Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Recyclable Heat-resisting Polymer Poly(ether azaindole ketone)-H^+ via Hydrogen Bonding Crosslinking

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Table of contents

1. Materials and Reagents

4-hydroxy-7-azaindole was purchased from TCI Development Co., Ltd. and used without further purification, 4,4'-difluorobenzophenone was purchased from J & K Technology Co., Ltd., and was purified by recrystallization from alcohol twice before use. The rest of materials and reagents were obtained from different commercial sources and used without further purification.

2. Measurements

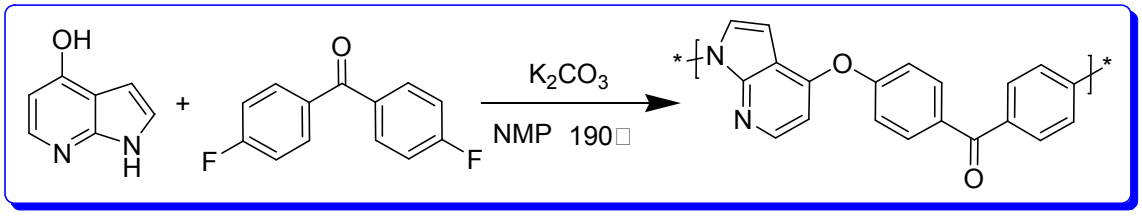
FTIR spectra were recorded on a Nicolt 6700 FTIR spectrometer. ^{1}H NMR were performed on Bruker AV-400 spectrometer at 400 MHz in DMSO-d_6 (δ 2.50 ppm), while ^{13}C NMR spectra were also recorded on a Bruker AV-400 spectrometer at 100 MHz in DMSO-d_6 (δ 2.50 ppm). The molecular weights and molecular weight distributions were estimated by gel permeation chromatography (GPC) on a Wyatt DAWNHELEOS using N,N-dimethylformamide (DMF) (adding 1% LiBr) as an eluent, testing temperature 50 ^{o}C. The glass transition temperature was obtained by DSC curve at a rate of 10 ^{o}C/min under flowing nitrogen gas. The thermogravimetric analysis (TGA) was performed on a Setarma TG-92 at a heating rate of 10 ^{o}C/min under nitrogen atmosphere. Absorption spectra were

detected on a SHIMADZU UV-3150 UV-vis-NIR sprectrophotometer.

3. Synthesis of Poly(ether azaindole ketone) (PEAINK)

A three-necked flask (25 mL) with a magnetic stirrer was evacuated and backfilled with nitrogen. Then the flask was charged with 4-hydroxy-7-azaindole 0.4024 g (3.0 mmol), 4,4'-difluorobenzophenone 0.6546 g (3.0 mmol), K_2CO_3 0.8292 g (6 mmol), and NMP (10.0 mL). The reaction mixture was evacuated and flushed with nitrogen and repeated this procedure for three times. The flask was immersed with continuous stirring in a 190 °C oil bath for 5 h. The resulting solution was allowed to slowly cool to room temperature and subsequently poured into cold water, filtered, washed with anhydrous ethanol, and then dried at 65 °C under vacuum for 24 h.

Yield: 93%; FTIR spectrum (KBr pellet), cm^{-1}: 3137, 1663, 1618, 1435, 1377, 1121, 1051, 876; ^1H NMR (600 MHz, DMSO-d_6), δ H, ppm: 6.47-6.89 (m, 2H), 7.16-7.31 (m, 2H), 7.38-7.61 (m, 3H), 7.79-8.36 (m, 5H); Anal. calcd. for $C_{20}H_{12}N_2O_2$, %: C, 76.92 ; H, 3.85; N, 8.97; Found, %: C, 76.87; H, 3.86; N, 8.89.



Scheme 1. Synthesis of PEAINK.

