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Alkyl-substituted carboxyl-containing polyaryletherketones and the crosslinking modifications with various bisphenols: Preparation and optical properties

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ABSTRACT

The birefringences, optical losses, refractive indices and their temperature dependency over a range of 30–90 °C for the films of carboxyl-containing polyaryletherketones with systematically varied alkyl substituents were investigated in detail. The results showed that the optical losses at 1310 nm were mainly affected by the content of C–H bond, whereas that at 1550 nm were more related to the presence of O–H bond. Moreover, two methyls and two bulky isopropyls on the phenylene rings led to the distorted polymer chain, which significantly reduced the chain packing density and disturbed the alignment of polymer chains along the substrate surface, and consequently resulted into the polymer films low refractive indices and birefringences. Furthermore, after conversion of carboxylic group to acyl chloride group, using rigid rod-like hydroquione and twisted phenolphthalein as bisphenol crosslinkers, respectively, the transparent smooth polymer films with three-dimensional network structures were readily obtained at the curing temperature below 200 °C without needing any additional catalyst. The cured polymers exhibited excellent resistance to organic solvents and good thermal stability as well as low birefringence of 0.0019 and greatly decreased optical loss at 1550 nm by about 78%.

1. Introduction

Amorphous polymer materials with high glass transition temperature have attracted considerable attention in applications of optical waveguide and optical interconnection because of their easy processability, relatively low cost compared to silica-based materials, good compatibility with semiconductor materials and facile controllability of optical properties [1–4]. Besides the advantages above, for the fabrication of optical component, an ideal polymer material should possess a variety of other comprehensive properties, including low propagation loss at the major telecommunication wavelength, low birefringence, precisely adjustable refractive index, good thermal stability, chemical and environmental resistance, as well as strong interfacial adhesion on substrates. However, these properties are often found to be contradictory to each other. For example, polyimides have good thermal stability and high T_g, but the rigid planar structures usually lead them to large birefringence values. For the fluorinated polymers, the improved refractive index, optical loss and moisture absorption are often accompanied by the sacrifice in adhesion property.

The development of polymeric materials with excellent properties requires both knowledge on property–structure correlation and proficiency at synthesizing polymers with predetermined structures. Over the past decade, a lot of works have been done in the synthesis of polymers to look for new polymer materials with the combination of excellent optical and physical properties [5–10]. The results showed that the polymeric optical materials could be affected by a variety of factors, such as glass transition temperature, substituent, configuration and conformation, chain packing and free volume, molecular polarity, inter-segmental distance and interaction, rigid and mobility ability, and crosslinking density, etc [11–19]. Nevertheless, the current understanding of physicochemical influences on optical properties, such as refractive index, birefringence, optical loss, and thermal-optical coefficient is still far less sufficient.

Polyaryletherketones are among the high-performance polymers, and have been considered as potential candidates as waveguide materials [20–23]. They can be easily prepared into films because of their good solubility in organic solvents, and the flexible ether and ketone groups in the backbones made these polymers tend to have low birefringence values than other high T_g polymers. In addition, in order to meet the requirements of multilayer coating process and environment stabilities, the after-curing procedure of film is usually necessary. Ding et al. introduced tetrafluorostyrene

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group onto the polymer chain, and the thermal curing could be carried out at 160 °C in the presence of dicumyl peroxide [20]. Chen and Jiang et al. used phenyl ethynyl as crosslinkable groups and the polyaryletherketones could cure at very high temperature of 370 °C [24,25]. Guiver et al. synthesized polyaryletherketones containing carboxylic acid groups and the carboxylic acid groups were used to react with poly(vinyl alcohol) (PVA) to prepare crosslinked polymers [26].

Recently, a series of polyaryletherketones (PEKs) were synthesized in our laboratory, which contain simultaneously carboxylic group and bulky alkyl substituents on the phenylene rings, endowing PEKs with high glass transition temperature, excellent heat-resistance and mechanical toughness as well as good film-formation property [27,28], In this paper, we systemically studied the influence of different alkyl substituents on optical properties of polymers, including birefringence, optical loss, refractive index and its temperature dependency. In addition, after conversion of carboxylic group into acyl chloride group, using rigid rod-like hydroquinone and kinked phenolphthalein as bisphenol curing agents, respectively, the polyaryletherketones could be readily crosslinked at relatively low temperature below 200 °C without using any catalyst, and their thermal and optical properties were examined in terms of the influences of a variety of structural factors. To the best of our knowledge, the preparations of crosslinked polyaryletherketones by means of esterification of acyl chlorides with bisphenols are rarely reported in the literature. Considering the versatility of bisphenol compounds, good miscibility between bisphenols and polyaryletherketones before curing and the ease of operation, this method is of great significance for investigating the structure-property relationship and developing new crosslinking polymeric optical materials.

2. Experimental

2.1. Materials

Phenolphthalein (PPH), 2′,2″-diisopropyl-5′,5″-dimethyl-phenolphthalein, 2′,2″-dimethyl-phenolphthalein and bis(4-fluorophenyl)ketone (DFDPK) were purchased from Aldrich Chemical Company and used without further purification. Hydroquinone (HQ) was obtained from Tianjin Chemical Reagent Factory, and purified by recrystallization from ethanol. 2-(bis(4-hydroxyphenyl)methyl) benzoic acid (PPL-1), 2-(bis(4-hydroxy-3-methylphenyl)methyl) benzoic acid (PPL-2), 2-(bis(4-hydroxy-3-isopropyl-5-methylphenyl)methyl)benzoic acid (PPL-3) were prepared in our laboratory according to the procedure described in the literature [29]. Thionyl chloride was provided by Shenyang Chemical Reagent Factory, and distilled just before use. Dimethyl sulfoxide (DMSO) and *N,N*-dimethylformamide (DMF) were provided by Fuyu Fine Chemical Industry Co., Ltd. and were purified by reduced pressure distillation prior to use. Other chemical reagents were of analytical grade and used without further purification unless otherwise stated.

