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Synthesis, characterization and optical properties of cross-linkable poly(phthalazinone ether ketone sulfone)

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Abstract

Cross-linkable poly(phthalazinone ether ketone sulfone) bearing tetrafluorostyrene groups (PPEKS–FSt) has been prepared by copolycondensation reaction for optical waveguide applications. The resulting amorphous polymer exhibits good solubility in some common polar organic solvents (e.g., *N*,*N*′-dimethylacetamide, *N*-methyl-2-pyrrolidinone, chloroform) at room temperature, and can be easily spin-coated into thin films with good optical quality. The glass transition temperature (T_g) and the temperature of 1% weight loss (1% T_d) are 261 °C and 494 °C, respectively, which could be further increased by 31 °C and 14 °C upon thermal cross-linking. The cross-linked polymer thin films exhibit high refractive index (~1.65, TE mode), high thermo-optic coefficient value (dn/dT) (-1.455×10^{-4}/°C, TE mode), low optical loss (less than 0.24 dB/cm at 1310 nm) and relatively low birefringence (~0.007).

Keywords: Polymer optical waveguide; Phthalazinone; Cross-linking

1. Introduction

Polymeric optical materials, with easy and rapid processability, good compatibility with semiconductor materials and facile controllability of optical properties, have addressed the demand for photonic components that meet economic criteria as well as technical requirements in telecom and datacom industries [1]. The key factors for their use include low optical loss at the major telecommunication wavelengths (1310 nm and 1550 nm), good refractive index controllability, thermal and environmental stability to withstand typical fabrication processing and operation condition, low birefringence, and good adhesion with semiconductor substrates. In addition, for the fabrication of a photonic device, including optical waveguides, a cross-linked polymer system has several advantages such as increased thermal stability, chemical resistance, and improved adhesion properties at the substrate [2]. Consequently, polymers with cross-linkable capabilities are also highly desired [3,4].

However, most hydrocarbon-based polymers have a high optical loss in the near infrared region due to the absorption associated with the vibrational overtones of C–H, O–H, and N–H bonds. Fortunately, substitution of hydrogen by a heavier atom (deuterium or halogens) can shift the associated vibrational overtone to longer wavelengths, thereby reducing the intrinsic optical loss in the infrared communication region [5]. Further studies revealed that the approach of replacing hydrogen by halogen was generally easier and cheaper than that by deuterium [6]. Furthermore, halogenations, particularly fluorination, can offer interesting opportunities for the

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alteration of properties such as refractive index, hydrophobicity and thermal stability [3,7]. Therefore, a wide range of fluorinated polymers such as fluorinated polyacrylates [8], fluorinated polyimide [9], perfluorocyclobutane [10], fluorinated dendrimer and hyperbranched polymers [11], fluorinated poly(arylene ether)s [2,12], and polysiloxanes and inorganic–organic hybrid polymers [13] have been synthesized and investigated for optical waveguide applications. Among those fluorinated polymers, highly fluorinated poly(arylene ether)s bearing various cross-linkable moieties have drawn much attention due to their low optical loss, excellent thermal stability and mechanical properties. Nevertheless, a very high curing temperature is traditionally required to yield those cross-linked polymers with high thermal stability [14]. At these temperatures, yellowing and even degradation of the polymers are usually observed. And these side effects contribute to larger optical loss [15]. Moreover, the high degree of fluorination makes adhesion to many substrates difficult [6].

It is supposed that poly(aryl ether) containing phthalazinone moieties will be particularly suitable to be used as potential polymeric optical materials after being partially fluorinated due to their extraordinarily high T_g (265–305 °C), excellent thermal stability, good thin film processability and cross-linking functionality [16]. However, there is no report on the preparation of this kind of material in the field of polymeric optical materials. In this study, we synthesized a novel kind of tetrafluorostyrene ended poly(phthalazinone ether ketone sulfone) copolymer by a two-step reaction. The chemical structure of the resulting polymer was confirmed by ^{1}H NMR, ^{19}F NMR and FT-IR methods. The thermal cross-linking of the PPEKS–FSt films and the optical properties, such as the refractive index, thermo-optic coefficient, optical loss and birefringence of the cross-linked films were also investigated by DSC and a Sairon SPA-4000 prism coupler.

