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ORIGINAL PAPER

Synthesis and characterization of poly(arylene ether ketone)s containing triazole units through click chemistry

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Abstract In order to develop a novel process for poly(arylene ether ketone)s with high thermal and chemical stability, a series of poly(aylene ether ketone)s containing triazloe moieties were synthesized via the click chemistry of 4,4′-bis(azidomethyl) diphenyl ketone (BADPK) and bisethynyl compounds (BEAE1-5). The resulting polymers were characterized by using IR and ^{1}H NMR techniques. The solubility data showed that samples possessed good solubility in highly polar solvents. Molecular mass of these samples was determined by GPC which indicated they exhibited reasonable molecules weights and relatively small polydispersity. Furthermore, thermal stability of the samples was evaluated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), which indicated that they possessed good thermal stability and high T_g (100–140 °C). All the polymers were amorphous confirmed by DSC and X-ray diffraction (WAXD).

Keywords Click chemistry · Poly(arylene ether ketone) · Thermal and chemical stability · High-performance polymer

Introduction

Poly(arylene ether ketone)s (PAEKs) are well accepted as a class of high-performance engineering thermoplastics with high thermal stability, excellent

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environmental resistance, good mechanical properties, and superior electrical insulating ability, due to containing rigid and thermally stable arylene moieties and flexible and heat resistant oxygen ether or sulfide bonds [1–4]. PAEKs have been receiving considerable attention for the past two decades due to their successful applications in aerospace, automobile, electronics and power fields, such as high-temperature coating, toughening agents, separation membranes and fibers [5, 6] and ionic exchange membrane carrying ionic exchange groups for fuel cell [7–12], and vanadium redox battery [13–16] so on.

Due to these advantages, PAEKs are well synthesized to obtain superior qualifications. There are various reactions for polymerization of PAEKs such as aromatic nucleophilic displacement, aromatic electrophilic reaction, oxidative coupling, Ullman ether synthesis, Scholl reaction, nickel catalyzed coupling of aromatic chlorides, and ring opening of cyclic oligomers. In these reactions, the most popular synthetic route to PAEKs is aromatic nucleophilic substitution of aromatic dihydroxy compounds and activated aromatic dihalo or dinitro compounds [17]. However, this polymerization generally needs high temperature (>160 °C) and long reaction time [17–19].

Recently, click chemistry, the copper (I)-catalyzed Huisgen's 1,3-dipolar cycloadditions of azides and terminal alkynes has attracted much attention [20, 21]. Click chemistry has recently drawn increasing attention in organic synthesis [22, 23], supermolecular chemistry [24, 25], and material surface modification [26–29] because of its high selectivity, near-perfect reliability, high yields, and exceptional tolerance towards a wide range of functional groups and reaction conditions [30]. To our knowledge, click chemistry is increasingly used in preparation of high-performance engineering thermoplastic polymers [31, 32]. However, these containing fluorine polymers developed by Zhu and Yao [31, 32] are related to fluorine monomers which are high-cost materials and harmful to environment. Therefore, it is essential to develop new non-fluorine PAEKs. To date, few of preparation and characterization of non-fluorine PAEKs containing triazole units via click chemistry has been reported. Although there are many non-fluorine PAEKs products on the market such as PEEK, PEKK [2], PPEK [33], etc., most of them are synthesized by condensation polymerization of nucleophilic substitution.

In this article, we described the synthesis and characterization of a novel class of linear aromatic ether ketone polymers containing triazole units from the click chemistry of new monomer 4,4′-bis(azidomethyl) diphenyl ketone and bisethynyl compounds.

Experimental

Materials

Acetone and DMSO were dried over CaH_2 and distillated before use. Other reagents or materials were used as received.

Measurements

Infrared spectra were obtained on Thermo Fisher Nicolet Avater 370 FT-IR spectrophotometer. Melting point ranges were determined on a WRS-2A capillary melting point apparatus. Mass spectrometry (MS) was recorded on a Finnigan-MAT-8430 instrument using EI ionization at 70 eV. ^{1}H NMR(400 MHz) was recorded on a Bruker AM-400 spectrometer with Me_4Si as internal standard. Relative molecular weights and molecular weight distributions were measured by gel permeation chromatography (GPC) system equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index (RI) detector, a Waters 2487 dual wavelength λ absorbance detector and a set of Waters Styragel columns (HR3, HR4 and HR5, 7.8 mm × 300 mm). GPC measurements were carried out at 35 °C using DMF as eluent at a flow rate of 1.0 mL/min. The system was calibrated with polystyrene standards. Differential scanning calorimetry (DSC) was conducted on a NetZSch (German) DSC 200F3 system under nitrogen calibrated with indium and zinc standards. Initial sample weight was set as 1–2 mg for each operation. The specimen was heated from 25 to 280 °C at a heating rate of 10 °C/min. Dynamic thermo-gravimetric analysis (TGA) was performed on NetZSch (German) TGA 209F1 system on powder samples at a heating rate of 10 °C/min under nitrogen atmosphere from 25 to 700 °C. Wide-angle X-ray diffraction (WAXD) patterns were obtained at room temperature on a Rigaku D/Max-2550 powder diffractometer with a scanning speed of 5°/min, and the patterns were recorded in the 2θ range of 5–60°.

