Supplementary Materials

Highly soluble fluorinated polyimides with promising gas transport performance and optical transparency

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1. Experimental

1.1 Measurements

FT-IR spectra were measured on a Thermo Nexus 470 spectrometer (Thermo Nicolet Corporation, Middletown, VA, USA) using the KBr pellet technique and polymer films. NMR spectra were recorded using an Avance AV 500 instrument (500 MHz; Bruker, Fällanden, Switzerland), DMSO-d_6 as the solvent, and tetramethylsilane as the internal standard. The intrinsic viscosities of polymers were determined for 0.5 g/dL solutions in 1-methyl-2-pyrrolidinone (NMP) using an Ubbelohde viscometer ($\varphi = 0.66$) in a water bath held at 30 °C. The thermal stability of polymers was determined by heating to 800 °C under N_2 at a rate of 10 °C/min (Q-500 TGA system, TA Instruments, USA). DSC (DSC 2920, TA Instruments, USA) was used to record the melting points (m.p.) of the diamine monomer and intermediates as well as the glass transition temperatures (T_g) of polymers at heating rates of 5 and 10 °C/min in nitrogen, respectively. In solubility tests, the polymer sample (10 mg) was placed in an organic solvent (1 mL) and observed at room temperature or upon heating. The optical properties of the polyimide films were characterized using a UV-3600 spectrophotometer (Shimadzu Corp., Japan) within a wavelength range of 200–800 nm. A densitometer (MatsuHaku GP-300s, Xiamen, China) instrument was used to measure the density of the polyimide films in water at 25 °C according to the Archimedes principle; temperature compensation was carried out during the test, and each membrane was tested five times. The crystalline phases of polymer films were probed at room temperature by wide-angle X-ray diffraction (WAXD; X'Pert PRO, PANalytical B.V., Almelo, the Netherlands) using a Cu K_α radiation source ($\lambda = 0.154$ nm) at 40 kV and 40 mA. The gas permeability coefficients (P) of polymer films were tested for pure CO_2, O_2, N_2, and He in this order using a constant-volume/variable-pressure method at 4 bar and 35 °C (VAC-V1, Labthink gas permeameter, China). Prior to being loaded with the membranes for the gas permeation test, the permeation cell was degassed via $in\ situ$ evacuation for 8 h. P was calculated from the slope of the downstream pressure vs. time plot (d$_p$(t)/dt) as

$$P = \frac{V_d l}{A T P_{up} \times 0.278} \times \frac{dp}{dt} \times 10^{10} \qquad (1)$$

where P_{up} is the upstream pressure (cm Hg), dp/dt is the steady-state pressure growth rate, V_d is the calibrated permeation volume (cm^3), l is the membrane thickness (μm), A is the effective test area of the membrane (cm^2), and T is the operating temperature (K). The ideal selectivity ($\alpha_{A/B}$) for a pair of gases is the ratio of their permeability coefficients:

$$\alpha_{A/B} = \frac{P_A}{P_B} \qquad (2)$$

The mechanical properties of the polyimide films (50 mm × 10 mm) were measured using an AG-I200 N universal testing machine at a tensile rate of 2 mm/min, and the value for each sample group was reported as the average of five replicates. All

simulations were performed using Materials Studio 7.0 (Accelrys). Hydrophobicity was measured by a contact angle analyzer (JY PHB, China) according to a high-dosage method.

1.2. Preparation of monomer

Preparation of 2,2-bis((4-N,N-dimethylthioacyl)hydroxyphenyl)hexafluoropropane (BMOA)

NaOH (2.74 g, 0.0475 mol), anhydrous methanol (25 mL), 4,4'-(Hexafluoroisopropylidene)diphenol (7.5 g, 0.0225 mol) and dimethylthiocarbamoyl chloride (6.115 g, 0.0475 mol) were mixed in a 100-mL three-neck round-bottom flask. The mixture was stirring upon cooling in the ice bath for 6 h. After reaction, the mixture was suction-filtered, and the filter cake was washed several times with ice-cold $CH_3OH:H_2O$ (1:1, v/v). The crude product was purified with $CHCl_3:CH_3OH$ (3.5:5, v/v) to obtain BMOA as a white powder. Yield: 73%; m.p. 210 °C (differential scanning calorimetry (DSC)). Fourier transform infrared (FT-IR) (KBr, cm^{-1}): 2942 (–CH_3), 1538 (C–N), 1138 (C–F), 1058 (C=S); ^{1}H NMR (δ, ppm, CDCl$_3$): 7.44 (d, 4H, $J = 8.2$ Hz), 7.11 (d, $J = 9.2$ Hz), 3.46 (s, 6H), 3.34 (s, 6H); ^{13}C NMR (δ, ppm, CDCl$_3$): 187.14, 154.48, 131.39, 130.72, 125.73, 122.89, 119.91, 115.54, 66.28, 43.53, 39.03. Elem. Anal. Calcd. for $C_{21}H_{20}F_6N_2O_2S_2$ (510.52): C, 49.41%; N, 5.49%; S, 12.56%. Found: C, 50.03%; N, 5.26 %; S, 12.38 %.

Preparation of 2,2-bis((4-N,N-dimethylthioacyl)mercaptophenyl)hexafluoropropane (BMAA)

A 100-mL three-neck round-bottom flask equipped with a mechanical stirrer, reflux condenser, and nitrogen inlet was charged with BMOA (5.00 g) and heated under nitrogen at 260 °C for 2 h. The resulting raw product was dried and recrystallized from $CH_3OH:H_2O$ (6:1, v/v) to obtain BMAA as a white powder. Yield: 75%; m.p. 151 °C (DSC). FT-IR (KBr, cm^{-1}): 2931 (–CH_3), 1671 (C–N), 1136 (C–F); ^{1}H NMR (δ, ppm, CDCl$_3$): 7.51 (d, 4H, $J = 8.3$ Hz), 7.41 (d, 4H, $J = 8.2$ Hz), 3.09 (d, 12H, $J = 20.5$); ^{13}C NMR (δ, ppm, CDCl$_3$): 166.32, 135.34, 134.05, 130.80, 130.69, 125.57, 124.00, 122.73, 64.85, 64.58, 50.88, 37.17. Elem. Anal. Calcd. for $C_{21}H_{20}F_6N_2O_2S_2$ (510.52): C, 49.41%; N, 5.49%; S, 12.56%. Found: C, 49.35%; N, 5.55%; S, 12.60%.

Preparation of 2,2-bis(4-mercaptophenyl)hexafluoropropane (BIA)

BMAA (12.5 g, 0.0245 mol), methanol (50 mL), pyridine (50 mL), deionized water (10 mL), and KOH (13.75 g, 0.245 mol) were mixed in a 250-mL three-neck flask. The reaction mixture was heated and refluxed under nitrogen for 10 h, cooled to room temperature, and dropwise supplemented with concentrated HCl (12 M, 60 mL) upon cooling in an ice-water bath. The white granular solid separated by suction filtration was dried overnight at 80 °C and recrystallized from $C_2H_5OH:H_2O$ (2:1, v/v) to obtain BIA as a white solid. Yield: 82%, m.p. 95 °C. FT-IR (KBr, cm^{-1}): 2571 (–SH), 1134 (C–F); ^{1}H NMR (δ, ppm, dimethyl sulfoxide-d$_6$ (DMSO-d_6)): 7.39 (d, 4H, $J = 8.8$ Hz), 7.16 (d, 4H, $J = 7.6$ Hz), 5.78 (s, 2H); ^{13}C NMR (δ, ppm, DMSO-d_6): 135.92, 131.35, 130.79, 129.08, 128.86, 127.29, 126.01, 123.15, 120.29, 65.05, 64.38, 63.07. Elem. Anal. Calcd. for $C_{15}H_{10}F_6S_2$ (368.36): C, 48.91%, S, 17.41%. Found: C, 49.25%, S, 17.33%.

