

Soluble and Cross-linkable Poly(phthalazinone ether ketone)s with Pendant Terminal Ethynyl Group: Synthesis, Characterization, and Click Modification

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Abstract: New poly(arylene ether ketone)s with pendent terminal ethynyl groups (PPHEKs) were synthesized by the aromatic nucleophilic substitution (S_NAr) polycondensation reaction of a new bisphenol monomer, 2-(3-ethynylphenyl) hydroquinone(EPH), with 4-(4'-hydroxyphenyl)phthalazin-1(2*H*)-one (DHPZ) and 4,4'-bis(4-fluorophenyl) ketone, followed by click modified reaction with 1-adizopryene. FT-IR and NMR data of model compound indicated that the terminal ethynyl group was stable to S_NAr reaction conditions, thus allowing the synthesis of the desired PPHEKs. The PPHEKs obtained with the glass-transition temperature (T_g) in the range of 152 to 245 °C were amorphous, characterized by Wide-angle X-ray diffraction, and dissolved in organic solvent to cast into transparent and flexible films. Differential scanning calorimetry results indicated that the curing reaction of the terminal ethynyl groups of the copolymers took place upon heating to 250°C. The T_g s of cured PPHEKs were updated to about 260°C. They also exhibited excellent thermal stability with 5% weight loss temperatures ranging from 482 to 527 °C. The selected PPHEK8020 was subsequently functionalized by pyrene through click chemical reaction. Its dilute chloroform solution exhibited a red-shifted emission profile.

Key words: poly(arylene ether ketone)s ethynyl group click modification

1. Introduction

Poly(arylene ether ketone)s (PAEKs) are a class of engineering thermoplastics and possess high mechanical properties, excellent thermooxidative stability and chemical resistance, making them find a wide variety of applications in automobile, aerospace, electronic fields[1]. The introduction of functional groups into the PAEK chains provides the feasible method to tailor the chemical and physical properties to expand their applications in specific fields. Up to now, a wide range of functional groups, including sulfonic acid [2,3], carboxyl [4,5], chloromethyl [6], amino [7], hydroxyl [8], iodo [9], cyano [10,11] and so on, have been incorporated into the PAEK chains. Maryam et al. reported that pendant sulfonic acid groups in poly(arylene ether ketone)s as proton charge carriers supplied appropriate proton conductivity for the fuel cell [3]. PAEKs containing carboxylic acid groups, prepared by Guiver et al., reacted with poly(vinyl alcohol) (PVA) to prepare cross-linked proton-exchange membrane [4]. Lin prepared side-chain phenol-functionalized polymer through a facile post-functionalization method. The phenol group of the polymer as cure sites reacted with epoxy resins to prepare flame-retardant and high-performance thermosets [8]. Zhang et al. introduced dicyanophenyl group onto the side-chain of PAEKs, and then converted them to phthalocyanine via the reaction of dicyano groups with excessive amount 1,2-dicyanobenzene and metal salt in quinoline. Those phthalocyanine polymers could be potential candidates as electroluminescent and electron transport material [11]. To the best of our knowledge, PAEKs with pendent terminal ethynyl groups

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has been hardly reported previously.

Ethynyl groups can offer a combination of properties, not available in other functional groups, such as long shelf life in air, low moisture absorption, low cross-linking temperature and excellent mechanical properties for the cured material [12,13,14]. In addition, terminal ethynyl groups are able to react with aryl or vinyl halides through a copper or palladium-mediated Sonogashira reaction, which is widely employed in synthesizing natural product, or building macrocyclic compounds and supramolecular chemicals [15,16]. However, most of the acetylenes' coupling reactions require careful selection of reaction condition and reagent to avoid undesirable side reactions such as Hay coupling product (homocoupling of terminal acetylenes, also called Glaser coupling) [17]. Hence, alternative mild methods to introduce them into PAEKs are highly desired.

Recently, click chemistry, the copper(I)-catalyzed Huisgen's azide-alkyne (3+2) cycloaddition reaction, has attracted more attention [18]. This type of reaction, characterized by very high yield, mild and simple reaction condition, oxygen and water tolerance and simple work-up of products, is highly chemoselective in the formation of the desired 1,4-disubstituted 1,2,3-triazole even in the presence of a large variety of functional groups. This methodology has been applied widely in organic chemistry [19], supramolecular chemistry [20], drug discovery [21], bioconjugations and materials science [22].

Therefore, it is an effective method to broaden the scope of application of PAEKs containing terminal ethynyl group through click chemistry. Herein we focused on the synthesis of a new bisphenol containing pendent terminal ethynyl group via a three-step synthesis procedure. Based on this monomer, a series of PAEKs were designed and synthesized. Subsequently, pyrene group was deliberately selected as the functional group and then introduced into the resulting PAEKs through a facile route of the copper-catalyzed Huisgen 1,3-dipolar click reaction.

2. Experimental section

2.1. Material

Benzoquinone was purchased from lideshi chemical company and sublimed at 90 °C in vacuum. 3-Aminophenylacetylene (Nanjing qike chemical reagent) was distilled under reduced pressure. 4-(4'-Hydroxyphenyl)phthalazin-1(2H)-one (DHPZ) was gifted by Dalian Polymer New Material Co. Ltd., PR China and used as received. 4,4'-Bis(4-fluorophenyl)ketone (DFK) was purified by recrystallization from ethanol. K_2CO_3 was ground and dried in vacuo at 100 °C for 24 h prior to use. 1-Azidopyrene was synthesized via the reported route previously [23]. NMP was stirred in the presence of CaH_2 overnight and then distilled under nitrogen. Other commercially available reagents were used without further purification.