Synthesis of 4,4′-bis(azidomethyl) diphenyl ketone compound BADPK

Synthesis of 4,4′-dimethyl benzophenone 1

According to [34], to a 500 mL three-necked flask equipped with a magnetic stirrer, dropping funnel, thermometer, and condenser upper with a $CaCl_2$ drying tube linked to a gas absorber was charged anhydrous aluminum chloride (75 g, 0.55 mol) and toluene (150 mL) and temperature was cooled to −5 to 0 °C. Then 4-methylbenzoyl chloride (77.3 g, 0.5 mol) was dropped from the dropping funnel over a period of 1 h at −5 to 0 °C, after complete addition of 4-methylbenzoyl chloride, the reaction was further stirred for 5–6 h at 0–5 °C to ensure complete consumption of 4-methylbenzoyl chloride (by observing no HCl gas escape in the gas absorber). The reaction mixture was then slowly poured into a mixture of crushed ice (2 kg) and conc. HCl (900 mL) at 0–10 °C. The products were extracted into ethyl acetate (1,000 mL). The ethyl acetate layer was separated and washed with water to neutral pH (6–7). Finally, ethyl acetate was concentrated on a rotary evaporator to obtain compound **1** as a white solid.

Compound **1** (80 g, 76.1%): m.p. 92.7–93.4 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz, ppm): δ 7.71 (4H, d, $J = 5.6$ Hz), 7.28 (4H, d, $J = 8.0$ Hz), 2.44 (6H, s). IR (KBr, cm^{-1}) ν 3035, 2919, 2855, 1924, 1650, 1605, 1558, 1446, 1406, 1314, 1279, 1177, 1148, 1112, 1041, 929, 825, 750.

Synthesis of 4,4′-bis(bromomethyl) diphenyl ketone 2

A mixture of compound **1** (50.4 g, 0.24 mol), N-bromosuccinimide (NBS, 85 g, 0.48 mol) and dry CCl_4 (400 mL) was stirred and refluxed under the light of two "IR 280 W" lamps until the starting material was completely transformed (ca. 5–6 h). When hot, the reaction mixture was filtered off and the solvent was removed on a rotary evaporator to give crude product. The crude product was recrystallized from chloroform to give compound **2** as a white solid.

Compound **2** (66.2 g, 75%): m.p. 126–128 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz, ppm): δ 7.79 (d, $J = 8.4$ Hz, 4H), 7.52 (d, $J = 8.4$ Hz, 4H), 4.54 (s, 4H). IR (KBr, cm^{-1}) ν 3072, 2916, 2848, 1700, 1646, 1608, 1437, 1412, 1348, 1278, 1175, 930, 851, 610.

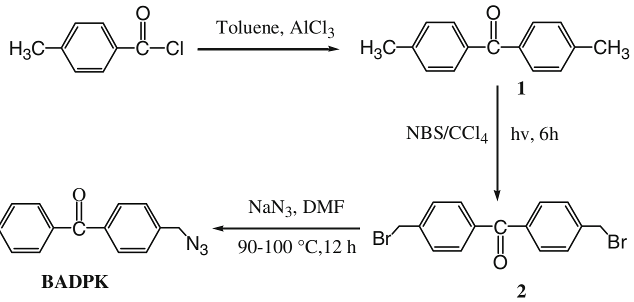
Synthesis of 4,4′-bis(azidomethyl) diphenyl ketone BADPK

To a 250-mL single-necked flask equipped with a reflux condenser and a magnetic stirrer were added compound **2** (60 g, 0.16 mol) and NaN_3 (20.8 g, 0.32 mol) in DMF (300 mL). The reaction mixture was stirred at 90 °C for 24 h. After the mixture was cooled to room temperature, the solution was diluted and extracted with ether (150 mL × 3). The combined organic layer was washed with saturated brine solution (100 mL × 2), dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (25:1) as eluent to give compound BADPK as a white solid.

Compound BADPK (42 g, 90%): m.p. 75.9–76.1 °C. 1H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.82 (d, $J = 8.0$ Hz, 4H), 7.45 (d, $J = 8.4$ Hz, 4H), 4.46 (s, 4H). IR (KBr, cm^{-1}) ν 3072, 2916, 2849, 2100, 1701, 1646, 1608, 1437, 1412, 1348, 1278, 1175, 930, 851. MS (EI): m/z 250, 236, 194, 132, 104, 76, 51. Anal. Calcd for $C_{15}H_{12}N_6O$: C, 61.64%; H, 4.14%; N, 28.75%. Found: C, 61.78%; H, 4.22% N, 28.59% (Scheme 1).

Synthesis of bisethynyl compounds BEAE1-5 containing arylene ether units

Compounds BEAE1-5 were prepared according to the [20].



