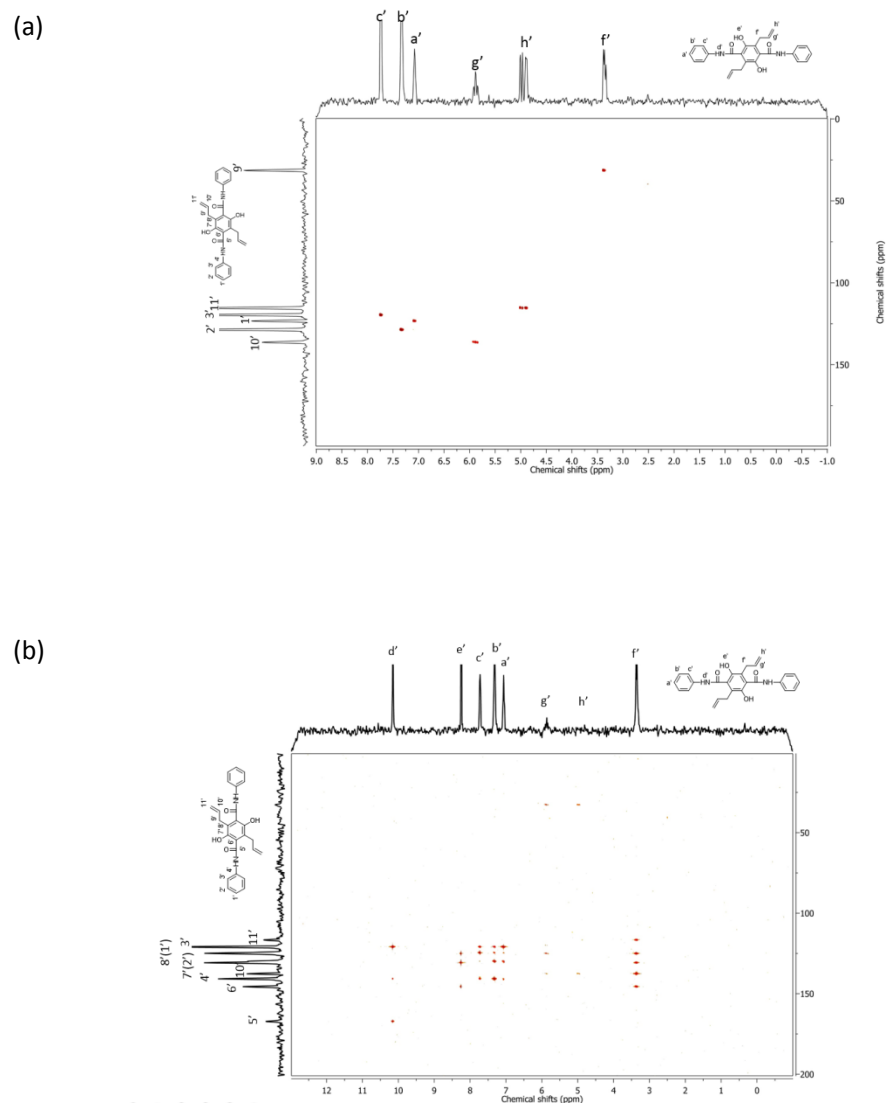


Fig. S2 HMQC (a) and HMBC (b) NMR spectra of 2,5-diallyl-3,6-dihydroxy-*N,N'*-diphenylterephthalamide measured in d_6 -DMSO at room temperature.

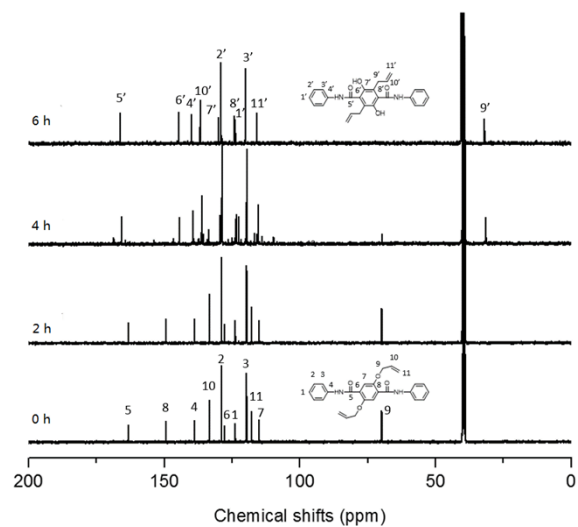


Fig. S3 ¹³C NMR spectra of 2,5-diallyloxy-*N,N'*-diphenylterephthalamide annealed at 170 °C for various time. Measured in d₆-DMSO at room temperature.