2.2. General measurement

Fourier-transform infrared (FTIR) spectra of the compounds were obtained with a Thermo Nicolet Nexus 470 Fourier transform infrared spectrometer using a KBr pellet or film. Nuclear magnetic resonance (NMR) spectra of synthesized compounds were recorded on Bruker Fourier Transform AVANCE400 spectrometers (400 MHz for 1H and 100 MHz for ^{13}C). Chemical shift of NMR was reported in part per million (ppm) using tetramethylsilane as an internal reference. Splitting patterns designated as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublets of doublet), m (multiplet), and br (broaden). Intrinsic viscosity data were obtained in *N*-methyl-2-pyrrolidinone (NMP) with a Ubbelohde viscosity meter at 25 °C. Gel permeation chromatography (GPC) analysis was carried out on a PL GPC-50 instrument equipped with 5 μm PL gel Mixed C columns (heated to 40 °C) arranged in series with chloroform as eluent and a RI detector. Thermogravimetric analysis

(TGA) and differential scanning calorimetry (DSC) were performed on a TA 2000 thermal analyzer system. T_g s of the polymers were obtained with DSC instrument at a heating rate of 10°C/min in N₂. TGA measurements were conducted at a heating rate of 20°C/min in N₂. Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDITOF/MS) analyses were performed on a Micromass GC-TOF CA 156 MALDI-TOF/MS. Absorption spectra were recorded on a Perkin-Elmer Lambda25 UV-Visible spectrophotometer. Fluorescence measurements were carried out with a Hitachi F-7000 spectrophotometer. Fluorescent quantum yield was determined using solutions in chloroform and calculated by comparing emission with that of a standard solution of the quinine sulphate (in 0.1 mol H₂SO₄ solution, Φ_F =55%) at room temperature.

2.3 Synthesis of 2-(3-ethynylphenyl)-1,4-benzoquinone (1)

In a three-necked round-bottomed flask equipped with a mechanical stirrer, a condenser and a dropping funnel, 3-aminophenylacetylene (18.7 g, 0.16 mol) was slowly dropped into 160 mL solution of 9% hydrochloric acid. The compound was then diazotized at 0–5°C using 11 g of sodium nitrite in 24 mL of water. This mixture was stirred for at least 1 h before the reaction mixture was filtered to obtain a clear solution.

To 200 mL of H₂O were added sodium acetate anhydrous (24.6 g, 0.3 mol) and 1,4-benzoquinone (19.2 g, 0.17 mol), followed by the addition of the diazonium. Then the resulting solution was stirred at 0–10°C for about 12 h. The precipitate was collected by filtration, washed thoroughly with water, and dried at room temperature in a vacuum oven for 24 h. The product was recrystallized from ethylene glycol monomethyl ether to give yellow crystals. Yield: 80%. Mass spectrum (m/e): 208.7; IR (KBr, ν , cm⁻¹): 3253, 3079, 2108, 1651, 1597, 1586, 1482, 1290, 1090, 914, 896; ¹H NMR (400MHz, CDCl₃, δ , ppm): 7.61 (s, 1H), 7.59-7.57 (d, J=7.6 Hz, 1H), 7.47-7.45 (d, J=8 Hz, 1H), 7.43-7.39 (t, J=6.4 Hz, 1H), 6.87 (t, 3H), 3.12 (s, 1H); ¹³C NMR (100 MHz, CDCl₃, δ , ppm): 187.3, 186.2, 145.0, 137.0, 136.3, 133.04, 132.8, 132.7, 129.5, 128.5, 122.7, 82.7, 78.15.

2.4 Synthesis of 2-(3-ethynylphenyl)-1,4-hydroquinone (2)

A solution of sodium dithionite (52.2 g, 0.3 mol) in 75 mL water was added to a solution of (1) (20.8 g, 0.1 mol) in 200 mL methanol and water (V=1/1). The mixture was vigorously stirred for 4 h. The aqueous layers obtained were extracted with ethyl ether (100 mL × 3). The combined organic layers were washed with the solution of saturated NaCl (50 mL × 2) and dried over anhydrous sodium sulfate. The solvent was removed by reduce pressure, and residue was recrystallized in benzene and dried under vacuum for 24 h at 40°C. Yield: 45%. Mass spectrum (m/e): 210.0688; IR (KBR, ν , cm⁻¹): 3327, 3278, 3065, 2105, 1611, 1594, 1573, 1519, 1453, 1406, 1234, 1200, 1118, 913, 865; ¹H NMR (400MHz, CDCl₃, δ , ppm): 8.88 (s, 1H), 8.80 (s, 1H), 7.59 (s, 1H), 7.52 (tt, J=6Hz, 1H), 7.40 (dd, J=7.2Hz, 2H), 6.75 (d, J=8.8Hz, 1H), 6.65 (d, J=3.2Hz, 2H), 6.59 (dd, J=2.8Hz, 1H); ¹³C-NMR (100MHz, CDCl₃, δ , ppm): 150.6, 147.2, 139.6, 132.6, 130.2, 130.1, 128.9, 127.3, 121.8, 117.4, 116.7, 115.9, 84.2, 80.9.

2.5 Model reaction of 2 and 4-fluoroacetophenone (3)

A 50 mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet, Deane-Stark trap, and condenser was charged with 2 (1.0504 g, 5 mmol), 4-fluoroacetophenone (1.6566 g, 12 mmol), K₂CO₃ (0.7865 g, 5.691 mmol), 5 mL of NMP, and 15 mL of toluene. The reaction mixture was heated to 135°C by vigorously stirring until no more water was formed by azeotropic distillation. Toluene was then removed slowly as the reaction mixture was heated to 160 °C. The reaction temperature was maintained at 160°C for 6 h. The product was precipitated into 300 mL water. The aqueous layers obtained was extracted with ether (100 mL × 3), and the combined organic layers were washed with

aqueous solution of saturated NaCl (50 mL × 2) and dried over NaSO₄. The solvent was filtered and removed by reduce pressure. Further purification was carried out by silica gel column chromatography using petroleum ether / ethyl acetate (v/v= 6/4, R_f=0.63) as an eluent to give light yellow solid (95.4% yield). Mass spectrum (m/e): Cal: 446.1518, Found: 446.1521; IR (KBr, ν, cm⁻¹): 3293, 3054, 3041, 2102, 1674, 1599, 1580, 1519, 1453, 1494, 1416, 1273, 1223, 1189, 959, 866; ¹H NMR (400MHz, CDCl₃, δ, ppm): 8.03 (d, J=7.2 Hz, 2H), 7.93 (d, J=8Hz, 2H), 7.65 (s, 1H), 7.59 (d, J=8Hz, 1H), 7.42 (d, J=8Hz, 1H), 7.38 (d, J=8Hz, 1H), 7.34 (d, J=4Hz, 1H), 7.30 (d, J=8Hz, 1H), 7.26 (dd, J=8Hz, 1H), 7.19 (d, J=8Hz, 2H), 6.98 (d, J=8Hz, 2H), 3.65 (s, 1H), 2.56 (s, 3H), 2.50 (s, 3H); ¹³C NMR (100MHz, CDCl₃, δ, ppm): 196.65, 196.63, 161.88, 161.66, 152.68, 148.36, 136.53, 135.24, 132.52, 132.29, 131.76, 131.54, 130.74, 130.58, 129.38, 128.35, 123.24, 122.51, 122.33, 120.74, 117.37, 116.44, 83.21, 77.56, 26.48, 26.41.