Preparation of 2,2-bis(4-(4-nitrophenylthio)phenyl)hexafluoropropane (BNTA)

BIA (5.00 g, 0.0135 mol), 1-chloro-4-nitrobenzene (4.725 g, 0.030 mol), K_2CO_3 (4.48 g), and N,N-dimethylformamide (DMF; 50 mL) were mixed in a 100-mL three-neck flask, and heated to reflux for 12 h. Subsequently, about two-thirds of the DMF was removed by rotary evaporation, and the mixture was poured into ice-water (1000 mL).

The resulting yellow precipitate was filtered, washed several times with cold water, dried, and recrystallized from $C_2H_5OH:C_3H_8O_2$ (5:1, v/v) to obtain BNTA as yellow needle-like crystals. Yield: 72%, m.p. 146 °C (DSC). FT-IR (KBr, cm^{-1}): 1514, 1343 ($-NO_2$), 1018 ($-S-$), 1137 (C–F); ^{1}H NMR (δ, ppm, DMSO-d_6): 8.20 (d, 4H, J = 8.8 Hz), 7.64 (d, 4H, J = 8.4 Hz), 7.48 (m, 8H, J = 3.2 Hz); ^{13}C NMR (δ, ppm, DMSO-d_6): 146.53, 145.39, 134.23, 133.49, 133.12, 131.89, 129.64, 128.65, 125.83, 125.18, 122.97, 120.12, 65.00, 64.56, 64.18.

Preparation of 2,2-bis(4-(4-nitrophenylsulfonyl)phenyl)hexafluoropropane (BNSA)

BNTA (2.50 g, 4.095 mmol), 30 wt% H_2O_2 (2.5 mL), and glacial acetic acid (25 mL) were mixed in a 50-mL three-neck flask, and the mixture was refluxed for 5 h and then left to stand overnight. The precipitate was filtered, washed several times with distilled water, dried, and recrystallized from DMF:C_2H_5OH (1:4, v/v) to obtain BNSA as a pale-yellow crystal. Yield: 73%, m.p. 201 °C. FT-IR (KBr, cm^{-1}): 1533, 1336 ($-NO_2$), 1270, 1169 ($-SO_2-$), 1103, 730 (C–F); ^{1}H NMR (δ, ppm, DMSO-d_6): 8.47 (d, 4H, J = 8.0 Hz), 8.31 (d, 4H, J = 8.4 Hz), 8.18 (d, 4H, J = 8.4 Hz);7.67 (d, 4H, J = 7.6 Hz); ^{13}C NMR (δ, ppm, DMSO-d_6): 151.32, 145.99, 141.84, 138.01, 132.15, 130.14, 129.18, 125.85, 124.70, 122.83, 119.32, 114.03, 70.00, 69.33, 68.34, 67.64, 66.99.

Preparation of 2,2-bis(4-(4-aminophenylsulfonyl)phenyl)hexafluoropropane (BASA)

BNSA (3.00 g, 0.0045 mol), 10 wt% Pd/C (0.50 g), and ethanol (75 mL) were mixed in a 100-mL three-neck round-bottom flask. The mixture was heated to reflux, supplemented with $N_2H_4 \cdot H_2O$ (7 mL), further refluxed for 12 h, and filtered hot to remove Pd/C. The filtrate was concentrated, and the residue was dried and recrystallized from $C_2H_5OH:H_2O$ (3:1, v/v) to obtain BASA as a pale-yellow crystal. Yield: 81%, m.p. 240.3 °C. FT-IR (KBr, cm^{-1}): 3442, 3365 ($-NH_2$), 1280, 1178 ($-SO_2-$), 739 (C–F); ^{1}H NMR (δ, ppm, DMSO-d_6): 7.97 (d, 4H, J = 7.6 Hz), 7.59 (m, 8H, J = 26.4 Hz), 6.66 (d, 8H, J = 8.4 Hz); 6.296 (s); ^{13}C NMR (δ, ppm, DMSO-d_6): 154.75, 145.28, 136.32, 131.57, 130.51, 124.75, 127.74, 118.01, 115.14，113.84, 111.24, 108.11,69.37 , 68.74, 68.41, 67.04, 66.31.

1.3. Preparation of polyimides

Polyimides BPADA/BASA, 6FDA/BASA, ODPA/BASA were synthesized by one-step high-temperature polycondensation as shown in Scheme 2. The specific polymerization process was illustrated by taking 6FDA-BASA as follows. A 50 mL Schlenk tube equipped with a mechanical stirrer, nitrogen inlet, and an oil bubbler was charged with BASA (1.5000g, 2.44 mmol), 6FDA (1.0844 g，2.44 mmol), m-cresol (22.5 mL) and isoquinoline(catalytic; 5−6 drops) under a continuous flow of nitrogen. The mixture was heated up to 50 °C under nitrogen atmosphere and mechanically stirred to achieve homogeneity and transparency. Subsequently, the reaction was heated to 80 °C for 3 h, 120 °C for 3 h, 180 °C for 3 h, and to 200 °C for 12 h. With the progress of the reaction, the water produced by the system was continuously taken away by the nitrogen flow. The resulting viscous polymer solution was cooled to room temperature and poured into methanol (400 mL). The precipitated white fibrous or strip-shaped polymer 6FDA-BASA was filtered, washed several times with methanol, dried, redissolved in an appropriate amount of DMF, precipitated in methanol, and vacuum-dried at 150 °C for 24 h. Other polymers were

synthesized similarly.

2. Characterization Data

Preparation of 2,2-bis(4-N,N-dimethylthioacyl hydroxyphenyl)hexafluoropropane (BMOA)

Compound BMOA was obtained by the reaction of 2,2-bis-(4-hydroxyphenyl)hexafluoropropane and N,N-dimethylthioacyl chloride in an ice bath under alkaline conditions. The FT-IR spectrum of BMOA (Fig. S1) showed characteristic absorption peak of methyl group at 2942 cm^{-1}. The characteristic absorption peak of C-F appears at 1138 cm^{-1}, and C=S at 1058 cm^{-1}. The structure of BMOA was also confirmed by NMR spectra. As shown in Fig. S7 (a), in the ^{1}H-NMR spectroscopy, the hydrogen atom (H^1) on methyl presents two single peaks, with chemical shifts of 3.34 ppm and 3.46 ppm, respectively. Because H^2 and H^3 are adjacent, they split into two peaks, and the chemical shifts appear at 7.11 ppm and 7.44 ppm, respectively. The ^{13}C-NMR spectrum (Fig. S7 (b)) exhibited 8 peaks for aromatic carbons of BMOA, and assignments of each carbon are given in the Fig. S7 (b), and the spectrum agrees well with the proposed molecular structure. The melting point of compound BMOA is shown in Fig. S13. It can be seen from Fig. S13 that there is only one melting peak at 210 °C, indicating that the compound has relatively high purity.

FT-IR (KBr, cm^{-1}): 2942 (-CH$_3$), 1538 cm^{-1} (C-N), 1138 cm^{-1} (C-F), 1058 cm^{-1} (C=S); ^{1}H NMR (δ, ppm, CDCl$_3$): 7.44 (d, 4H, J = 8.2 Hz), 7.11 (d, J = 9.2 Hz), 3.46 (s, 6H), 3.34 (s, 6H); ^{13}C NMR (δ, ppm, CDCl$_3$): 187.14, 154.48, 131.39, 130.72, 125.73, 122.89, 119.91, 115.54, 66.28, 43.53, 39.03; Elem. Anal. Calcd. for C$_{21}$H$_{20}$F$_6$N$_2$O$_2$S$_2$ (510.52): C, 49.41%; N, 5.49%; S, 12.56%. Found: C, 50.03%; N, 5.26 %; S, 12.38 %. m.p. 210 °C (by DSC at a scan rate of 5 K/min)

Preparation of 2,2-bis(4-N,N-dimethylthioacyl mercaptophenyl)hexafluoropropane (BMAA)

The structure of compound BMAA was tested by infrared spectrometer, and the results are shown in Fig. S2. The peak at 2931 cm^{-1} belongs to the characteristic absorption peak of -CH$_3$. The C=O stretching vibration peak appears at 1760 cm^{-1}, the characteristic absorption peak of C-N appears at 1671 cm^{-1}, and C-F appears at 1136 cm^{-1}. The ^{1}H-NMR and ^{13}C-NMR spectra of BMAA are shown in Fig. S8 (a) and (b), the values of H^3 at 7.51 ppm corresponded to the methyl group, and the values at 7.41 ppm and 3.08 ppm were corresponded to the protons of H^2 and H^1 in the similar chemical. The chemical shifts of carbon atom C^a on methyl group are 43.53 ppm and 36.73 ppm, while those at 166.07 ppm are C^b on C=O, and the carbon atoms at 134.19 and 134.96 ppm belong to C^c and C^d on benzene ring. The chemical shifts of C^e and C^g coincided at 130.82 ppm. C^h and C^f split into quadruple peaks due to the coupling effect of C-F bond. The results of FT-IR and NMR show that compound BMAA is consistent with the molecular design. The melting point of compound BMAA is shown in Fig. S14, it can be seen that there is a melting peak at 151 °C.