2.2. Synthesis

2.2.1. Synthesis of carboxyl-containing poly(aryl ether ketone)s

PEK-1 was prepared via solution polycondensation reaction according to the procedure described in our previous paper [25]. 6.4069 g (0.02 mol) PPL-1, 4.3640 g (0.02 mol) DFDPK, 5.5282 g (0.04 mol) anhydrous K_2CO_3, 18 ml toluene and 16 ml DMSO were added into a three-necked round bottom flask equipped with Dean–Stark trap, N_2 inlet, mechanical stirrer and thermometer. When the temperature was raised to 140 °C, water began to be collected in the Dean–Stark trap. After toluene and water were distilled out, the reactant was heated gradually to 175 °C, and allowed to react at this temperature for 12 h to obtain a viscous solution finally. The product was diluted with DMF, then precipitated in a stirred mixed solution of ethanol and 0.1 N aqueous hydrochloric acid solution (v/v, 1:2) to separate white polymer. The polymer was dried at 100 °C for 12 h after complete removal of inorganic salt by washing with boiled water for several times. The yield was 92%. FTIR (cm^{-1}): 3030, 2988, 1720, 1698, 1655, 1592, 1499, 1245, 724; ^1H NMR (400 MHz, DMSO-d_6/TMS, ppm): 12.99 (s, 1H), 7.80 (d, 1H), 7.72 (d, 4H), 7.46 (t, 1H), 7.32 (t, 1H), 7.08 (d, 9H), 6.68 (s, 1H), 1.98 (s, 3H).

The syntheses of PEK-2 and PEK-3 were carried out in the similar procedure to that for PEK-1 except that the bisphenols used was PPL-2 and PPL-3 instead of PPL-1, with the yield of 90% and 92%, respectively. PEK-2: FTIR (cm^{-1}): 3030, 2993, 2987, 1726, 1702, 1655, 1592, 1500, 1245, 738; ^1H NMR (400 MHz, DMSO-d_6/TMS, ppm): 12.99 (s, 1H), 7.81 (d, 1H), 7.72 (d, 4H), 7.47 (t, 1H), 7.32 (t, 1H), 7.08 (d, 13H), 6.68 (s, 1H). PEK-3: FTIR (cm^{-1}): 3030, 2961, 2967, 2869, 1726, 1669, 1655, 1592, 1500, 1245, 735; ^1H NMR (400 MHz, DMSO-d_6/TMS, ppm): 12.99 (s, 1H), 7.82 (d, 1H), 7.68 (d, 4H), 7.47 (t, 1H), 7.36 (t, 1H), 6.98 (d, 5H), 6.67 (d, 4H), 6.68 (s, 1H), 2.83 (s, 2H), 0.97 (s, 12H).

2.2.2. Synthesis of PEK-COCl

The synthesis procedure for poly(aryl-ether-ketone) bearing pendant aroyl chloride group (PEK-COCl) was described as follows: 0.9971 g PEK-1 (2.0 mmol) was added to a dry 50-mL round flask equipped with magnetic stirring bar, condenser and drying tube. It was dissolved immediately after adding 25 mL thionyl chloride (34.7 mmol). The solution was then stirred and refluxed for 24 h to ensure that the reaction finished. Excess thionyl chloride was distilled off under reduced pressure. The product was dried under vacuum at 60 °C for 24 h to give pale-yellow solid of PEK-COCl.

2.3. Film preparations

For PEK-1 film, a polymer solution was prepared by dissolving PEK-1 in cyclohexanone (15 wt%). Then the solution was filtered through a 0.22-μm Teflon filter and spin coated onto a silicon wafer or a quartz substrate. The resulting films were dried at 60 °C for 0.5 h and 120 °C for 4 h to remove the residual solvent under vacuum. The preparation procedures for PEK-2 and PEK-3 films were similar to that of PEK-1.

For the crosslinked polymer films, a typical procedure for PEK-HQ was described as follows: 3.000 g PEK-COCl (5.8 mmol) was dissolved in 10 mL of dried cyclohexanone. Then a solution of 0.319 g HQ (2.9 mmol) in 10 mL of dried cyclohexanone was added, followed by stirring vigorously for 10 min. The solution was filtered through a 0.22-μm Teflon filter, and then the film was prepared by spin coating on a cleaned silicon wafer. After drying, the film was cured at 80 °C for 12 h, 160 °C for 5 h, at 200 °C under vacuum for 12 h, and allowed to slowly cool to room temperature. The thermal crosslinking procedure for PEK-PPH film was similar to that for PEK-HQ except that the crosslinker was PPH instead of HQ.

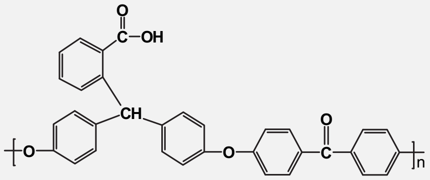
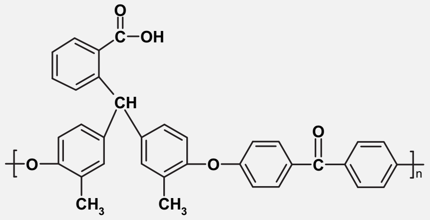
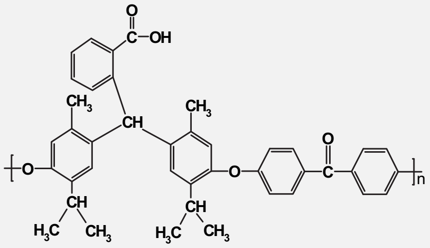
2.4. Measurements

Fourier transform infrared spectra (FTIR) were recorded using a Nicolet 20XB FTIR spectrophotometer in the 400–4000 cm^{-1} region with KBr flake.

