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# Multi-Methyl-Substituted Polyphenylquinoxalines with High Solubility and High Glass Transition Temperatures: Synthesis and Characterization

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New polyphenylquinoxalines (PPQs) containing methyl substituents have been synthesized and characterized. The PPQs were prepared by the polycondensation of a newly-developed aromatic tetraketone, 4,4′-bis(4-benzilyloxy)-3,3′,5,5′-tetramethylbiphenyl (III) and aromatic tetraamines. Compared with the non-methyl-substituted PPQs derived from 1,4-bis (4-benzilyloxy)benzene (I) and 4,4′-bis(4-benzilyloxy)biphenyl (II), the obtained polymers exhibited better solubility. They were soluble not only in the common *m*-cresol and chloroform, but in polar aprotic solvent *N*-methyl-2-pyrrolidinone (NMP). The polymers showed glass transition temperatures of 325°C for PPQ-III$_a$ (from III and 3,3′,4,4′-tetraaminobiphenyl) and 287°C for PPQ-III$_b$ (from III and 3,3′,4,4′-tetraaminodiphenyl ether), which were much higher than their analogues. The PPQs exhibited good thermal stability up to 470°C in nitrogen and good optical transparency at 450 nm with a thickness of around 10 $\mu$m. The refractive indices and birefringences of the PPQs were in the range of 1.6998–1.7739 and 0.0002–0.0007, respectively.

**Keywords:** Polyphenylquinoxaline, solubility, thermal stability, refractive index

## 1 Introduction

Polyphenylquinoxalines (PPQs), first developed by Hergenrother in 1967, represent a class of high performance heteroaromatic polymers (1). The special molecular structures of PPQs endow them many desirable properties, such as high thermal stability resulting from their highly conjugated backbones; good solubility in common solvents caused by the bulky molecular packing; and relatively low dielectric constants and low moisture absorption due to their low contents of polar components (2). Thus, PPQs have been utilized in many high-tech fields including composites for extreme environments (3), foams for microelectronic fabrication (4,5), structural adhesives for high temperature bonding (6), proton exchange membranes for fuel cell (7–9), electron transport materials for organic light-emitting diodes (10), and nonlinear optical materials (11).

Although PPQs have been utilized in many areas, the functionality and modification of conventional PPQs progressed slowly in the past decades. This is mainly attributed to the relatively high cost of the starting monomers, tetraamines and tetraketones compounds. Compared with the tetraamines, the synthesis of tetraketones is more complicated. The conventional synthesis procedures of tetraketones inevitably used the highly-toxic oxidizing agent (such as selenium dioxide), which greatly limited their widespread application (12). An alternative route to synthesize tetraketones is via the palladium-catalyzed coupling of halo-substituted benzenes and arylalkynes and subsequent oxidation of the triple bonds leading to the target compounds (13). However, the high cost of palladium reagents makes it not suitable for mass-production. Recently, Harris group developed a new approach to synthesize PPQs via self-polymerizable quinoxaline monomers (14–16). The route is through the aromatic nucleophilic substitution reactions of an AB monomer containing preformed quinoxaline ring.

Relles reported a synthesis procedure of ether-linkaged tetraketones via the nucleophilic aromatic nitro displacement reactions of 4-nitrobenzil and aromatic diols (17). This procedure is thought to be one of the most promising low-cost routes to develop tetraketones due to the easily available starting materials. However, the obtained ether-bridged PPQs often exhibit lower glass transition temperatures ($T_g$s) in comparison with their non-ether analogues

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due to the rotational flexibility along the diphenyl ether units in their backbones. Such a flexible unit is thought to enhance the chain mobility, thus decrease the $T_g$. One method to prevent the internal rotation along the diphenyl ether units is to introduce bulky substituents at the 2- and 2′-positions of the diphenyl ether moiety. The rotational flexibility along the biphenyl ether units is expected to be decreased due to the steric effects of the substituents.