FT-IR (KBr, cm^{-1}): 2931 cm^{-1} (-CH$_3$), 1671 cm^{-1} (C-N), 1136 cm^{-1} (C-F); ^{1}H NMR (δ, ppm, CDCl$_3$): 7.51 (d, 4H, J = 8.3 Hz), 7.41 (d, 4H, J = 8.2 Hz), 3.09 (d, 12H, J = 20.5); ^{13}C NMR (δ, ppm, CDCl$_3$): 166.32, 135.34, 134.05, 130.80, 130.69, 125.57, 124.00, 122.73, 64.85, 64.58, 50.88, 37.17; Elem. Anal. Calcd. for C$_{21}$H$_{20}$F$_6$N$_2$O$_2$S$_2$

(510.52): C, 49.41%; N, 5.49%; S, 12.56%. Found: C, 49.35%; N, 5.55%; S, 12.60%. m.p. 151 °C (by DSC at a scan rate of 5 K/min).

Preparation of 2,2-bis(4-mercaptophenyl)hexafluoropropane (BIA)

The infrared spectrum of compound BIA is shown in Fig. S3. The stretching vibration absorption peak of -SH appears at 2571 cm^{-1}, while the stretching vibration absorption peak of C-F appears at 1173 cm^{-1} and 1134 cm^{-1}. The structure of compound BIA was further characterized by NMR, and the ^{1}H-NMR spectrum is shown in Fig. S9 (a). The values of H^1 at 5.78 ppm corresponded to the hydrogen atom on -SH. The adjacent H^2 and H^3 on the benzene ring split into two peaks, in which H^3 at 7.39 ppm is greater than H^2 at 7.16 ppm due to the electron absorption and deshielding effect of trifluoromethyl. In Fig. S9 (b), the splitting peaks of C^e and C^f are related to the coupling effect of C-F, and the coupling effect decreases with the increase of the distance of C-F bond. The 4 different carbons in the structure, which corresponded to 135.92, 130.79, 129.08 and 128.26 ppm is attributed to C^a, C^b, C^c and C^d on the benzene ring, respectively. The structure of compound BIA was consistent with the molecular design. Fig. S15 shows the melting point spectrum of compound BIA. It can be seen from the Fig. S15 that there is a sharp melting peak at 95 °C and the melting range is narrow, indicating that the purity of the intermediate compound BIA is very high.

FT-IR (KBr, cm^{-1}): 2571 (-SH), 1134 (C-F); ^{1}H NMR (δ, ppm, DMSO): 7.39 (d, 4H, $J = 8.8$ Hz), 7.16 (d, 4H, $J = 7.6$Hz), 5.78 (s, 2H); ^{13}C NMR (δ, ppm, DMSO): 135.92, 131.35, 130.79, 129.08, 128.86, 127.29, 126.01, 123.15, 120.29, 65.05, 64.38, 63.07; Elem. Anal. Calcd. for $C_{15}H_{10}F_6S_2$ (368.36): C, 48.91%, S, 17.41%，Found: C, 49.25%, S, 17.33%. m.p. 95 °C (by DSC at a scan rate of 5 K/min).

Preparation of 2,2-bis(4-(4-nitrophenylthio)phenyl)hexafluoropropane (BNTA)

Fig. S4 is the infrared spectrum of intermediate BNTA. It can be seen from Fig. S4 that 1514 cm^{-1} and 1343 cm^{-1} correspond to the asymmetric and symmetric stretching vibration peaks of -NO_2, 1177 cm^{-1} and 1137 cm^{-1} correspond to the characteristic absorption peak of C-F, and the characteristic absorption peak at 1018 cm^{-1} also confirms the existence of -S- bond. Fig. 10 (a) and Fig. 10 (b) are ^{1}H-NMR and ^{13}C-NMR spectra of intermediate BNTA, respectively. The hydrogen atoms in the molecular structure of intermediate BNTA are on the aromatic ring, and the corresponding chemical shift range in ^{1}H-NMR spectrum is δ=7.48-8.20 ppm, which is consistent with the expected structure. The signal peaks in the ^{13}C-NMR spectrum are also consistent with the designed structure. The splitting of C^i and C^j into multiple peaks is due to the coupling effect of fluorine atoms, and the coupling constant decreases with the increase of the distance from C-F bond. Fig. 16 shows the melting point of compound BNTA with a sharp melting peak at 146 °C.

FT-IR (KBr, cm^{-1}): 1514, 1343 cm^{-1} (-NO_2), 1018 cm^{-1} (-S-), 1137 cm^{-1} (C-F); ^{1}H NMR (δ, ppm, DMSO): 8.20 (d, 4H, $J = 8.8$ Hz), 7.64 (d, 4H, $J = 8.4$ Hz), 7.48 (m, 8H, $J = 3.2$ Hz); ^{13}C NMR (δ, ppm, DMSO): 146.53, 145.39, 134.23, 133.49, 133.12, 131.89, 129.64, 128.65, 125.83, 125.18, 122.97, 120.12, 65.00, 64.56, 64.18. m.p. 146 °C (by DSC at a scan rate of 5 K/min).

Preparation of 2,2-bis(4-(4-nitrophenylsulfonyl)phenyl)hexafluoropropane (BNSA)

It can be seen from the Fig. S5 that there are the characteristic absorption peaks of -NO$_2$ at 1533 cm^{-1} and 1336 cm^{-1}, characteristic absorption peaks of -SO$_2$- at 1270 cm^{-1} and 1169 cm^{-1}, and C-F bond at 1103 cm^{-1}. In addition, the signal peaks in the ^{1}H-NMR spectrum (Fig. S11 (a)) and ^{13}C-NMR spectrum (Fig. S11 (b)) of intermediate BNSA are also consistent with the designed structure. In the ^{13}C-NMR spectrum, C^i and C^j split into multiple peaks is also due to the coupling effect of C-F bond. The melting point of compound BNSA is showed in Fig. S17. It can be seen from the Fig. S17 that a sharp melting peak appears at 201 °C, indicating that the obtained compound is relatively pure.

FT-IR (KBr, cm^{-1}): 1533, 1336 cm^{-1} (-NO$_2$), 1270, 1169 cm^{-1} (-SO$_2$-), 1103, 730 cm^{-1} (C-F); ^{1}H NMR (δ, ppm, DMSO): 8.47 (d, 4H, J = 8.0 Hz), 8.31 (d, 4H, J = 8.4 Hz), 8.18 (d, 4H, J = 8.4 Hz);7.67 (d, 4H, J= 7.6Hz); ^{13}C NMR (δ, ppm, DMSO): 151.32, 145.99, 141.84, 138.01, 132.15, 130.14, 129.18, 125.85, 124.70, 122.83, 119.32, 114.03, 70.00, 69.33, 68.34, 67.64, 66.99. m.p. 201 °C (by DSC at a scan rate of 5 K/min).