Gel permeation chromatography (GPC) analyses were carried out on a PL-GPC220 system using polystyrene (PS) as standard and tetrahydrofuran (THF) as the eluent.

Wide-angle X-ray diffraction (WAXD) measurements were performed on a D/Max-2400 X-ray diffractometer with CuKα_1 radiation ($\lambda = 1.54$ Å) over the 2θ range of 4–60°. Film samples of

Table 1
Three carboxyl-containing PEKs and their physical properties.

Sample	Structure	M_n (kg/mol)	M_w (kg/mol)	PD	T_g (°C)	d-spacing (Å)	R_D (cm^3/mol)	R (cm^3/g)
PEK-1		84.4	222	2.64	228	4.68	144	0.290
PEK-2		44.5	88.0	1.98	211	4.88	153	0.292
PEK-3		48.2	124	2.56	231	6.69	181	0.298

ca. 40-μm thickness were vacuum dried at 180 °C for at least 24 h before measurement.

The atomic force microscopy (AFM) images were recorded with an Agilent PicoPlusII microscope in the tapping mode at room temperature. The images were recorded in tapping mode to avoid the possible deformation and indentation of the polymer surface by the tip. The values of root mean square (rms) roughness were calculated over the whole captured film area using the accessory software of instrument.

Thermogravimetric analyses (TGA) were run on NETZSCH TG209C under nitrogen atmosphere in the 50–700 °C region and conducted with a heating rate of 10 °C·min^{-1}.

Refractive index, thermo-optic coefficients, birefringence, and optical loss were measured at room temperature on a Sairon SPA-4000 prism coupler with a gadolinium gallium garnet (GGG) prism. For each sample, at least three pieces of films were measured and their values were averaged.

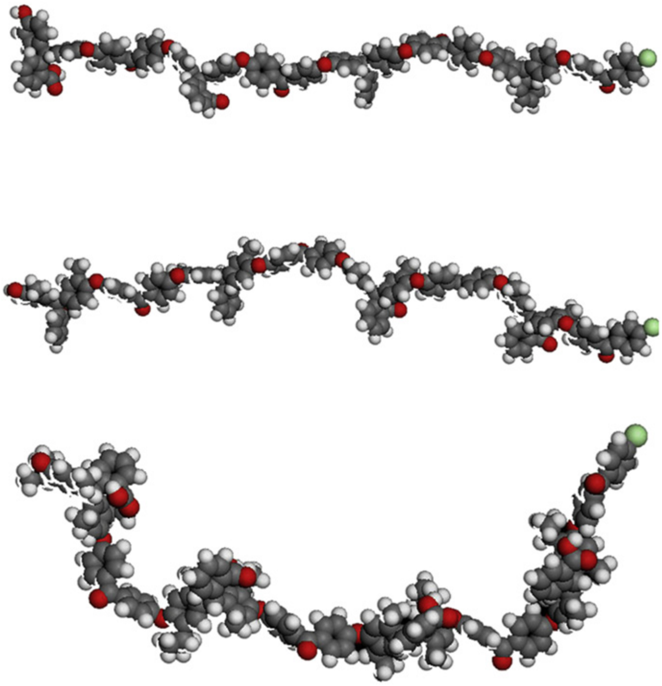


Fig. 1. Chain conformations of PEKs containing four repeating units: (up) PEK-1; (middle) PEK-2; (down) PEK-3.

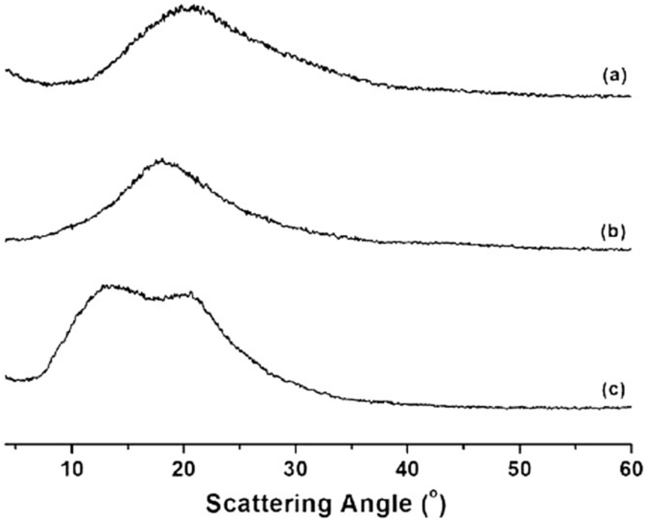


Fig. 2. WAXD patterns of (a) PEK-1, (b) PEK-2, and (c) PEK-3.

Table 2
Refractive indices and birefringences of PEKs.

Sample	Wavelength (1310 nm)			Wavelength (1550 nm)		
	n_{TE}	n_{TM}	Δn[a]	n_{TE}	n_{TM}	Δn[a]
PEK-1	1.619	1.608	0.011	1.616	1.605	0.011
PEK-2	1.601	1.594	0.007	1.598	1.591	0.007
PEK-3	1.572	1.565	0.006	1.569	1.563	0.006

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

Table 4
Optical loss values of PEK films.

