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Crosslinkable fluorinated poly(aryl ether ketone)s containing pendent phenylethynyl moieties for optical waveguide devices

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Abstract

A type of novel crosslinkable fluorinated poly(aryl ether ketone) containing pendent phenylethynyl moieties (PEP-3F-PEEK$_n$) have been synthesized by copolycondensation reaction of difluoro-monomer with potassium salt of 4-phenylethynylphenyl hydroquinone (PEP-PH) and (3-trifluoromethyl) phenyl hydroquinone (3F-PH). The resulting polymers could be thermally crosslinked at 370 °C. The cured polymers showed good solvent resistance, high thermal stability up to 500 °C under nitrogen. They had small light absorption at the telecommunication wavelengths of 1.3 and 1.55 μm. The refractive index of the cured films was in the range of 1.6154–1.6274 at 1.55 μm wavelength.

Keywords: Phenylethynyl; Fluoropolymers; Crosslinking behavior; Polymer optical waveguide

1. Introduction

Fluorine-containing polymers are of considerable interest for optical and electronic applications in recent years [1–5] because of their thermal and chemical stability, easy processability, low dielectric constant, refractive index, optical loss, and moisture absorption [6,7]. Based on low-loss polymer materials, various optical waveguide devices such as optical interconnection devices, thermo-optic switches, arrayed waveguide grating (AWG) wavelength multiplexers, and tunable wavelength filters have been demonstrated [8–11]. To obtain a polymer device with good performance, the polymer should satisfy several requirements: low optical transmission loss; sufficient thermal stability and chemical resistance; low birefringence.

3F-PEEK has been synthesized for optical and electric applications by our group [12]. The materials exhibit low moisture absorption, low isotropic dielectric constant values, and good mechanical properties. Moreover, 3F-PEEK based on 3F-PH has low inherent optical absorption at the near-infrared region because the C–H bond in the polymer is substituted by the C–F bond. 3F-PEEK are dissolved easily by organic solvents such as tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP) and cyclohexanone. The good solubility is of great advantage for making thin film and coating. However, good solubility shows limit in the proceeding of multilayer coating operation and brings some problems to the devices including sharp-cleaving property and chemical nonresistance.

For the fabrication of a waveguide device, a crosslinked polymer system has several advantages such as increased thermal stability, chemical resistance, gap filling ability, and improved adhesion properties at the substrate. Containing phenylethynyl moieties polymers are good candidates for crosslinked optical waveguide materials due to easy synthesis, absence of an aliphatic C–H bond leading to significant optical absorption loss, and absence of catalyst and evolution of any volatile during the curing process. The incorporation of acetylenic moieties into polymers has been studied extensively. The most common approach has been to introduce the acetylenic groups as end caps on oligomers which can then be molded into the final shape and subsequently crosslinked by heating [13–17].

We introduce a new efficient synthetic method to prepare these crosslinkable 3F-PEEKs containing pendent phenylethynyl moieties with high molecular weights and linear structure [18,19]. The crosslinking behavior and some properties

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of such polymers, including thermal property, solubility, and optical properties, will be discussed.

2. Experimental

2.1. Materials

Phenyl acetylene, dichlorobis(triphenyl-phosphine)palladium(II), copper(I) iodide were purchased from Aldrich Chemical Co. and used without further purification; (3-trifluoromethyl) phenylhydroquinone (3F-PH) was synthesized in our laboratory. 4,4′-Difluorobenzophenone was obtained from Yanji Chemical Plant (China) and distilled under vacuum before use. 4-Bromoaniline (Jingjiang Malong Chemical Manufacturing Co. Ltd., China); 1,4-benzoquinone (Dalian Jizhou Chemical, China); 4,4′-difluorobenzophenone (DFP, Yanji Chemical Plant) and all of other reagents were obtained commercially and used as received.

2.2. Measurements

IR spectra (KBr pellets or films) were measured on a Nicolet Impact 410 Fourier transform infrared (FTIR) spectrometer. ^{1}H (500 MHz), and ^{13}C (125.7 MHz) NMR spectra were recorded on a Bruker 510 NMR spectrometer with tetramethyl silane as a reference. Gel permeation chromatograms (GPC) were obtained on a Waters 410 instrument with tetrahydrofuran (THF) as an eluent and monodisperse polystyrene as standards. Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC821^e instrument at a heating rate of 20 °C/min under nitrogen. Thermal gravimetric analyses (TGA) were determined in nitrogen atmosphere using a heating rate of 10 °C/min and polymers were contained within open aluminum pans on a PERKIN ELMER TGA-7. The elemental analysis was carried out with a Thermoquest CHNS-O elemental analyzer. Mass spectra were obtained on a Finnigan 4510 mass spectrometer.