2. Experimental

2.1. Materials

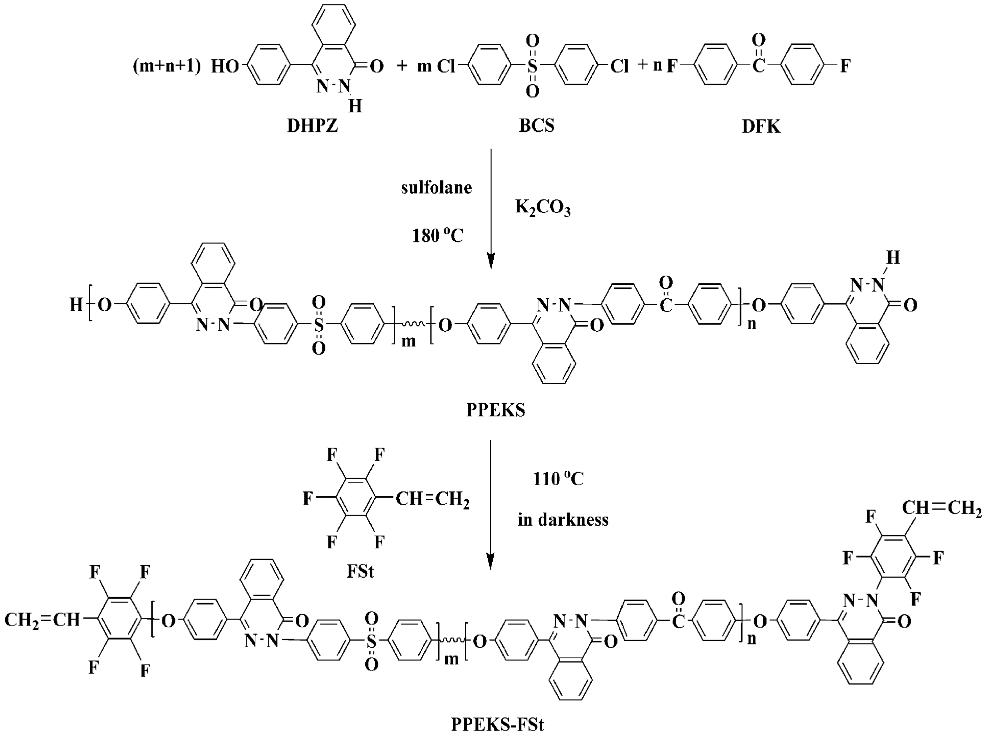
4-(4′-Hydroxyphenyl)phthalazin-1(2*H*)-one (DHPZ) was gifted by Dalian Polymer New Material Co. Ltd., PR China. 4,4′-Bis(4-chlorophenyl)sulfone (BCS) and 4,4′-difluorobenzophenone (DFK) were purchased from commercial sources and purified by recrystallization from isopropanol and ethanol, respectively. Pentafluorostyrene (FSt) was purchased from Aldrich–Sigma, and used as received. Analytical-grade anhydrous potassium carbonate (K_2CO_3) (Tianjin Fuyu Fine Chemical Industry Co., Ltd., PR China) was ground and dried in vacuum at 100 °C for 24 h before use. Sulfolane was dried over sodium hydroxide pellets and purified by reduced pressure distillation prior to use. *N*,*N*′-Dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidinone (NMP) (Tianjin Fuyu Fine Chemical Industry Co., Ltd., PR China) were purified by reduced pressure distillation prior to use, subsequently, the middle fractions were collected and stored over molecular sieves (Type 4 Å). All the other chemicals were purchased from Tianjin Fuyu Fine Chemical Industry Co., Ltd., PR China, and used without further purification.

2.2. Measurements

^{1}H NMR (400 MHz) and ^{19}F NMR (376 MHz) spectra were obtained with a Varian Unity Inova 400 spectrometer at an operating temperature of 25 °C using $CDCl_3$ as a solvent and were listed in parts per million downfield from tetramethylsilane (TMS) and potassium fluoride (KF), respectively. Fourier transform infrared (FT-IR) spectra were recorded by reflection method with a Thermo Nicolet Nexus 470 Fourier transform infrared spectrometer. Gel permeation chromatography (GPC) analysis was carried out on a HP 1090 HPLC instrument equipped with 5 μm Phenogel columns (linear, 4×500 Å) arranged in series with chloroform as solvent and a UV detector at 254 nm. And the values were calibrated versus polystyrene standard. The glass transition temperature (T_g) was determined with a Mettler DSC 822 differential scanning calorimetry (DSC) in flowing nitrogen at a heating rate of 10 °C min^{-1} from 50 to 400 °C. Thermogravimetric analysis (TGA) of the polymer was performed on a Mettler TGA/SDTA851 thermogravimetric analysis instrument in a nitrogen atmosphere at a heating rate of 20 °C min^{-1} from 100 to 700 °C. Wide-angle X-ray diffraction (WAXD) was performed at room temperature on a Shimadzu XRD-6000 automatic X-ray diffractometer with Ni-filtered Cu Kα radiation. The rotated velocity of the goniometry was 4° min^{-1}.