Scheme 1 Synthesis of 4,4′-bis(azidomethyl) diphenyl ketone compound BADPK

Synthesis of polymer PEK1-5

In a 50 mL flask $CuSO_4 \cdot 5H_2O$ (7 mg, 5 mol%) and sodium ascorbate (12 mg, 10 mol%) dissolved in H_2O (10 mL) were added dropwise to a solution of bisethynyl compounds BEAE1-5 (0.50 mmol) and compound BADPK (146 mg, 0.50 mmol) in DMSO (15 mL). The reaction mixture was stirred at 45 °C overnight. The solvent was decanted to leave a gum residue in the flask. The residue was then stirred in H_2O (20 mL) and concentrated ammonia (5 mL) for another 1 h. The mixture was filtered and the resulting filter cake was washed with H_2O (20 mL × 3). The filter cake was then dissolved in DMSO, filtered again and precipitated into a 2:1 solution of water and methanol. The solid was separated and washed repeatedly with aqueous methanol before dried in a vacuum oven. The desired polymers PEK1-5 were obtained as pale yellow solids, respectively.

PEK1: 68% yield. 1H NMR (DMSO-d6, 400 MHz, ppm) δ: 8.32 (2H, s), 7.73 (4H, br), 7.48 (4H, br), 6.96 (4H, br), 5.74 (4H, br), 5.08 (4H, br). IR (KBr, cm^{-1}): ν 3134, 3079, 2934, 2870, 1650, 1608, 1570, 1505, 1460, 1414, 1313, 1278, 1221, 1204, 1109, 1049, 1016, 928, 821, 745, 710.

PEK2: 56% yield. 1H NMR (DMSO-d6, 400 MHz, ppm) δ: 8.33 (2H, s), 7.72 (4H, br), 7.45 (4H, br), 7.17 (1H, br), 6.71 (1H, br), 6.62 (2H, br), 5.73 (4H, br), 5.12 (4H, br). IR (KBr, cm^{-1}): ν 3138, 3062, 2939, 2872, 1656, 1607, 1586, 1490, 1460, 1415, 1313, 1278, 1223, 1178, 1149, 1104, 1049, 1019, 928, 807, 762, 738.

PEK3: 69% yield. 1H NMR (DMSO-d6, 400 MHz, ppm) δ: 8.32 (2H, s), 7.72 (4H, br), 7.44 (4H, br), 7.10 (4H, br), 6.70 (4H, br), 5.70 (4H, br), 5.11 (4H, br), 1.56 (6H, br). IR (KBr, cm^{-1}): ν 3135, 3075, 2965, 2934, 2872, 1649, 1605, 1570, 1508, 1460, 1413, 1312, 1229, 1204, 1109, 1050, 1012, 928, 821, 742, 709.

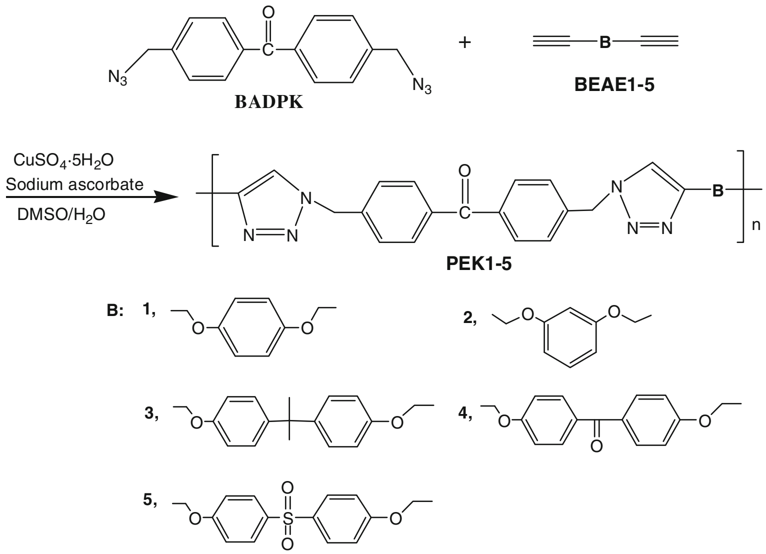
PEK4: 66% yield. 1H NMR (DMSO-d6, 400 MHz, ppm) δ: 8.36 (2H, s), 7.75 (4H, br), 7.68 (4H, br), 7.48 (4H, br), 7.17 (4H, br), 5.72 (4H, br), 5.23 (4H, br). IR (KBr, cm^{-1}): ν 3136, 3063, 2938, 2872, 1707, 1648, 1598, 1569, 1505, 1460, 1415, 1306, 1279, 1246, 1204, 1165, 1148, 1114, 1048, 1029, 998, 946, 925, 848, 766, 727.

PEK5: 67% yield. 1H NMR (DMSO-d6, 400 MHz, ppm) δ: 8.35 (2H, s), 7.85 (4H, br), 7.76 (4H, br), 7.57 (4H, br), 7.22 (4H, br), 5.72 (2H, br), 5.23 (4H, br). IR (KBr, cm^{-1}): ν 3133, 3076, 2931, 2872, 1650, 1598, 1569, 1498, 1460, 1415, 1310, 1285, 1255, 1164, 1148, 1110, 1047, 1028, 947, 828, 727.