To measure the refractive index and near–IR absorption, polymers were dissolved into cyclohexanone at concentrations of 10–20 wt%. Then the solution was filtered with a syringe through 0.22 μm Teflon membrane filter. The filtered solution was spin coated on the Si wafer and quartz substrates. The thickness of film was controlled by adjusting the spin rate. After coating, gradually increased temperature to volatilize solvent and then cured at 370 °C for 2 h under a vacuum to produce insoluble optical quality films.

2.3. Synthesis of 4-bromophenyl hydroquinone (Br-PH)

To a 1000-mL beaker containing 4-bromoaniline (17.2 g, 0.1 mol) and water (20 mL) was added 35% hydrochloric acid (34 mL, 0.4 mol). The mixture was heated slowly until 4-bromoaniline (17.2 g, 0.1 mol) was dissolved and then quickly cooled to 0–5 °C to result in precipitate. To this mixture was added dropwise with stirring a solution of sodium nitrite (6.9 g, 0.1 mol) in water (80 mL) at 0–5 °C and stirred for 2 h, and a clear solution was obtained. The resulting solution was added dropwise to a mixture of 1,4-benzoquinone (10 g, 0.093 mol), sodium bicarbonate (25.2 g, 0.3 mol) and water (80 mL). The reaction mixture was stirred at 8–12 °C for about 2 h and then at room temperature for 2 h. The precipitate was collected by filtration, washed thoroughly with water, and dried at 60 °C in a vacuum oven to give a yield of 86%. The product was recrystallized from *n*-butanol and gave yellow crystals.

This product and Zn powder (19.5 g, 0.3 mol), and 100 mL deionized water were placed into a 250 mL three-necked flask equipped with a mechanical stirrer, a condenser, and a dropping funnel. The mixture was heated to 90 °C with stirring, followed by the addition of hydrochloric acid (25.5 mL 0.3 mol) dropwise at a rate of 30 drops per min. After addition, the reaction mixture was allowed to reflux for 3 h. Then, the hot mixture was filtered. The filtrate was cooled to room temperature and poured into a large amount of deionized water. The white solid was collected and recrystallized from toluene. mp: 133 °C (DSC). *m/z*: 265.

2.4. Synthesis of 4-phenylethynylphenyl hydroquinone (PEP-PH)

Acetic anhydride (22.44 g, 220 mmol) was added dropwise to a solution of pyridine (17.16 g, 220 mmol) in 4-bromophenyl hydroquinone (26.5 g, 100 mmol) under nitrogen atmosphere. The stirred solution was heated at 70 °C for 2 h. After cooling down to room temperature, the reaction mixture was poured into 200 mL water. The precipitated solid was filtered, purified by recrystallization from methanol and dried at 50 °C under vacuum to afford white yellow solid. Yield: 95%. mp: 101 °C (DSC).

In a 500 mL three-necked flask, the resulting product (25 g, 70 mmol) and triphenylphosphine (0.785 g, 3 mmol) was dissolved in 50 ml of DMAc under nitrogen atmosphere. To the solution phenyl acetylene (9 g, 88 mmol), $PdCl_2(PPh_3)_2$ (0.3 g, 0.43 mmol) and triethylamine (60 mL) were added. The mixture was slowly heated to 60 °C, and then CuI (0.2 g, 1 mmol) was added with 60 mL triethylamine. The reaction mixture was heated to 80 °C and maintained for 12 h. After cooling, the reaction mixture was filtered to remove inorganic salts, and evaporate the triethylamine. The concentrated product was poured into acidic water. The precipitated solid was filtered and purified by recrystallization from ethanol and dried at 50 °C under vacuum to afford while solid. mp: 123 °C (DSC). *m/z*: 369.7.

In a 500 mL three-necked flask equipped with a mechanical stirrer, a condenser, and a dropping funnel the resulting product was dissolved in a mixture of THF (120 mL) and methanol (120 mL). Sodium hydroxide (9.6 g, 240 mmol) dissolved in 80 mL water was added to this reaction mixture. After being refluxed for 12 h with stirring, the reaction mixture was cooled and poured into 200 mL of acidic water. The organic layer was extracted with methylene chloride and dehydrated with anhydrous sodium sulfate. After filtration and distillation, the residue was purified by decolourization with activated carbon and recrystallization from toluene to afford a white solid, PEP-PH.

mp: 146 °C (DSC). *m/z*: 286.3. Elem. Anal. Calculated for $C_{20}H_{14}O_2$: C, 83.90%; H, 4.93%; O, 11.18%. Found: C, 83.88%, H, 4.99%, O, 11.08%. ^{1}H NMR ($CDCl_3$, δ, ppm): 6.75 (dd,

$J = 7.5$ Hz, 1H), 6.76 (s, 1H), 6.86 (dd, $J = 6.5$ Hz, 1H), 7.34–7.40 (m, 3H), 7.46 (d, $J = 8.5$ Hz, 2H), 7.54–7.58 (m, 2H), 7.64 (d, $J = 8$ Hz, 2H). ^{13}C NMR: 88.9, 90.3 (ethynyl), 116.1, 116.5, 117.0, 122.9, 123.1, 128.3, 128.4, 128.9, 131.6, 132.3, 136.8, 146.4, 149.4 (phenyl).

