

Study on Synthesis of PAEKs Containing Triazole Units through Click Reaction and Their Properties

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A series of novel linear aromatic ether ketone polymers containing triazole units were synthesized by click chemistry and their structures and properties were characterized by FT-IR, ¹H NMR, GPC, TGA, DSC and WAXD. The results showed that these polymers exhibited relatively small molecular weights distributions, good thermal stability and solvent-repelling which could have potential applications as engineering thermoplastic.

Key Words : Click chemistry, Poly(arylene ether ketone), Triazoles, Engineering thermoplastic

Introduction

Poly(arylene ether ketone)s (PAEKs) are well accepted as a class of high performance engineering thermoplastics known for their excellent combination of thermal and chemical stability and mechanical properties such as creep resistance, high strength and durability and superior electrical insulating ability, due to containing rigid and thermally stable arylene and flexible and heat resistant oxygen ether or sulfide bonds.¹⁻⁴ These advanced materials have been receiving considerable attention for past decades due to their successful applications in aerospace, automobile, electronics and other high technology fields,⁵ such as high-temperature coating, toughening agents, ultrafiltration membranes and ionic exchange membrane after carrying ionic exchange groups for fuel cell and vanadium redox battery so on.

Due to these advantages, Poly(arylene ether ketone)s are being synthesized to obtain superior qualifications. The most popular synthetic route to poly(arylene ether ketone)s is aromatic nucleophilic substitution of aromatic dihydroxy compounds and activated aromatic dihalo- or dinitro- compounds. However, this polymerization generally needs high temperature (> 160 °C) and long reaction time.⁶

Recently, click chemistry, the copper (I)-catalyzed Huisgen's 1,3-dipolar cycloadditions of azides and terminal alkynes has attracted much attention.^{7,8} Because of their high selectivity, near-perfect reliability, high yields, and exceptional tolerance towards a wide range of functional groups and reaction conditions, click chemistry have recently attracted increasing attention in organic synthesis,⁹ supermolecular chemistry and material surface modification.^{10,11} In particular, click chemistry is increasingly used in engineering thermoplastic polymer synthesis.^{12,13}

In this article, we describe the synthesis and characterization of a novel class of linear aromatic ether ketone/sulfone polymers containing triazole units from the click chemistry of new monomer 4,4'-bis(azidomethyl) diphenyl

ketone and bisethynyl compounds.

Experimental Part

Materials. Acetone, DMSO were dried from CaH₂, and distilled before use. Other reagents (*N,N*-dimethylformamide (DMF), 1-methyl-2-pyrrolidinone (NMP), dimethylacetamide (DMAc), Methanol (MeOH), tetrahydrofuran (THF), toluene) or materials were used as received.

Measurements. Infrared spectra were obtained on Thermo Electron Corporation Nicolet 380 FT-IR spectrophotometer. ¹H NMR (400 MHz) was recorded on a BrukerAM-400 spectrometer with Me₄Si (¹H NMR) 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 DMSO 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 204 F1 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. Thermogravimetric analysis (TGA) was performed on NetZSch (German) TGA 209 F1 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.

Synthesis of 4,4'-dimethyl Benzophenone: To a 500 mL three-necked flask equipped with a magnetic stirrer, a dropping funnel, a condenser upper with a CaCl₂ drying tube linked to a gas absorber was added anhydrous aluminium chloride (75 g, 0.55 mol), toluene (150 mL). Then stirring to mixture uniform, 4-methylbenzoyl chloride (77.3 g, 0.5 mol) was dropped from the dropping funnel over a period of 1 h maintaining temperature between -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 gas absorber). The reaction mixture was then slowly poured in to a mixture of crushed ice (2 Kg) and conc. HCl (900 mL) maintaining temperature between 0 to 10 °C. The products were extracted into ethyl acetate (1000 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 give 4,4'-dimethyl benzophenone as a solid.

(80.4 g, 52%): mp 92.7-93.4 °C. ¹H NMR (CDCl₃, 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): 3035, 2919, 2855, 1924, 1650, 1605, 1558, 1446, 1406, 1314, 1279, 1177, 1148, 1112, 1041, 929, 825, 750. MS (EI): *m/z* 210, 195, 119, 91, 65. Anal. Calcd for C₁₅H₁₄O: C, 85.68%; H, 6.71%. Found: C, 85.91%; H, 6.74%.