2.3. Synthesis of PPEKS–FSt

Cross-linkable poly(phthalazinone ether ketone sulfone) bearing tetrafluorostyrene groups (PPEKS–FSt) was synthesized via a nucleophilic aromatic substitution (S_NAr) as illustrated in Scheme 1. The synthetic procedure of PPEKS–FSt was conducted in a 100 mL three-necked round-bottom flask equipped with a Dean-Stark trap, a condenser, a nitrogen inlet/outlet, and a mechanical stirrer. The flask was loaded with 4-(4′-hydroxyphenyl)phthalazin-1(2*H*)-one (DHPZ) (8.82 mmol), 4,4′-bis(4-chlorophenyl)sulfone (BCS) (6.78 mmol), 4,4′-difluorobenzophenone (DFK) (1.69 mmol), anhydrous potassium carbonate (13.20 mmol), sulfolane (4.4 mL) and toluene (6.0 mL). Nitrogen was purged through the reaction mixture with stirring for 10 min, and then the mixture was slowly heated to 150 °C to azeotrope off the water generated in the reaction with toluene. After 3 h of dehydration, the mixture was heated to 180 °C by stepwise removal of toluene from the Dean–Stark trap and kept at this temperature for 5 h. After cooling to room temperature, 1.40 mmol pentafluorostyrene (FSt) was added into the reaction mixture. Then the mixture was stirred under nitrogen at 110 °C in darkness for 3 h to prepare PPEKS–FSt. After cooling, the resulting mixture was slowly poured into sufficient boiling pure water containing a few drops of concentrated hydrochloric acid under vigorous stirring to precipitate the product. After filtered and dried, the polymer was purified by filtering its *N*,*N*′-dimethylacetamide (DMAc) solution



Scheme 1. Synthetic route of PPEKS–FSt.

through a thin layer of Celite before precipitating it into sufficient ethanol. The white powder was collected by filtration and then treated thoroughly with boiling pure water and methanol, and then drying at 50 °C under vacuum for 24 h. The total yield of PPEKS–FSt was 91%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.12–7.26 (m, 4H), 7.60–8.03 (m, 11H), 8.55 (s, 1H), 6.64 (FSt, dd, $J = 17.5$ Hz, 11.5 Hz), 6.08 (FSt, d, $J = 17.5$ Hz), 5.69 (FSt, d, $J = 11.5$ Hz). ^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ: −143.73 (m, 2F), −155.55 (m, 2F). IR (film, cm^{-1}): 1670 (C=O), 1588, 1488 (Ar stretching), 1430 (CH_2=CH), 1325, 1154 (O=S=O), 1242 (aromatic ether bond), 975, 932 (CH_2=CH–).

2.4. Thermal cross-linking of PPEKS–FSt

To study the thermal cross-linking of PPEKS–FSt, the polymer was firstly dissolved in chloroform at a concentration of 16.7 wt%. Then the films were cast from the solution and dried at room temperature under high vacuum. The thermal cross-linking behaviors of the films were then performed by heating the polymer films at either 160 °C in the presence of a free radical initiator, dicumyl peroxide (1 wt% relative to the polymer) for 4 h under vacuum, or at 220–280 °C in the absence of any initiator for 20 min in air atmosphere. Then the effect of thermal cross-linking on T_g was detected by DSC.

2.5. Film preparation and optical properties measurements

The substrates used in the experiments were highly polished Si/SiO_2 wafers. Organic residues on the silicon surfaces were removed by the successive ultrasonic cleaning with acetone, alcohol and ion free pure water. The polymer solution was prepared by dissolving the PPEKS–FSt (~16.7 wt%) and a thermal cross-linking initiator (dicumyl peroxide, 1 wt% of PPEKS–FSt) in *N*-methyl-2-pyrrolidinone (NMP). Then the solution was filtered through a 0.45 μm Teflon microfilter and spin-coated on a Si/SiO_2 substrate. The spin-coating speeds ranged from 1000 to 6000 rpm. In order to guarantee the quality of the spin-coated films, the whole spin-coating procedure was carried out in a 1000 class ultra-clean room. The resulting films were dried at 60 °C (30 min) and 120 °C (2 h) to remove the residual solvent under vacuum. Thermal cross-linking was then performed by heating the films slowly to 160 °C and maintaining at this temperature for 4 h under vacuum. The uniformity of film thickness and refractive index was investigated by using a Sairon SPA-4000 prism coupler. It was carried out on a 2-inch silicon wafer to investigate the uniformity of the obtained polymer films. And six points were tested per spin-coated film. The refractive indices of the polymer films were measured by the prism-coupling method at the wavelengths of 1310 nm and 1550 nm with the tolerance of ±0.0002. The optical losses of the polymer films were measured on slab waveguide samples using the high-index liquid immersion technique [17]. In this technique, light was coupled to a slab waveguide by prism coupling. After propagating for a certain distance, the light was out-coupled from the waveguide by immersing it into a high-index liquid. And the propagation loss could be calculated with the out-coupled optical power described as a function of the propagation distance.

3. Results and discussion

3.1. Synthesis of PPEKS–FSt

Introducing FSt moiety into non-fluorinated poly(phthalazinone ether ketone sulfone) (PPEKS) by a one-pot condensation reaction is illustrated in Scheme 1. There were two steps: PPEKS with the end-capped O–H or N–H groups of DHPZ was firstly synthesized via a nucleophilic aromatic substitution (S_NAr), and then reacted with pentafluorostyrene to yield the cross-linkable PPEKS–FSt with tetrafluorostyrene at the chain end. As a bisphenol-like monomer, the phthalazinone N–H group in DHPZ behaves like the phenolic O–H group with result that DHPZ can react with the activated dihalo compounds to produce high molecular weight polymers via combined C–N and C–O coupling reactions [18]. To avoid branching or cross-linking side reactions, the second step of the end-capped reaction was therefore conducted at a temperature of 110 °C in darkness. And no peak attributing to branch structure existed in the ^{19}F NMR (Fig. 2b) spectra suggested that a good control of the FSt end-capped linear structure was obtained for PPEKS–FSt under this reaction condition.