Results and discussion

Synthesis and characterization of polymers

The polymers containing triazole unites PEK1-5 were obtained from the click reactions of 4,4′-bis(azidomethyl) diphenyl ketone BADPK and bisethynyl compounds BEAE1-5 (Scheme 2). Click reactions were carried out in a 3:2 solvent ratio of DMSO to H_2O using 5 mol% $CuSO_4 \cdot 5H_2O$ with 10 mol% sodium ascorbate as the in situ reducing agent to generate the active Cu(I) species [28]. From experiments, it was found that the reaction temperature played a key part in the



Scheme 2 Synthesis of polymer PEK1-5

formation of the polymers and further that the polymers with reasonable molecular weight were obtained when the click reactions were carried out at 45 °C.

It can be seen from the infrared spectra of PEK1-5 (Fig. 1b) that the strong absorption peaks at 3,300 and 2,100 cm^{-1} assigned to stretched vibration of ≡C–H and –N_3, respectively (Fig. 1a) are disappeared, while there are absorption peaks at 3,062–3,079 cm^{-1} attributed to stretched vibration of =C–H of 1,2,3 triazole. A representative ^{1}HNMR spectrum of monomer BADPK and its polymer PEK3 is shown in Fig. 2. It is clear that the proton chemical shifts of monomer BADPK (Fig. 2a) appear correspondingly in ^{1}HNMR spectrum of its polymer PEK3 (Fig. 2b). Furthermore, the 1,2,3-triazole rings of the polymer are characterized by signals near 8.32 ppm of the triazole protons in ^{1}HNMR spectrum of its polymer PEK3. It is confirmed that the resulting polymers by click chemistry contain triazole units corresponding to IR analysis (Fig. 1). These indicate that polymerization between 4,4′-bis(azidomethyl) diphenyl ketone BADPK and bisethynyl compounds BEAE1-5 by the click chemistry is successful.

Properties of polymers

Solubility of polymers

The solubility of polymers PEK1-5 in common organic solvents was determined quantitatively by dissolving 5.0 mg of solid polymers in 1.0 mL of solvents (Table 1). In the solubility experiments, it was found that, at room temperature, these polymers could not dissolve in MeOH, THF, Acetone, and Toluene while they were slowly dissolved in highly polar solvents such as DMF, NMP, DMAc, and

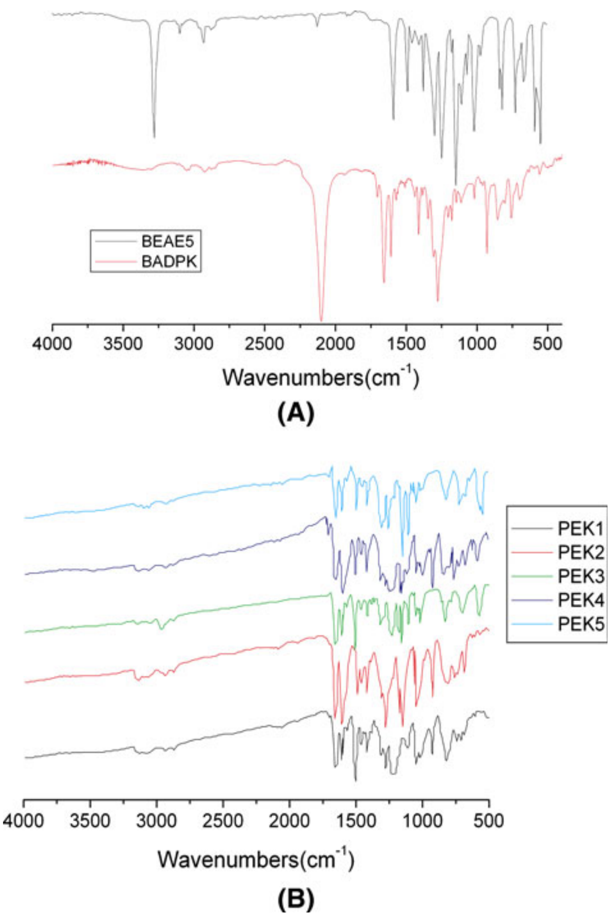


Fig. 1 IR spectra of samples: **a** monomers BADPK and BEAE5; **b** polymer PEK1-5

DMSO, when heating, the rate of dissolving was increased. These polymers show good solubility in the highly polar solvents, which makes them easy to process into films, membranes, fibers, and paints. According to literatures, as a well known member of PAEKs, Poly(aryl ether ether ketone)s (PEEK, e.g. 'Victrex' PEEK from ICI [2]) synthesized by condensation polymerization of nucleophilic substitution can not be processed by casting method because of its poor solubility in most highly polar solvents due to its semicrystalline structure [35], which restricted its applications. In order to increase the solubility without sacrificing the thermal stability, considerable research effort has been devoted to develop new polymers containing heterocyclic moieties. Mami et al. [36] developed a novel Naphthalene-based poly(arylene ether ketone) by polycondensation of nucleophilic displacement, which showed good solubility in polar solvents such as NMP, THF, etc. Xia et al. [33] have synthesized poly(phthalazinone ether ketone)s (PPEK) through a typical polycondensation and the resulting PPEK possessed good solubility. Click reaction