2.6 Synthesis of poly(phthalazinone ether ketone)s containing pendant terminated-ethynyl groups (PPHEKs)

Poly(phthalazinone ether ketone)s containing pendant terminated-ethynyl groups were synthesized via a nucleophilic aromatic substitution (S_NAr). The numbers in the sample name indicated the molar percentages of compound 2 relative to DHPZ. For example, the PPHEK containing 80 mol% phthalazinone moiety (relative to the total bisphenols in the polycondensation reaction) was denoted as PPHEK8020. All PPHEKs were prepared in the similar procedures. Therefore, only the preparation of PPHEK8020 (4b) was depicted as a typical example. A 50 mL three-necked round-bottomed flask was equipped with a mechanical stirrer, a nitrogen gas inlet tube and a Dean–Stark trap. The flask was charged with a mixture of DHPZ (1.1427 g, 4.8 mmol), 2 (0.2521 g, 1.2 mmol), DFK(1.3080 g, 6 mmol) and K₂CO₃ (0.9936 g, 7.2 mmol), and then rinsed with 5 mL NMP and 15 mL toluene. The mixture was stirred and heated to the reflux temperature for 3 h to dehydrate the system. The temperature was raised to 160 °C and the reaction mixture was stirred for 8 h. The polymer was slowly poured into a solution of sufficient boiling water containing a few drops of concentrated hydrochloric acid under vigorous stirring. The resulting precipitate was filtrated and washed with hot water twice to give white precipitate. The obtained polymer was Soxhlet-extracted with methanol for 48 h. The product was dried at 60 °C under vacuum for 48 h. The yield of 4b was 95 wt%.

Selected data of 4b: IR (film, ν, cm⁻¹): 3297, 3077, 3012, 1667, 1596, 1499, 1413, 1327.2, 1309, 1280, 1242, 1166, 1133, 929, 873, 755; ¹H NMR (400MHz, CDCl₃, δ, ppm): 8.63 (s, 1H), 7.92-7.70 (m, 16H), 7.61(s, 1H), 7.47 (s, 1H), 7.40 (s, 1H), 7.26-6.92 (m, 12H), 3.05 (s, 1H); ¹³C NMR (100MHz, CDCl₃, δ, ppm): 194.40, 194.10, 161.65, 161.44, 160.84, 160.59, 158.90, 157.03, 152.71, 148.45, 147.49, 145.26, 145.08, 136.61, 135.22, 133.62, 132.91, 132.85, 132.59, 132.41, 132.08, 131.55, 131.38, 130.86, 130.68, 130.45, 129.48, 128.95, 128.41, 128.02, 126.89, 125.32, 123.27, 122.57, 122.33, 120.82, 117.98, 117.24, 116.39, 83.26, 77.63.

2.7 Functional modification of PPHEK via click reaction (5).

Into a 25mL one-neck round-bottomed flask equipped with a stirring bar under air atmosphere, a solution of 0.06g (0.25 mmol) of 1-azidopyrene and 0.3g (0.012 mmol) 4b in 10 mL of NMP, CuSO₄ (0.4mmol), sodium ascorbate (0.45 mmol) was added with stirring. The resulting mixture was heated at 80 °C for 8 h to drive the reaction to completion. Then the mixture was precipitated into ethanol. The resulting polymer was collected and dried. The dried polymers dissolved in CHCl₃ and the solution was passed through a column of neutral alumina to remove metal salt before poured into ethanol. The polymer 5 was filtered and dried in vacuum at 60 °C for 24 h.

IR (film, ν , cm^{-1}): 3068, 3009, 1666, 1596, 1499, 1414, 1326, 1308, 1277, 1241, 1166, 929, 846, 754; ^1H NMR (400 MHz, CDCl_3 , δ , ppm): 8.63 (s, 1H), 8.18 (s, 1H), 8.04 (s, 1H), 7.92-7.70 (m, 18H), 7.59-7.37 (m, 4H), 7.26-6.98 (m, 15H); ^{13}C NMR (100 MHz, CDCl_3 , δ , ppm): 194.41, 194.11, 160.79, 160.61, 158.88, 156.97, 152.82, 148.40, 147.45, 145.26, 145.07, 144.99, 136.18, 136.08, 136.04, 133.56, 132.83, 132.57, 132.39, 132.35, 132.26, 132.21, 132.04, 131.37, 131.27, 131.04, 130.84, 130.64, 130.42, 130.26, 129.77, 129.05, 128.89, 127.98, 126.86, 126.74, 126.46, 126.39, 126.12, 125.30, 125.07, 124.98, 124.75, 124.07, 123.55, 123.26, 122.79, 120.98, 120.78, 119.76, 117.97, 117.80, 117.28, 116.28, 115.61, 115.39.

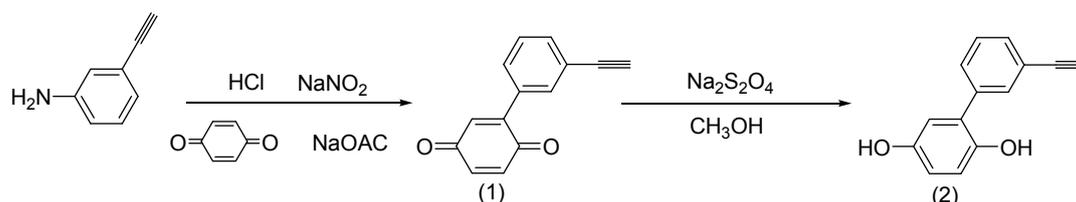
2.8 Preparation of PPHEK films

The polymer 4a-4d and polymer 5 samples were dissolved in NMP at a concentration of 0.1 g/mL. The solution was cast on a glass plate. The wet films were dried at 60 °C to remove most of the solvent. The semidried film was further dried in vacuo at 150 °C for 48 h. The obtained films were about 30–50 μm in thickness and were used for X-ray diffraction measurements, solubility tests and thermal analyses.

