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ORIGINAL PAPER

Poly(ether ketone azomethane)s and poly(ether ketone imide)s containing naphthylene moieties

Ming Zhu · Xiao Liu · Baijun Liu · Zhenhuan Jiang · Toshihiko Matsumoto

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Abstract A new diamine monomer, 1,5-bis[4-(4-aminophenoxy)]benzoyl-2,6-dimethoxynaphthalene, was synthesized via a Friedel–Crafts acylation reaction followed by an aromatic nucleophilic substitution reaction. Six ether–ketone linked polymers, named as poly(ether ketone azomethane)s and poly(ether ketone imide)s, were successfully prepared through the polycondensations of the diamine monomer with dialdehydes and dianhydrides, respectively. These naphthylated polymers exhibited high T_g values (142–288 °C), due to their bulky and rigid chemical structure. Meanwhile, they showed good thermal stability and improved solubility. Typically, some of them were casted into thin flexible film and showed high moduli.

Keywords High-performance polymer · Polyetherketone · Polyimide · Polyazomethine · Solubility

Introduction

Aromatic polymers, such as polyetherketones (PEKs), polyimides (PIs), and polyazomethines (PAMs), are widely applied in aerospace, automobile, electronics, and other high technology fields due to their excellent thermal, mechanical, and some special properties [1–3]. Most of PEKs, PIs, and PAMs have rigid molecular chains, resulting in poor solubility in common organic solvents, and this inevitably affects their synthesis, processing, and application. One of the research topics in the aromatic polymer filed is the rational design of the chemical structure to improve

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M. Zhu · X. Liu · B. Liu (✉) · Z. Jiang
Alan G. MacDiarmid Institute, Jilin University, Changchun 130012, People's Republic of China
e-mail: liubj@jlu.edu.cn

T. Matsumoto
Center for Nano Science and Technology, Tokyo Polytechnic University, Atsugi,
Kanagawa 243-0297, Japan

the solubility and processability. Liu reported a series of aromatic PEKs bearing fluorophenyl pendants. Because of their good solubility, these aromatic polymers could be processed through both thermal press and solution casting [4]. Matsumoto et al. [5] designed and synthesized two novel diamines having a bulky tetraphenylethylene structure, and accordingly, PAMs with good solubility were obtained based on above monomers. Imai and coworkers [6] reported several aromatic PAMs with diphenylfluorene moiety and these polymers with bulky moieties also had good solubility and thermal properties.

It is widely accepted that the introduction of bulky groups into the polymer side chain or main chain, not only can improve the solubility, but also can enhance the polymer's glass transition temperature (T_g). The T_g is one of the most important indicators to evaluate the using temperature of amorphous polymers. The heat-resistant polymers containing naphthalene are preferred because of their good solubility and high T_g values. However, some of reported naphthylated aromatic polymers showed low molecular weight and poor mechanical properties. Harsh synthesis conditions were needed to get the high-molecular weight products [7, 8]. Preparing good soluble polymers without loss of thermal and mechanical properties is attractive in the high-performance polymer field [9, 10].

It will be of interest to introduce the C=N bonds and imide rings into the polyetherketones, which may increase the rigidity of the molecular chains and enhance the T_g values. Usually, the PEKs were prepared via high-temperature aromatic nucleophilic substituents or electrophilic route [11]. In this study, we synthesized some novel naphthylated ether–ketone linked polymers, poly(ether ketone azomethane)s and poly(ether ketone imide)s, through the polycondensations of an diamine monomer with dialdehydes and dianhydrides, respectively. Their chemical structure and properties have been well studied.