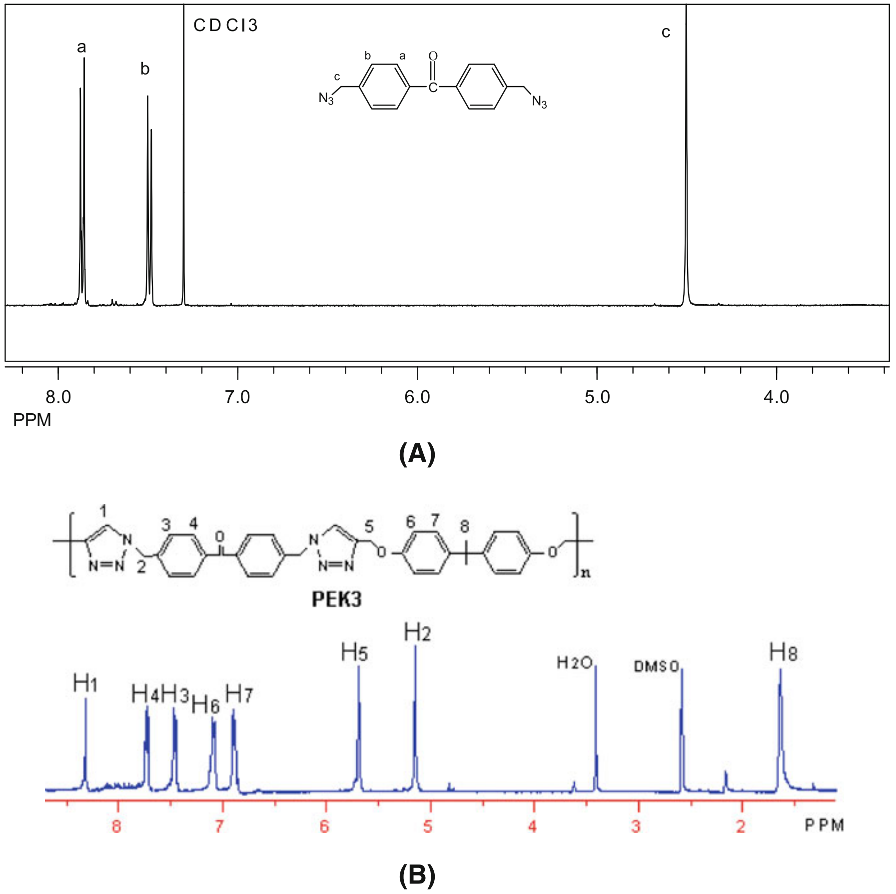


Fig. 2 ^{1}H NMR of samples: **a** monomer BADPK; **b** PEK3

could link the well-designed monomers and make backbones of PEK1-5 carry triazole units linked to benzene rings through methylene or methylene ether, which decreases the crystallinity of PEK1-5 and increases their solubility. As for the polycondensation of nucleophilic displacement with the monomers designed intentionally for PAEKs like PPEK, polycondensation could make the polymer backbones contain heterocyclic moieties and decrease coplanarity, which decreases their crystallinity and increases their solubility.

Molecular weights and their distributions of polymers

The corresponding data of GPC analysis in DMF for polymers PEK1-5 were listed in Table 2. The data show that the polymerization via click chemistry produced polymers PEK1-5 with fairly high molecular weights and narrow distributions. The number average molecular weights of them are around 20,000 and the distributions range from 1.4 to 1.5 with the exception of polymer PEK3 which distribution is

Table 1 Solubility of polymers PEK1-5

Polymers	DMF	NMP	DMAc	DMSO	MeOH	THF	Acetone	Toluene
PEK1	+−	+−	+−	+−	−	−	−	−
PEK2	+−	+−	+−	+−	−	−	−	−
PEK3	+−	+−	+−	+−	−	−	−	−
PEK4	+−	+−	+−	+−	−	−	−	−
PEK5	+−	+−	+−	+−	−	−	−	−

Note: (+) Soluble; (+−) Soluble when heating; (−) insoluble; (sw) swell

Table 2 Molecular weights and their distributions of polymers PEK1-5 using GPC

Polymers	M_n^a	M_w^a	$(M_w/M_n)^a$
PEK1	18,543	27,355	1.47
PEK2	17,851	27,213	1.52
PEK3	22,165	24,232	1.09
PEK4	19,190	26,988	1.41
PEK5	15,580	21,806	1.40

[a] GPC in DMF vs. polystyrene at 35 °C

narrower (1.09). All polydispersites of polymers are less than 2 which is typical for polycondensation reaction [37]. In the case of the polycondensation of nucleophilic displacement, Mami et al. [36] found that Naphthalene-based poly(arylene ether ketone) showed only unimodal peak with M_n 34,900 (M_w/M_n 1.96). Berti et al. [38] reported that the molecular weights of random copoly(arylene ether-thioether ketone)s varied from 19,000 to 32,000 with the polydispersites in a range of 1.65–2.86. It is indicated that the click chemistry is an efficient way for polymerization of block polymers.