Sample	Optical loss (dB cm^{-1})	
	1310 nm	1550 nm
PEK-1	0.237	2.876
PEK-2	0.470	2.735
PEK-3	0.517	2.426

The refractive indices n_{TE} and n_{TM} for the transverse electric (TE) and transverse magnetic (TM) modes of the films were measured by using a Sairon SPA-4000 prism coupler at room temperature at the wavelengths of 1310 nm and 1550 nm, respectively, with the accuracy of 0.001 and the resolution of ±0.0005. The birefringences (Δn) were calculated as the difference between n_{TE} and n_{TM}. The curves of refractive index as a function of temperature was obtained by measuring the refractive indices at different sample temperature, and their slopes were thermo-optic coefficient. The optical losses of the films were measured on slab waveguide samples at 1310 nm and 1550 nm, respectively, using the technique of high-index liquid immersion on the Sairon SPA-4000 prism coupler, which gave a highly precise measurement down to 0.05 dB cm^{-1}.

3. Results and discussion

3.1. Structure-property relationship of linear PEKs

Three polyaryletherketones and their physical properties containing different alkyl substituents are shown in Table 1, and the chemical structures were confirmed by means of FTIR and ^{1}H NMR methods. The number-average molecular weights (M_n) were in the range from 44.5 kg/mol to 84.4 kg/mol with the PD values from 1.98 to 2.64. These polymers had high glass transition temperatures above 211 °C and were soluble in polar organic solvents such as dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethlyacetamide (DMAc), cyclohexanone, *N*-methylpyrrolidone (NMP), tetrahydrofuran (THF) at the room temperature, exhibiting good film-formation properties.

The energy-minimized polymer backbones containing four repeating units by molecular modeling are illustrated in Fig. 1. For conformation simulations, molecular models were generated using energy minimization via conjugate-gradient method. The algorithm was set to Polak-Ribiere, convergence and line search were equal to 0.1 and 0.5, respectively. Molecular dynamics simulations were performed using COMPASS force field. Because the results by energy minimization were affected by the initial structures, several structures with different torsions, e.g., 0, 60, 120, 180, 240, 300 were constructed, and calculated, respectively. The structure with lowest energy was the best optimal result. The calculation results of total potential energies were relative energies, and there were not absolute meaning. The total potential energies for PEK-1, PEK-2 and PEK-3 were −210.13, −149.15 and −255.54, respectively. As a result, PEK-1 had rigid and straight polymer chain, while the chain conformation of PEK-2 was relatively twisted when the two hydrogen atoms on phenylene ring were replaced by methyl group, and this trend became more pronounced if another two bulky isopropyl groups were introduced for PEK-3. The kinked polymer structure serious restricted PEK-3 effective chain packing, leading to it the most disordered and loose aggregation structure among the three polymers.

Table 3
Thermo-optic coefficients of PEKs.

Sample	Wavelength (1310 nm)		Wavelength (1550 nm)	
	dn_{TE}/dT (°C)	dn_{TM}/dT (°C)	dn_{TE}/dT (°C)	dn_{TM}/dT (°C)
PEK-1	-1.42×10^{-4}	-1.15×10^{-4}	-1.32×10^{-4}	-1.25×10^{-4}
PEK-2	-1.41×10^{-4}	-1.25×10^{-4}	-1.41×10^{-4}	-1.28×10^{-4}
PEK-3	-1.43×10^{-4}	-1.25×10^{-4}	-1.50×10^{-4}	-1.31×10^{-4}

As shown from the WAXD diffractive patterns in Fig. 2, all the three polymers were amorphous, but relative to PEK-1 and PEK-2, the peak halo of PEK-3 was very wide and shifted toward a larger diffraction angle (2θ). The interchain distance (d-spacing) can be used as a measure of the chain packing density and free volume or the “tightness” of polymer structure. According to the Bragg’s equation: $\lambda = 2d\sin\theta$, the d-spacing could be calculated, and used to indicate the openness of chain packing. The results in Table 1 showed that the introduction of alkyl substituents made the d-spacing increase from 4.68 Å of PEK-1 to 4.88 Å of PEK-2, and finally reach to 6.69 Å of PEK-3, implying that PEK-3 had the most loose chain packing and the largest free volume among the three polymers.

In this study, all the polymer films were controlled to almost the same thickness by adjusting solution concentration and spin-coating speed so that an effective comparison could be made based only on the molecule structure. The average thickness of thin film was in 4–5 μm, measured by Sairon SPA-4000 prism coupler. Specifically, the film thickness values for PEK-1, PEK-2, and PEK-3 are 4.57 μm, 4.82 μm and 4.63 μm, respectively. The systematic structural variations in the three polymers were reflected by the results of refractive indices and birefringences. The birefringence of a polymer material comes mainly from its optical anisotropy due to the preferred orientation of rigid groups and polymer chains along the surface of substrate [30]. As shown in Table 2, for PEK-1, the rigid and straight polymer chain is advantageous for well aligning in parallel with the film surface during the spin-coating process and consequently, the birefringences of PEK-1 were the highest among

