Supporting Information

Novel Synthetic Method for Tubular Nanofibers

Jiqi Wang [1], Zuoting Yang [1], Mudasir Ahmad [1], Hepeng Zhang [1, 2], Qiuyu Zhang [1, 2], Baoliang Zhang[1, 3 *]

[1] School of Applied and Natural Sciences, Northwestern Polytechnical University, Xi'an, 710129, P. R. China

[2] MOE Key Laboratory of Material Physics and Chemistry under Extraordinary Condition, Ministry of Education, Northwestern Polytechnical University, Xi'an, 710129, P. R. China

[3] Sunresin New Materials Co. Ltd., Xi'an, 710072, PR China

Materials and instruments

Materials

Alpha,alpha'-dichloro-p-xylene, alpha,alpha'-dichloro-m-xylene, alpha,alpha'-dichloro-o-xylene, alpha,alpha'-dibromo-p-xylene, alpha,alpha'-dibromo-m-xylene, 1,3-bis(bromomethyl)-5-methylbenzene, and 1,3,5-tris(bromomethyl)benzene were purchased from J&K Scientific Ltd. Polydimethylsiloxane (viscosity 100±8 mPa·s), liquid paraffin (0.85 g/mL at 20 ℃), solid paraffin (m.p 52-54℃), n-hexane, cyclohexane, n-heptane, and kerosene (b.p 190-250 °C) were obtained from Macklin. Anhydrous $FeCl_3$ was supplied by Sinopharm Chemical Reagent Co., Ltd. Absolute ethanol and 1,2-dichloroethane were purchased from Guangdong Guanghua Sci-tech Co., Ltd.

Instruments

The morphology and structure of samples were observed by field emission scanning electron microscope (FESEM, FEI Verios G4) and transmission electron microscope (TEM, FEI TALOS-F200X). X-ray diffraction (XRD) characterized by Thermo Scientific 7000. Specific surface areas and pore size distribution were

* Corresponding author tel: +86-029-88431675; fax: +86-029-88431675; Northwestern Polytechnical University, Youyi Road 127#, Xi'an (710072), China.
Email： blzhang@nwpu.edu.cn

computed from the results of N_2 physisorption (Tristar3020, Micromeritics) by using the BET (Brunauer-Emmet-Teller). The magnetic properties were determined by vibrating sample magnetometer (VSM, Lake Shore 7307). Fourier Transform Infrared (FTIR) spectra was analyzed on the TENSOR27 FTIR spectrometer (Bruker).

Experiments

100 mL of polydimethylsiloxane (or n-hexane, cyclohexane, n-heptane, liquid paraffin, solid paraffin, kerosene) was added into a 250 mL three-necked flask. The DCE solution of benzyl halide with certain concentration and volume was added to the three-necked flask at room temperature under stirring. Then, a certain concentration and volume DCE solution of $FeCl_3$ was added to the system. After stirring for 30 min, the temperature was raised to 82℃ and the reaction was carried out for 12 h at constant temperature. The tubular polymer nanofibers were obtained after filtration, ethanol extraction, and vacuum drying. The vacuum carbonization process was as follows: the heating rate was 5°C/min, the carbonization temperature was 550°C, and the carbonization time was 5 h. The specific feeding parameters were shown in Table.S1.

The tubular polymer nanofibers were also prepared by α,α'-dichloro-m-xylene, alpha,alpha'-dichloro-o-xylene, alpha,alpha'-dibromo, alpha,alpha'-dibromo-m-xylene, 1,3-bis(bromomethyl)-5-methylbenzene, 1,3,5-tris(bromomethyl)benzene as the monomers. For the preparation, the dosage of DCE for dissolving monomer was 8 mL, the addition amount of FeCl3 and DCE were 0.45 g and 6 mL.