Experimental

Materials

2,6-Dimethoxynaphthalene (Phentex Corporation, Beijing), 4-fluorobenzoyl chloride (Jiangsu Haixiang Chemical Industry Co, Ltd), 4-aminophenol (Sinopharm Chemical Reagent Co, Ltd), hexamethylphosphoramide (HPMA, Sinopharm Chemical Reagent Co, Ltd), terephthalaldehyde (Sinopharm Chemical Reagent Co, Ltd), Glutaraldehyde 25 wt% solution in water (Sinopharm Chemical Reagent Co, Ltd), 2-hydroxybenzaldehyde (Sinopharm Chemical Reagent Co, Ltd), and anhydrous lithium chloride (Tianjin North Union Fine Chemicals Development Co, Ltd) were used without further purification. 5,5′-Methylenebis(salicylaldehyde) was prepared from 1,3,5-trioxane and 2-hydroxybenzaldehyde according to a reported procedure and recrystallized twice from acetone before use [12]. Promellitic dianhydride (PMDA, Aladdin Reagent), 4,4′-oxydiphthalic anhydride (ODPA, Tokyo Kasei Kogyo Co, Ltd), and 4,4′-hexafluoroisopropylidenediphthalic anhydride (6FDA, Alfa Aesar) were purified by recrystallization from acetic anhydride.

All other chemicals used for the synthesis of monomers and polymers were obtained from commercial sources and used without further purification.

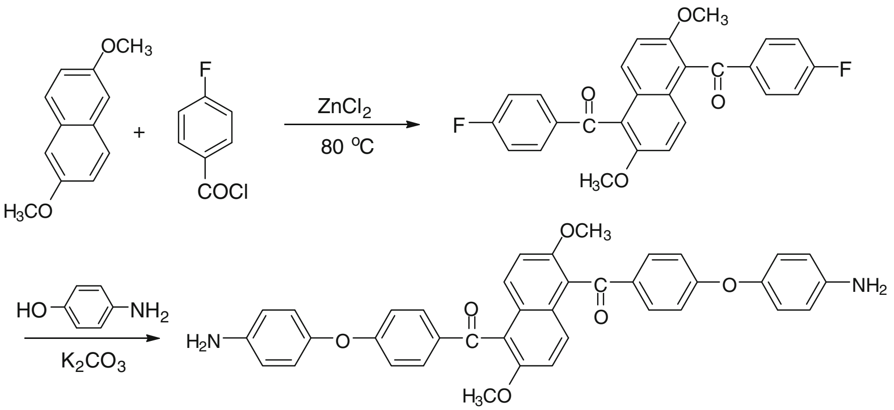
Instruments

FTIR was recorded on a Nicoler Impact 410 Fourier transform infrared spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded using a Bruker 510 NMR spectrometer with tetramethylsilane as the internal reference. The elemental analysis was carried out with a VarioMICRO. MALDI-TOF Mass spectra were obtained on a Kratos (Shimadzu company), equipped with a nitrogen laser ($\lambda = 337$ nm). Differential scanning calorimetry (DSC) measurements were performed on a METTLER TOLEDO DSC 821e instrument at the heating rate of 10 °C/min under nitrogen. Thermal gravimetric analyses (TGAs) were performed using a PERKIN ELMER TGA-7 thermal analyzer system at the heating rate of 10 °C/min under nitrogen. Inherent viscosities were measured by an Ubbelohde viscometer in DMAc at a concentration of 0.1 g/dL at 25 °C.

Synthesis of the diamine monomer (Scheme 1)

The diamine monomer, 1,5-bis[4-(4-aminophenoxy)]benzoyl-2,6-dimethoxynaphthalene, was synthesized in two step as follows: Into a 1 L three-necked flask equipped with a nitrogen inlet were placed 500 mL of 1,2-dichloroethane, 5.10 g of anhydrous zinc chloride, 47.00 g of 2,6-dimethoxy-naphthalene, and 118.90 g of 4-fluorobenzoyl chloride. After stirring at room temperature for 1 h, the temperature was gradually elevated to 80 °C. The reaction mixture was poured into dilute hydrochloric acid after 12 h. The obtained yellow solid, 1,5-bis(4-fluoro)benzoyl-2,6-dimethoxynaphthalene, was washed several times by acetone. The yield is about 75%.

M.p.: 260 °C (DSC). *m/z*: 432. ELEM. ANAL. Calcd. for $C_{26}H_{18}F_{2}O_{4}$ (432.12 g/mol): C, 72.22%; H, 4.20%. Found: C, 72.13%; H, 4.24%.