3 Results and Discussion

3.1 Synthesis and characterization of 2-(3-ethynylphenyl)-1,4-hydroquinone

The synthesis of 2-(3-ethynylphenyl)-1,4-hydroquinone (named as monomer 2) was conducted according to the synthetic route shown in Scheme 1. 3-Aminophenyl acetylene was firstly employed in the traditional diazotization reaction in the presence of sodium acetate at 0-5 °C for 12 h, subsequently by reduction with sodium dithionite. The structure of the resulting bisphenol monomer was confirmed by convenient organic characterization prior to polymerization reaction, including FT IR, ^1H and ^{13}C NMR spectroscopy and mass spectrometry.



Scheme 1. Synthetic route of the target bisphenol monomer 2

In the FT-IR spectra, as shown Fig 1, 2-(3-ethynylphenyl)-1,4-benzoquinone (1) showed an absorption at around 1651 cm^{-1} attributed to the symmetric stretching vibration of carbonyl groups in quinone and an absorption at 3253 cm^{-1} owing to stretching vibration of ethynyl group. After reduction, carbonyl groups characteristic absorption in compound 1 disappeared, and meanwhile hydroxyl group at around 3327 cm^{-1} in monomer 2 was found. The characteristic peak of ethynyl group still existed at 3278 cm^{-1} during the reaction, implying reduction condition of carbonyl groups had no influence on alkyne triple bond.

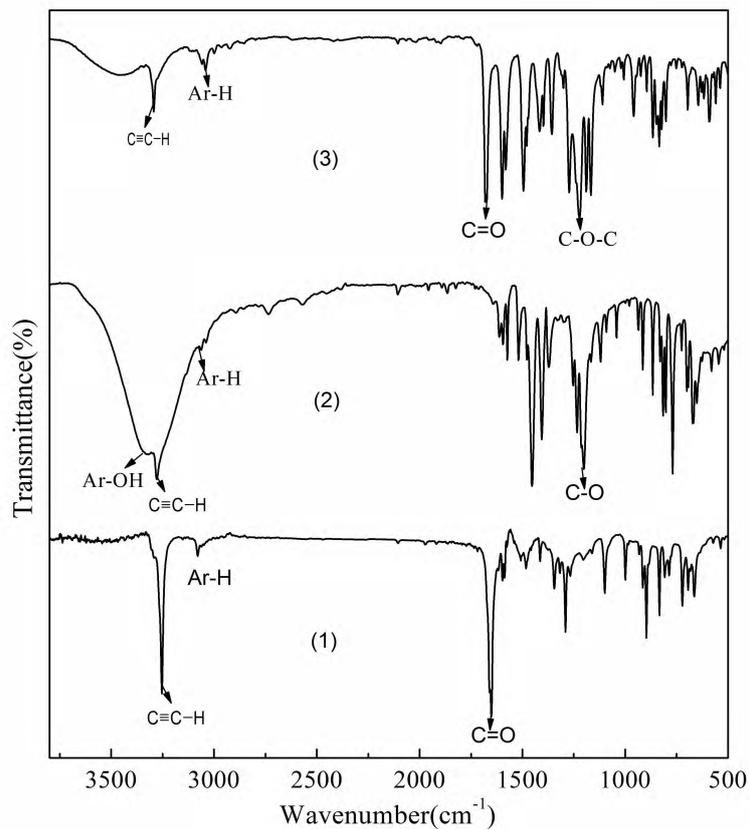


Fig 1 FT-IR spectra of compound 1, monomer 2 and model compound 3

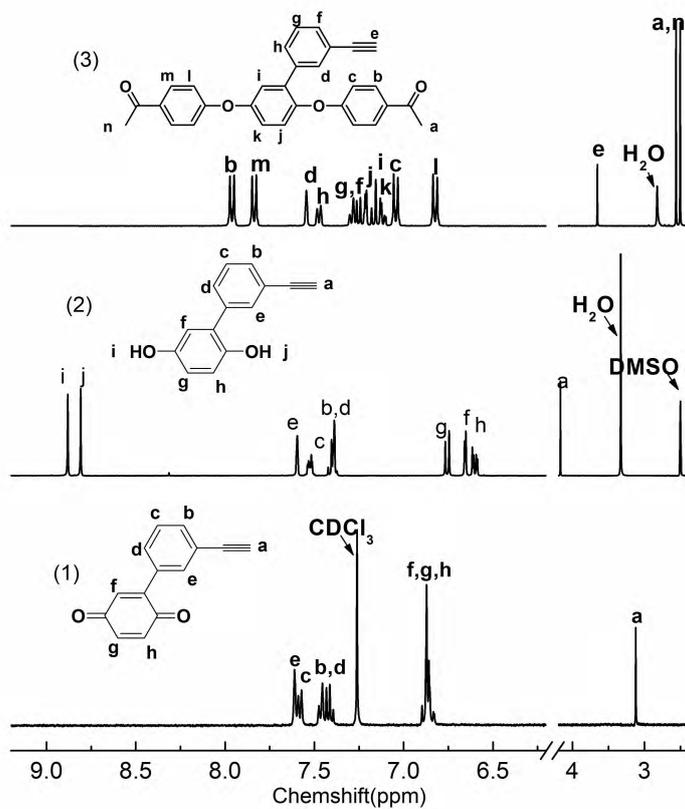
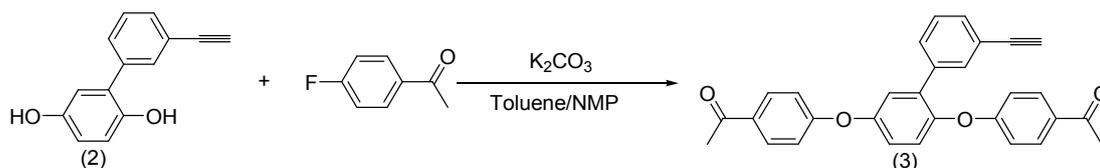


Fig 2 ^1H NMR spectra of compound 1, monomer 2 and model compound 3

The ^1H NMR spectra of compound 1 and monomer 2 were shown in Fig. 2, respectively. The signals at 8.88 and 8.80 ppm were assigned to the hydrogen atoms of hydroxyl group in the monomer 2, which could not be observed in the spectrum of the corresponding quinone 1. The peak at around 3.12 ppm in the compound 1 were assigned to the hydrogen atoms of ethynyl group, and this peak transferred to 4.17 ppm due to inductive effect of hydroxyl group in the monomer 2 after reduction. ^{13}C NMR spectra of the compound 1 and monomer 2 all exhibited 13 peaks, and two signals in the 75–85 ppm region were assigned to carbon atoms of ethynyl group.