The inorganic salts in the reaction system should be eliminated completely during the purifying process to avoid the undesirable optical loss. The purification of the resulting PPEKS–FSt involved filtering its DMAc solution through the Celite layer before precipitating it into sufficient ethanol containing a few drops of concentrated hydrochloric acid, and boiling in pure water, followed by filtration, washing thoroughly with pure water and methanol. Herein hydrochloric acid was used to neutralize the excess potassium carbonate to potassium chloride which could be soluble in water. Thus the inorganic salts could be eliminated by washing thoroughly with pure water.

GPC analysis, using chloroform as the eluent and polystyrene as standards, indicated that the number-average molecular weight of PPEKS–FSt ($M_n = 0.95 \times 10^4$) was close to the designed value ($M_n = 1.1 \times 10^4$). Additionally, the weight-average molecular weight (M_w) and molecular weight distribution (M_w/M_n) of PPEKS–FSt was 2.47×10^4 and 2.6, respectively. It has been demonstrated that initial low concentration of the reactive monomers could favor the formation of cyclic oligomers during the polycondensation reaction [19,20]. In this reaction, if the cyclic oligomers of PPEKS once formed during the first step of the synthetic procedure, the introduction of FSt moiety will be prevented. Thus it was necessary to minimize the formation of the cyclics. Examination of the GPC curves of PPEKS (see Fig. 1) revealed that the content of cyclic oligomers contributed about 10% (peak a in Fig. 1) to the final product at a 23 wt% initial monomer concentration while the amount of those oligomers decreased to 0.32% (peak b in Fig. 1) as the initial concentration reached 50 wt%, which demonstrated that higher initial monomer concentration could effectively minimize the formation of cyclic oligomers in the reaction. As a consequence, the initial concentration of the reactants was 50 wt% in our reaction system.

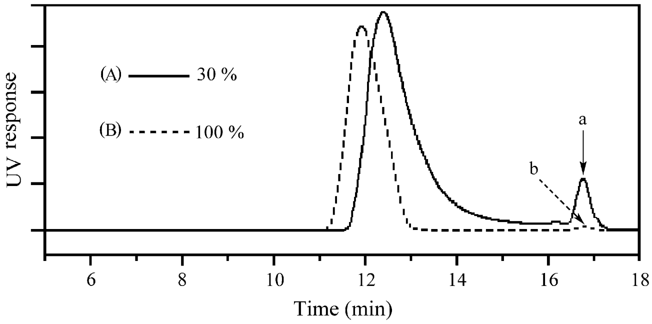


Fig. 1. GPC curves of PPEKS with different initial monomer concentrations: (A) 23 wt%; (B) 50 wt%.

3.2. Characterization of PPEKS–FSt

The chemical structure of PPEKS–FSt was characterized by ^{1}H NMR, ^{19}F NMR, and FT-IR spectra. The fact in Fig. 2b that the *para*-fluorine (F^c) peak of pentafluorostyrene at −156.48 ppm disappeared completely, the *ortho*-fluorine (F^a) peak centered at −143.79 ppm shifted slightly to −143.73 ppm ($F^{a'}$), and the *meta*-fluorine (F^b) peak also shifted from −163.49 ppm to −155.55 ppm ($F^{b'}$) due to the resonance effect of the main chain indicated that the tetrafluorostyrene group was introduced at the end of the main chain successfully during the reaction. Meanwhile, no peak attributed to branch structure in the ^{19}F NMR spectra suggested that the FSt end-capped linear structure was obtained for PPEKS–FSt. And the emergence of peaks at 6.64, 6.08 and 5.69 ppm (the three kinds of protons on the vinyl group of FSt) in ^{1}H NMR spectrum (see Fig. 2a) also indicated that the FSt units were attached to the polymer and kept stable during the synthetic procedure. The IR spectrum of PPEKS–FSt (see Fig. 4b) showed the characteristic absorption bands near 1670 cm^{-1} (C=O stretching), 1588 cm^{-1}, 1488 cm^{-1} (C=C stretching vibration of the aromatic ring), 1325 cm^{-1}, 1154 cm^{-1} (asymmetric SO_2 stretching), 1242 cm^{-1} (Ar–O–Ar stretching), 1430 cm^{-1} (stretching vibration of the vinyl double bond in FSt group, CH_2=CH), 932 cm^{-1} and 975 cm^{-1} (out of plane vibrations of the vinyl group, CH_2=CH–). These characteristic bands in IR spectrum correlate sufficiently well with the expected structure of the target substance.