2.5. Synthesis of PEP-PEEK

In a 100 mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet, a Dean–Stark trap, and a condenser were placed PEP-PH (1.43 g, 5 mmol), 4,4-difluorobenzophenone (1.09 g, 5 mmol), anhydrous potassium carbonate (K_2CO_3, 0.725 g, 5.3 mmol), *N*,*N*-dimethylformamide (DMF) (10 mL), and benzene (30 mL) and the mixture was allowed to reflux for 2 h. After benzene was removed by distillation, the system was heated at 130–140 °C for 6 h. The viscous mixture was poured into 1000 mL acidic water. The threadlike polymer was pulverized, washed with hot methanol and water several times, and dried at 80 °C under vacuum to give essentially quantitative yield of white polymer, PEP-PEEK.

GPC in THF: $M_n = 32{,}794$; $M_w/M_n = 3.9$. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.83 (d, $J = 8.5$ Hz, 1H), 7.78 (d, $J = 8.5$ Hz, 1H), 7.72 (d, $J = 8.5$ Hz, 1H), 7.67 (d, $J = 8.5$ Hz, 1H), 7.43–7.55 (m, 6H), 7.29–7.35 (m, 3H), 7.05–7.26 (m, 5H), 6.93 (d, $J = 8.5$ Hz, 1H), 6.89 (d, $J = 8.5$ Hz, 1H). ^{13}C NMR ($CDCl_3$, δ, ppm): 89.0, 90.4 (ethynyl), 116.2, 117.2, 120.6, 122.4, 122.9, 123.0, 123.3, 128.3, 128.9, 131.6, 131.6, 131.9, 132.2, 132.3, 132.5, 132.6, 135.5, 136.2, 152.7, 161.2, 161.4, 194.0 (phenyl).

2.6. Synthesis of PEP-3F-PEEK$_n$

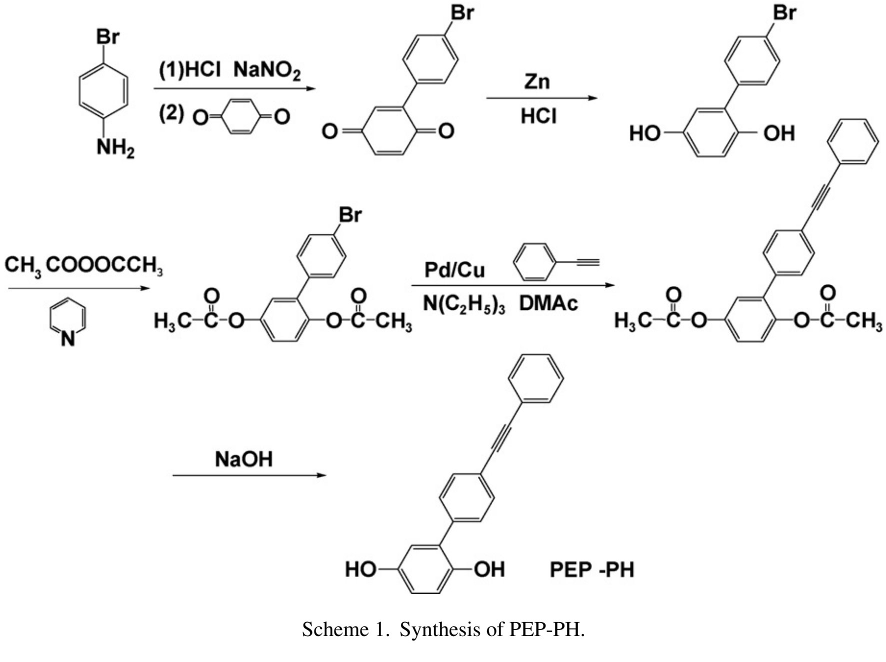
3F-PH (4.572 g, 18 mmol), DFP (4.3 g, 20 mmol), anhydrous K_2CO_3 (2.61 g, 18.9 mmol), 34 mL *N*-methyl-2-pyrrolidone (NMP), and 30 mL toluene were placed in a 100 mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet, a Dean–Stark trap, and a condenser. The reaction mixture was allowed to reflux for 2 h to remove the water from the reaction mixture as an azeotrope with toluene and then the toluene was removed by distillation. The mixture was heated to 180–190 °C and maintained for 6 h. Then the viscous mixture was poured into 1000 mL acidic water. The threadlike polymer was pulverized into a powder, washed with hot methanol and water several times, and dried at 80 °C under vacuum afford a nearly quantitative yield of white polymer, 3F-PEEK$_{20}$.