Scheme 1 Synthetic route of the diamine monomer containing ether and ketone linkages

IR (KBr, cm^{-1}): 1661(–C=O). ^1H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.91 ~ 7.86 (m, H), 7.64–7.61 (d, 2H), 7.28–7.25 (d, 2H), 7.14–7.09 (m, 4H), 3.78 (s, 6H). ^{13}C NMR (500 MHz, $CDCl_3$, δ, ppm): 195.85, 167.19, 165.16, 152.76, 134.32, 132.36, 127.30, 127.00, 122.19, 115.86, 114.97, 56.64.

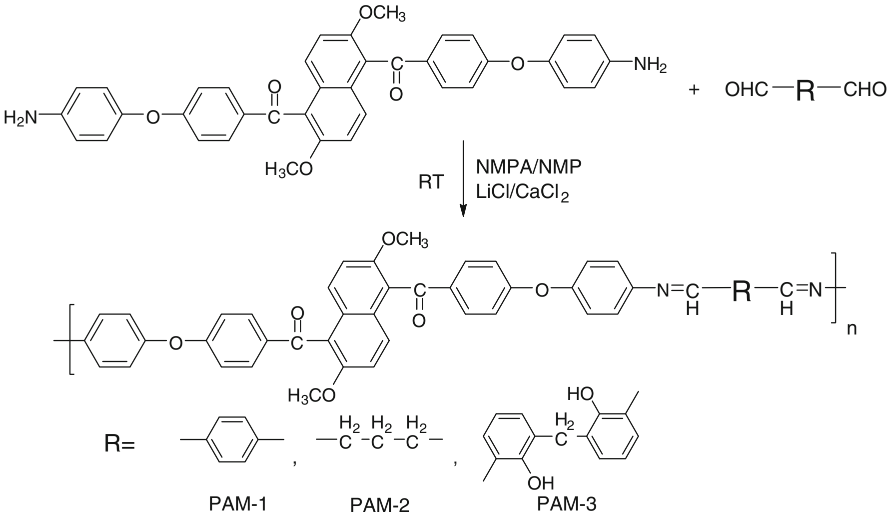
Into a 100 mL three-necked flask equipped with a reflux condenser, a Dean-Stark and a nitrogen inlet were placed 4.32 g of 1,5-bis(4-fluoro)benzoyl-2,6-dimethoxynaphthalene, 2.4 g of 4-aminophenol, 1.6 g of anhydrous potassium carbonate, 30 mL of DMF, and 20 mL toluene. The mixture was kept at 130 °C for 2.5 h, and then toluene was removed. After stirring at 150 °C for 5 h, the reaction mixture poured into ice water. The precipitated solid, 1,5-bis[4-(4-aminophenoxy)]benzoyl-2,6-dimethoxynaphthalene, was dried and purified by column chromatography using a mixture of methylene chloride and tetrahydrofuran (1:1 vol/vol) as an eluent. The yield is about 50%.

M.p.: 286 °C (DSC). *m/z*: 610. ELEM. ANAL. Calcd. for $C_{38}H_{30}N_2O_6$ (610.21 g/mol): C, 74.74%; H, 4.95%; N, 4.59%. Found: C, 73.90%; H, 5.08%; N, 4.74%.

IR (KBr, cm^{-1}): 3461, 3364 ($-NH_2$), 1658 (–C=O). ^1H NMR (500 MHz, DMSO, δ, ppm): 7.72–7.69 (d, 4H), 7.49–7.47 (m, 4H), 6.93–6.90 (d, 4H), 6.84–6.81 (m, 4H), 6.62–6.59 (m, 4H), 5.08 (s, 4H), 3.74 (s, 6H). ^{13}C NMR (500 MHz, DMSO, δ, ppm): 195.02, 162.87, 151.42, 145.77, 142.68, 131.05, 130.74, 126.08, 126.00, 122.46, 120.85, 115.19, 113.89, 55.71.