Thermal properties of polymers

Thermal stability of PEK1-5 was determinated by means of thermogravimetric analysis (TGA) (Fig. 3) and differential scanning calorimetry (DSC) (Fig. 4). The resulting data are summarized in Table 3. The polymers PEK1-5 start to decompose at about 330 °C which probably attribute to chain scission of aromatic ether. There was the second stage of weight loss at 363–377 °C. It was seen from Fig. 3 that rate of weight loss of PEK3 was lager than the other polymers. The reason is that the former might be caused by the decomposition of isopropyl group, the latter by decomposition of methylene group.

The values of T_g were determinated from the DSC curves and listed in Table 3. T_g values of polymers PEK1-5 were found to be in the increasing order of PEK2 < PEK1 < PEK3 $\approx$ PEK4 < PEK5. T_g of PEK5 is the highest due to the rigid sulfone groups in the polymer backbone which could hinder molecular rotation while that of PEK2 was the lowest owing to the meta-phenylene groups which could increase flexibility of molecular chain. The curves of DSC (Fig. 4) also show that that all polymers are amorphous, which are required to be confirmed by X-ray of diffraction studies of these polymers.

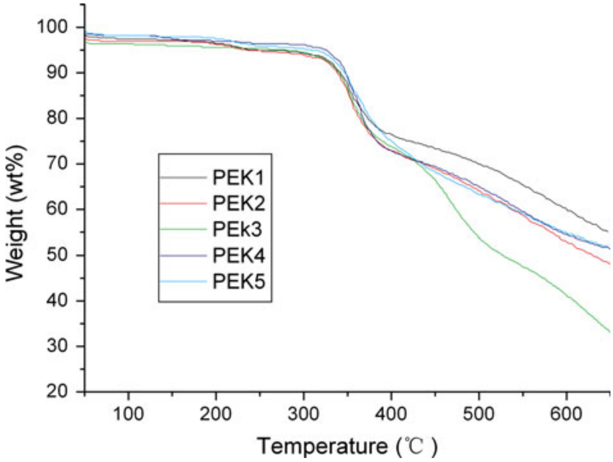


Fig. 3 TG curves of polymers PEK1-5

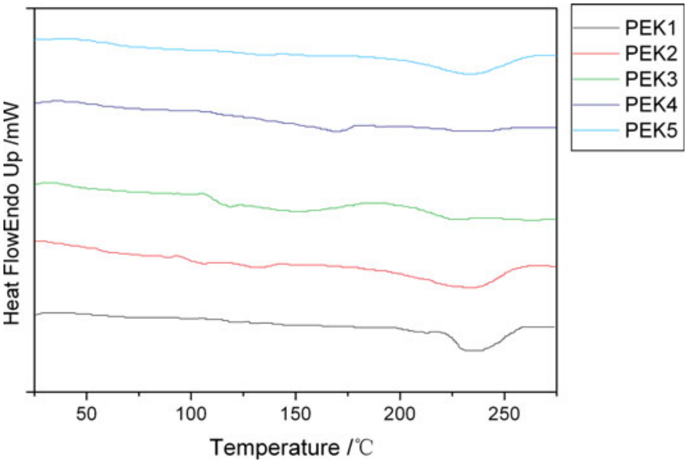


Fig. 4 DSC curves of polymers PEK1-5

In terms of thermal stability of polymers by the polycondensation of nucleophilic displacement, PEEK has a glass transition temperature around 140–160 °C and a melting temperature around 340–360 °C [39], exhibiting excellent thermal stability. However, the low T_g of PEEK restricted its performance in high temperature conditions. To increase thermal properties of the polymers by this conventional method of polymerization, PPEK with T_g at 263 °C and the 5% weight loss temperature at 500 °C was reported by Xia et al. [33]. Ding et al. [40] developed cross-linkable poly(phthalazinone ether ketion)s with T_g at 250–270 °C and the 5% weight loss temperature at 450–500 °C. Consequently, it is clear that the introduction of the rigid unsymmetrical phenyl phthalazinone moiety into the polymer backbone or the crosslinking reaction when thermally curing gives the

Table 3 Data of DSC and TGA of polymer PEK1-5

Polymers	T_g (°C)[a]	T_d (°C)[a]	T_s (°C)[a]	R_w (%)[b]
PEK1	104	330	374	55.6
PEK2	96	326	363	47.8
PEK3	110	325	365	33.2
PEK4	112	332	368	51.3
PEK5	142	334	377	51.3

[a] Measured at 10 °C/min in N_2; T_d: onset decompositon temperature; T_s: 20% weight loss at the second stage

[b] Residual weight retention at 650 °C

polymers higher glass transition temperature and thermal stability. T_g and T_d of PEK1-5 by click polymerization are lower than those of PPEK attributed to the fact that backbones of PEK1-5 did not contain the rigid unsymmetrical phenyl phthalazinone moiety. Further research is required to develop novel PAEKs containing such rigid unsymmetrical phenyl phthalazinone units by click chemistry reaction.

X-ray diffraction studies of polymer PEK1-5

The X-ray diffractogram curves of polymer PEK1-5 were shown in Fig. 5. X-ray diffractograms of all polymers exhibit broad halo at about $2\theta \approx 15$–30° in the wide angle region indicating that the polymers PEK1-5 are amorphous in nature which is corresponding to the DSC analysis. Actually, amorphous phase of PEK1-5 is favorable to their good solubility.