Table.S1 Data for the synthesis of tubular polymer nanofibers

No.	DCX (g)	DCE for dissolving DCX (mL)	$FeCl_3$ (g)	DCE for dissolving $FeCl_3$ (mL)
1	0.4	8	0.45	8
2	0.4	10	0.45	8
3	0.4	12	0.45	8
4	0.8	8	0.45	8
5	0.8	10	0.45	8
6	0.8	12	0.45	8
7	1.2	8	0.45	8
8	1.2	10	0.45	8
9	1.2	12	0.45	8
10	0.8	8	0.25	6
11	0.8	8	0.25	8
12	0.8	8	0.25	10
13	0.8	8	0.45	6
14	0.8	8	0.45	8
15	0.8	8	0.45	10
16	0.8	8	0.9	6
17	0.8	8	0.9	8
18	0.8	8	0.9	10
19	0.8	6	0.45	10
20	0.8	10	0.45	6

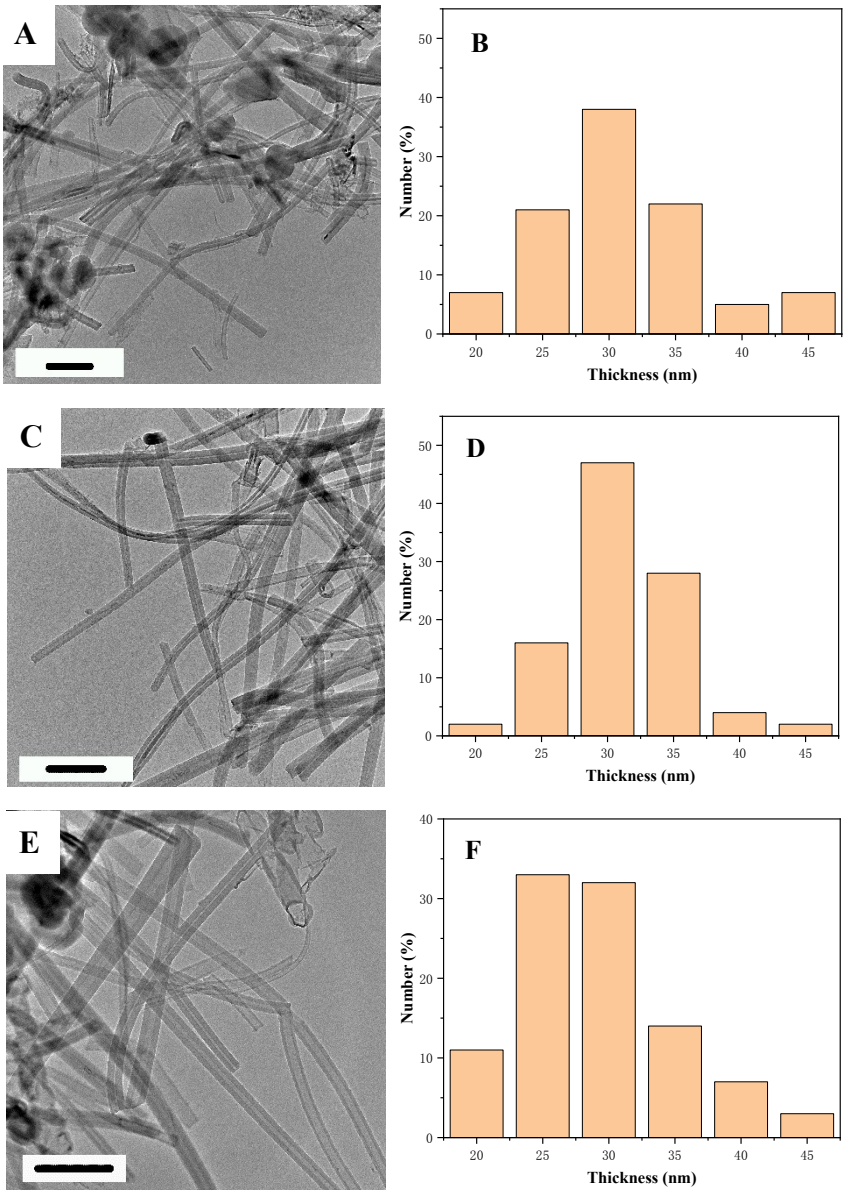

Fig.S1 TEM images and the wall thickness distributions of tubular polymer nanofibers: the dosage of DCE was 8 mL, at DCX concentrations of 50 mg/mL (A, B), 100 mg/mL (C, D), 150 mg/mL (E, F). The scale bar is 200 nm. The wall thickness distributions are obtained by the statistics from TEM images.