Synthesis of the naphthylated poly(ether ketone azomethine)s (Scheme 2)

Three ether–ketone linked PAMs were prepared by the polycondensation of the diamine and the dialdehydes at room temperature under nitrogen purge. The



Scheme 2 Synthesis of the naphthylated poly(ether ketone azomethine)s

polymers were washed repeatedly with water and ethanol several times. And they were dried under vacuum at 80 °C.

PAM-1 was obtained by the polycondensation of 1,5-bis[4-(4-aminophenoxy)]-benzoyl-2,6-dimethoxynaphthalene (0.500 g) and terephthalaldehyde (0.1098 g) in 4 mL of HMPA/NMP (1:l in volume) containing LiCl (0.24 g) and $CaCl_2$ (0.30 g) for 48 h.

ELEM. ANAL. Calcd. for $C_{46}H_{32}N_2O_6$ (708.23 g/mol): C, 77.95%; H, 4.55%; N, 3.95%. Found: C, 77.27%; H, 4.77%; N, 4.17%. IR (KBr, cm^{-1}): 1629 (C=N).

PAM-2 and PAM-3 were prepared using the similar procedure. Glutaraldehyde 25 wt% solution in water and 5,5′-methylenebis(salicylaldehyde) were used as dialdehydes, respectively.

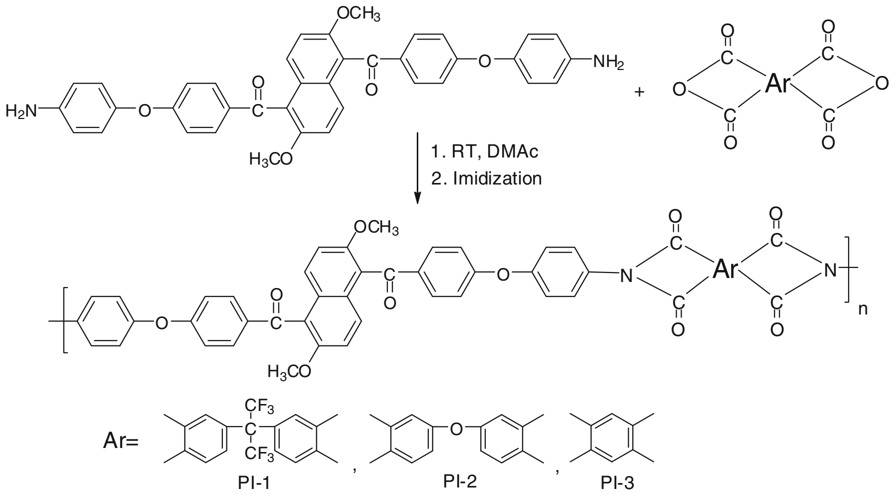
Film preparation of the PAMs

Thin films were casted from NMP solution of PAM-1, 2, and 3 onto flat glass plates, and dried at 80 °C for 12 h. The films were finally obtained after drying at 120 °C for 5 h in a vacuum oven.

Synthesis of the poly(ether ketone imide)s (Scheme 3)

Three ether–ketone linked PIs were synthesized based on the obtained diamines and commercially available dianhydrides.

PI-1 was prepared as follows: 1,5-bis[4-(4-aminophenoxy)]benzoyl-2,6-dimethoxynaphthalene (0.4000 g) and DMAc (4 mL) were placed into a 50-mL three-necked flask equipped with a magnetic stirrer and a nitrogen inlet. After the diamine was entirely dissolved, 6FDA (0.2910 g,) was added to the solution. The mixture was stirred at 40 °C for 24 h to yield polyamic acid solution. And then, the temperature was



Scheme 3 Synthesis of the naphthylated poly(ether ketone imide)s

increased to 60 °C. Acetic anhydride (1.2 mL) and pyridine (1 mL) were added. After 4 h, the solution was poured into ethanol to get the PI-1 powder.