3.3. Solubility of PPEKS–FSt

No obvious diffraction peak observed in wide-angle X-ray diffraction (WAXD) diagram (Fig. 3) and the absence of crystalline melting peak in the DSC curve (Fig. 5) revealed the amorphous nature of PPEKS–FSt. The resulting amorphous polymer exhibited good solubility in polar organic solvents, such as chloroform, DMAc, DMF, NMP at room temperature. The excellent solubility of PPEKS–FSt can be ascribed to the crank and twisted noncoplanar phthalazinone structure and the flexible ether linkages, which help to cumber the close packing of the polymer chains, enlarge the average intermolecular distance of the polymer and enable solvent molecules to diffuse

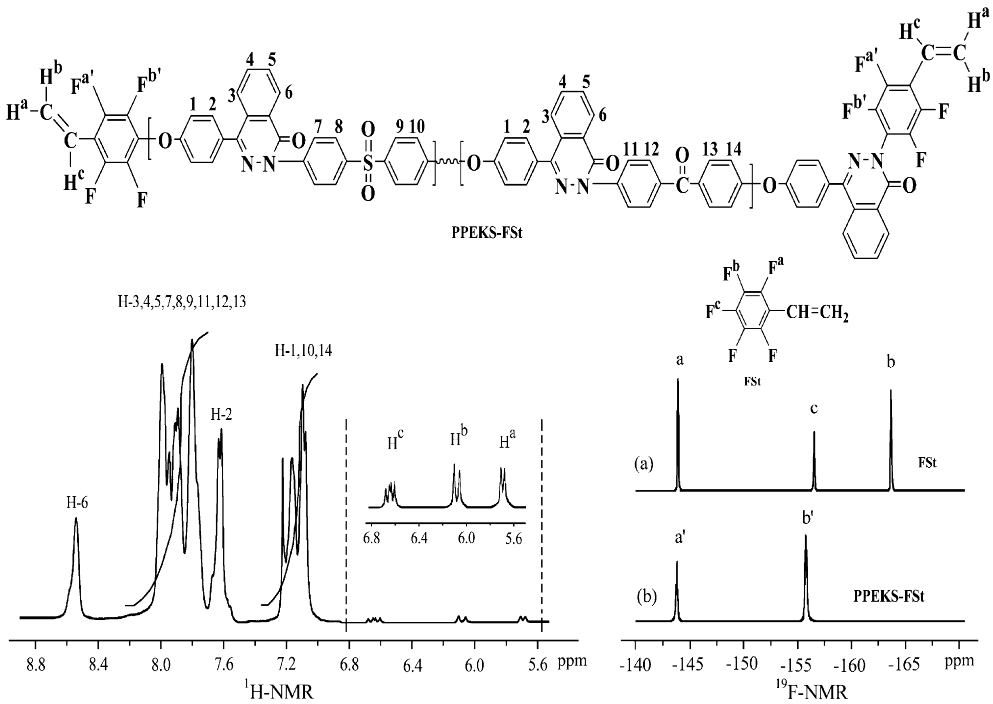


Fig. 2. ^{1}H NMR and ^{19}F NMR spectra of PPEKS–FSt (in $CDCl_3$).

easily into the polymer chains [21]. The excellent solubility of PPEKS–FSt makes it easier for film preparation by spin-coating, and it also shows the potential for further device fabrication.

3.4. Thermal cross-linking of PPEKS–FSt

It has been found that the tetrafluorostyrene (FSt) units could undergo cross-linking reactions by both thermal heating and UV irradiation under mild conditions in the presence of a suitable initiator [12c]. In this work, the thermal cross-linking of PPEKS–FSt was studied by heating the polymer films at either 160 °C in the presence of a free radical initiator, dicumyl peroxide (1 wt% relative to the polymer) for 4 h under vacuum, or at 220–280 °C in the absence of any initiator for 20 min in air atmosphere.

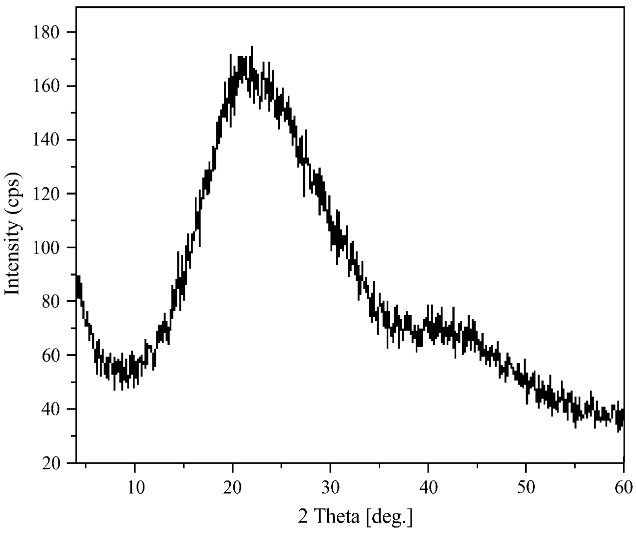


Fig. 3. WAXD diffractogram of PPEKS–FSt.