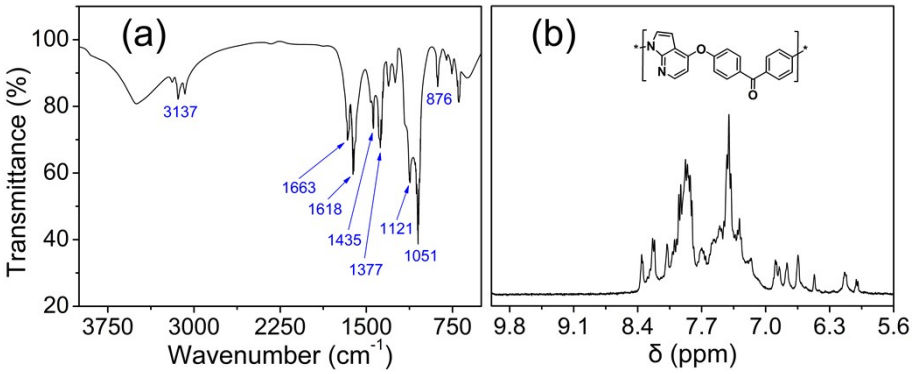


Fig. S1. FT-IR and ^{1}H NMR spectra of PEAINK.

4. Preparation of PEAINK film

0.0625 g polymer PEAINK was dissolved in 2.5 mL NMP to form a 2.5 wt % solution, the polymer solution was filtered and subsequently cast onto a clean glass sheet, and dried in a convection oven at 70 °C for 24 h and then further dried under vacuum at 70 °C for another 24 h to afford the PEAINK polymer film (about 14 μm thickness).

5. Preparation of PEAINKH^{+} film

0.0625 g polymer PEAINK was dissolved in 2.5 mL NMP to form a 2.5 wt % solution, the polymer solution was filtered, and the desired mole equivalent of the HCl ($n_{(H^{+})}$:$n_{(azaindole)}$=1:1) was added into the PEAINK polymer solution, the solution was subsequently cast onto a clean glass sheet, and dried in a convection oven at 70 °C for 24 h and then further dried under vacuum at 70 °C for another 24 h to afford the PEAINKH^{+} polymer film (about 15 μm thickness).

6. Solubility of the PEAINK and PEAINKH$^+$ films

Table S1. Solubility of PEAINK and PEAINKH$^+$ films

Sample	DMAc	DMSO	DMF	NMP	THF
PEAINK film	+ +[a]	+ +	+ +	+ +	- -[b]
PEAINKH$^+$ film	- -	- -	- -	- -	- -

[a]+ +: The polymer can be completely dissolved at room temperature; [b]- -: the polymer was insoluble at both room temperature and 50 °C.

7. The powder wide-angle X-ray diffraction of PEAINKH$^+$

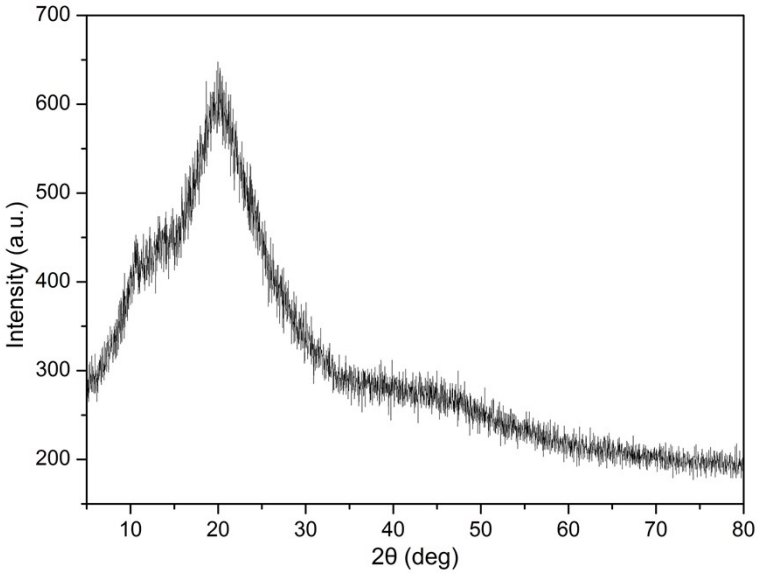


Fig. S2. The powder wide-angle X-ray diffraction of PEAINKH$^+$ polymer.