ELEM. ANAL. Calcd. for $C_{57}H_{32}F_6N_2O_{10}$ (1018.20 g/mol): C, 67.19%; H, 3.17%; N, 2.75%. Found: C, 66.93%; H, 3.37%; N, 2.87%. IR (KBr, cm^{-1}): 1779, 1732 (–C=O); 1375 (C–N–C).

PI-2 was prepared using the similar procedure, and ODPA was used to replace 6FDA.

PI-3 derived from the new diamine and PMDA were synthesized using the thermal cyclization method. The polyamic acid solution was cast on a glass plate and then heated in vacuo by the following procedure: 80/3, 110/0.5, 150/0.5, 180/0.5, 210/0.5, 240/0.5, and 270 °C/0.5 h.

Results and discussion

A bulky diamine monomer, 1,5-bis[4-(4-aminophenoxy)]benzoyl-2,6-dimethoxynaphthalene, was synthesized via a Friedel–Crafts acylation reaction followed by an aromatic nucleophilic substitution reaction. The chemical structure for both 1,5-bis(4-fluoro)benzoyl-2,6-dimethoxynaphthalene (difluoro precursor) and diamine monomer was well characterized by FTIR and ^{1}H NMR spectroscopy. In their FTIR spectra, characteristic absorption bands of carbonyl groups around 1700 cm^{-1} were observed (Fig. 1). Characteristic absorptions at 3200–3400 cm^{-1} corresponding to $–NH_2$ groups of the diamine were clearly observed, indicating successful synthesis of the aimed product. The ^{1}H and ^{13}C NMR spectra of the diamine monomer further confirmed its chemical structure. As shown in Fig. 2, all the proton signals could be well assigned. The peaks at 7.72–6.59 ppm were from the protons of aromatic rings. The peaks around 5.08 and 3.74 ppm were belonged to the protons of $–NH_2$ and $–OCH_3$ groups, respectively.

Six novel naphthylated polymers containing ether and ketone linkages were successfully prepared. One-step room temperature polycondensation was adopted to prepare PAMs. PIs were prepared according to a typical two-step polymerization method, including the formation of a polyamic acid intermediate and the completion of the imidization. Despite the existence of rigid and bulky naphthylene moieties, which often led to the difficulty in the preparation of high-molecular weight polymers [7, 10], the resulting polymers had acceptable viscosities (Table 1).

The structure of the polymers was characterized by ^{1}H NMR spectroscopy. Typical ^{1}H NMR spectra of PAM-1 and PI-1 are shown in Figs. 3 and 4, and the spectra were well agreed with their expected chemical structure. Both PAM-1 and PI-1 showed the characteristic peaks around 3.70 ppm, corresponding to $–OCH_3$ groups. Also, the peak from azomethine groups could be observed around 8.75 ppm in Fig. 3.

It was noticed that the existence of the bulky methoxylated naphthylene moieties improved the solubility of the polymers. Despite the symmetric chemical structure, PAM-1,2,3 and PI-1,2 were readily soluble in aprotic polar solvents such as NMP, DMAc, and DMF at room temperature. PAM-1 and PI-1 could even be dissolved in the less polar solvents, like chloroform and THF. However, PI-3 obtained by