Synthesis of 4,4'-bis(bromomethyl) diphenyl Ketone: A mixture of 4,4'-dimethyl benzophenone (50 g 0.24 mol), N-bromosuccinimide (NBS, 85 g, 0.48 mol) and dry CCl₄ (400 mL) was stirred and refluxed under the light of two "IR 275 W" lamps until the starting material was completely transformed (*ca.* 1-3 h). The reaction mixture was cooled to room temperature, succinimide was filtered off and the solvent was removed on a rotary evaporator to give crude product. The crude product was recrystallized from ethanol to afford 4,4'-bis(bromomethyl) diphenyl ketone.

(81.9 g, 72%): mp 126-128 °C. ¹H NMR (CDCl₃, 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. MS (EI): *m/z* 367, 289, 287, 180, 118, 104, 90, 89, 63, 39. Anal. Calcd for C₁₅H₁₂Br₂O: C, 48.95%; H, 3.29%. Found: C, 49.13%; H, 3.37%.

Synthesis of 4,4'-bis(azidomethyl) diphenyl Ketone: To a 500 mL single necked flask equipped with a reflux condenser and a magnetic stirrer were added 4,4'-bis(bromomethyl) diphenyl ketone (73.6 g, 0.20 mol) and NaN₃ (26 g, 0.40 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 with and extracted with ether (3 mL × 100 mL). The combined organic layer was washed with saturated brine solution (100 mL), dried and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (10:1) as eluent to give 4,4'-bis(azidomethyl) diphenyl ketone.

(5.3 g, 90%): mp 75.9-76.1 °C. ¹H NMR (CDCl₃, 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 C₁₅H₁₂N₆O: C, 61.64%; H, 4.14%; N, 28.75%. Found: C, 61.94%; H, 4.24%; N, 27.27%.

Synthesis of Bisethynyl Compounds 26a-e Containing Arylene Ether Units.

Compounds **Ia-e** were prepared according to the ref. 7.

Synthesis of Polymer IIa-e: CuSO₄·5H₂O (7 mg, 5 mol %) and sodium ascorbate (12 mg, 10 mol %) dissolved in H₂O (10 mL) were added dropwise to a solution of bisethynyl compounds (0.50 mmol) and 4,4'-bis(azidomethyl) diphenyl ketone (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 H₂O (20 mL) and concentrated ammonia (5 mL) for another 1 h. The mixture was filtered and the resulting filter cake was washed with H₂O (3 mL × 20 mL). 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 **IIa-e** were obtained as pale yellow solids, respectively.

IIa: 66% yield. ¹H NMR (DMSO-*d*₆, 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. Mn = 18543, Mw = 27355, PI = 1.47.

IIb: 51% yield. ¹H NMR (DMSO-*d*₆, 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. Mn = 17851, Mw = 27213, PI = 1.52.

IIc: 70% yield. ¹H NMR (DMSO-*d*₆, 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. Mn = 22165, Mw = 24232, PI = 1.09.

IId: 65% yield. ¹H NMR (DMSO-*d*₆, 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. Mn = 19190, Mw = 26988, PI = 1.41.

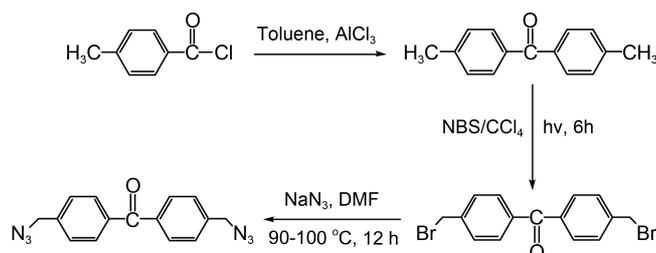
IIe: 62% yield. ¹H NMR (DMSO-*d*₆, 400 MHz, ppm) δ 8.35 (2H, s), 7.85 (4H, br), 7.76 (4H, br), 7.57 (4H, br), 7.22 (4H, br), 5.72 (2H, br), 5.23 (4H, br). IR (KBr, cm⁻¹): ν 3133, 3076, 2931, 2872, 1650, 1598, 1569, 1498, 1460, 1415, 1310, 1285, 1255, 1164, 1148, 1110, 1047, 1028, 947, 828, 727. Mn = 15580, Mw = 21806, PI = 1.40.