A reaction flask equipped with the same apparatus described above was charged with 3F-PEEK (8.6 g), PEP-PH (0.5434 g, 1.9 mmol), anhydrous K_2CO_3 (0.414 g, 3 mmol) NMP (34 mL), and benzene (30 mL). The reaction mixture was allowed to reflux for 2 h then the benzene was removed by distillation. The system was heated to 140–150 °C. As the polymerization was complete after 6 h, the viscous mixture was poured into 1000 mL acidic water. The threadlike polymer was pulverized into a powder after cooling, washed with hot methanol and water several times and dried at 80 °C under vacuum to give an essentially quantitative yield of white polymer, PEP-3F-PEEK$_{20}$. GPC in THF: $M_n = 101{,}581$; $M_w/M_n = 3.1$, ^{13}C NMR ($CDCl_3$, δ, ppm): 89.0, 90.4 (ethynyl).

3. Results and discussion

3.1. Synthesis and characterization of monomer

The novel bisphenol monomers containing pendent diphenylacetylene moiety (PEP-PH) were synthesized and the main steps are shown in Scheme 1. The bisphenol was synthesized in a two-step synthetic process starting from the diazonium coupling reaction of 4-bromoaniline to yield 4-bromophenyl hydroquinone (Br-PH). Then PEP-PH was readily synthesized



Scheme 1. Synthesis of PEP-PH.

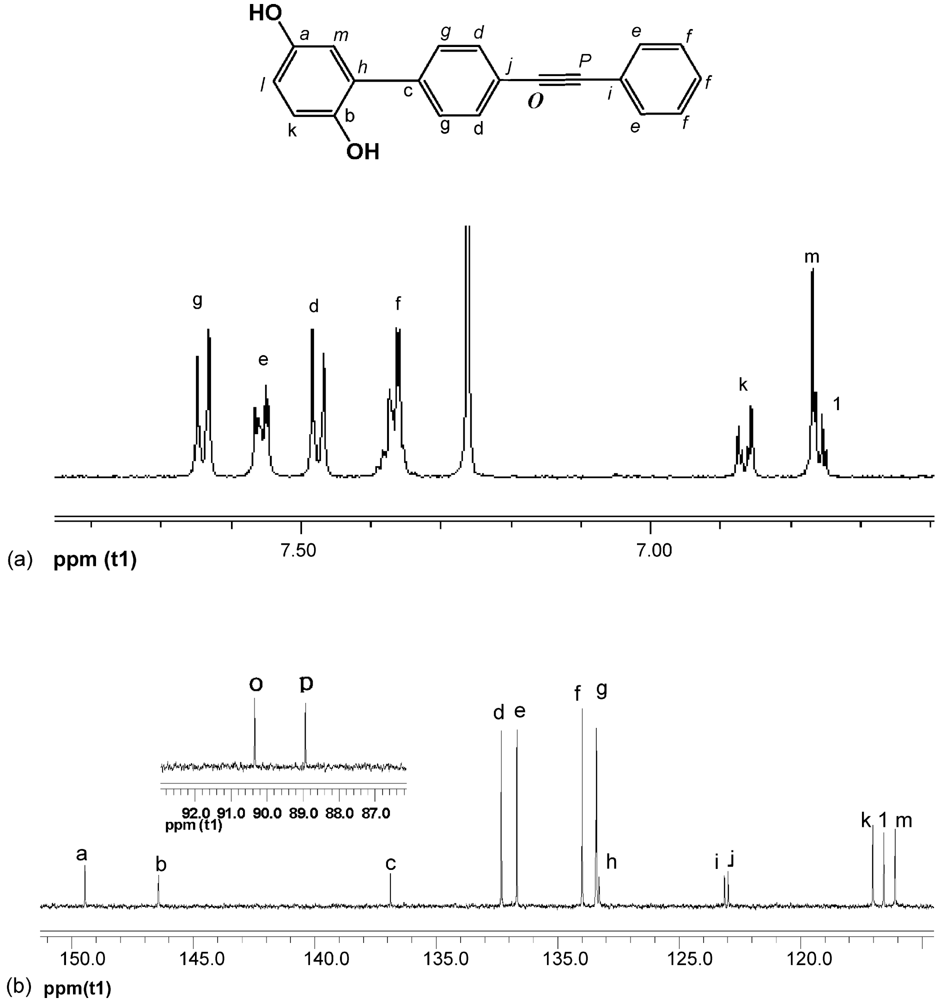
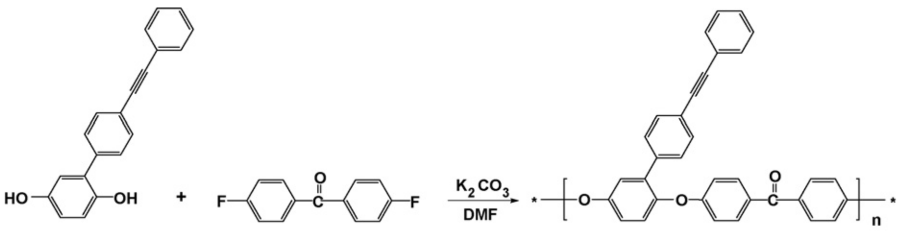


Fig. 1. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of PEP-PH.