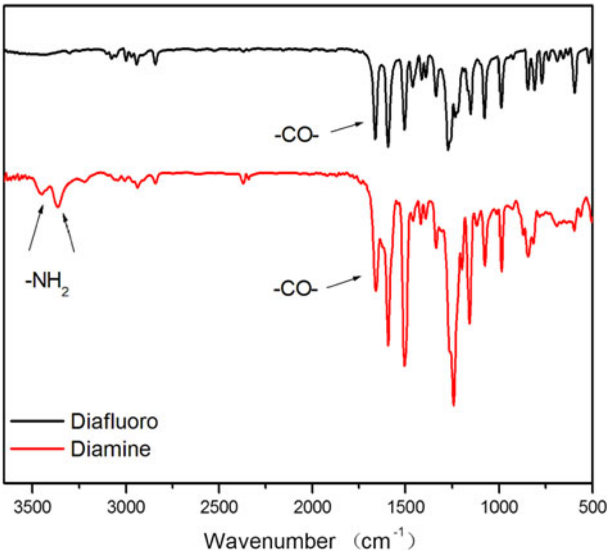


Fig. 1 FTIR spectra of difluoro precursor and diamine monomer

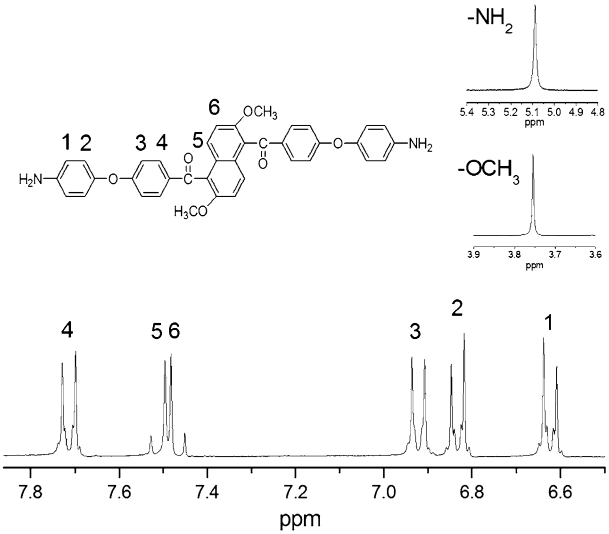


Fig. 2 ^{1}H NMR spectrum of the diamine monomer in DMSO-d_6

thermal cyclization showed poor solubility in above solvents due to its regular or rigid chemical structure.

The thermal properties of the polymers were evaluated by DSC and TGA. The naphthylated polymers showed high T_gs in the range of 142–288 °C (Table 1). Obviously, the T_g values of PI series were much higher than those of PAM ones due to their more rigid molecular chains. PAM-2 had lowest T_g because of the existence

Table 1 Molecular weights and properties of the polymers

Polymer	η (dL/g)[a]	T_g (°C)[b]	TD_5 (°C)[c]	TD_{10} (°C)[d]
PAM-1	0.49	219	390	435
PAM-2	0.45	142	238	314
PAM-3	0.47	194	234	271
PI-1	0.94	274	445	459
PI-2	0.87	258	418	437
PI-3	–	288	432	453

[a] Inherent viscosities measured in DMAc at a concentration of 0.1 g/dL at 25 °C

[b] Glass transition temperature from the second heating cycle of DSC

[c] Temperature at 5% weight loss measured by TGA under nitrogen

[d] Temperature at 10% weight loss measured by TGA under nitrogen

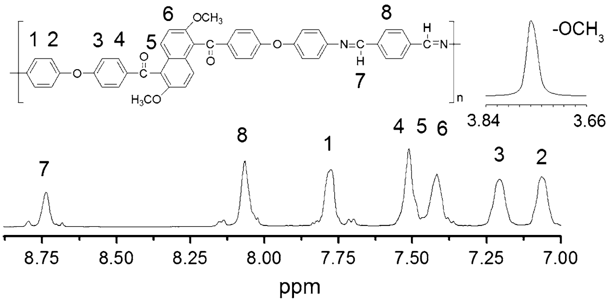


Fig. 3 ^{1}H NMR spectrum of PAM-1 in DMSO-d_6

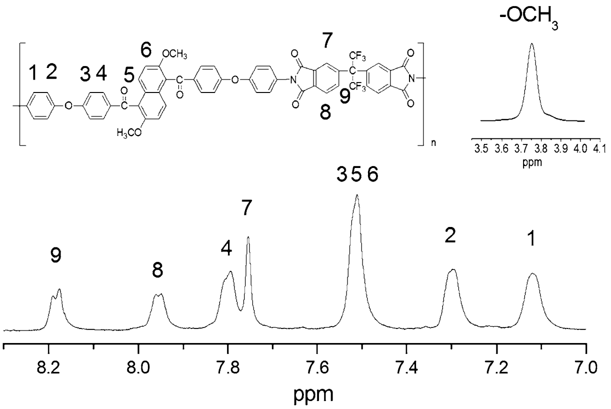


Fig. 4 ^{1}H NMR spectrum of PI-1 in DMSO-d_6

of the aliphatic moieties. The T_g values of PAM-1 and PI-1, 2, and 3 were much higher than those (204–213 °C) of previously reported naphthylated PEKs [10]. Except that PAM-2 and 3 containing aliphatic linkages in the backbones, all the