Results and Discussion

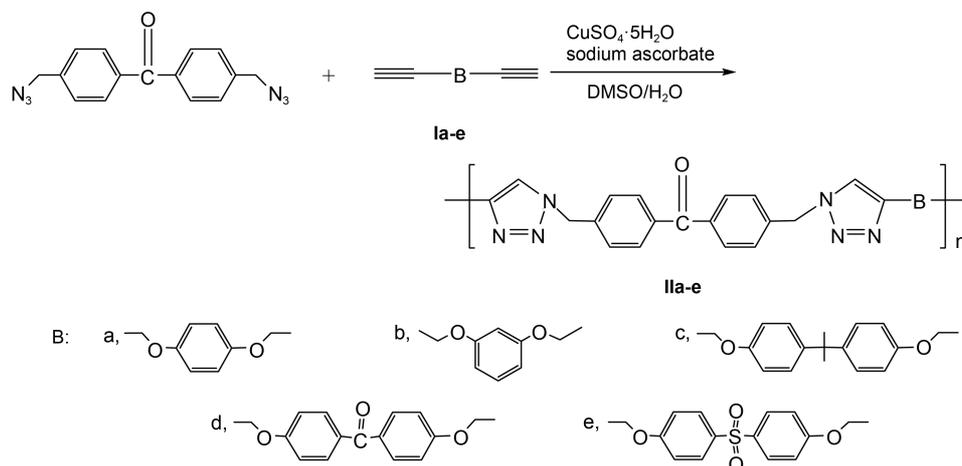
Synthesis and Characterization of Polymers. The polymers containing triazole unites **IIa-e** were obtained from the click reactions of monomers 4,4'-bis(azidomethyl) diphenyl ketone and **6a-f** respectively (Scheme 1 and 2). Click reactions were carried out in a 3:2 solvent ratio of DMSO to H₂O using 5 mol % CuSO₄·5H₂O with 10 mol% sodium ascorbate as the in situ reducing agent to generate the active Cu(I) species.⁸ The reaction temperature played key role in the formation of the polymers. It was found that the polymers with reasonable molecular weight were obtained when the click reactions were carried out at 45 °C.

Properties of Polymers.

Solubility of Polymers: The solubility of polymers **IIa-e** in common organic solvent was determined quantitatively by dissolving 5.0 mg of solid polymers in 1.0 mL of solvents (Table 1). It can be seen that solubility of these polymers is poor in solvents listed in Table 1 at room temperature. When



Scheme 1. Synthesis of 4,4'-bis(azidomethyl) diphenyl ketone compound.



Scheme 2. Synthesis of polymer **IIa-e**.

Table 1. Solubility of polymers

Polymers	DMF	NMP	DMAc	DMSO	MeOH	THF	Acetone	Toluene
IIa	+	+	+	+	-	-	-	-
IIb	+	+	+	+	-	-	-	-
IIc	+	+	+	+	-	-	-	-
IIId	+	+	+	+	-	-	-	-
IIe	+	+	+	+	-	-	-	-

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

heating, these polymers all show good solubility in highly polar solvents such as DMF, NMP, DMAc and DMSO, while they can not dissolve in MeOH, THF, Acetone, Toluene. All these polymers possess film forming ability. The polymer solutions (8%) in polar solvents with LiCl were processed into thin films by casting onto glass plates. The free-standing films having a thickness in the range of tens of micrometers were flexible, tough, and maintained their integrity after repeated bendings.

Molecular Weights and their Distributions of Polymers:

The corresponding data of GPC analysis in DMF for polymers **IIa-e** were listed in Table 2. The data show that the polymerization between 4,4'-bis(azidomethyl) diphenyl ketone and bisethynyl compounds *via* click chemistry produced polymers **IIa-e** with fairly good molecular weights and the distributions. The number average molecular weights of them are around 20000 and the distributions range from 1.4 to 1.5 with the exception of polymer **IIc** which distribution is narrower (1.09). The reason for the difference is

Table 2. Molecular weights and their distributions of polymers **IIa-e** using GPC

Polymers	Mn ^a	Mw ^a	(Mw/Mn) ^a
IIa	18543	27355	1.47
IIb	17851	27213	1.52
IIc	22165	24232	1.09
IIId	19190	26988	1.41
IIe	15580	21806	1.40

^aPC in DMF vs. polystyrene at 35 °C.

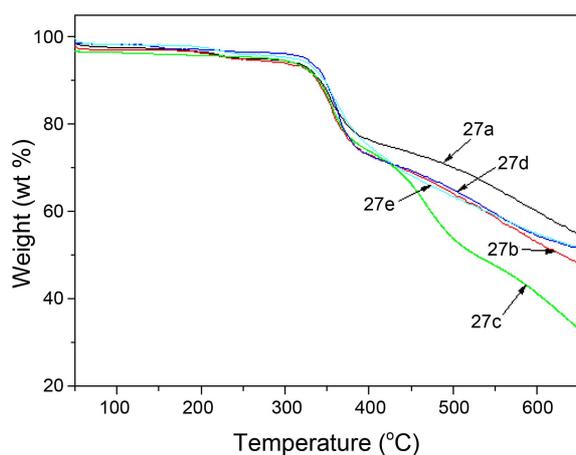


Figure 1. TG curves of polymers **IIa-e**.