Thus, in the present work, in order to increase the $T_g$s of the ether-PPQs, a new aromatic tetraketone, 4,4′-bis(4-benzilyloxy)-3,3′,5,5′-tetramethylbiphenyl (III) was synthesized. A series of PPQs were synthesized from III and aromatic tetraamines. For comparison, another two series of analogous PPQs were prepared from 1,4-bis (4-benzilyloxy)benzene (I) and 4,4′-bis(4-benzilyloxy)biphenyl (II), respectively. The effects of the structure on the thermal properties, mechanical properties, solubility, and optical properties of the PPQs were investigated and compared.

## 2 Experimental

### 2.1 Materials

4-Nitrobenzil was synthesized in our laboratory according to the literature (18). 3,3′,5,5′-Tetramethyl-4,4′-biphenol was synthesized in our laboratory. Hydroquinone, 4,4′-dihydroxybiphenyl and 3,3′,4,4′-tetraaminobiphenyl (a) were purchased from Acros and used as received. 3,3′,4,4′-Tetraaminodiphenyl ether (b) was synthesized according to the reported procedure (19). *N*-methyl-2-pyrrolidinone (NMP), dimethylsulfoxide (DMSO), *m*-cresol, $N,N-$dimethylacetamide (DMAc), cyclopentanone (CPA), and other solvents were purified by distillation prior to use. The other commercially available reagents were used without further purification.

### 2.2 Monomer Synthesis

#### 2.2.1. *Synthesis of 4,4′-bis(4-benzilyloxy)-3,3′,5,5′-tetramethylbiphenyl (III)*

Into a 250-mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet, and a condenser, 53.60 g (0.21 mol) of 4-nitrobenzil, 24.23 g (0.01 mol) of 3,3′,5,5′-tetramethyl-4,4′-biphenol, and 240 mL of anhydrous DMSO were added. The reaction mixture was then heated to 60°C and 69.11 g (0.5 mol) of anhydrous $K_2CO_3$ was added. The reaction was maintained for 20 h. Upon confirmation of the completion of the reaction by thin-layer chromatography, the solution was cooled to room temperature and then poured into a mixed solvent containing 2400 mL of 1 mol/L HCl and 600 mL of chloroform. The organic phase was collected and washed thoroughly with deionized water. Then, the chloroform solution was dried with $MgSO_4$. After distilling off the chloroform, a tan solid was obtained. The solid was purified by a two-step recrystallizations, first from acetic acid and then from a mixture of benzene-cyclohexane (4:3, v/v). The purified tetraketone III was obtained as pale yellow crystals (36.2 g, yield: 55%).

Melting point: 201.7°C (DSC peak temperature). FT IR (KBr, $cm^{-1}$): 2962, 2918, 1672, 1593, 1502, 1470, 1236, 1213, 1157 and 808.2.$^1$H-NMR (DMSO-$d_6$): 2.11 (s, 12H), 6.97–6.99 (d, 4H), 7.53 (s, 4H), 7.59–7.63 (t, 4H), 7.76–7.79 (t, 4H), and 7.90–7.94 (m, 8H). Mass [m/e (relative intensity)]: 553 ($M^+$-105, 100). Elemental analysis: calculated for $C_{44}H_{34}O_6$: C, 80.23%; H, 5.20%. Found: C, 80.08%; H, 5.33%.

1,4-Bis (4-benzilyloxy)benzene (I) and 4,4′-bis(4-benzilyloxy)biphenyl (II) were similarly prepared except that 3,3′,5,5′-tetramethyl-4,4′-biphenol was replaced by hydroquinone for I and 4,4′-dihydroxybiphenyl for II.

I. **Melting point**: 159.0°C (DSC peak temperature). FT IR (KBr, $cm^{-1}$): 1672, 1597, 1500, 1250, 1215, 1161, and 881.$^1$H NMR ($CDCl_3$): $\delta$ =7.04–7.06 (d, 4H), 7.13 (d, 4H), 7.50–7.54 (t, 4H), 7.65–7.68 (t, 2H), and 7.96–7.99 (m, 8H). Mass [m/e (relative intensity)]: 421 ($M^+$-105, 100). Elemental analysis: calculated for $C_{34}H_{22}O_6$: C, 77.56%; H, 4.21%. Found: C, 77.35%; H, 4.24%.