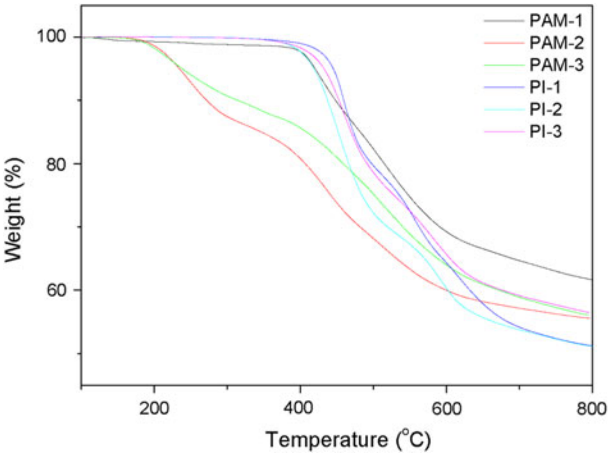


Fig. 5 TGA curves of PAMs and PIs under nitrogen

Table 2 Mechanical properties of the polymers

Polymer	Youngs' modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
PAM-1	2.2	89.2	8.5
PAM-2	–	–	–
PAM-3	2.0	61.1	4.1
PI-1	2.6	104.7	6.8
PI-2	2.4	102.7	7.6
PI-3	2.3	100.8	8.8

other exhibited good thermal stability. The temperature at 5% weight loss of these polymers having aromatic backbones was above 390 °C under nitrogen (Fig. 5 and Table 1).

The membranes of PAM-1,3 and PI-1,2,3 even showed acceptable mechanical properties (Table 2). The samples had tensile strength of 89.2–104.7 MPa, Young's moduli of 2.2–2.6 GPa, and elongation at break of 4.1–8.8%, indicating that they were strong materials.

As shown in Fig. 6, the UV–vis absorptions of the dilute polymer solution were investigated. PAM-1 and 3 exhibited two clear absorption peaks around 290 and 360 nm, which were attributed to naphthylene and azomethine containing moieties, respectively. A systematic bathochromic shift of PAM-1 caused by its improved conjugation was also observed. However, PI-1 and PAM-2 having less locally conjugated moieties only had one obvious absorption peak around 280 nm.

Conclusions

Some poly(ether ketone azomethane)s and poly(ether ketone imide)s containing symmetric naphthylene moieties were successfully prepared which was derived

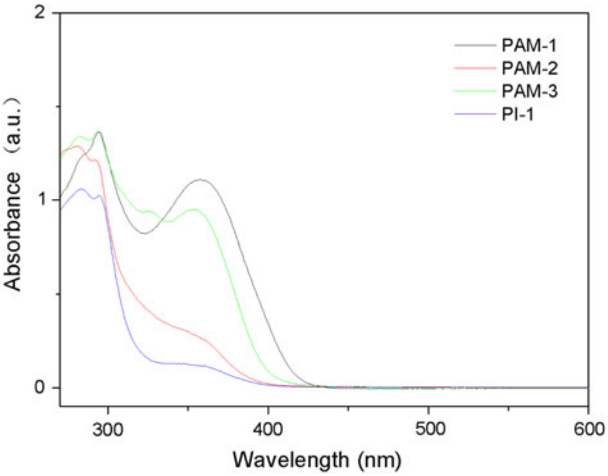


Fig. 6 UV–vis spectra of the polymers in chloroform (0.5 wt%)

from a novel bulky diamine monomer. Some of them exhibited improved solubility, high T_g, good thermal stability, and high moduli. These properties suggested that they would be promising high-performance materials.

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