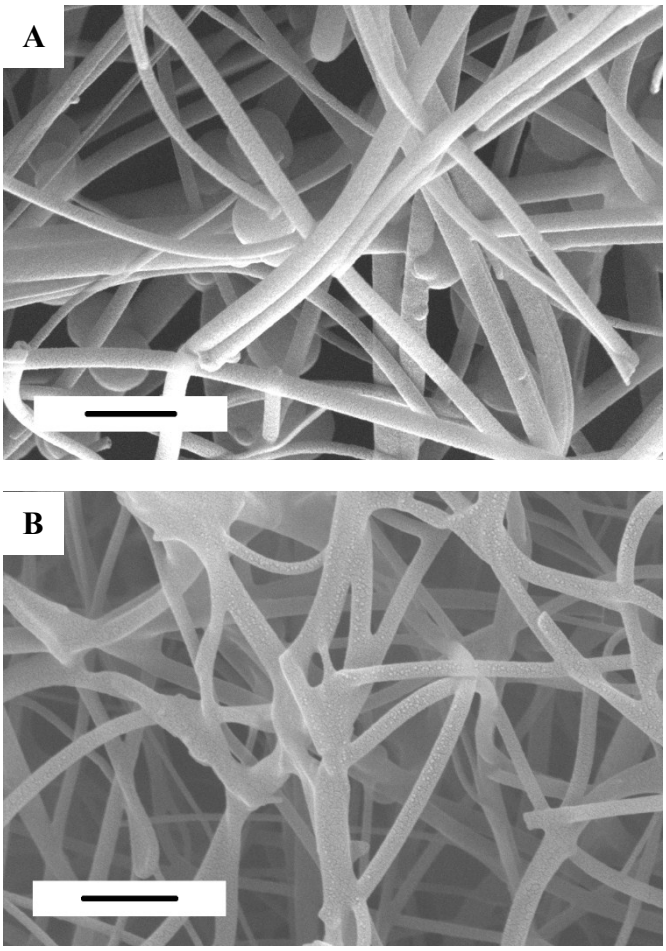

Fig.S2 SEM images of tubular polymer nanofibers: the dosages of DCE for dissolving DCX and $FeCl_3$ were 10 mL and 6 mL (A); the dosages of DCE for dissolving DCX and $FeCl_3$ were 6 mL and 10 mL (B). The scale bar is 0.5 μm.

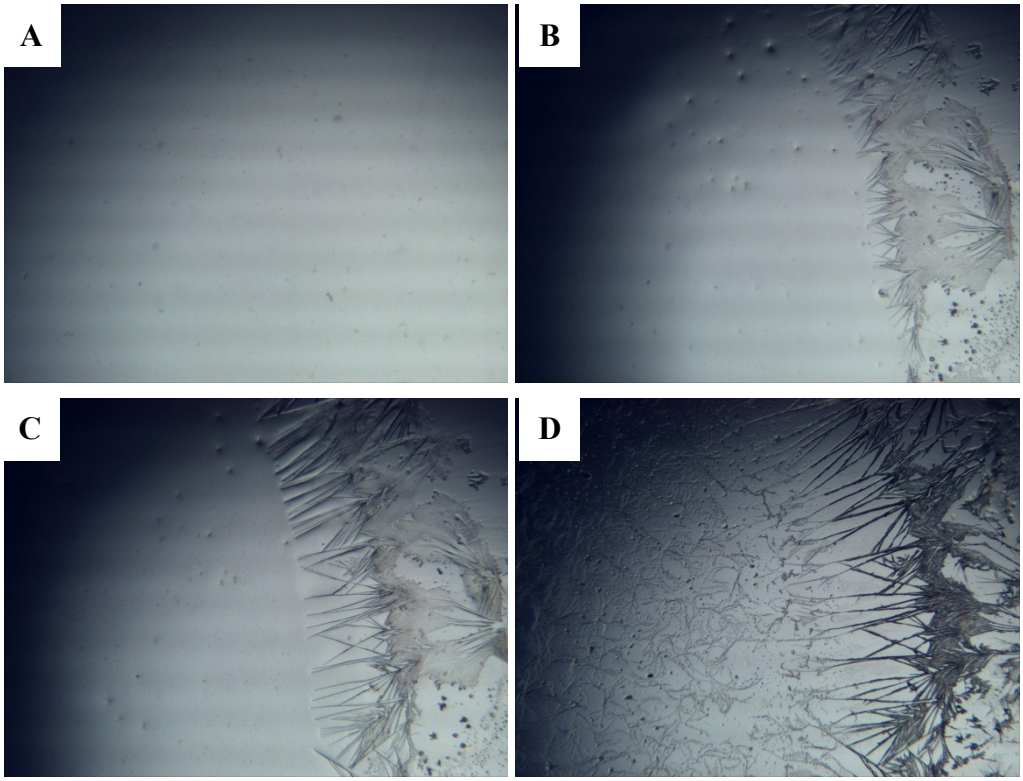

Fig.S3 Optical microscope images of $FeCl_3$ crystallization process at different stages. The DCE solution of $FeCl_3$ (A); the crystalline state of $FeCl_3$ during the volatilization of DCE (B, C, the DCE volatilization amount in B is less than C); the $FeCl_3$ crystals after complete evaporation of DCE (D)