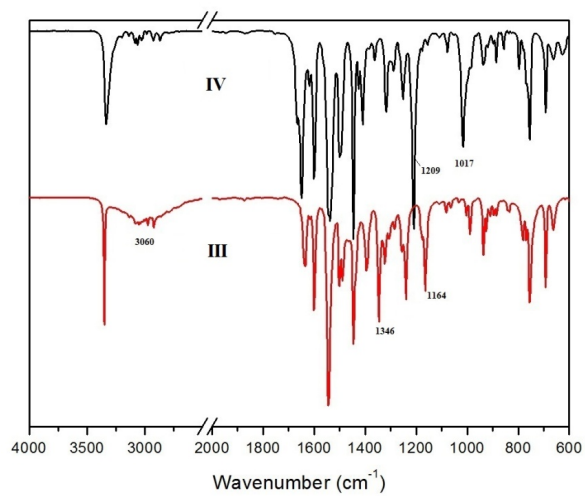


Fig. S4 FT-IR spectra of 2,5-diallyl-3,6-dihydroxy-*N,N'*-diphenylterephthalamide and 2,5-diallyloxy-*N,N'*-diphenylterephthalamide.

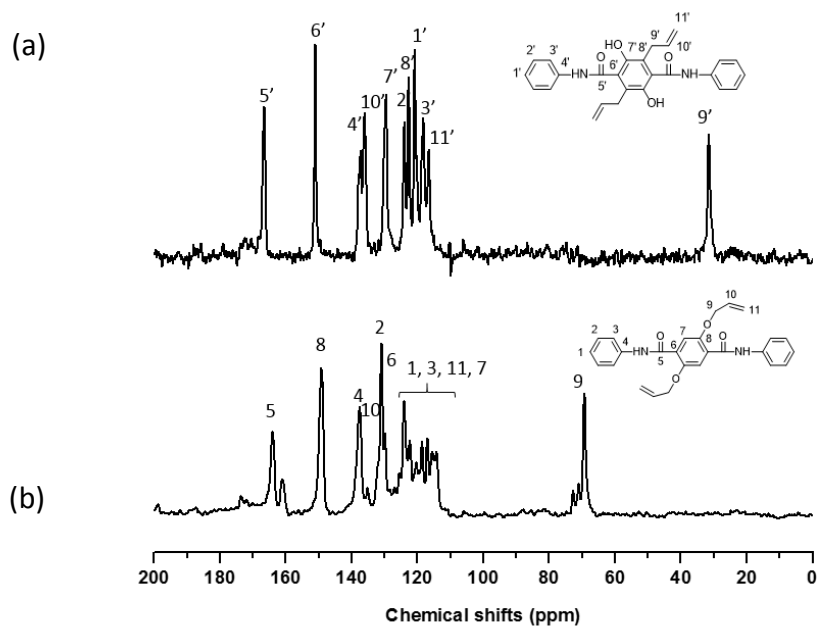


Fig. S5 Solid state ^{13}C NMR spectra of 2,5-diallyloxy- N,N' -diphenylterephthalamide (a) and its rearranged product annealed at 170 °C for 6 h (b).

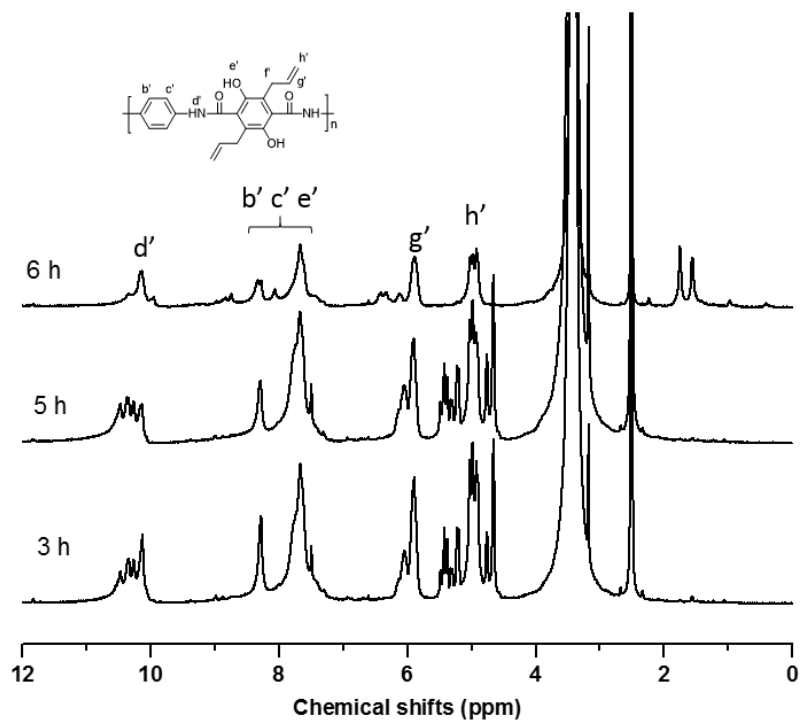


Fig. S6 ^1H NMR spectrum of **II** annealed in NMP at 190 °C for different times. Measured in d_6 -DMSO at room temperature.