II. **Melting point**: 167.7°C (DSC peak temperature). FT IR (KBr, $cm^{-1}$): 1674, 1591, 1491, 1252, 1161, and 891.$^1$H NMR ($CDCl_3$): 7.07–7.08 (d, 4H), 7.15–7.17 (d, 4H), 7.50–7.54 (t, 4H), 7.59–7.60 (m, 2H), 7.65–7.68 (m, 4H), and 7.96–7.99 (m, 8H). Mass [m/e (relative intensity)]: 497 ($M^+$-105, 100). Elemental analysis: calculated for $C_{40}H_{26}O_6$: C, 79.72%; H, 4.35%. Found: C, 80.32%; H, 4.43%.

### 2.3 Polymer Synthesis and Film Preparation

Three series of PPQs, including PPQ-$I_{a\sim b}$, PPQ-$II_{a\sim b}$ and PI-$III_{a\sim b}$ were synthesized via a two-step procedure with *m*-cresol as the solvent. The detail procedure was illustrated by the synthesis of PPQ-$III_a$. Thus, 3,3′,4,4′-tetraaminobiphenyl (a) (4.2854 g, 0.02 mol) was added to a 250-mL three-necked flask equipped with a mechanical stirrer, a condensator, and a nitrogen inlet. Anhydrous *m*-cresol (50 mL) was added and a gentle stream of nitrogen was passed through the solution. After stirring for 10 min, a clear tetraamine solution was obtained. III (13.1750 g, 0.02 mol) was then added in one batch and an additional volume of *m*-cresol (20 mL) was added to wash the residual III, and at the same time to adjust the solid content of the reaction system to be 20 wt%. The mixture was stirred at room temperature for 1 h to yield a viscous brown solution. Then, the solution was heated to 120°C and maintained for another 6 h. The obtained viscous pale solution was cooled to room temperature and slowly poured into an excess of methanol (500 mL) to yield a silky resin, yellow in color. The precipitate was immersed into methanol for 24 h, then collected and dried at 80°C in vacuum overnight to afford PPQ-$III_a$ resin. Yield: 16.06 g (92%).

The well-dried silky PPQ-$III_a$ resin was dissolved in NMP at room temperature with a solid content of 15 wt%. The obtained PPQ solution was filtered through a 0.45 $\mu$m Teflon syringe filter to remove any contaminates that might affect the quality of the film. Then, the solution was cast onto a clean glass and PPQ-$III_a$ film was obtained by thermally baking the solution with the following heating procedure: 80°C/2 h, 150°C/1 h, 200°C/1 h, and 250°C/1 h.

The other PPQ resin and films, including PPQ-$I_{a\sim b}$, PPQ-$II_{a\sim b}$, and PPQ-$III_b$ were prepared according to a similar procedure as mentioned above.

### 2.4 Characterization

Inherent viscosity was measured using an Ubbelohde viscometer with a 0.5 g/dL NMP solution at 30°C. Absolute viscosity was measured using a Brookfield DV-II+ Pro viscometer at 25°C. FT-IR spectra were obtained with a Tensor 27 Fourier transform spectrometer. UV-Vis spectra were recorded on a Hitachi U-3210 spectrophotometer at room temperature. Prior to test, PPQ samples were dried at 100°C for 1 h to remove the absorbed moisture. $^1$H-NMR was performed on a AV 400 spectrometer operating at 400 MHz in DMSO-$d_6$ or $CDCl_3$. DSC and TGA were recorded on a TA-Q series thermal analysis system at a heating rate of 10°C/min and 20°C/min in nitrogen, respectively. The tensile properties were performed on an Instron 3365 Tensile Apparatus with $80 \times 10 \times 0.05$ mm$^3$ specimens in accordance with GB1447-83 at a drawing rate of 2.0 mm/min.