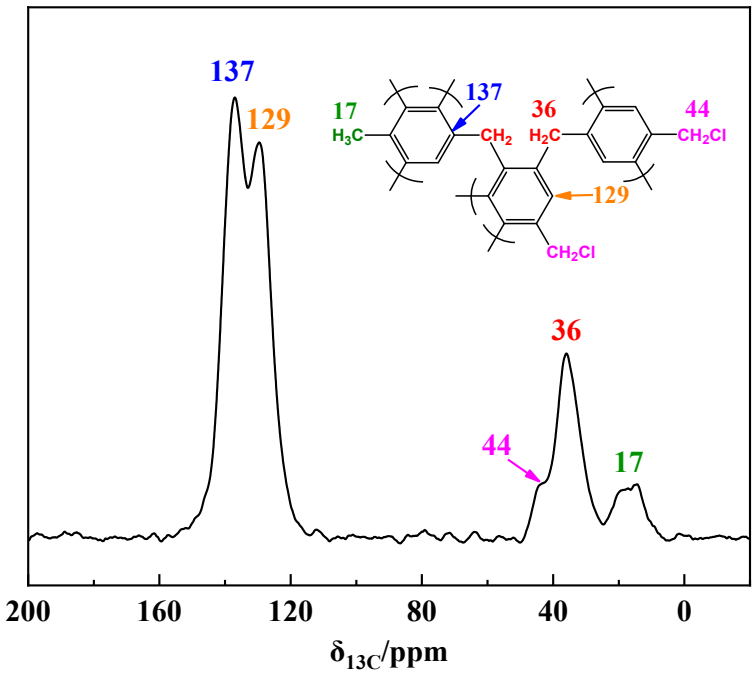

Fig.S4 ^{13}C solid state NMR spectrum of tubular polymer nanofibers

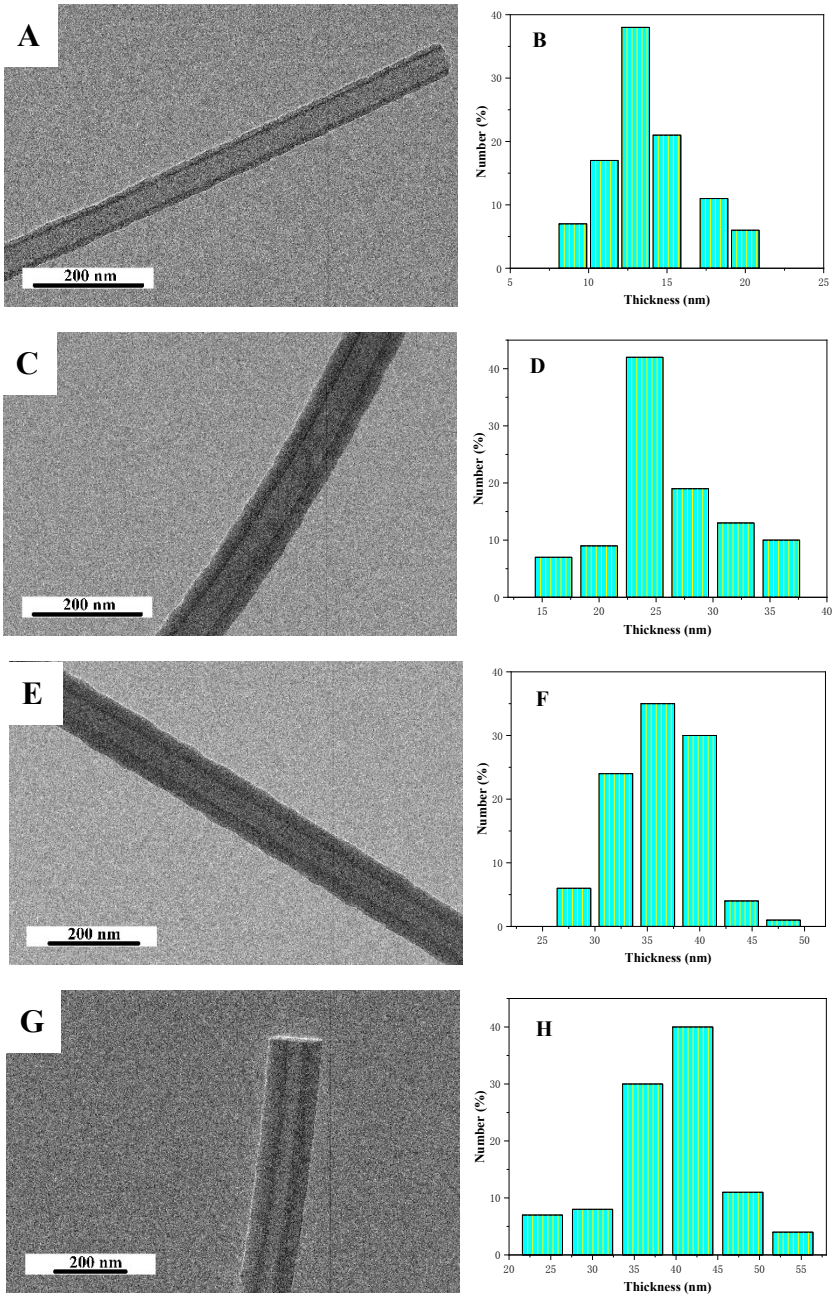

Fig.S5 TEM images and the wall thickness distributions of tubular polymer nanofibers obtained under different reaction time: 6 h (A, B), 9 h (C, D), 