Since the vinyl group has the specific IR absorption and it could give information on the chemical structure change during the cross-linking process, the thermal cross-linking reaction was monitored by FT-IR spectroscopy. And the characteristic bands near 1430 cm^{-1} (stretching vibration of the vinyl double bond in FSt group, $CH_2{=}CH$), 932 cm^{-1} and 975 cm^{-1} (out of plane vibrations of the vinyl group, $CH_2{=}CH-$) were selected for reference. The comparisons of FT-IR spectra of the monomer FSt (a) and PPEKS–FSt films during thermal cross-linking process at various heating temperatures with (f) or without (b–e) an initiator are depicted in Fig. 4. It can be clearly seen that, without any initiator, the samples give little changes in the FT-IR spectra before being heated to 260 °C (b–d). However, the absorption peaks near 975 cm^{-1} ($CH_2{=}CH-$), 932 cm^{-1} ($CH_2{=}CH-$) and 1430 cm^{-1} ($CH_2{=}CH$) quickly decrease with increasing the temperature over 260 °C and then almost disappear at 280 °C (e), which suggests the completeness of thermal cross-linking reaction of the FSt units. Similar phenomena of the absorption peaks near 975 cm^{-1}, 932 cm^{-1} and 1430 cm^{-1} are also observed (see Fig. 4f) by heating the film at 160 °C for 4 h under vacuum with an initiator of dicumyl peroxide (1 wt% relative to PPEKS–FSt). The results above indicated that this initiator is highly efficient in inducing the thermal cross-linking of FSt units in PPEKS–FSt. Considering the side effects such as yellowing of the polymer films which were usually observed when heated at high temperature, the samples should be cured at 160 °C in the presence of 1 wt% dicumyl peroxide as an initiator for 4 h under vacuum to yield stable cross-linked films.

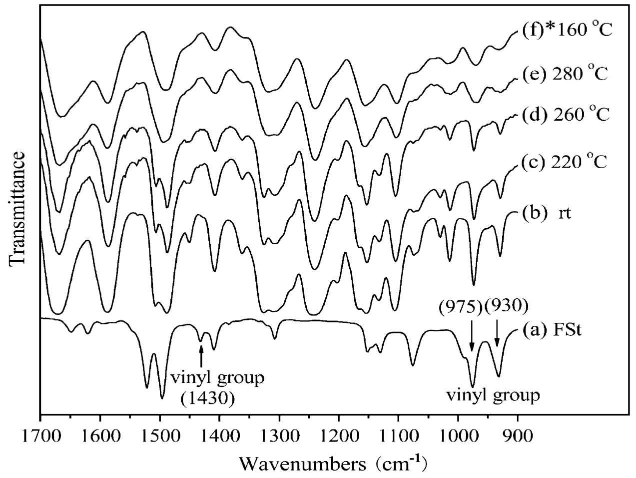


Fig. 4. FT-IR spectra of (a) FSt and PPEKS–FSt films during thermal cross-linking process with different initiator contents; (b–e) 0 (in air) and (f) 1 wt% (under vacuum).

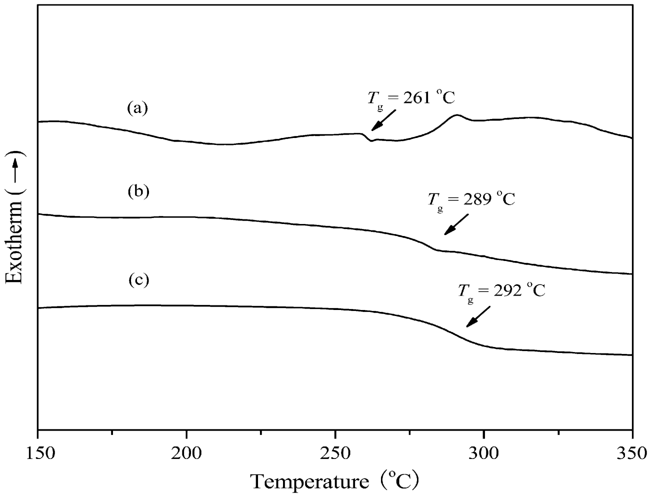


Fig. 5. Effect of the degree of curing on the T_g of PPEKS–FSt: (a) the first scan; (b) the second scan and (c) the third scan.

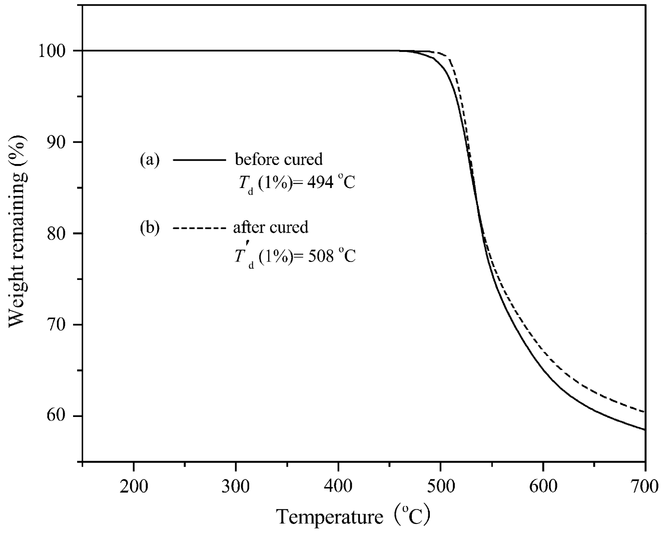


Fig. 6. TGA thermograms of PPEKS–FSt: (a) before thermal cross-linking and (b) after thermal cross-linking.