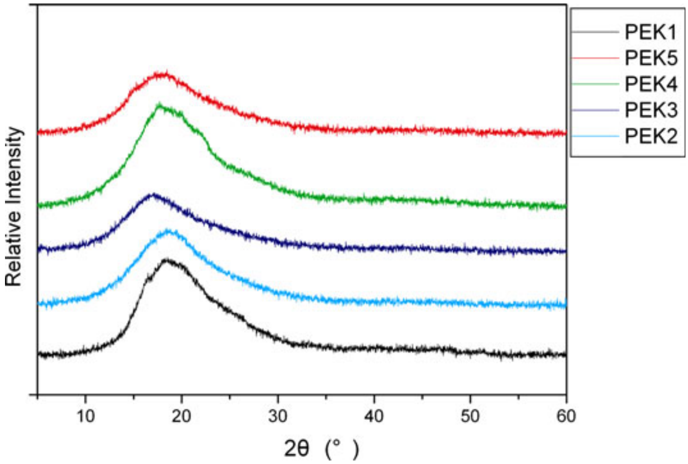


Fig. 5 X-ray diffractogram curves of polymer PEK1-5

Conclusions

The click chemistry of 4,4′-bis(azidomethyl) diphenyl ketone and bisethynyl compounds BEAE1-5 successfully provided a novel class of linear aromatic ketone polymers containing triazole unites. The IR and ^{1}H NMR identified that these copolymers produced by the click chemistry contained triazole units. The resulting polymers have good solubility in most strong polar solvents. GPC showed they exhibited reasonable molecules weights and relatively small polydispersity. TGA and DSC indicated that they possessed good thermal stability and have high T_g (100–140 °C), but were amorphous which was confirmed by WAXD.

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References

1. Rose JB (1974) Preparation and properties of poly(arylene ether sulphones). Polymer 15(7):456–465
2. Blundell DJ (1992) The crystal structures of aryl ether ketone polymers containing meta-phenyl links. Polymer 33(18):3773–3776
3. Gardner KH, Hsiao BS, Faron KL (1994) Polymorphism in poly(aryl ether ketone)s. Polymer 35(11):2290–2295
4. Ji XL, Yu DH, Zhang WJ, Wu ZW (1997) The multiple melting behaviour of immiscible poly(ether ether ketone)/poly(ether diphenyl ether ketone) blend. Polymer 38(14):3501–3504
5. Jian X, Dai Y, He G, Chen G (1999) Preparation of UF and NF poly (phthalazine ether sulfone ketone) membranes for high temperature application. J Membr Sci 161(1–2):185–191
6. Yang Y, Yang D, Zhang S, Wang J, Jian X (2006) Preparation and characterization of poly(phthalazinone ether sulfone ketone) hollow fiber ultrafiltration membranes with excellent thermal stability. J Membr Sci 280(1–2):957–968
7. Kerres JA (2001) Development of ionomer membranes for fuel cells. J Membr Sci 185(1):3–27
8. Shin CK, Maier G, Scherer GG (2004) Acid functionalized poly(arylene ether)s for proton-conducting membranes. J Membr Sci 245(1–2):163–173
9. Xing PX, Robertson GP, Guiver MD, Mikhailenko SD, Kaliaguine S (2004) Sulfonated poly(aryl ether ketone)s containing the hexafluoroisopropylidene diphenyl moiety prepared by direct copolymerization, as proton exchange membranes for fuel cell application. Macromolecules 37(21): 7960–7967
10. Muthu Lakshmi RTS, Meier-Haack J, Schlenstedt K, Vogel C, Choudhary V, Varma IK (2005) Sulphonated poly(ether ether ketone) copolymers: synthesis, characterisation and membrane properties. J Membr Sci 261(1–2):27–35
11. Tian SH, Shu D, Wang SJ, Xiao M, Meng YZ (2007) Poly(arylene ether)s with sulfonic acid groups on the backbone and pendant for proton exchange membranes used in PEMFC applications. Fuel Cells 7(3):232–237
12. Liu BJ, Hu W, Robertson GP, Guiver MD (2008) Poly(aryl ether ketone)s with carboxylic acid groups: synthesis, sulfonation and crosslinking. J Mater Chem 18(39):4675–4682
13. Chen D, Wang S, Xiao M, Han D, Meng Y (2010) Sulfonated poly (fluorenyl ether ketone) membrane with embedded silica rich layer and enhanced proton selectivity for vanadium redox flow battery. J Power Sources 195(22):7701–7708
14. Jia C, Liu J, Yan C (2010) A significantly improved membrane for vanadium redox flow battery. J Power Sources 195(13):4380–4383
15. Chen D, Wang S, Xiao M, Meng Y (2010) Preparation and properties of sulfonated poly(fluorenyl ether ketone) membrane for vanadium redox flow battery application. J Power Sources 195(7): 2089–2095