Preparation of 2,2-bis(4-(4-aminophenylsulfonyl)phenyl)hexafluoropropane (BASA)
As showed in Fig. S6, compared with the infrared spectrum of the intermediate BNSA, it can be found that the characteristic absorption peak corresponding to -NO$_2$ in the spectrum disappears, and the stretching vibration peak corresponding to N-H bond appears at 3442 cm^{-1} and 3365 cm^{-1}, confirming the formation of -NH$_2$ group. In addition, the characteristic absorption peak corresponding to -SO$_2$- at 1280 cm^{-1} and 1178 cm^{-1} and the characteristic absorption peak corresponding to C-F bond at 1112 cm^{-1} still exist. As shown in Fig. S12, the ^{1}H NMR spectrum of BASA (Fig. S12 (a)) is showed the characteristic aromatic peaks at 6.30 ppm and the proton signal peaks on other aromatic rings of BASA appeared at 6.66 ~ 7.97 ppm. Furthermore, the ^{13}C spectrum resonances is also corresponded to the target molecular structure. The specific assignment of carbon atoms is shown in the Fig. S12 (b). The splitting of C^i and C^j into multiple peaks is due to the coupling effect of fluorine. Obviously, the FT-IR and NMR results showed that the new diamine monomer containing hexafluoroisopropyl and sulfonyl groups were successfully prepared. The melting point of the diamine monomer BASA was determined by DSC, and the result is 240.3 °C. As shown in Fig. S18, there is only one sharp melting peak on the melting curve, indicating that the purity of the monomer is high enough.

FT-IR (KBr, cm^{-1}): 3442, 3365 cm^{-1} (-NH$_2$), 1280, 1178 cm^{-1} (-SO$_2$-), 739 cm^{-1} (C-F); ^{1}H NMR (δ, ppm, DMSO): 7.97 (d, 4H, J = 7.6 Hz), 7.59 (m, 8H, J = 26.4 Hz), 6.66 (d, 8H, J = 8.4 Hz); 6.296 (s); ^{13}C NMR (δ, ppm, DMSO): 154.75, 145.28, 136.32, 131.57, 130.51, 124.75, 127.74, 118.01, 115.14，113.84, 111.24, 108.11,69.37 , 68.74, 68.41, 67.04, 66.31. m.p. 240.3 °C (by DSC at a scan rate of 5 K/min).

Polyimides (PIs)
BPADA-BASA
^{1}H NMR (500 MHz, DMSO) δ 8.49–8.07 (m, 8H), 8.07–7.88 (m, 2H), 7.74 (t, J = 13.4 Hz, 4H), 7.71–7.54 (m, 4H), 7.53–7.24 (m, 8H), 7.27–6.83 (m, 4H), 6.81–6.37 (m, 1H), 1.66 (d, J = 41.6 Hz, 6H).

6FDA-BASA
^{1}H NMR (500 MHz, DMSO) δ 8.30–8.17 (m, 2H), 8.16–8.08 (m, 1H), 8.09–7.82 (m, 2H), 7.77 (d, J = 7.7 Hz, 2H), 7.70–7.43 (m, 2H), 6.70–6.41 (m, 1H).

ODPA-BASA

^{1}H NMR (500 MHz, DMSO) δ 8.27–8.17 (d, *J* = 8.2 Hz, 2H), 8.16–8.12 (d, *J* = 8.4 Hz, 2H), 8.12–8.01 (m, 1H), 7.90–7.73 (m, 2H), 7.71–7.50 (m, 3H), 6.70–6.46 (m, 1H).

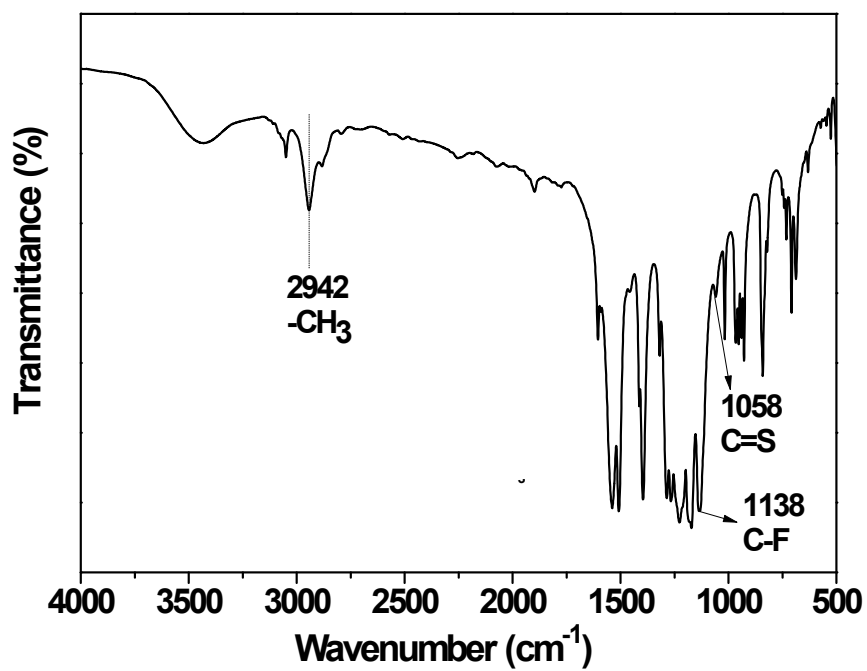## 3. The FT-IR Spectra of compounds
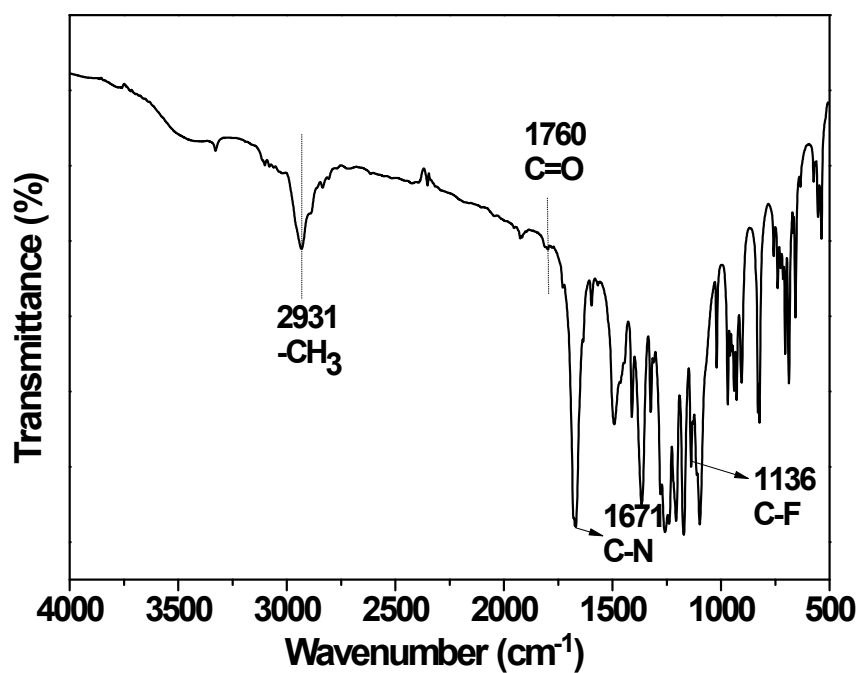

Fig. S1 FT-IR spectrum of compound BMOA

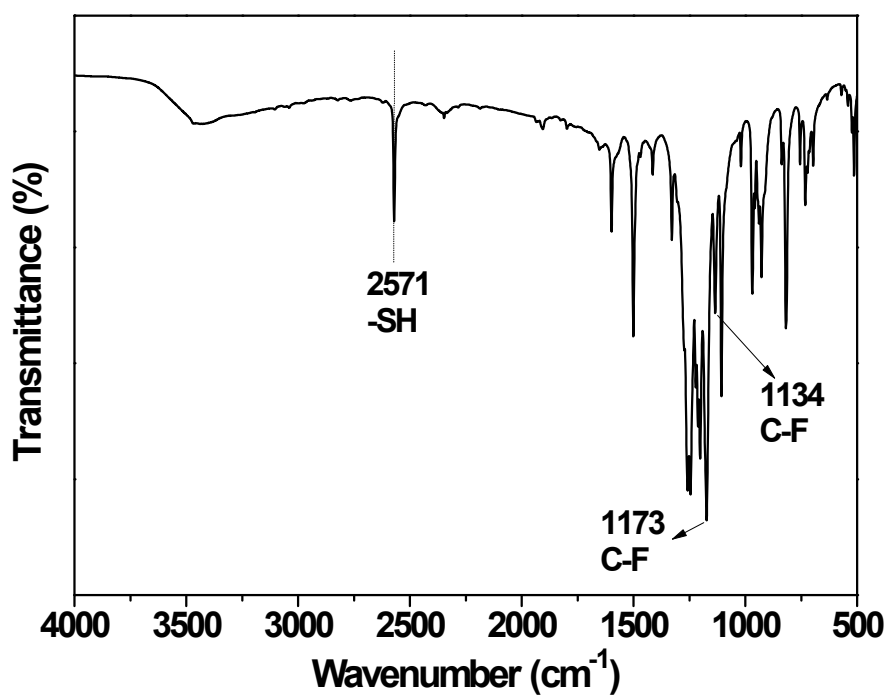**Fig. S2** FT-IR spectrum of compound BMAA