12 h (E, F) and 15 h (G, H). The wall thickness distributions are obtained by the statistics from TEM images.

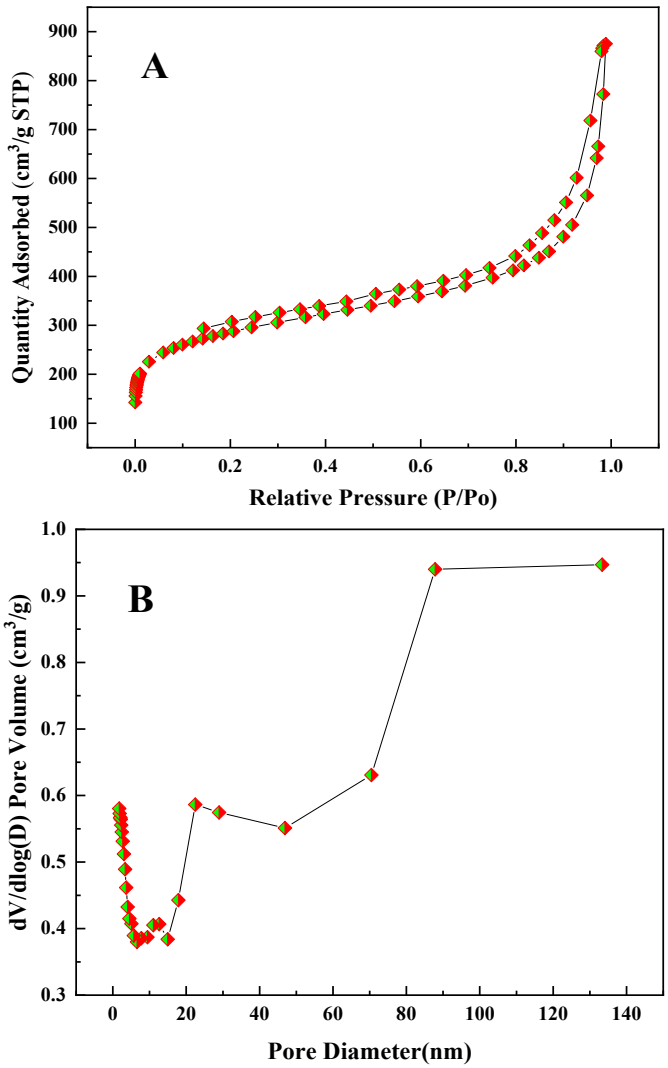

Fig.S6 The BET and pore size distribution curves of the traditional hypercrosslinked polymer by DCX, DCE and $FeCl_3$ without polydimethylsiloxane