16. Chen D, Wang S, Xiao M, Meng Y (2010) Synthesis and properties of novel sulfonated poly(arylene ether sulfone) ionomers for vanadium redox flow battery. Energy Convers Manag 51(12):2816–2824
17. Hergenrother PM (2003) The use, design, synthesis, and properties of high performance/high temperature polymers: an overview. High Perform Polym 15(1):3–45
18. Hergenrother PM, Jensen BJ, Haynes SJ (1988) Poly(arylene ethers). Polymer 29:358–364
19. Chen YL, Meng YZ, Wang SJ, Tian SH, Chen Y, Hay AS (2006) Sulfonated poly(fluorenyl ether ketone) membrane prepared via direct polymerization for PEM fuel cell application. J Membr Sci 280:433
20. Hartmuth CK, Finn MG, Sharpless KB (2001) Click chemistry: diverse chemical function from a few good reactions. Angew Chem Int Ed 40(11):2004–2021
21. Qin A, Lam JWY, Tang BZ (2010) Click polymerization. Chem Soc Rev 39(7):2522–2544
22. Wang ZX, Qin HL (2003) Regioselective synthesis of 1,2,3-triazole derivatives via 1,3-dipolar cycloaddition reactions in water. Chem Commun (19):2450–2451
23. Zeng Q, Li Za, Li Z, Ye C, Qin J, Tang BZ (2007) Convenient attachment of highly polar azo chromophore moieties to disubstituted polyacetylene through polymer reactions by using “click” chemistry. Macromolecules 40(16):5634–5637
24. Badjic JD, Balzani V, Credi A, Lowe JN, Silvi S, Stoddart JF (2004) A mechanically interlocked bundle. Chemistry 10(8):1926–1935
25. Li Za, Wu W, Li Q, Yu G, Xiao L, Liu Y, Ye C, Qin J, Li Z (2010) High-generation second-order nonlinear optical (NLO) dendrimers: convenient synthesis by click chemistry and the increasing trend of NLO effects. Angew Chem Int Ed 49(15):2763–2767
26. Yao RX, Wang LJ, Li HQ, Meng WD, Qing FL (2008) Chemical modification of poly(vinylacetylene) via click reaction. E-Polymers 137:1–10
27. Parrish B, Breitenkamp RB, Emrick T (2005) PEG- and peptide-grafted aliphatic polyesters by click chemistry. J Am Chem Soc 127(20):7404–7410
28. Helms B, Mynar JL, Hawker CJ, Fre′chet JMJ (2004) Dendronized linear polymers via ‘click chemistry’. J Am Chem Soc 126:15020–15021
29. Carroll JB, Jordan BJ, Xu H, Erdogan B, Lee L, Cheng L, Tiernan C, Cooke G, Rotello VM (2005) Model systems for flavoenzyme activity: site-isolated redox behavior in flavin-functionalized random polystyrene copolymers. Organ Lett 7(13):2551–2554
30. Di′az DD, Punna S, Holzer P, Mcpherson AK, Sharpless KB, Fokin VV, Finn MG (2004) Click chemistry in materials synthesis. 1. Adhesive polymers from copper-catalyzed azide-alkyne cycloaddition. J Polym Sci A 42:4392–4403
31. Zhu YQ, Huang Y, Meng WD, Li HQ, Qing FL (2006) Novel perfluorocyclobutyl(PFCB)-containing polymers formed by click chemistry. Polymer 47(18):6272–6279
32. Yao R-X, Kong L, Yin Z-S, Qing F-L (2008) Synthesis of novel aromatic ether polymers containing perfluorocyclobutyl and triazole units via click chemistry. J Fluor Chem 129(10):1003–1010
33. Xia J, Zhang J, Liao G, Jian X (2007) Copolymerization and blending of poly(phthalazinone ether ketone)s to improve their melt processability. J Appl Polym Sci 103(4):2575–2580
34. Agarwal SK, Maikap GC, Kumar P (2007) WO 2007074474 05 July
35. Dawson PC, Blundell DJ (1980) X-ray data for poly(aryl ether ketones). Polymer 21(5):577–578
36. Mami O, Toshikazu T, Takeshi E (1995) Synthesis of a novel naphthalene-based poly(arylene etherketone) by polycondensation of 1,5-bis(4-fluorobenzoyl)-2,6-dimethylnaphthalene with bisphenol a. J Polym Sci A 33(15):2647–2655
37. Mansour IB, Alouani K, Chauveau E, Martin V, Schiets F, Mercier R (2010) Synthesis and characterisation of poly(ester-amide)s from aromatic bisoxazoline precursors. Eur Polym J 46(4):814–820
38. Berti C, Celli A, Marianucci E, Vannini M (2007) Preparation and characterisation of novel random copoly(arylene ether-thioether ketone)s containing 2,2-bis(4-phenylene)propane units. Eur Polym J 43(6):2453–2461
39. Bourgeois Y, Devaux J, Legras R, Parsons IW (1996) Synthesis of a soluble poly(ether ketone) prepolymer. Polymer 37(14):3171–3176
40. Ding FC, Wang SJ, Xiao M, Han DM, Meng YZ (2007) Synthesis and characterization of crosslinkable poly(phthalazinone ether ketone)s. J Appl Polym Sci 106(3):1821–1827