Fig. S3 FT-IR spectrum of compound BIA
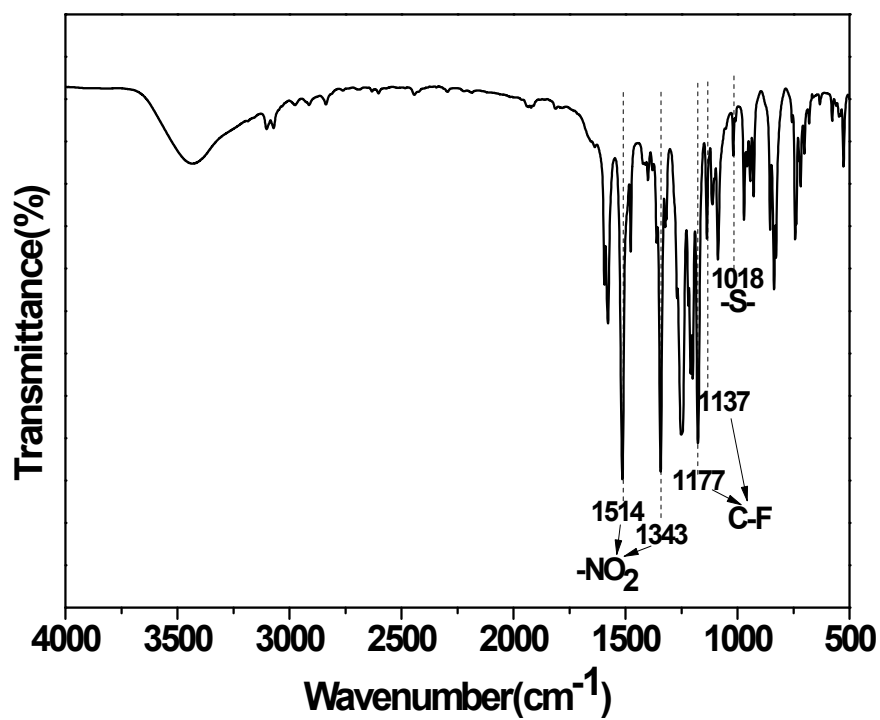
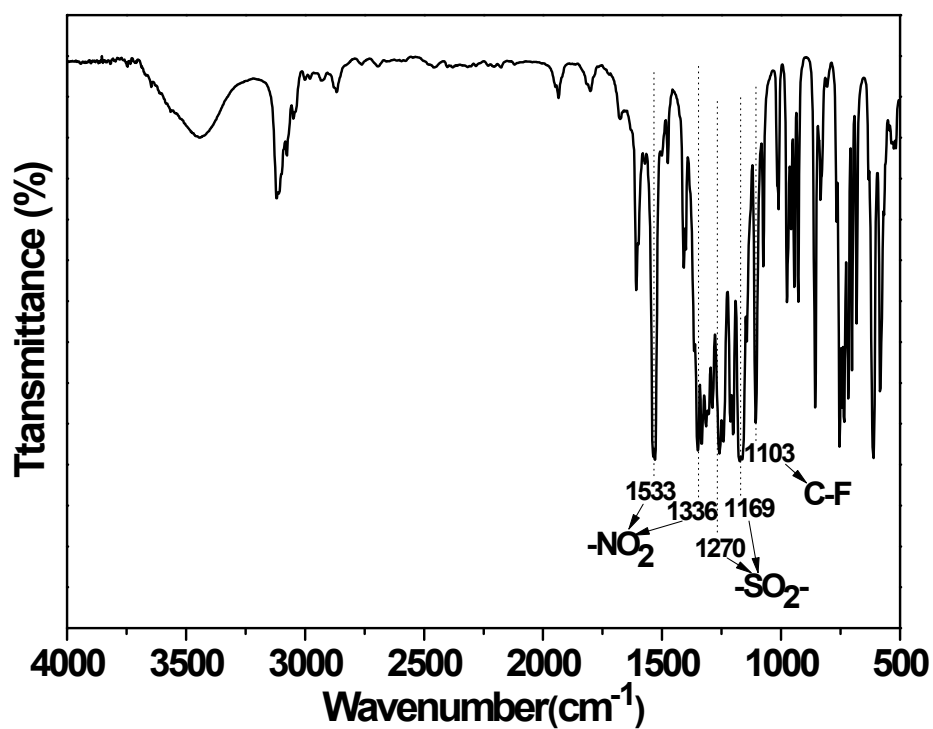**Fig. S4** FT-IR spectrum of compound BNTA

Fig. S5 FT-IR spectrum of compound BNSA
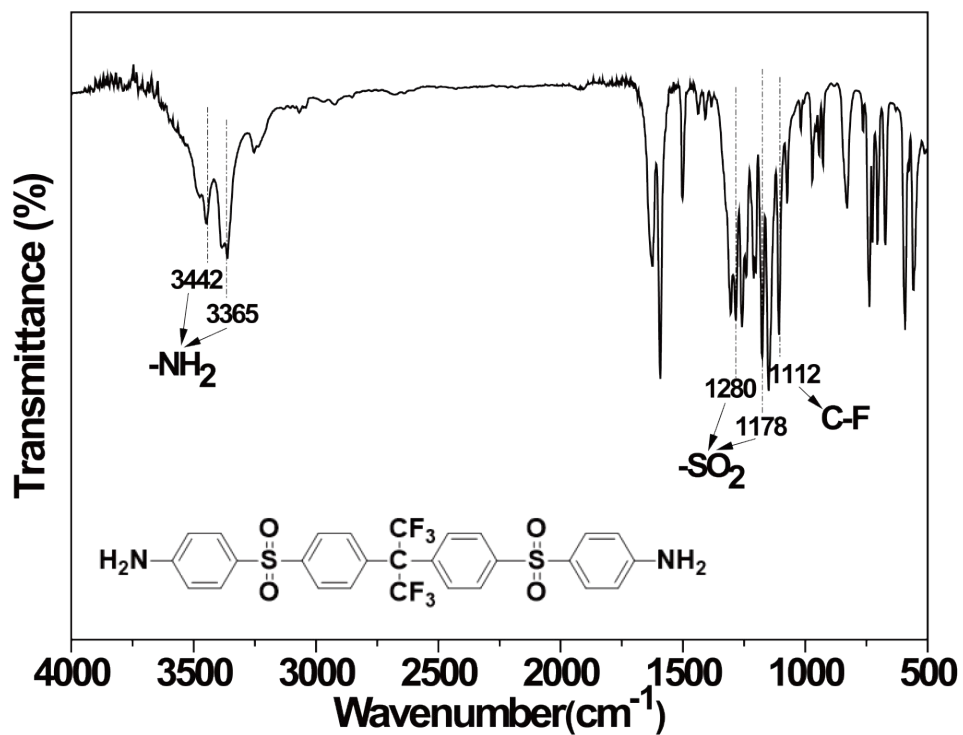
Fig. S6 FT-IR spectra of compound BASA