Table 1
Uniformity[a] of film thickness and refractive index

Spinning speed (rpm)	Average thickness[b] (μm)	Uniformity of thickness (%)	Uniformity of refractive index[c] (%)
1000	6.45	<2.0	<0.03
3000	2.70	<1.5	<0.04
4000	1.64	<0.8	<0.05
6000	1.10	<0.5	<0.04

[a] The values were calculated as follows: uniformity(%) = $|A - A_{\text{ave}}|/A_{\text{ave}} \times 100\%$, where A and A_{ave} denote the maximum/minimum and average value of film thickness or refractive index, respectively.

[b] Six points were tested per spin-coated film.

[c] The values of TE mode were tested by the prism-coupling method at the wavelength of 1310 nm.

The cross-linking process of PPEKS–FSt was also investigated by DSC, and the results are represented in Fig. 5. It can be observed that, the exothermic peak, which attributed to the reaction of the styrol group in Fig. 5a, disappeared in Fig. 5b and c. In addition, as the scan number of DSC increased, the T_g of PPEKS–FSt increased from 261 to 292 °C, clearly indicating the occurrence of cross-linking reactions.

The thermal decomposition temperature, defined as the temperature of 1% weight loss, at a heating rate of 20 °C min^{-1} in a nitrogen atmosphere, was also measured by TGA as shown in Fig. 6. The cross-linked polymer exhibits a 14 °C increase in thermal decomposition temperature; thus the temperature of 1% weight loss is up to 508 °C, which is much higher than most of the cross-linkable polymers used as optical materials [2,3,12].

3.5. Optical properties

To measure the optical properties such as refractive index and optical loss, PPEKS–FSt was dissolved in NMP at a concentration of 16.7 wt%, and then spin-coated on a Si/SiO$_2$ wafer substrate. In order to guarantee the quality of the spin-coated films, the whole spin-coating procedure was carried out in a 1000 class ultraclean room, and the polymer solution was filtered by a 0.45 μm Teflon membrane filter. The obtained films exhibited good membrane quality and their thickness could be controlled into a range of 1–7 μm by spin-coating with different speeds, 1000–6000 rpm.

The uniformity of film thickness and refractive index was investigated by using the prism-coupling method. The results are summarized in Table 1.

From the test results showed in Table 1, the uniformity of film thickness and refractive index are found to be better than 2% and 0.05%, respectively, which meets the requirements of optical waveguide applications. Additionally, the test results show that the spinning speed has a tremendous influence on the control of the film thickness. The uniformity of the film thickness gets better and better with the increase of spinning speed. Therefore, we could achieve perfect film thickness uniformity by controlling the spinning speed.

Birefringence is quantified by the difference between the refractive indices of parallel and perpendicular to the plane of orientation. Perpendicular indices of anisotropic waveguide materials are labeled n_{TE} and n_{TM}, whereupon the subscripts denote the transverse electric (TE) and transverse magnetic (TM) modes in the medium, respectively. Unlike silica glass, whose birefringence arises from the stress formed in processing, the birefringence of polymer materials comes mainly from the preferred orientation of rigid groups and polymer chains [6]. In addition, a polymer film usually undergoes molecular orientation during spin-coating. The refractive indices and birefringence of the polymer films at the wavelengths of 1310 nm and 1550 nm were measured by a Sairon SPA-4000 prism coupler. The results are shown in Table 2.

In general, the high speed of spinning during the spin-coating process causes the polymer chains to extend in a direction parallel to the film plane. Therefore, in such cases, the refractive index in the TE mode is larger than that of the TM mode [5]. Similar to other conventional spin-coated polymer films, PPEKS and PPEKS–FSt show a larger n_{TE} than n_{TM}. As shown in Table 2, before thermal cross-linking, the birefringence ($\Delta n = n_{TE} - n_{TM}$) of PPEKS and PPEKS–FSt are observed to have similar values about 0.02. However, the birefringence of the thermally cross-linked PPEKS–FSt reduces from 0.02 to 0.007. It can be ascribed to the reduction of electronic polarizability in the polymer chains. It has been proved that [22], birefringence depends on the polarizability and van der Waals volume of the repeating unit. Larger polarizability leads to high birefringence. During thermal cross-linking, the reaction of tetrafluorostyrol units leads to the break of π-conjugation, and consequently, results in a decrease in electronic polarizability of the polymer chains. As a result, a large decrease in birefringence was observed. However, it should be noted that the birefringence was a little higher in this work. Some further structural modifications, such as inserting FSt units into the polymers both as end-caps and pendant groups, still need to be explored. And the preparation of these polymers is currently under way in order to reduce the birefringence to an acceptable value.