3.2 Model reaction

A model compound 2-(3-ethynylphenyl)-1,4-bis(*p*-acetyl phenoxy)benzene (3) was synthesized by the typical nucleophilic displacement reaction to investigate the influence of this reaction condition on the stability of terminated ethynyl group as well as the reactivity of monomer 2 (Scheme 2). Reaction of monomer 2 with two equivalents of *p*-fluorine acetophenone was carried out in the presence of K_2CO_3 as a base in NMP as a solvent at 20 w/v % of solid content. Toluene was used to allow azeotropic distillation of water formed as a byproduct during the incipient stage of the reaction. The reaction mixture was heated to 160°C. The whole reaction was monitored by thin-layer chromatography to confirm the completion of the reaction for about 4 hours. The desired compound 3 was obtained in 85% yield. The FT-IR spectroscopic (Fig.1) analyses of the model compound 3 displayed the successful formation of the ether linkages without destroying terminal ethynyl group. Its ^1H -NMR spectrum also gave the same proof that the peaks of the aryl acetylene protons at 3.65 ppm still existed, as shown in Fig.2.

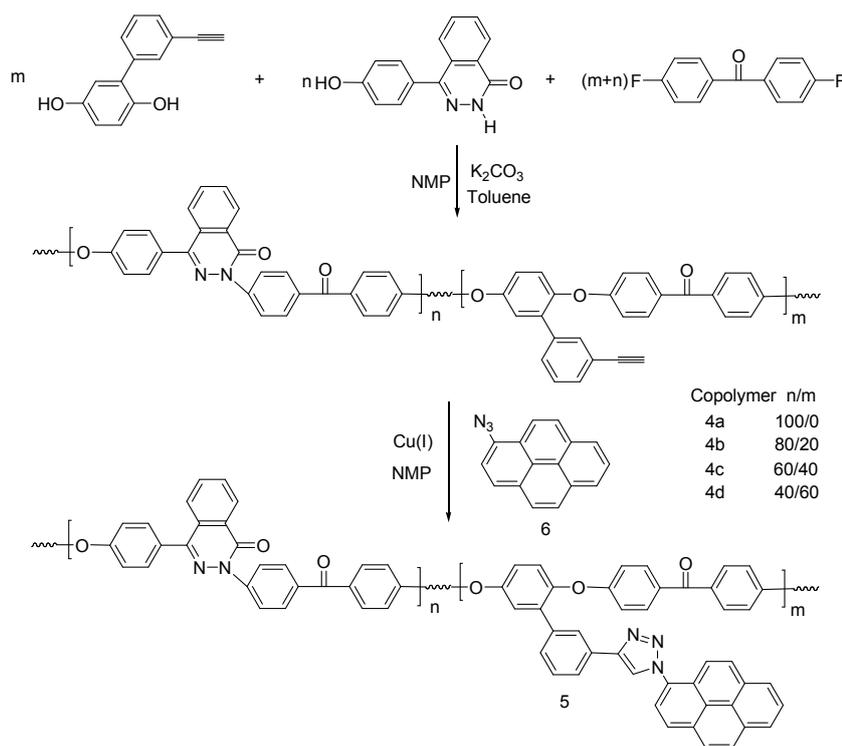


Scheme 2 Model reaction of monomer 2 and *p*-fluorine acetophenone

3.3 Synthesis and characterization of PPHEKs

Based on the above model reaction, the bisphenol monomer 2 was then designed to copolymerize with different molar percentage of 4-(4-hydroxyphenyl)phthalazin-1 (*2H*)-one (DHPZ) and 4,4'-difluorobenzophenone (DFK) to afford poly(phthalazinone ether ketone)s containing pendant terminal ethynyl group (PPHEKs) via traditional $\text{S}_{\text{N}}\text{Ar}$ reaction (Scheme 3). The polycondensation reactions were carried out at 160 °C for 8 h. The white rod-like polymers were obtained by precipitating into enough hot water containing a few drops of concentrated hydrochloric acid in essentially quantitative yields (exceeding 94%). PPHEKs had inherent viscosities (η_{inh}) in the range of 0.87–1.23 dL/g. From the table 1, it could be seen that the number average molecular weights of PPHEKs were over 1.6×10^4 , and their polydispersities values ranged from 1.96 to 2.65. According to the GPC results in Tab. 1, the molecular weight and polydispersities values of pyrene-modified PPHEK8020, named as polymer 5, did not significantly change in comparison with the primal polymer during the click reaction process.

The structures of the polymers were confirmed by FTIR, ^1H NMR, and ^{13}C NMR spectroscopy. As shown in Fig.3, the absorption occurring at around 3297 cm^{-1} was characteristic peak of the ethynyl group, suggesting the successful introduction of ethynyl unit into the polymer side chain. After treatment with pyrene using CuSO_4 and sodium ascorbate as catalyst in NMP, disappearance of this absorption peak indicated the complete conversion from ethynyl group to triazole ring.



Scheme 3. Synthesis of PPHEKs and then their click modification

Table 1 Synthetic data of PPHEKs

PPHEKS	Composition DHPZ/ monomer 2	M_n^a	PDI ^b	η_{inh}^c	yield
4a	100/0	21000	1.96	1.23	96
4b	80/20	20000	2.17	1.16	96
4c	60/40	16000	2.23	0.87	94
4d	40/60	19000	2.06	0.98	95
5	80/20	21000	2.65	1.14	96

^a Determined by GPC using chloroform as eluting solvent at 40 °C with polystyrene standards.

^b Measured in NMP at 25 °C at a concentration of 0.5g/dL.

^c Polydispersity Index = M_w/M_n .

The chemical shift assignments of 4a, 4b and 5 were illustrated in Fig. 4. The characteristic peaks shifting downfield at around 8.63 ppm, which could always be used as the reference signal to assign the other protons, was diagnostic peak of the typical H-1 signal of phthalazinone moiety. Compared with 4a and 4b, a new peak of ethynyl group at about 3.05ppm in the figure of 4b, different from 4a, was observed. According to the integral area of this peak, the comonomer composition was determined by taking into account the ratios of the integrals of ethynyl group to the integrals of reference signal at around 8.63 ppm as disclosed in eq 1.