Solubility was determined as follows: 1.0 g of the tested PPQ resin was mixed with 9.0 g of the solvent at room temperature (10 wt% solid content), which was then mechanically stirred in nitrogen for 24 h. The solubility was determined visually as three grades: completely soluble, partially soluble, and insoluble. The complete solubility is defined as a homogenous and clean solution is obtained, in which no phase separation, precipitation or gel formation is detected.

The alkaline stability of the PPQ films was evaluated as follows: the PPQ film sample ($80\times10\times0.05$ mm$^3$) was boiling with an aqueous sodium hydroxide (NaOH) solution (20 wt%) in a flask equipped with a reflux condensator. The hydrolysis of the sample was observed visually. After boiling for 100 h, the sample was dried at 120°C in vacuo and evaluated by TGA and tensile measurements.

Refractive index of the PPQ films formed on a 3-inch silicon wafer was measured at room temperature with a prism coupler (Metricon, model PC-2010) equipped with a He-Ne laser light source (wavelength: 632.8 nm). The in-plane ($n_{TE}$) and out-of-plane ($n_{TM}$) refractive index were determined using linearly polarized laser light parallel (transverse electric, TE) and perpendicular (transverse magnetic, TM) polarizations to the film plane, respectively. The average refractive index ($n_{av}$) was calculated according to Equation 1:

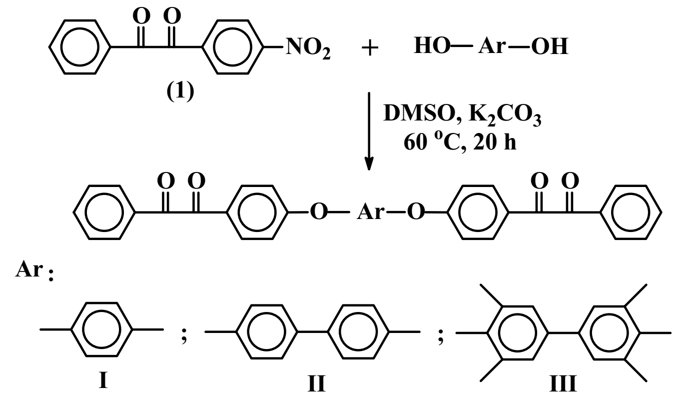

**Fig. 1.** Synthesis of tetraketone monomers.

$$n_{av} = (2n_{TE} + n_{TM})/3 \tag{1}$$

## 3 Results and Discussion

### 3.1 Monomer Synthesis

A new tetraketone monomer having four *ortho*-substituted methyl groups to the ether linkage per molecule, III, was synthesized in one step starting from 4-nitrobenzil and 3,3′,5,5′-tetramethyl-4,4′-biphenol, as shown in Figure 1. The nitro group was activated by the *para*-substituted electron-withdrawing benzil moiety, thus its nucleophilic substituent reaction with hydroxyl proceeded smoothly under a moderate condition. The obtained III could be easily purified by a two-step recrystallization procedure. The structure of III was confirmed by spectroscopic and elemental analysis. In the FT-IR spectra, the characteristic absorption of carbonyl in benzil moiety was clearly observed at 1672 cm$^{-1}$. In the $^1$H-NMR spectrum, the protons *ortho*-to the electron-withdrawing benzil moiety appeared at the lowest field in the spectrum.

Elemental analysis of the compound was also in good agreement with calculated results for the proposed structure. All the characterization revealed a high purity of the monomer, which could be used for the following polymerization.