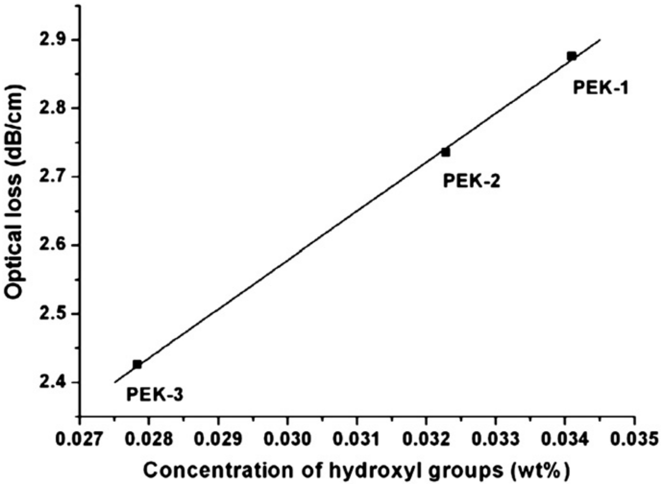
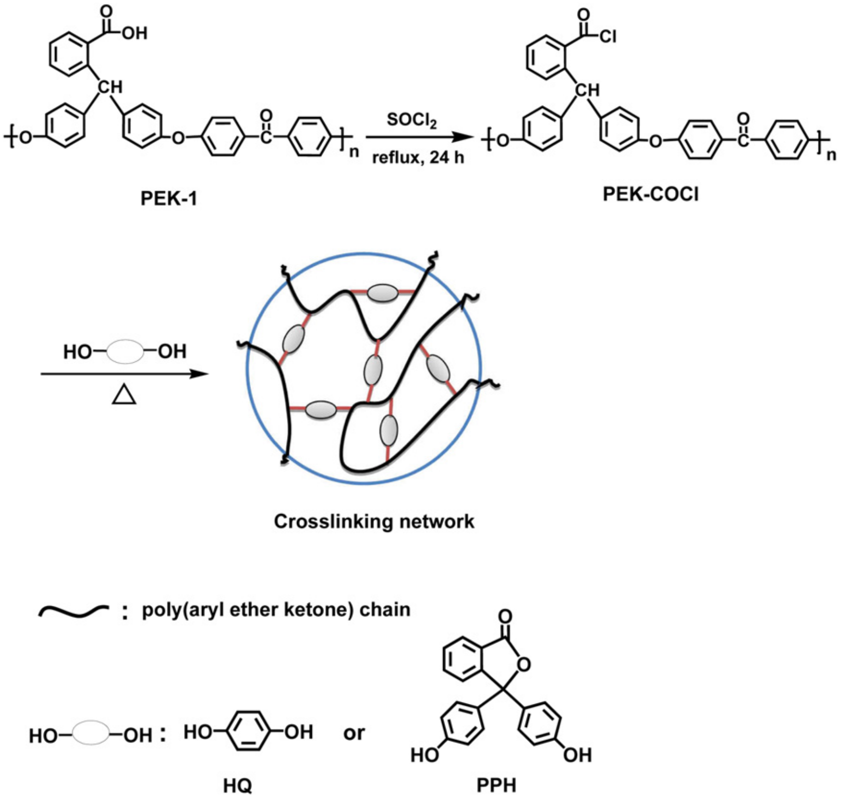


Fig. 3. Optical loss as a function of content of hydroxyl groups for the three polymer films.



Scheme 1. Synthesis route to PEK-COCl and crosslinked PEK-HQ and PEK-PPH.

the three polymers with the birefringence values of 0.011 both at 1310 nm and 1550 nm. As a contrast, for PEK-3, the twisted chain structure and disordered chain packing led to its more isotropic characteristic, exhibiting decreased birefringence values by about 44% compared to PEK-1.

It is well known that the relationship between refractive index and polymer molecular structure agrees with the Lorentz–Lorenz equation [31]:

$$\frac{n_D^2-1}{n_D^2+2}=\frac{R_D\rho}{M} \tag{1}$$

where n_D is the refractive index, ρ the density, R_D and M are the molecular polarizability and molecular weight of the polymeric repeating unit, respectively.

From Eq. (1), the following expressions for the refractive index can be easily derived:

$$n_D=\sqrt{\frac{1+\rho\frac{2R_D}{M}}{1-\rho\frac{R_D}{M}}}=\sqrt{\frac{1+2\rho R}{1-\rho R}} \tag{2}$$

where R_D value can be calculated according to the group contribution method [32], and $R=R_D/M$ is defined as molecular polarizability per mass unit. Their values are presented in Table 1. It can be seen from Eq. (2), that the larger R and density values are favorable for material higher refractive index. As could be seen, for this series of polymers, R values are similar, so the differences in refractive indices were mainly dominated by the chain packing densities. As a result, compared to PEK-1 and PEK-2, the wide chain d-spacing and loose chain packing rendered PEK-3 the obviously decreased refractive indices at the wavelength of both 1310 and 1550 nm.

Besides refractive index and birefringence, another important optical parameter is the thermal-optical coefficient. For some applications such as thermal-optical switch or variable optical attenuator, the polymers with high thermo-optical coefficient are preferred since a small temperature change is enough for the function of optical switching or optical attenuation and thus the power consumption is reduced. On the other hand, for arrayer waveguide grating application, thermo-optical coefficient should be as low as possible to reduce the wavelength shift caused by the fluctuation of environmental temperature. Fig. 2S-4S (Supporting Information) showed that the refractive indices of three polymers at 1310 and 1550 nm linearly decreased with temperature over the range from 30 to 90 °C. From the slopes, the thermo-optical