The molar percent of ethynyl group in the backbone of 4b was about 19.8%, which was in good agreement with the feed ratio, as estimated from ¹H NMR spectrum. Moreover, disappearance of this peak in pyrene-modified PPHEK spectrogram and the appearance of the characteristic aromatic peaks of the pyrene units in the range of 8.18–6.98 implied that pyrene was successfully incorporated into

the copolymer by click chemical reaction. The content of pyrene group grafted to PPHEK8020 could be also assessed from eq 2.

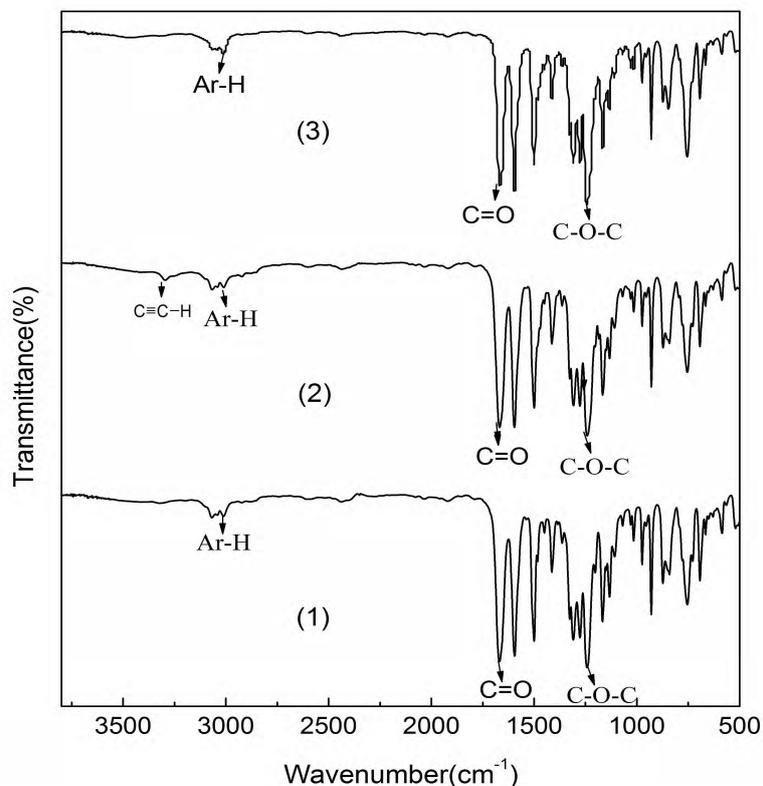


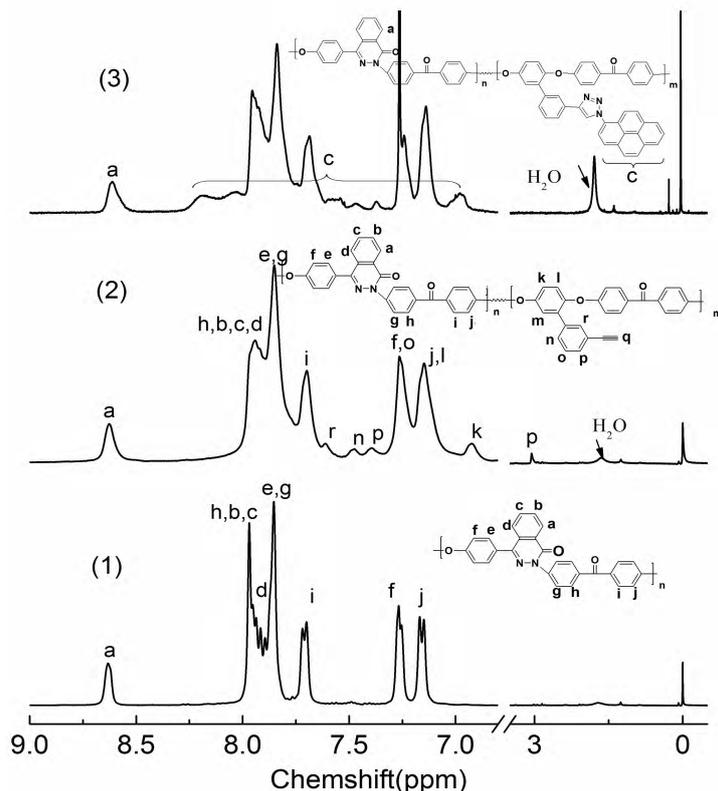
Fig 3 FT-IR spectra of 4a (1), 4b (2) and 5 (3)

Thus, 19.3% of pyrene group percentage was calculated, and the functional group conversion was then calculated according to the equation 3:

$$\text{Conversion (\%)} = \frac{\% \text{pyrene}}{\% \text{ethynyl group}} \times 100 \quad (3)$$

The conversion of ethynyl group was 97%, indicating that the azide-alkyne (3+2) cycloaddition reaction was efficient to incorporate illuminophore pyrene group into the poly(arylene ether ketone)s.

The ^{13}C NMR data of PPHEK8020 were also found to be in accordance with its chemical structures (see Section 2.6 and 2.7 for details). Assigned carbon peaks consisted of the proposed repeating unit structure and the presence of terminal ethynyl groups were identified by signals at 83.2 and 77.6 ppm. These characteristic bands in corresponding spectra correlated sufficiently well with the expected structure of the target substance.


 Fig 4 ^1H NMR spectra (CDCl_3) of 4a (1), 4b (2) and 5 (3)

3.4 Polymer solubility and thermal properties

The solubility of PPHEKs was summarized in Table 2. All copolymers were soluble in selected solvents such as NMP, chloroform and 1,1,2,2-tetrachloroethane at room temperature. However, they could hardly dissolve in other common organic solvents like THF, toluene and acetone, even at elevated temperatures. 4a and 4b were also soluble in dimethyl sulfoxide (DMSO), and *o*-dichlorobenzene (ODCB) at room temperature. The lower solubility of 4c than 4a and 4b was observed, presumably due to lower content of twisted non-coplanar phthalazinone segment resulting in decreasing the free volume between the polymer's chains. Thus solvent molecules hardly diffused into the copolymer chains. The polymer 5 was soluble in DMAc on heating because the introduction of bulk pendent pyrene unit into the backbone improved its solubility. Transparent, pale yellow and flexible films were prepared by casting from NMP solutions of the copolymers.