### 3.2 Polymer Synthesis and Film Properties

As mentioned in the Introduction part, there are several routes to prepare PPQs. The procedure from tetraketone and tetraamine monomers is the most common route. The reaction condition is often affected by several factors, including the reactivity of the starting monomers and the solubility of the obtained PPQs in the reaction medium. For instance, Wrasidlo synthesized a series of PPQs

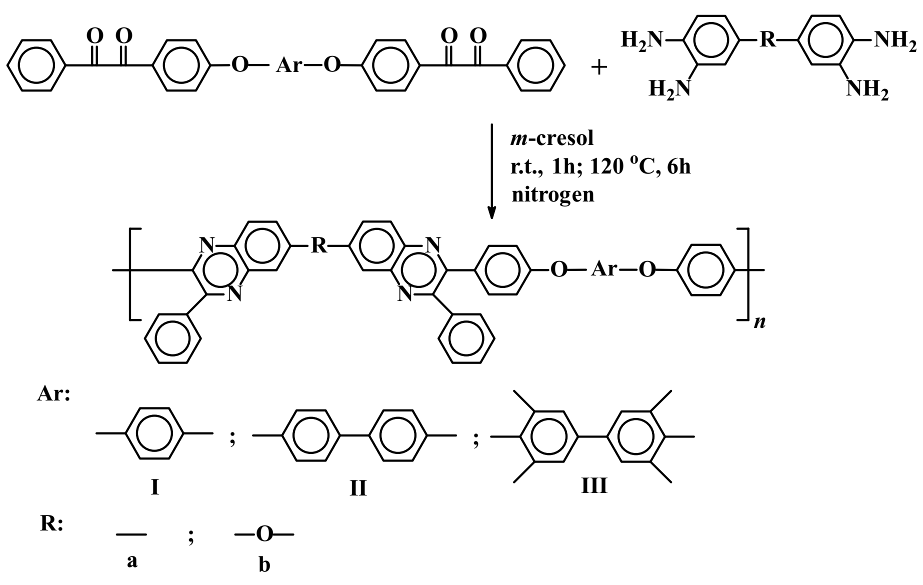

**Fig. 2.** Synthesis of PPQs.

containing flexible groups at ambient temperature and high-molecular-weight soluble PPQs were obtained (12). However, in some other reports, much higher polymerization temperature (>100°C) had to be adopted (20).

Considering the potential effects of the structures on the reactivity of the monomers, a two-step polymerization procedure, including an initial reaction at room temperature for 1 h, and a following reaction at 120°C for another 6 h was utilized in the present work (Figure 2). The inherent viscosities of the PPQs are in the range of 0.45–0.95 dL/g (Table 1), indicating the good reactivity and high purity of the starting monomers. Flexible and tough PPQ films were obtained by casting their solution in NMP, which confirmed the high molecular weights of the polymers.

It can be seen from the FT-IR spectra of III and PPQ films that the characteristic absorption peak at 1672 cm$^{-1}$ attributed to the carbonyl groups in III disappeared after polycondensation, which confirmed the formation of the polymers. The structures of the PPQs could be further identified by the $^{1}$H-NMR measurements.

**Table 1.** Inherent viscosities, thermal and mechanical properties of PPQ films

| *Sample* | *[η]$_{inh}$ (dL/g)* | *$T_g$ (°C)* | *$T_{5\%}$ (°C)* | *$T_{10\%}$ (°C)* | *$R_{w750}$ (%)* | *$T_s$ (MPa)* | *$E_b$ (%)* | *$T_M$ (GPa)* |
|---|---|---|---|---|---|---|---|---|
| PPQ-I$_a$ | 0.45 | 280 | 550 | 566 | 76 | 88 | 5.3 | 2.3 |
| PPQ-I$_b$ | 0.58 | 243 | 532 | 546 | 66 | 77 | 4.7 | 2.2 |
| PPQ-II$_a$ | 0.68 | 286 | 566 | 577 | 67 | 96 | 6.8 | 2.4 |
| PPQ-II$_b$ | 0.77 | 255 | 559 | 569 | 65 | 86 | 6.0 | 2.1 |
| PPQ-III$_a$ | 0.83 | 325 | 488 | 497 | 56 | 75 | 5.2 | 2.2 |
| PPQ-III$_b$ | 0.95 | 287 | 479 | 487 | 55 | 70 | 4.7 | 2.1 |

[η]$_{\mathrm{inh}}$: inherent viscosities measured with a PPQ resin at a concentration of 0.5 g/dL in NMP at 25°C; $T_g$: glass transition temperature; $T_{5\%}$, $T_{10\%}$: temperatures at 5% and 10% weight loss, respectively; $R_{w750}$: residual weight ratio at 750°C in nitrogen; $T_s$: tensile strength; $E_b$: elongation at break; $T_M$: tensile modulus.