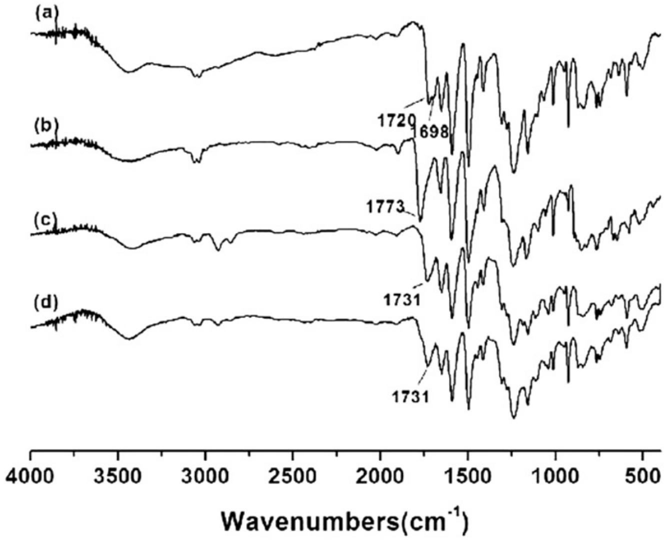


Fig. 4. FTIR spectra of (a) PEK-1, (b) PEK-COCl, (c) PEK-HQ, and (d) PEK-PPH.

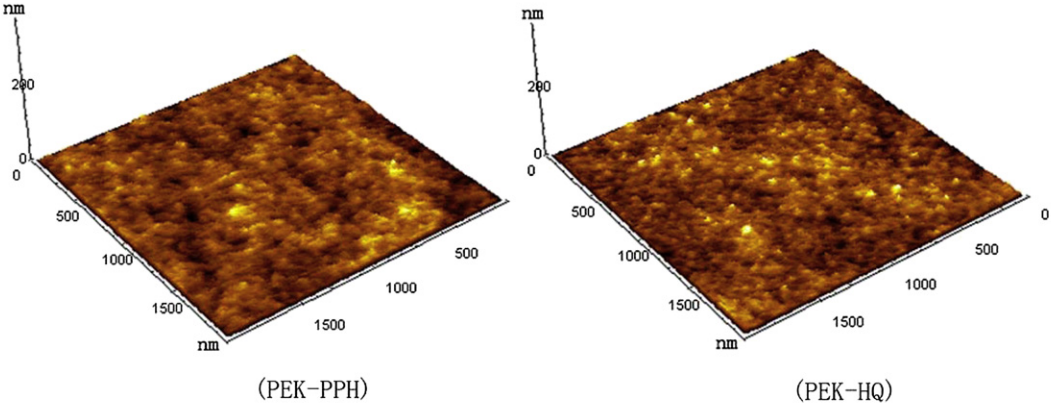


Fig. 5. AFM topography image of PEK-PPH and PEK-HQ films.

coefficients (dn/dT) were calculated and are listed in Table 3. It was found that the temperature dependency of refractive indices were also anisotropic, displaying the higher absolute values of dn_{TE}/dT than that of dn_{TM}/dT. Moreover, for the three polymers, at shorter wavelength of 1310 nm, the thermo-optical coefficients were similar, but showed apparent difference from -1.32×10^{-4} to -1.50×10^{-4}/°C at the longer wavelength of 1550 nm as in the order: PEK-3 > PEK-2 > PEK-1. The higher thermo-optical coefficient for PEK-3 could be attributed to its loose chain packing structure, similar to other polymer systems [33]. Generally, the dn/dT values of PEKs are one order of magnitude larger than those of inorganic glasses, showing potential in applications of thermo-optic active optical components such as thermo-optic switches [34] and tunable filters [35], etc.

The optical losses of PEKs at the wavelength of 1310 nm and 1550 nm are summarized in Table 4. The loss values at 1310 nm were in the range of 0.237–0.517 dB cm^{-1} and that at 1550 nm were from 2.426 to 2.876 dB cm^{-1}. Of interest was the observation that the ranking order of loss values at 1310 nm was PEK-3 > PEK-2 > PEK-1, which was opposite to that at 1550 nm. For PEK-1, the lowest loss value among the three polymers was due to the reason that the optical losses at 1310 nm were mainly affected by the content of C—H bond in polymers.

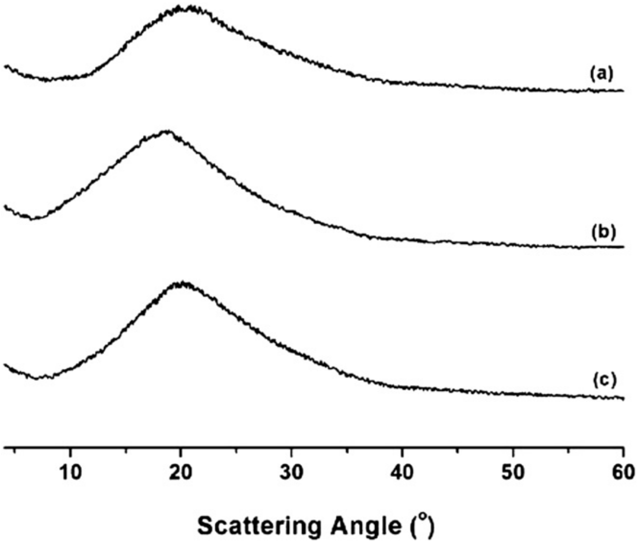


Fig. 6. WAXD patterns of (a) PEK-1, (b) PEK-HQ, and (c) PEK-PPH.