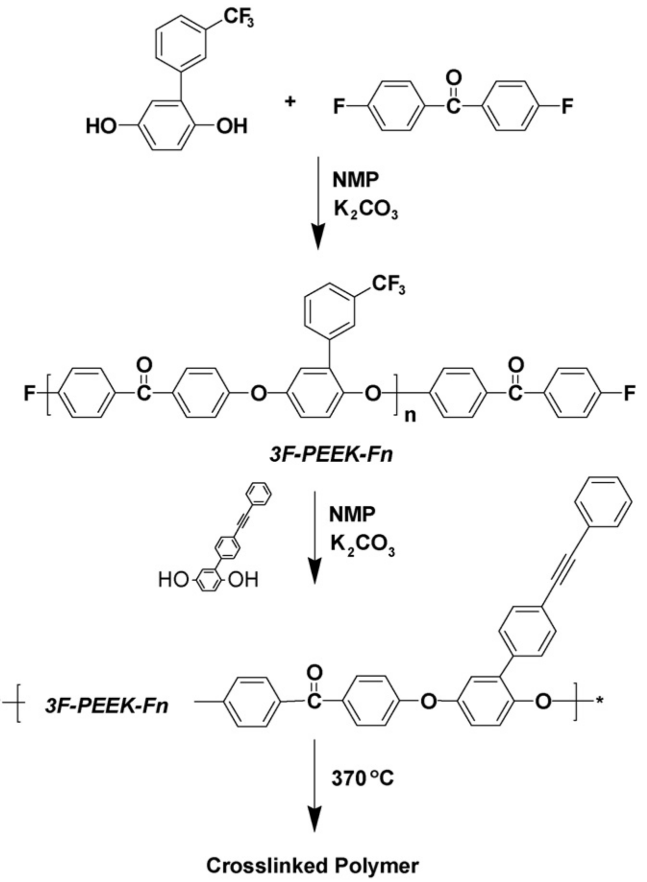
by the coupling of phenyl acetylene with a Pd(0)/Cu(1) catalyst. The structures of PEP-PH were confirmed by mass spectrometry, FTIR, NMR spectroscopy, and elemental analysis. The FTIR spectrum of PEP-PH shows the peaks at 2220, 3382 and 3532 cm^{-1} due to the characteristic absorption of ethynyl groups, hydroxy bands, respectively. ^{1}H and ^{13}C NMR spectra of PEP-PH are shown in Fig. 1. The peaks in ^{1}H NMR spectra at 7.52–5.18 ppm are assigned to the aromatic protons, respectively. ^{13}C NMR spectra of PEP-PH exhibit 15 peaks. Two peaks at 88.9 and 90.3 ppm are attributed to the ethynyl groups. The result of elemental analysis accorded with these values by calculated.

3.2. Synthesis and characterization of polymers

Scheme 2 shows the structural formula of PEP-PEEK with the phenyl ethynyl group at the side chain. The phenylethynyl group, as a crosslinkable moiety, was introduced into a fluorinated poly(ether ether ketone) by a two-step aromatic nucleophilic substitution reaction. In the first step, the oligomers terminated with activated fluorines were obtained by the polymerization of a bisphenol monomer with an excess bisfluoro monomer in the presence of potassium carbonate as a base in DMAc. The crosslinkable PEEKs were obtained by the further reactions of the oligomers (various molecular weights) with



Scheme 2. Synthesis of PEP-PEEK.



Scheme 3. Synthesis of PEP-3F-PEEK$_n$.

4-phenylethynylphenyl hydroquinone, as shown in Scheme 3. The number n in the polymer codes is the degree of polymerization calculated for monomer imbalance. The number-average molecular weights (M_n) and polydispersities of the resulting polymers are in the range of 37,000–135,000 and 1.7–3.1, respectively, as shown Table 1.