Table 2 Solubility of PPHEKs

PPHEKs	NMP	DMAc	DMF	DMSO	THF	CHCl ₃	TCE	ODCB	Toluene
						3			
4a	++	+ -	+ -	++	-	++	++	+	-
4b	++	+ -	+ -	++	-	++	++	+	-
4c	++	+ -	+ -	+	-	++	++	+	-
4d	++	+ -	+ -	+	-	+	++	+ -	-
5	++	+	-	-	-	++	++	+ -	-

Abbreviations: NMP (*N*-methyl pyrrolidone), DMAc (*N,N*-dimethylacetamide), DMF (*N,N*-dimethyl formamide), DMSO (dimethyl sulfoxide), THF (tetrahydrofuran), CHCl_3 (chloroform), TCE (1,1,2,2-tetrachloroethane), CB (chlorobenzene), ODCB (*o*-dichlorobenzene).

++: Soluble at room temperature, +: soluble on heating, + -: partially soluble, -: insoluble.

The thermal properties of the resulting copolymers were evaluated by a combination of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in nitrogen atmosphere with the data depicted in Table 3.

Table 3 Thermal analysis data of PPHEKs

PPHEKs	T_g^a (°C)		$T_{d5\%}^b$ (°C)		Cy ^c (%)	
	F.Scan	S.Scan	uncured	cured	uncured	cured
4a	244	-	491	-	65	-
4b	211	261	496	519	58	68
4c	185	264	487	511	61	67
4d	164	266	501	527	60	68
5	239	-	521	-	68	-

^a Glass transition temperature (T_g) tested by DSC at heating rate of 10°C/min in nitrogen atmosphere.

^b Temperature for 5% mass-loss in nitrogen determined by TGA at a heating rate of 20 °C/min in nitrogen atmosphere.

^c Char yield in nitrogen determined by TGA.

The temperature of 5% weight loss ($T_{d5\%}$), measured by TGA in nitrogen atmosphere at a heating rate of 20 °C/min, was used to describe the thermal stability of 4a, 4b, cured 4b and 5. They all demonstrated excellent thermal stability without significant weight loss near to 500 °C. Char yields of the resulting polymers in nitrogen atmosphere were in the range of 58%-70% at 800 °C. The $T_{d5\%}$ value of the cured 4b was slightly higher by about 20 °C than the uncured 4b. The $T_{d5\%}$ value of 5 was similar to that of the cured 4b, indicating that introducing pyrene unit into the polymer's side chain could also improve the thermal stability of the polymer.

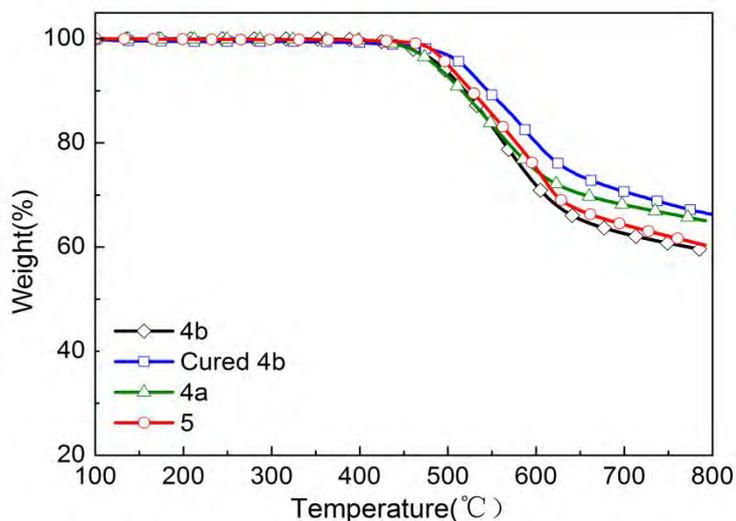


Fig 5. TGA curves of the polymer 4a, 4b, cured 4b and 5

DSC analysis was also performed to study the glass transition temperature of the copolymers at a heating rate of 10°C/min. The T_g values of the polymers were taken as the midpoint of the change in slope of the baseline in DSC curve. A single distinct T_g was found for every copolymer in the range of 153-265°C, depending on the content of phthalazone moiety in the main chain of the polymer, at the first scan in Table 3 and Fig. 6. Meanwhile, an intense exothermic peak in the DSC curve of every

copolymer, attributed to the thermal crosslinking reaction of the ethynyl group, in the range of 220–320 °C was observed. After cured, the T_g values of the cured copolymers (4b, 4c, 4d) increased to approximately 260 °C as the second scan in Fig.6. Moreover, the modified polymer 5 presented the higher T_g of 239 °C than 4b ($T_g=211$ °C), as shown in Table 3, most possibly due to the introduction of bulky pyrene unit into the side chain to prevent the rotation of the molecular chain of the polymer 5.

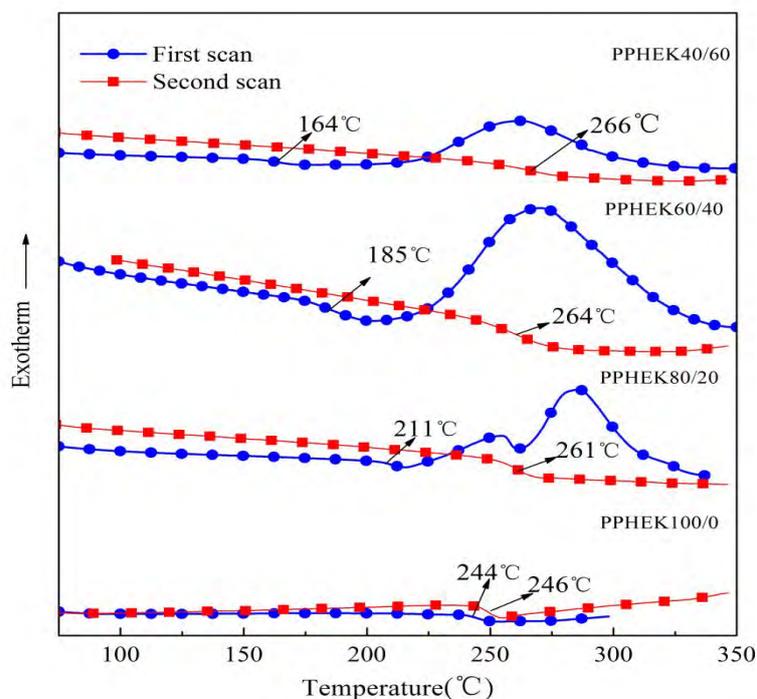


Fig. 6 DSC first scan and second scan curves of PPHEKs

3.5 Polymer crystallinity and photophysical properties

Crystallinity of 4a, 4b and 5 was investigated by means of wide-angle X-ray diffraction (WAXD) on film samples at room temperature. Fig. 7 illustrated WAXD diffractograms of the obtained copolymers. No sharp peak crystalline nature was observed in their WAXD patterns to demonstrate their amorphous nature, ascribed to the presence of the cranked, twisted non-coplanar of the phthalazinone moieties in the polymers, which was also reflected in their good solubility in common polar solvents.