In our study, the film-formations were carried out in a 1000 class ultra-clean room to avoid the introduction of dust and particles. Thus, the optical loss mainly depended on absorption loss. According to Beer's law, $A = \varepsilon \bullet b \bullet c$, the optical loss can be represented as $A/b = \varepsilon \bullet c$, where A is absorbance, ε the molar absorbtivity, b the path length of the sample and c the concentration of the absorption unit, respectively, while the concentration of hydroxyl groups in the samples is calculated in term of mass percent for repeated unit. As a consequence, the relationship between the optical loss and concentration of hydroxyl groups for PEKs can be quantitatively obtained. As shown in Fig. 3, the optical loss has a very good linear relationship with the concentration of hydroxyl groups, demonstrating that the optical losses at 1550 nm were more related to the relative content of O—H bond in structural unit of a polymer since the O—H bond had strong absorption at this wavelength. As a result, PEK-1 with larger weight percentage of OH group displayed the higher optical loss than the other two polymers.

3.2. Synthesis and properties of three-dimensional crosslinked polymers

The synthetic routes to the crosslinked polyaryletherketones PEK-HQ and PEK-PPH are illustrated in Scheme 1. At first, PEK-COCl was synthesized through acyl chlorination of PEK-1 with thionyl chloride. The product exhibited good solubility in dichloromethane, chloroform, tetrahydrofuran and cyclohexanone, and could be easily mixed with HQ or PPH to form transparent uniform solution with equivalent stoichiometric ratio of acyl chloride and hydroxy group. Then the solution was spin coated on a clean silicon wafer to obtain a film. To avoid the possible sublimation of HQ and PPH, the curing process of PEK-COCl films containing bisphenols was firstly carried out at 80 °C for 12 h, then the temperature was increased gradually to 160 °C, and finally to 200 °C under vacuum to ensure complete curing. After curing, the films became insoluble in any

Table 5
DSC and TGA data of PEK-1, PEK-HQ and PEK-PPH.

Sample	T_g (°C)	T_5[a] (°C)	T_{10}[a] (°C)	T_{20}[a] (°C)	RW [b] (%)
PEK-1	228	425	450	486	58
PEK-HQ	232	437	464	561	72
PEK-PPH	239	397	435	473	57

[a] T_5, T_{10} and T_{20} are referred to the temperature at 5%, 10% and 20% weight loss, respectively.
[b] RW is referred to the residual weight percentage at 700 °C.

Table 6
Refractive indices and birefringences of PEK-HQ and PEK-PPH films.

Sample	Wavelength (1310 nm)			Wavelength (1550 nm)		
	n_{TE}	n_{TM}	Δn[a]	n_{TE}	n_{TM}	Δn[a]
PEK-1	1.619	1.608	0.011	1.616	1.605	0.011
PEK-HQ	1.620	1.615	0.005	1.616	1.612	0.005
PEK-PPH	1.615	1.613	0.002	1.612	1.610	0.002

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

Table 7
Optical loss values of PEK-HQ and PEK-PPH films.

Sample	Optical loss (dB cm^{-1})	
	1310 nm	1550 nm
PEK-1	0.237	2.876
PEK-HQ	0.379	0.622
PEK-PPH	0.413	0.667

common organic solvents, indicating the improved chemical resistance.

Fig. 4 shows the FTIR spectra of PEK-1, PEK-COCl, PEK-HQ and PEK-PPH. For PEK-1, the peaks at 1720 cm^{-1} and 1698 cm^{-1} were assigned to the C=O absorptions of free and hydrogen-bonded carboxylic groups, respectively. The conversions of carboxyl groups to acyl chloride groups were confirmed by the absorption at 1773 cm^{-1} and disappearance of the peaks of carboxylic group (Fig. 4b). After curing, for PEK-HQ and PEK-PPH, it was observed that the characteristic peak of COCl group at 1773 cm^{-1} disappeared completely, and alternatively, a new peak at 1731 cm^{-1} due to the ester linkage appeared (Fig. 4c and d). The above FTIR results confirmed that the esterification reaction between acyl chloride groups in PEK-COCl and hydroxyl groups of HQ or PPH carried out smoothly, and eventually formed crosslinked poly(aryl-ether-ketone) networks.

As shown in the AFM topography image (Fig. 5), the surfaces of PEK-PPH and PEK-HQ films were very smooth with the root mean square (RMS) roughness values of only 0.29 nm and 0.52 nm, respectively, and no aggregation phenomenon of HQ or PPH could be observed. The WAXD patterns of PEK-1, PEK-HQ, and PEK-PPH are illustrated in Fig. 6. It could be seen that PEK-HQ, and PEK-PPH displayed the amorphous structures with the wide hump very similar to that of uncrosslinked PEK-1 except for that the halo of PEK-HQ slightly shifted toward the small diffractive angle. The possible reason could be that the rigid rod-like HQ opened up the polymer chain, leading to PEK-HQ the increased inter-segmental spacing. Moreover, no obvious diffractive peaks for small molecule HQ or PPH could be detected in the WAXD pattern of either PEK-HQ or PEK-PPH, agreeing well with the FTIR and AFM observation that HQ and PPH had been uniformly mixed with PEK-1 and participated into the crosslinking reaction completely.

Thermal stabilities of PEK-HQ and PEK-PPH were evaluated by DSC and thermogravimetric analysis (TGA) methods. As expected, after curing, the crosslinked PEK-HQ and PEK-PPH exhibited the increased glass transition temperature due to the restricted segmental motion, and this effect was more obvious if using the rigid and twisted PPH as crosslinker. The TGA data are summarized in Table 5. PEK-HQ displayed 5% thermal decomposition loss at 437 °C, which was about 11 °C higher than that of uncrosslinked PEK-1, whereas a decreased thermal decomposition temperature for PEK-PPH was observed because of the introduction of relatively weak lactone bonds (Figs. 5S and 6S, Supporting Information).