4. NMR Spectra of compounds
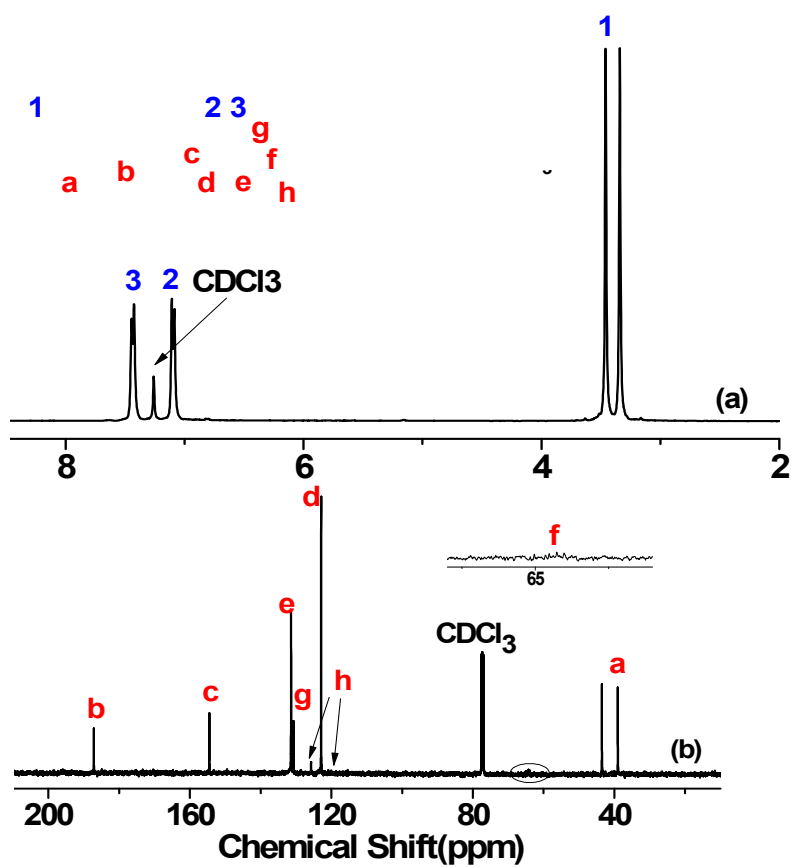
Fig. S7 ^{1}H NMR and ^{13}C NMR spectra of compound BOMA
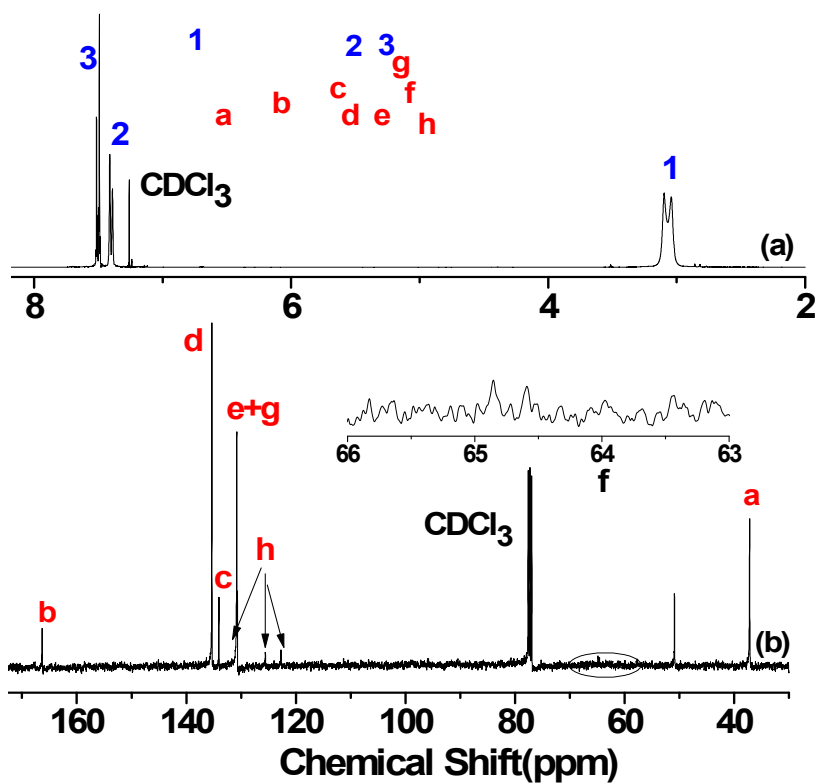
Fig. S8 ^{1}H NMR and ^{13}C NMR spectra of compound BMAA
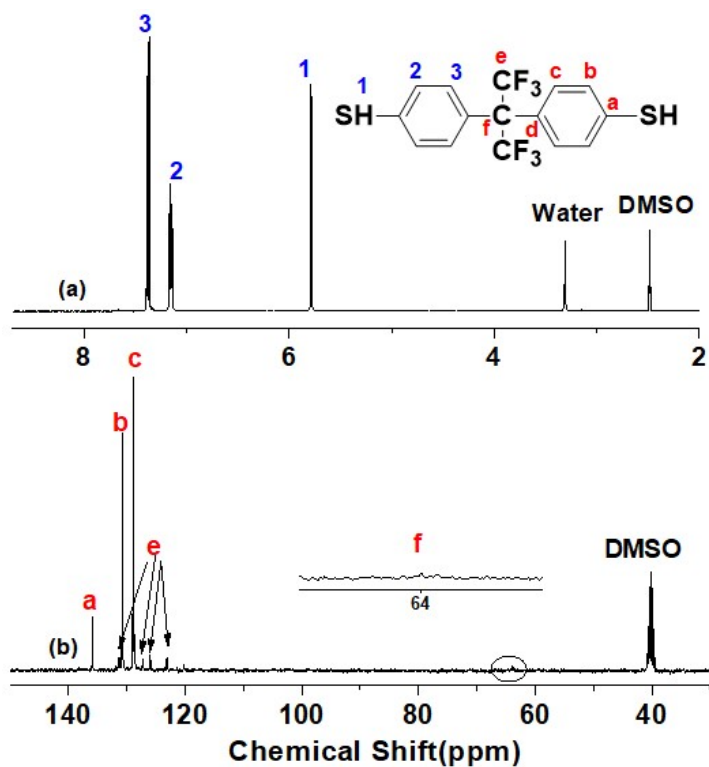
Fig. S9 ^{1}H NMR and ^{13}C NMR spectra of compound BIA