As is known that, low optical loss in the near IR region is one of the most important requirements for optical waveguide materials. The optical loss of PPEKS–FSt was evaluated from the slab waveguide loss using high index liquid immersion method. The values were found to be less than 0.24 dB/cm at 1310 nm and 0.52 dB/cm at 1550 nm, indicating a high transparency of the polymer at the telecommunication wavelengths. Compared with the commercial materials reported by Ma et al. [3], the optical loss of the PPEKS–FSt is even a little lower than some highly fluorinated polymers due to the low content of aliphatic C–H bonds in its backbone.

Table 2
Refractive indexes and birefringences of PPEKS[a] and PPEKS–FSt[b]

Polymers	Wavelength (1310 nm)			Wavelength (1550 nm)		
	n_{TE}[c]	n_M[c]	Δn[d]	n_{TE}[c]	n_{TM}[c]	Δn[d]
PPEKS	1.6569	1.6352	0.0217	1.6537	1.6320	0.0217
PPEKS–FSt 1	1.6552	1.6341	0.0211	1.6523	1.6311	0.0212
PPEKS–FSt 2	1.6518	1.6450	0.0068	1.6486	1.6419	0.0067

[a] PPEKS, without FSt units, produced in the first step of the synthetic procedure.

[b] PPEKS–FSt 1, the polymer before thermal cross-linking; PPEKS–FSt 2, the polymer after thermal cross-linking.

[c] Refractive index of the TE- or TM-optical guided mode.

[d] Birefringence, $\Delta n = n_{TE} - n_{TM}$.

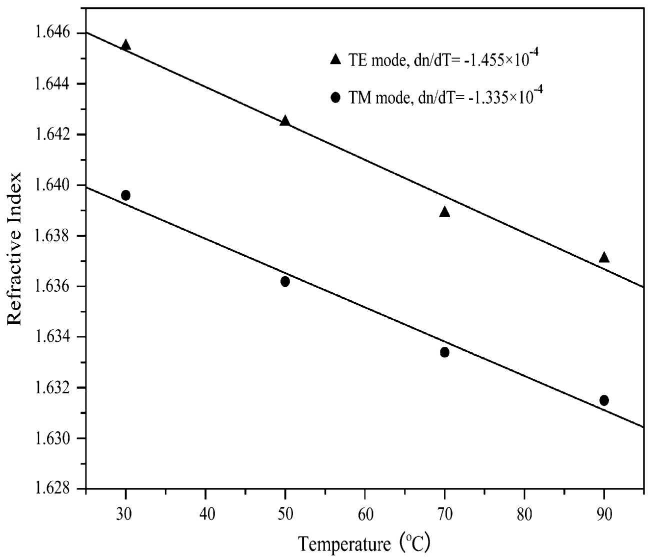


Fig. 7. Refractive index of PPEKS–FSt versus temperature at 1550 nm.

Besides optical loss, refractive index and birefringence, thermo-optic (T-O) coefficient (dn/dT) also plays a vital role in indicating the optical properties of the polymer. The dn/dT values of PPEKS–FSt were calculated by linear fit of the refractive indices at different temperatures at the wavelengths of 1310 nm and 1550 nm. Fig. 7 shows the refractive indices of PPEKS–FSt at different temperatures at a wavelength of 1550 nm. The slopes of the curves represent the dn/dT values of the polymer. It can be seen that the refractive index decreases linearly with increasing temperature, namely, the polymer has a negative temperature coefficient of the refractive index. The dn/dT values of PPEKS–FSt for TE and TM mode are -1.455×10^{-4}/°C and -1.355×10^{-4}/°C, respectively. As is known that, large T-O coefficient corresponds to a small temperature change and thus a small power input for causing the necessary change in the refractive index of polymer waveguides. These large dn/dT values of PPEKS–FSt, which are one order of magnitude larger than those of inorganic glasses [3], are especially useful for devices in which thermal jump actuation is utilized for switching optical communication signals from one optical circuit to another.

4. Conclusions

Tetrafluorostyrene-terminated novel cross-linkable poly(phthalazinone ether ketone sulfone) (PPEKS–FSt) has been designed and synthesized by the copolymerization of DHPZ, BCS and DFK with FSt. The obtained polymer exhibits good solubility in some polar organic solvents and excellent thermal stability, which could simplify device fabrication and processing. The reactive tetrafluorostyrene units attached at the chain end of the polymer not only lower the birefringence but also improve the thermal stability up to 508 °C (1% T_d) by thermal cross-linking reaction. The optical loss of PPEKS–FSt exhibits a relatively low value (less than 0.24 dB/cm at 1310 nm) compared to some highly fluorinated polymer. Additionally, the thermo-optic (T-O) coefficient (dn/dT) values of PPEKS–FSt for TE and TM modes are $-1.455 \times 10^{-4}/°C$ and $-1.355 \times 10^{-4}/°C$, respectively, which are one order of magnitude larger than those of inorganic glasses. These results indicate that the application of PPEKS–FSt in the field of low cost optical waveguide appears feasible and promising.

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