## 3.3 Solubility

One of the main purposes of the present work is to improve the solubility of PPQs by decreasing the molecular packing density of the polymer chains. The aim was achieved by the incorporation of methyl substituents into the PPQs. PPQ-III$_a$ and PPQ-III$_b$ exhibited the best solubility in the tested solvents. They were soluble not only in the conventional chloroform and *m*-cresol, but in polar aprotic solvents, such as NMP and DMAc. PI-III$_b$ was also partially soluble in cyclopentanone and tetrahydrofuran. All the PPQs exhibited good resistance to the alcohol solvents.

Although the PPQs are all soluble in NMP, they exhibited quite different solubility in the solvent. For example, plots of the absolute viscosity vs. solid contents of PPQ-I$_b$ and PPQ-III$_b$ are shown in Figure 3. As expected, the viscosity of both PPQ-I$_b$ and PPQ-III$_b$ increases with the increasing of the solid contents. However, at the same solid content, such as 25 wt%, the viscosity of PPQ-III$_b$ (14390 mPa s) is much lower than that of PPQ-I$_b$ (55246 mPa s), indicating the relatively higher solubility of the former. Apparently, the synergic effects of methyl groups and ether linkages increased the disorder of the PPQ-III$_b$ chains, hindered the dense chain packing, and thus reduced the intermolecular interactions. All the effects are beneficial for the penetration of the solvents.

## 3.4 Thermal and Tensile Properties

PPQ has been well known for their excellent thermal and thermal-oxidative stabilities. The influence of methyl

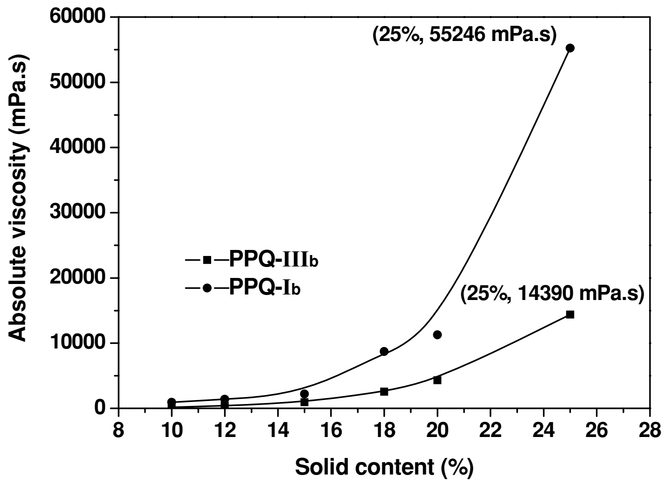

**Fig. 3.** Correlations of solid contents and absolute viscosities of PPQ solution.

substituents on the thermal stability of the present PPQs was investigated by TGA and DSC measurements and the data are tabulated in Table 1. It could be clearly observed that the introduction of methyl groups brought different effects on the thermal decomposition behavior and glass transition behavior of PPQs. As shown in Table 1, PPQ-III$_a$ undergoes a 5% weight loss at 488°C, which is 62°C and 78°C lower than those of PPO-I$_a$ and PPQ-II$_a$, respectively. PPQ-III$_a$ maintains 56% of its original weight at 750°C in nitrogen, which is also 20% lower than that of PPQ-I$_a$ (76%). The sacrifice of thermal stability of the PPQs could mainly be attributed to the unstable nature of methyl groups at elevated temperatures. Conversely, the introduction of methyl groups effectively increased the glass transition temperatures ($T_g$s) of the PPQs. For example, PPQ-III$_a$ has a $T_g$ of 325°C, which is 45°C and 39°C higher than those of PPQ-I$_a$ and PPQ-II$_a$ (Table 1). The higher $T_g$ values are most likely due to the methyl groups *ortho*-substituted to the ether linkage, which restrict the rotation of ether bond along the phenyl ring, resulting a hindrance to the glass transition of the PPQs.