12
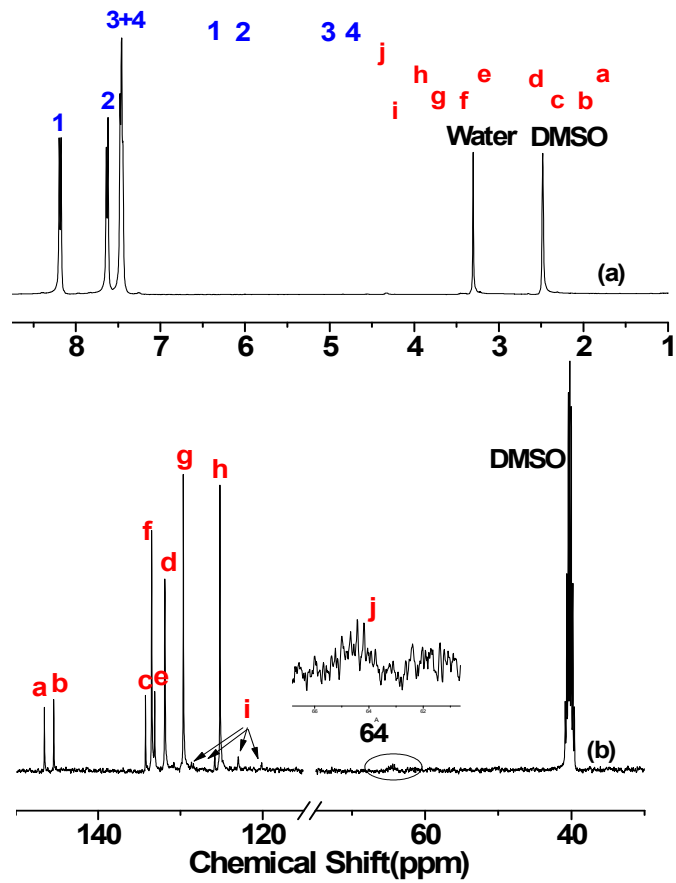
Fig. S10 ^{1}H NMR and ^{13}C NMR spectra of compound BNTA
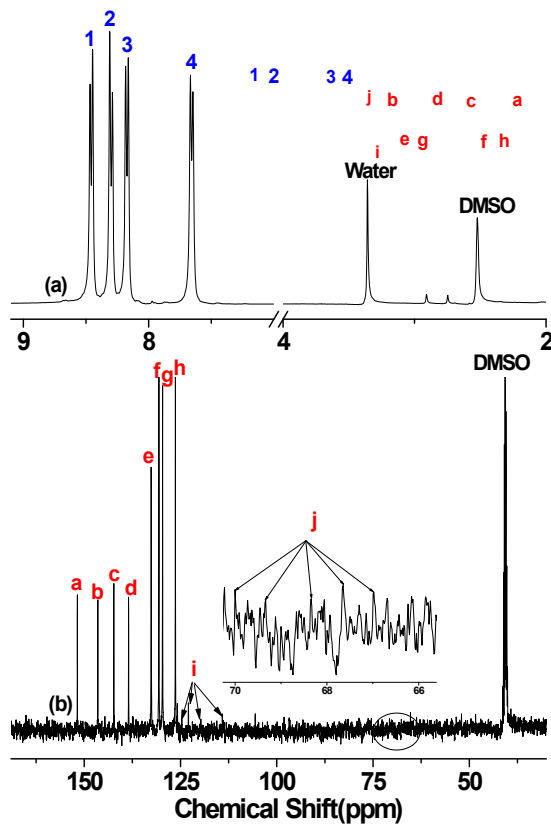
Fig. S11 ^{1}H NMR and ^{13}C NMR spectra of compound BNSA
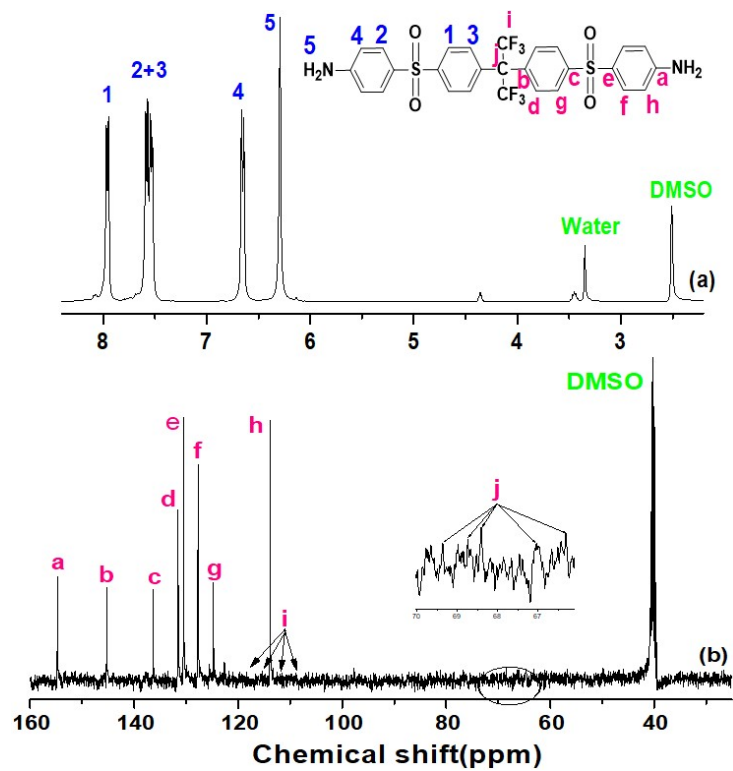
Fig. S12 ^{1}H NMR and ^{13}C NMR spectra of compound BASA

5. The DSC curve of compounds
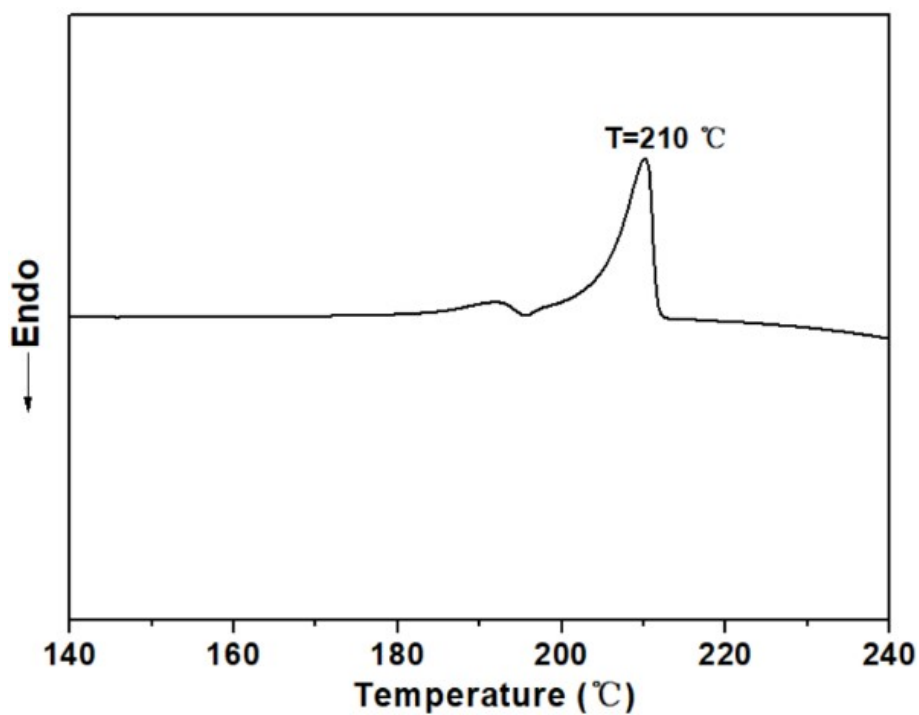
Fig. S13 DSC curve of compound BMOA
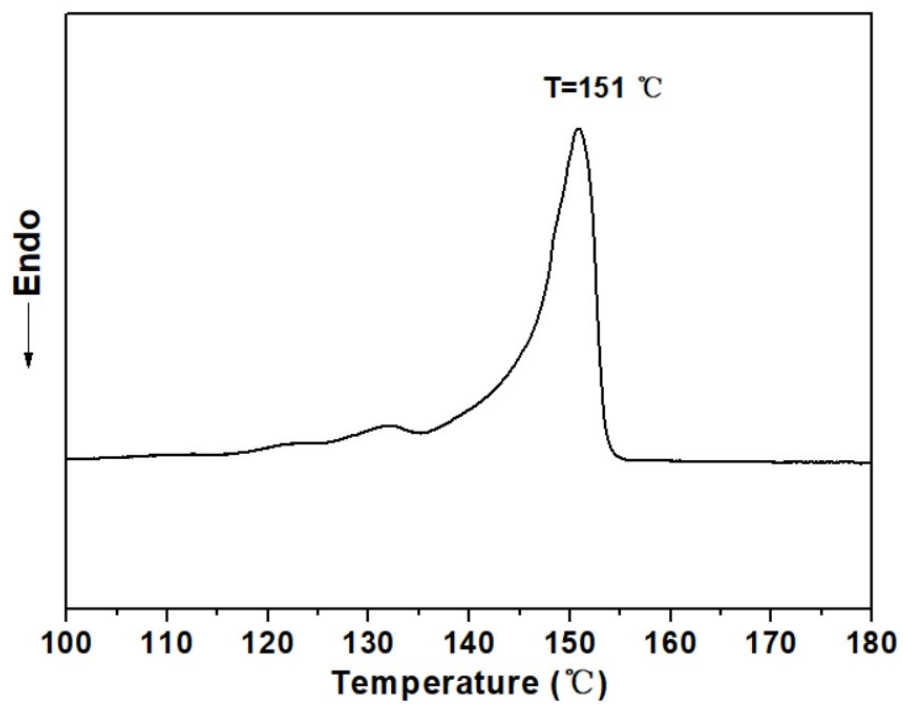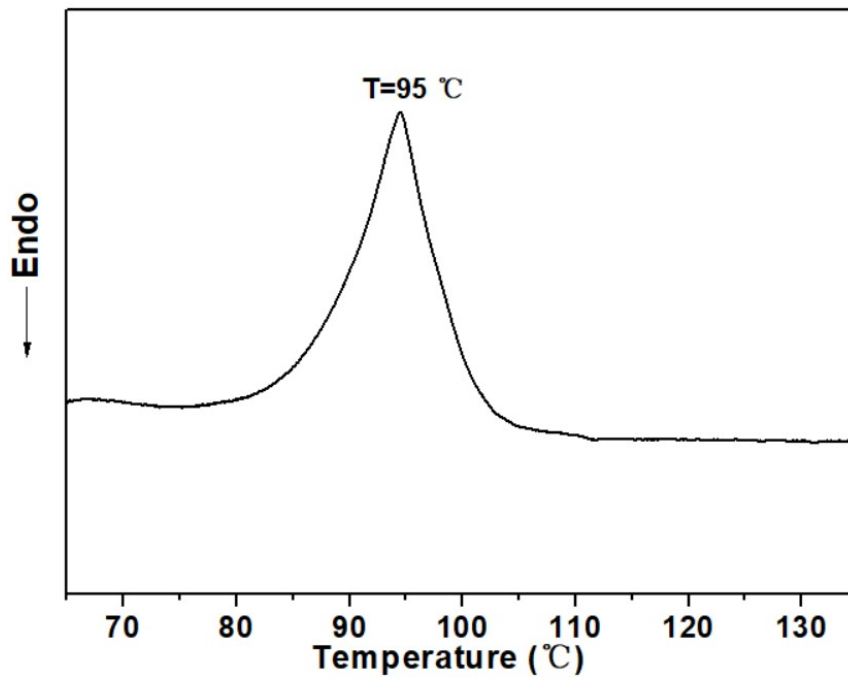
Fig. S14 DSC curve of compound BMAA