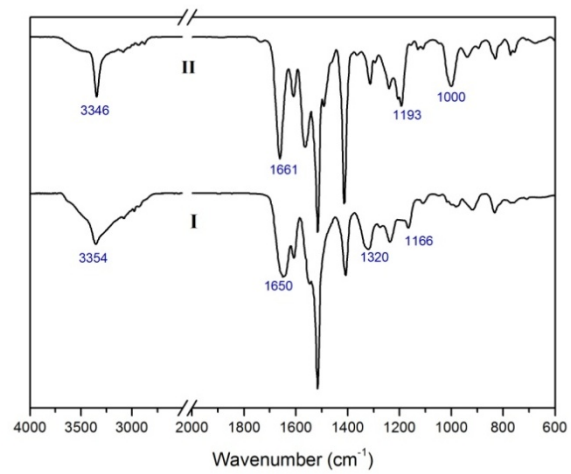


Fig. S7 FT-IR spectra of polymers **II** and **I**

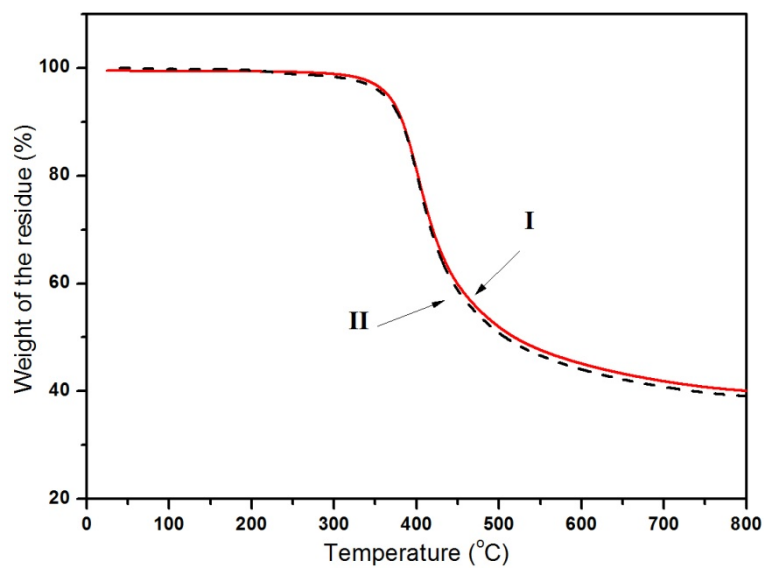


Fig. S8 TGA curves of polymers **I** and **II**

Table S1. Solubilities^a of PPTA, **II** and **I**

Sample	PPTA	II	I
NMP	-	-	++
DMF	-	-	++
H ₂ SO ₄	++	+-	++
<i>m</i> -Cresol	-	+-	++
DMSO	-	-	++
NMP+5%LiCl	-	+-	++
DMF+5%LiCl	-	-	++
Acetonitrile	-	-	-
Dioxane	-	-	-
THF	-	-	-

^a: For 2 mg polymer in 1 ml solvent: ++, soluble at 25°C; +, soluble at 60°C; +-, partly soluble at 60°C; -, insoluble.

Table S2. Results of single fibre pull-out force test. The fiber was treated with NMP solution of polymer **I** at various concentrations as sizing agents.

Concentration of I (wt%)	Adhesive force (N)				
	1	2	3	4	average
0	21.8	19.5	19.2	22.9	20.9
0.1	23.8	23.4	27.7	25.0	25.0
0.5	29.2	30.6	28.6	32.1	30.1
1.0	19.6	24.3	19.7	20.9	21.1
2.0	34.7	34.3	33.8	31.0	33.5

Reference

- [1] Henke, S.; Schneemann, A.; Wütscher, A.; Fischer, R. A. *J. Am. Chem. Soc.* **2012**, *134*, 9464.
- [2] Itami, K.; Palmgren, A.; Thorarensen, A.; Bäckvall, J.E. *J. Org. Chem.* **1998**, *63*, 6466.
- [3] Steuer, M.; Rehahn, M.; Ballauff, M. *Makromol. Chem.* **1993**, *194*, 2395.
- [4] Zhang, X.B.; Tang, B.C.; Zhang, P.; Li, M.; Tian, W.J. *J. Mol. Struct.* **2007**, *846*, 55.