The ^{1}H and ^{13}C NMR spectra of PEP-PEEK are shown in Fig. 2. From ^{1}H NMR spectra it can be seen that there are a aromatic peak at 7.48 ppm due to the PEP group and peaks at 7.6–7.9 ppm due to the 4,4′-difluorobenzophenone, area ratio of these two peaks is 1.48:1, consist with feed ratio of PEP-PH and 4,4′-difluorobenzophenone. The pendent ethynyl carbon peaks show at 89.0 and 90.4 ppm. Assigned hydrogen and carbon peaks consist of the proposed repeating unit structure. The ^{1}H NMR spectrum of PEP-3F-PEEK$_{10}$ presented in Fig. 3 shows the peaks at 7.48 and 7.32, 7.46 and 7.54, 6.89–7.12 and 7.64–7.85 ppm due to PEP-PH, 3F-PH, 4,4′-difluorobenzophenone and 4,4′-difluorobenzophenone and 3F-PH, respectively, and the mole ratio of 3F-PH and PEP-PH calculated is 4.2:1, almost consist with their feed ratio 4:1. The pendent ethynyl carbon peaks showed at 89.0 and 90.4 ppm in ^{13}C NMR spectrum of PEP-3F-PEEK$_{10}$, indicated the success of polymerization in producing PEP-3F-PEEK$_{10}$.

3.3. Crosslinking behaviors and thermal properties

DSC analysis was performed to study the thermal crosslinking behavior of the polymers. The DSC trace of PEP-PEEK is shown in Fig. 4. Traces a and b are for the first heating run of the origin sample and second heating run of the thermal treatment sample at 340 °C for 2 h, respectively. A glass transition at 179 °C and an exothermal peak ranged from 300 °C to 470 °C can be seen from trace a. PEP-PEEK had higher T_g value was due to its bulky rigidity pendent group. For trace b, T_g and exotherm could not be detected. Fig. 5 showed the repeat scan DSC traces of PEP-3F-PEEK$_{10}$. T_g of this polymer increase with increase of scan times and exothermal trace gradually disappeared. These all are attributed to crosslinking reaction of the phenylethynyl moieties.

The TGA trace of PEP-PEEK heated at 370 °C under nitrogen was shown in Fig. 6. A straight line almost paralleled to X-axis indicates without the evolution of volatiles during crosslinking.

Some parameters of PEP-PEEKs are shown in Table 2. It can be seen that the glass transition temperature is increased after crosslinking and the temperatures at a 5% weight loss (TD$_5$) are above 500 °C under a N_2 atmosphere. The high thermal stability is attributed to the aromatic structures and strong C–F bonds of 3F-PEEK, and the importance of conjugate alkene and aromatic ring in cured structure of phenylethynyl group should not be disregarded.

3.4. Solubility of polymers

It is well known that the conventional PEEK could not be dissolved in most known organic solvents. In sharp contrast, the precursor forms, PEP-3F-PEEK$_n$ were soluble at room tem-

Table 1
Synthetic data of polymers

	$[B]_0/[D]_0$[a]	M_n[b]	M_w[b]	Polydispersity[b]
PEP-3F-PEEK$_{40}$	19:1	135,052	408,513	3.0
PEP-3F-PEEK$_{20}$	9:1	101,581	315,513	3.1
PEP-3F-PEEK$_{10}$	4:1	43,848	77,831	1.8
PEP-3F-PEEK$_7$	7:3	37,759	63,926	1.7
PEP-PEEK	–	32,794	131,005	3.9

[a] Calculated from the feed ratio of (3-trifluoromethyl) phenyl hydroquinone (3F-PH) and 4-phenylethynylphenyl hydroquinone (PEP-PH).

[b] Determined by GPC calibrated with polystyrene standards in THF at 25 °C.

Table 2
Thermal properties of polymers

	T_{g1}	T_{g2}	ΔT_g	TD$_5$	n
PEP-3F-PEEK$_{40}$	141	149	8	557	1.6154
PEP-3F-PEEK$_{20}$	140	156	16	564	1.6176
PEP-3F-PEEK$_{10}$	142	165	23	553	1.6197
PEP-3F-PEEK$_7$	144	190	46	561	1.6274
PEP-PEEK	179	–	–	526	–

T_{g1}: second heat in the DSC after heat at 160 °C/5 min in N_2, quenching. T_{g2}: second heat in the DSC after cure at 370 °C/120 min in N_2, quenching; TD$_5$: temperature of weight loss 5% after cure at 370 °C/120 min in N_2; n: the refractive index of cured films at 1.5 μm.