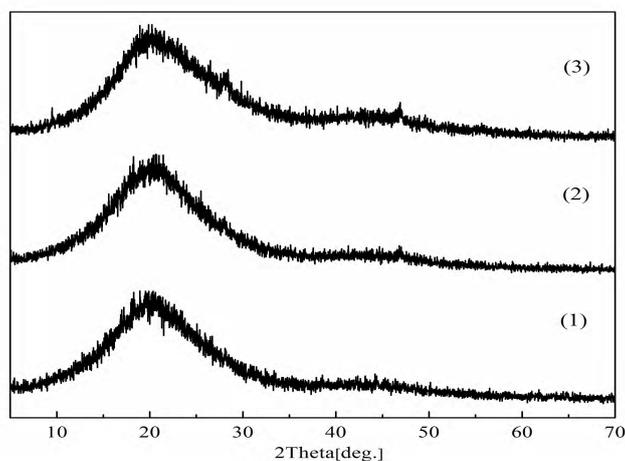


Fig. 7 WAXD diffractogram of 4a(1), 4b(2) and 5(3)

Photophysical properties of 4b, 5 and 1-azidopyrene (6) in CHCl_3 solution were characterized by UV-vis spectra and fluorescence emission spectra, as shown in Fig. 8. Four peaks at 275 nm, 285 nm, 344 nm and 361 nm, respectively, in the UV-vis spectrum of the compound 6 appeared. However, the UV-vis spectrum of 4b in CHCl_3 solution displayed single peak at 297nm. In the UV-vis spectrum of the pyrene-modified polymer 5, two weak peaks at 280 nm and 297 nm, respectively, and shoulder at 340 nm, similar to the compound 6, were detected. These absorption peaks for the polymer 5 and the compound 6 were associated with $\pi-\pi^*$ transition in the conjugated structure of pyrene. In the fluorescence spectra, three substances exhibited similar emission profiles in CHCl_3 solution. 4b showed blue emission with maximum peak at 449 nm, and 6 showed red emission with maximum at 519 nm. Compared to 4b, the emission peak of the polymer 5 in a dilute chloroform solution was slightly red-shifted and exhibited yellowish green fluorescence at 458 nm derived from pyrene units.

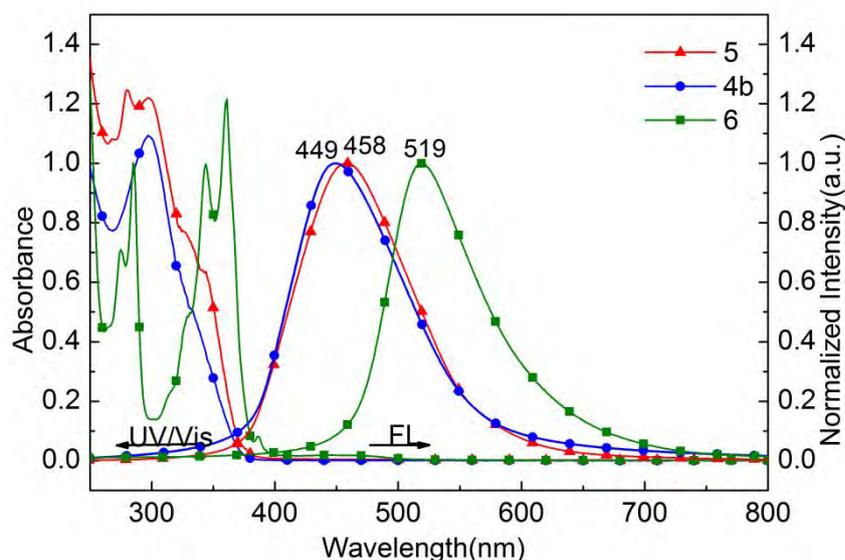


Fig.8 The normalized UV-Vis absorption and FL of 4b, 5 and 6 in CHCl_3 solution at the same concentration

The fluorescence quantum yields (Φ_F) of 4b, 5 and 6 in chloroform solution were found to vary from 2.1% to 6.4%, respectively, relative to the quinine sulfate (in 0.1 M H_2SO_4 solution, $\Phi_F = 55\%$), as listed in Table 4. The higher quantum efficiency of 5 could be attributable to the presence of rigid, highly fluorescent pyrene chromophore.

Table 4 Optical properties of 4b, 5 and 6

Substance	$\lambda_{\text{max}}^{\text{abs}}/\text{nm}^{\text{a}}$	$\lambda_{\text{max}}^{\text{FL}}/\text{nm}^{\text{a}}$	$\Phi_F(\%)^{\text{b}}$
4b	297	449	2.4
5	280, 297, 340	458	6.4
6	275, 285, 344, 361	519	2.1

^a The concentration was $1 \times 10^5 \text{ mol L}^{-1}$ in CHCl_3 .

^b Fluorescent quantum yield estimated using solutions in chloroform and calculated by comparing emission with that of a standard solution of the quinine sulphate (in 0.1M H_2SO_4 solution, $\Phi_F = 55\%$) at room temperature.

4. Conclusions

Herein we developed a straightforward and versatile strategy for the introduction of terminal ethynyl groups into a poly(arylene ether ketone). The functional monomer contained terminal ethynyl

group, 2-(3-ethynylphenyl)-1,4-hydroquinone, was synthesized in good yield by three-step synthesis procedure. FT-IR and NMR spectroscopy of the model compound indicated that the terminal ethynyl groups were stable to nucleophilic displacement reaction conditions. Then a series of novel poly(phthalazinone ether ketone)s containing pendant terminal ethynyl groups were successfully prepared. These amorphous polymers could be soluble in a wide range of organic solvents. Their terminal ethynyl groups could undergo thermal curing reaction at elevated temperature and azide-alkyne cycloaddition reaction to incorporate the fluorescence pyrene group into the side chain of the polymer. The stable monomer, 2-(3-ethynylphenyl)-1,4-hydroquinone, provides a versatile platform for the modification of PAEK systems without directly disturbing the composition of the polymer backbone.

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