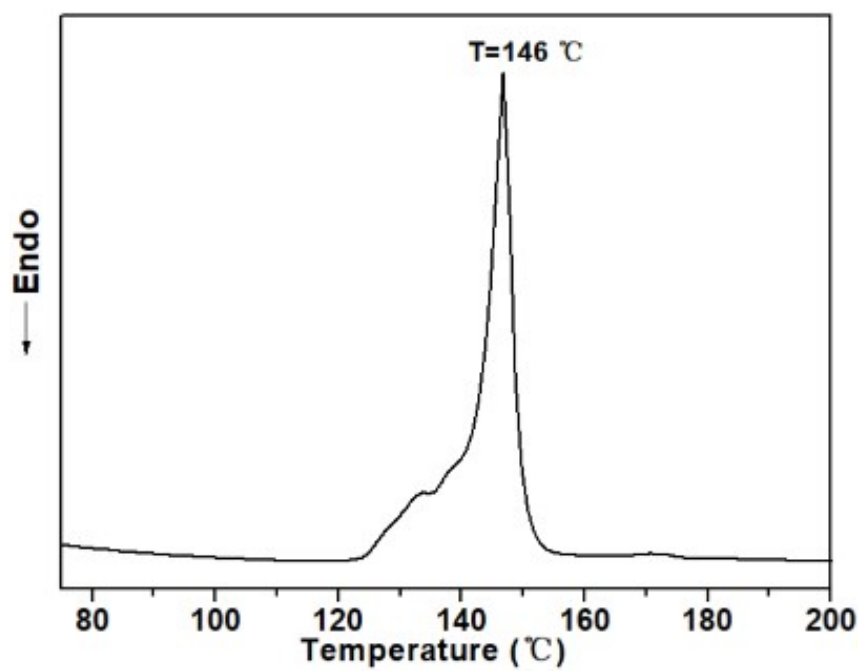**Fig. S15** DSC curve of compound BIA
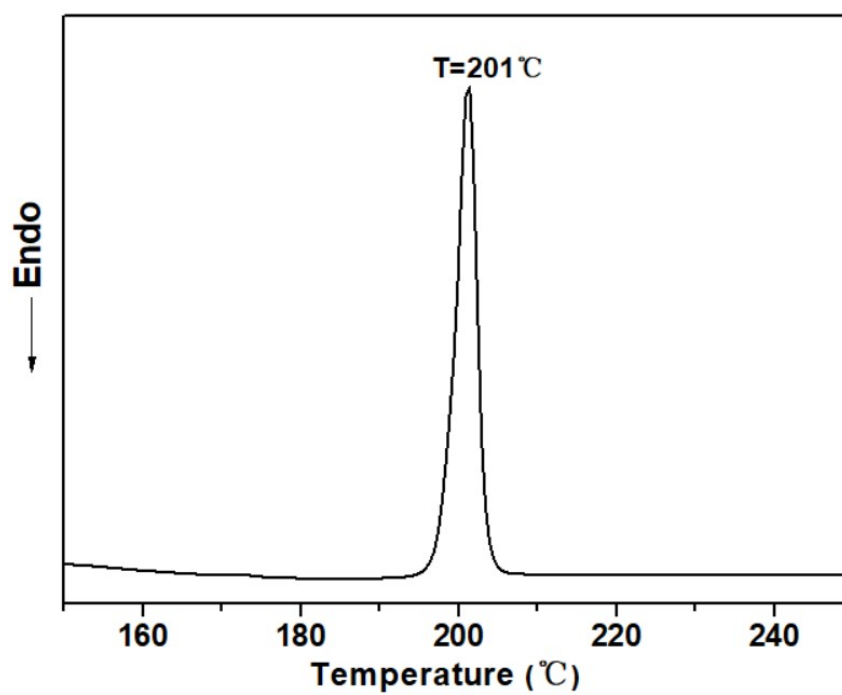
Fig. S16 DSC curve of compound BNTA

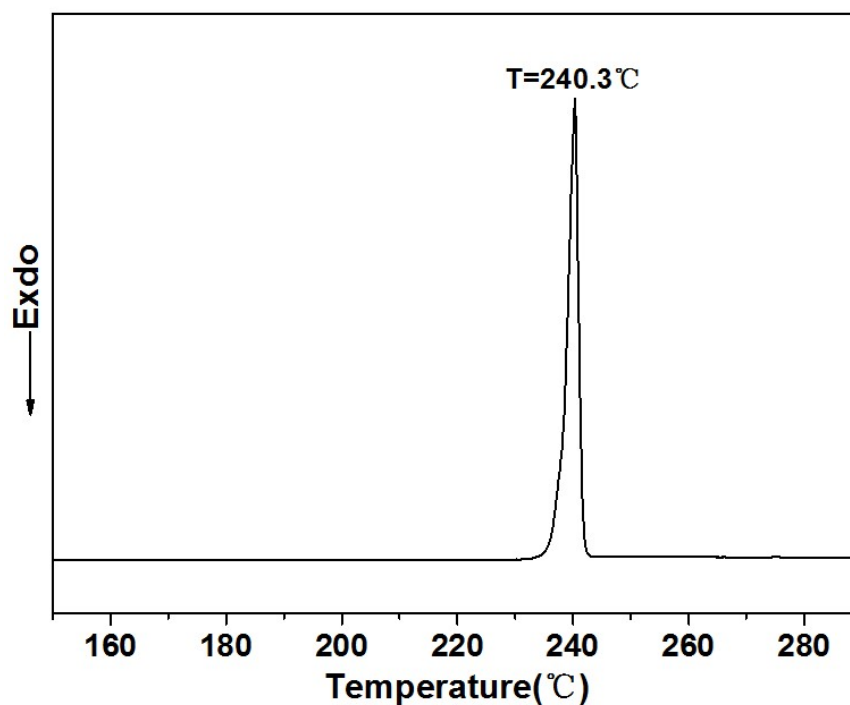**Fig. S17** DSC curve of compound BNSA

Fig. S18 DSC curve of compound BASA

6. Membrane thickness information

The membrane thickness is measured by taking five points, one in the middle of membrane, the other four around middle, and finally take the average value of five points.

Table S1 The average of membrane thickness

Polymers	Membrane thickness (μm)					Average(μm)
BPADA-BASA	66	66	68	67	67	66.8
6FDA-BASA	63	61	62	60	60	61.2
ODPA-BASA	57	59	58	57	56	57.4