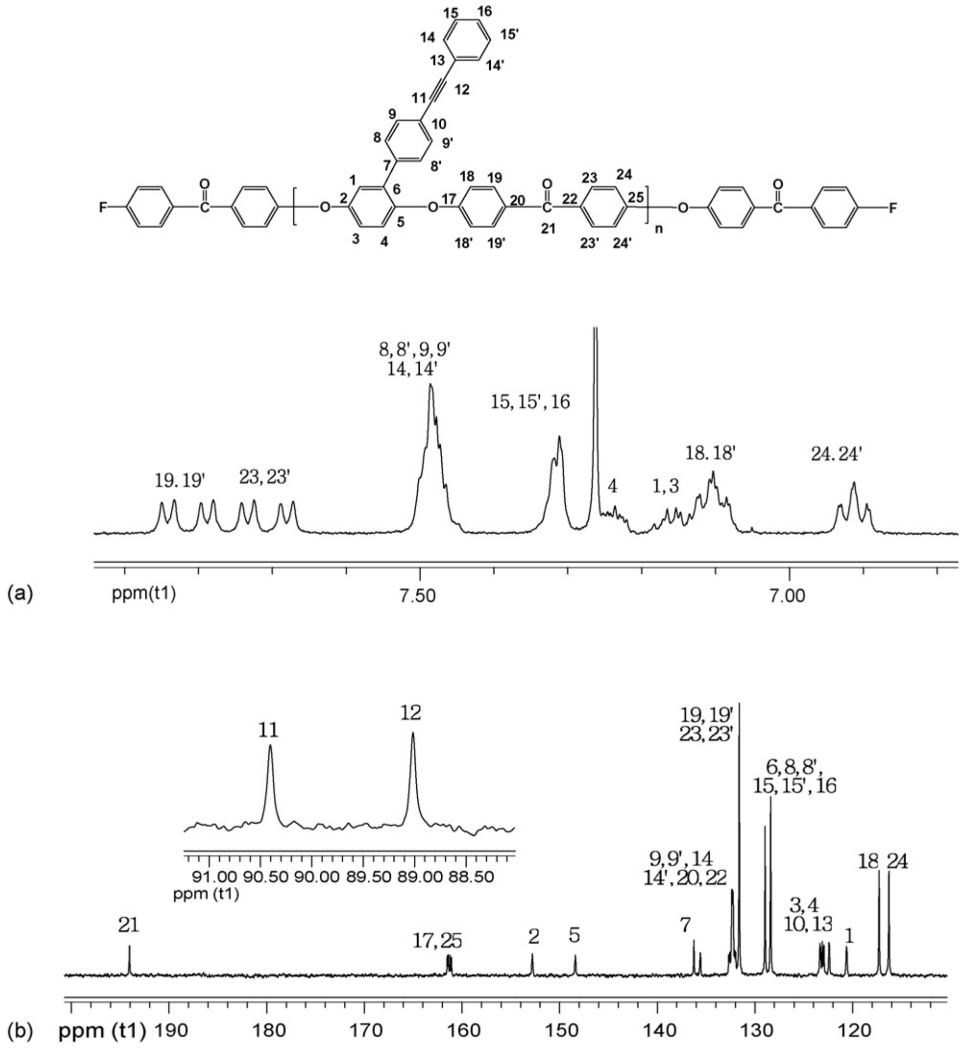


Fig. 2. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of PEP-PEEK.

perature in aprotic polar solvents such as NMP, DMAc and DMF as well as in the less polar solvents such as chloroform and THF. This was attributed to their molecular structures with a bulky pendant group. Therefore, they could be readily processed by the solution casting. However, they did not show good chemical resistance for the multicoated thin-film process and sharp-cleaving property for optical fiber coupling at the end face of a device. The cured PEP-3F-PEEK$_n$ showed good solvent resistance property. They could not dissolve in the above mentioned solvents after treatment at 370 °C for 2 h under N_2 atmosphere.

3.5. Optical properties

It is known that the absorption in the near–IR region is mainly caused by the harmonics and their coupling with the stretching vibration of the chemical bonds. Carbon–hydrogen (C–H) and oxygen–hydrogen (O–H) bands strongly affect the absorption in the near–IR region. The low absorption at the optical wavelengths, 1.3 and 1.55 μm, is regarded to be an important consideration if polymers are to be used for optical devices. Therefore, fewer C–H bonds in the polymer would lead to lower absorption in the near–IR region [2,20,21]. The effect of the

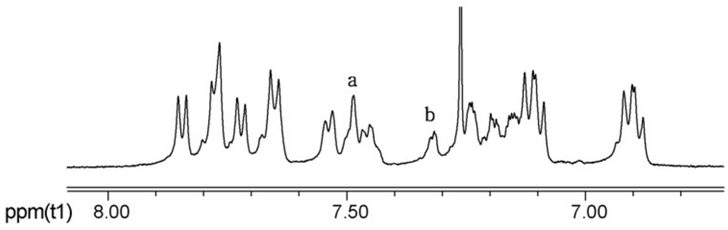


Fig. 3. ^{1}H NMR spectra of PEP-3F-PEEK$_{20}$ (a, $\delta = 7.48$ ppm; b, $\delta = 7.32$ ppm).