Before curing, the values of PEK-HQ and PEK-PPH are 6.84 μm and 6.55 μm which, after curing, are shrank to 6.37 μm and 5.93 μm, respectively. The optical properties of crosslinked PEK-HQ and PEK-PPH films were measured using the same way as that of PEKs, and the data are listed in Table 6. Compared to PEK-1, the crosslinked PEK-HQ and PEK-PPH films did not display obvious change in refractive indices, but the birefringence values at 1310 nm were significantly decreased from 0.113 to 0.005 and 0.002, respectively, implying that the three-dimensional network of polymer was an effective way to decrease the difference of segmental orientation in the plane and out of plane of film on the substrate. Moreover, it was found that the birefringence PEK-PPH film at both 1310 nm and 1550 nm were more than twice lower than that of PEK-HQ, indicated that, relative to the rigid rod-like HQ molecule, the distorted structure of PPH led to the more isotropic segmental orientation in crosslinked PEK-PPH network.

The optical losses of PEK-HQ and PEK-PPH were evaluated from the slab waveguide loss using high-index immersion method, and the results are given in Table 7. The loss values were found to be 0.379 and 0.413 dB cm^{-1} at 1310 nm, respectively, slightly higher than that of PEK-1. However, the losses at 1550 nm of crosslinked PEK-HQ and PEK-PPH decreased dramatically, about 78% lower than the uncured PEK-1 due to the complete conversion of carboxyl groups to ester groups by the crosslinking reaction, which in fact further demonstrated that the presence of O–H bond was the main reason for the large optical loss at 1550 nm of a polymer material. Fig. 7 shows the refractive indices of PEK-HQ and PEK-PPH at different temperatures. For rigid polymeric systems, their volume coefficient of thermal expansions (α) generally decrease after the

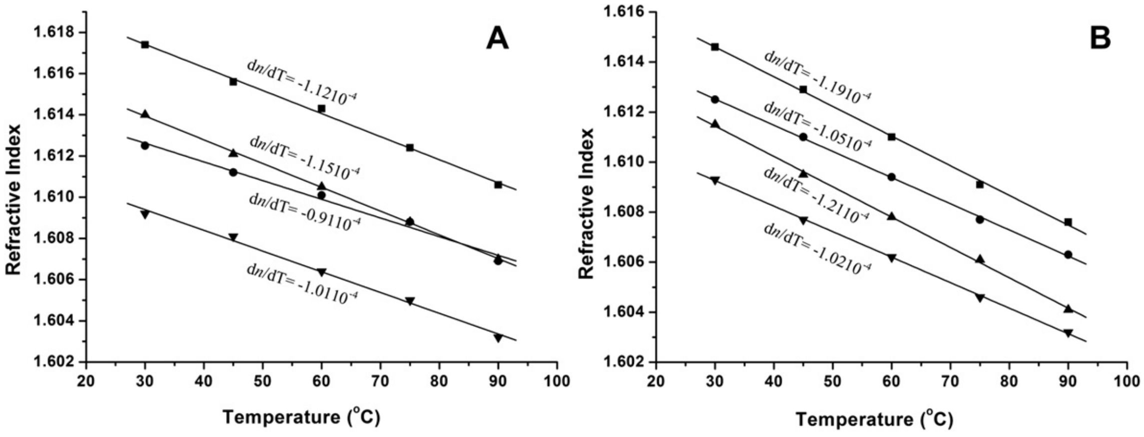


Fig. 7. Refractive index versus temperature for (A) PEK-HQ and (B) PEK-PPH: (■) 1310 nm, TE mode; (●) 1310 nm, TM mode; (▲) 1550 nm, TE mode; (▼) 1550 nm, TM mode.

crosslinking modification, whereas the α value is proportional to the thermal-optical coefficient (dn/dT) [33]. As a consequence, the dn/dT values of PEK-HQ and PEK-PPH ranged from -0.91×10^{-4}/°C to -1.21×10^{-4}/°C, apparently lower than that of linear PEK-1.

4. Conclusions

The films of three carboxyl-containing polyaryletherketones with different alkyl substituents were prepared and the influences of systematic structural variation on optical properties were examined by means of molecular modeling, WAXD, calculation of molecular polarizability as well as the measurements of refractive index, birefringence, optical loss, and thermo-optical coefficient. After the acyl chlorination reaction with thionyl chloride, poly(aryl-ether-ketone)-bearing pendant acyl chloride group (PEK-COCl) was obtained, which exhibited good solubility in some polar organic solvents. The film obtained from the mixture solution of PEK-COCl with HQ or PPH could be thermally crosslinked readily at the temperature below 200 °C without using any catalyst.

For linear polymers, the introduction of bulky alkyl substituents severely restricted the effective chain packing and disturbed the chain orientation along the substrate surface, leading to apparently increased interchain spacing and isotropic characteristics of polymer films, exhibiting the decreased refractive indices and birefringences. Moreover, the optical loss values at 1310 nm were mainly affected by the content of C–H bond, whereas that at 1550 nm were more related to the presence of O–H bond.

After curing, the crosslinked polymers became insoluble in any organic solvents, displaying excellent chemical resistance. Moreover, the films were very smooth with roughness values of 0.29–0.52 nm. Compared to the linear PEK-1, the cured PEK-HQ and PEK-PPH did not display obvious change in refractive indices, but the birefringences were significantly decreased. Especially for PEK-PPH, the twisted crosslinker structure resulted into its birefringence at 1310 nm decreased from 0.011 to 0.002, and the optical loss value at 1550 nm decreased by about 78% due to the disappearance of OH group.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2010.04.054.

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