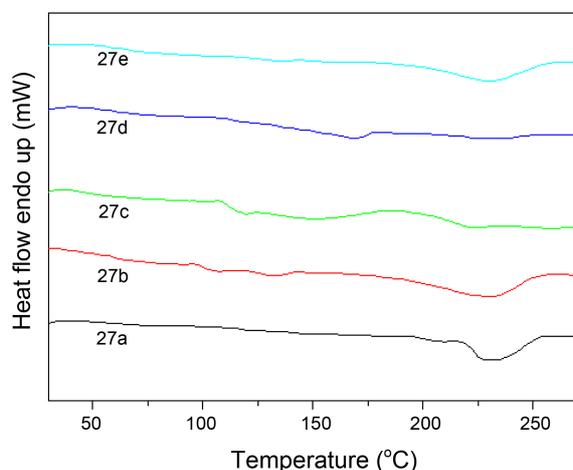


Figure 2. DSC curves of polymers **IIa-e**.

that **IIa**, **IIb**, **IId** and **IIe** contain more small molecular polymers with azido than **IIc**. All polydispersities of polymers are less than 2 which indicated that the click chemistry is a efficient way for polymerization of block polymers.

Thermal Properties of Polymers: Thermal stability of the polymers **IIa-e** was determined by means of thermogravimetric analysis (TGA) (Fig. 1) and differential scanning calorimetry (Fig. 2). The resulting data are listed in Table 3. The polymers **IIa-e** started to decompose at about 330 °C which probably attribute to breakage of aromatic ether in molecular chain. There were the second stage of weight loss at 363-377 °C. It was seen from Figure 1 that rate of weight loss of **IIa** was larger 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 determined from the DSC curves and listed in Table 3. T_g values of polymers **IIa-e** were found to be in the increasing order of **IIb** < **IIa** < **IIc** \approx **IId** < **IIe**. T_g value of **IIe** is the highest due to the rigid sulfone groups in the polymer backbone which hinder molecular rotation while that of **IIb** was the lowest owing to the meta-phenylene group which increase flexibility of molecular chain. The curves of DSC (Fig. 2) also show that

Table 3. Data of DSC and TGA of polymer **IIa-e**

Polymers	T_g (°C) ^b	T_d (°C) ^b	T_s (°C) ^b	R_w (%) ^c
IIa	104	330	374	55.6
IIb	96	326	363	47.8
IIc	110	325	365	33.2
IId	112	332	368	51.3
IIe	142	334	377	51.3

^bMeasured at 10 °C/min in N₂; T_d : onset decomposition temperature; T_s : 20% weight loss at the second stage. ^cResidual weight retention at 650 °C.

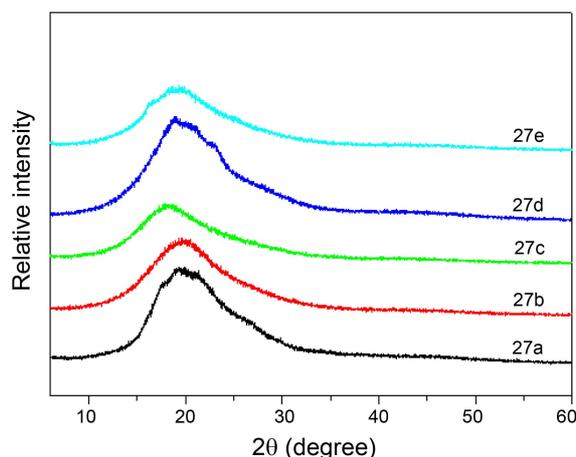


Figure 3. X-ray diffractogram curves of polymer **IIa-e**.

that all polymers are amorphous, which are required to be confirmed by X-ray of diffraction studies of these polymers.

X-ray Diffraction Studies of Polymer **IIa-e:** The X-ray diffractogram curves of polymer **IIa-e** were shown in Figure 3. X-ray diffractograms of all polymers exhibit broad halo at about $2\theta \approx 15-25^\circ$ in the wide angle region indicating that the polymers **IIa-e** are amorphous in nature which is corresponding to the DSC analysis.

Conclusions

A novel monomer 4,4'-bis(azidomethyl) diphenyl ketone was prepared. The click chemistry of 4,4'-bis(azidomethyl) diphenyl ketone and bisethynyl compounds **Ia-e** provided a novel class of linear aromatic ketone polymers containing triazole units. The resulting polymers mostly are amorphous and have good solubility in most strong polar solvents and thermal stability.

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