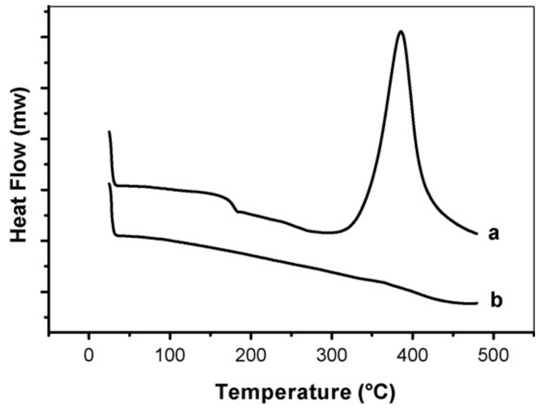


Fig. 4. DSC traces of PEP-PEEK (a) first scan (b) second scan after thermal treatment at 340 °C for 2 h.

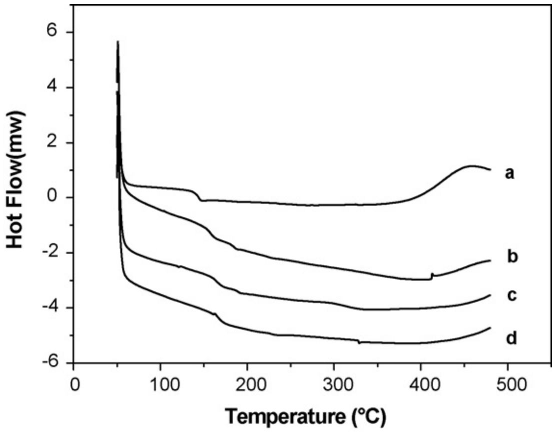


Fig. 5. DSC traces of PEP-3F-PEEK$_{10}$ (a) first scan, (b) second scan, (c) third scan, and (d) fourth scan.

fluorinated moieties on the optical loss was evaluated by the near–IR spectrum of the polymer films. As shown in Fig. 7, the cured PEP-3F-PEEK$_{10}$ film (about 30 μm thick) didn't increase compared with 3F-PEEK, and showed low absorption at the telecommunication wavelengths of 1.3 and 1.55 μm [21].

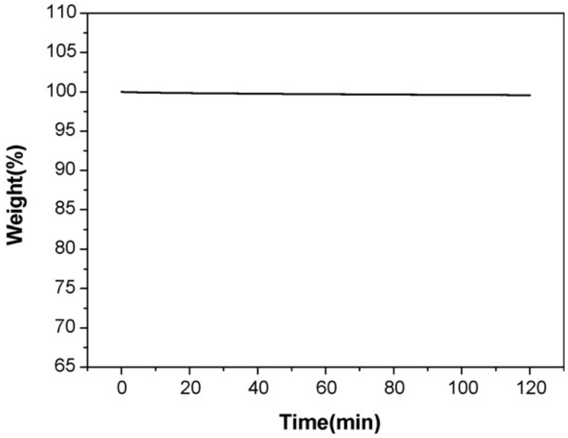


Fig. 6. TGA traces of constant temperature thermal treatment of PEP-PEEK at 370 °C.

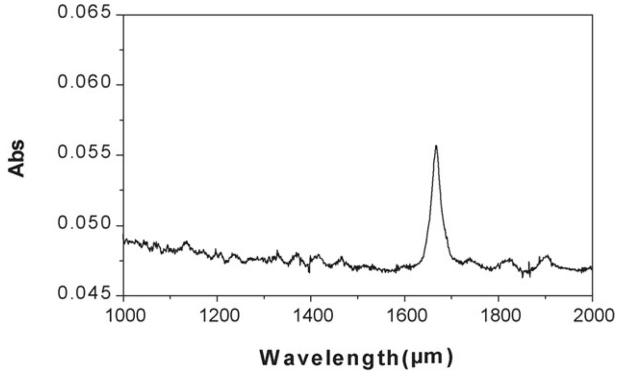


Fig. 7. Absorption spectra of the cured PEP-3F-PEEK$_{10}$ film (about 30 μm thick) at near-infrared region.

The fluorine content of the polymers decreases with the increase in the bisphenol PEP-PH of the polymers. As expected, shown in Table 2, the refractive indices of the polymers increase with the increase in content of bisphenol PEP-PH from 1.6154 to 1.6274. The resulting birefringence of the cured PEP-3F-PEEK$_{10}$ and PEP-3F-PEEK$_7$ was $\Delta n = n_{\mathrm{TE}} - n_{\mathrm{TM}}$; 0.003 and 0.006 at 1.55 μm, separately. According to the optical properties mentioned above, we could design the optical devices based on the precise refractive index with low birefringence.

4. Conclusion

A series of crosslinkable fluorinated poly(aryl ether ketone)s have been successfully synthesized in a two-step synthetic route. The flexible films could be prepared by solution casting of the precursors, and then curing at 370 °C. The crosslinked polymer offered highly thermal stability, higher glass transition temperature, and good solvent resistance. They showed small optical absorptions at 1.3 and 1.55 μm and lower birefringence. These polymers may be considered as potential candidates for high-temperature microelectronic and optical materials.

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