The PPQ films exhibited excellent resistance in a NaOH solution at a concentration of 20 wt%. After boiling with the base for 100 h, the films maintained their thermal-stable backbone. A 2% weight loss occurred at about 250°C, which could be attributed to the release of the absorbed water.

The tensile properties of the PPQ films are summarized in Table 1. The flexible and tough PPQ films showed tensile strength of 67–96 MPa, elongations at break of 4.0–6.8%, and tensile moduli of 2.1–2.4 GPa. PPQs derived from biphenyl tetraketone (II) exhibited the best tensile properties. When the methyl groups were introduced, the tensile properties were slightly decreased. It is interesting that PPQ-III$_b$ film showed a tensile strength of 80 MPa after treatment with a 20 wt% NaOH solution for 100 h, which was about 10 MPa higher than that of the virgin sample. This phenomenon, on one hand, reflects the possible internal plasticization effects of water molecules; on the other hand, the excellent alkaline-resistance of the film. The good mechanical properties of the present PPQs are essentially beneficial for their applications in high-tech fields.

**Table 2.** Optical properties of the PPQ films

| | | | | *Refractive indices at 632.8 nm* | | | |
|---|---|---|---|---|---|---|---|
| *Sample* | $\lambda$ *(nm)* | $T_{450}$ *(%)* | *d* *(μm)* | $n_{TE}$ | $n_{TM}$ | $n_{av}$ | $\Delta n$ |
| PPQ-I$_a$ | 415 | 73 | — | — | — | — | — |
| PPQ-I$_b$ | 403 | 84 | — | — | — | — | — |
| PPQ-II$_a$ | 412 | 79 | 1.9 | 1.7741 | 1.7734 | 1.7739 | 0.0007 |
| PPQ-II$_b$ | 406 | 81 | 2.0 | 1.7356 | 1.7353 | 1.7355 | 0.0003 |
| PPQ-III$_a$ | 420 | 75 | 2.9 | 1.7333 | 1.7331 | 1.7332 | 0.0002 |
| PPQ-III$_b$ | 403 | 89 | 2.2 | 1.6999 | 1.6996 | 1.6998 | 0.0003 |

$\lambda$: cutoff wavelength; $T_{450}$: transmittance at 450 nm; *d*: film thickness for refractive index measurements; $n_{\mathrm{TE}}$, $n_{\mathrm{TM}}$, $n_{\mathrm{av}}$,: see section 2.4; $\Delta n = n_{\mathrm{TE}} - n_{\mathrm{TM}}$.

## 3.5 Optical Properties

The optical data of the PPQ films are summarized in Table 2. The cutoff wavelengths are in the range of 403–420 nm. The transmittances of the films measured at 450 nm are all higher than 70% at a thickness of 10 μm. The PPQs derived from ether-bridged tetraamine (PPQ-I$_b$, II$_b$, and III$_b$) show better optical transmittances than those of their analogues derived from biphenyl tetraamine (PPQ-I$_a$, II$_a$, and III$_a$). This trend is mainly attributed to the inhibition of conjugated structures by the ether linkage in the former polymers. The optical transparency of PPQ-III$_b$ was further enhanced by the bulky methyl substituents, which efficiently reduced the molecular packing density and the intermolecular interactions of the polymer chains. This reduction is quite beneficial for the penetration of the visible light, thus PPQ-III$_b$ exhibited a high transmittance of 89% at 450 nm.

The conjugated aromatic components in PPQs endow them with very high aromatic contents. According to Lorentz-Lorenz equation, the polymer possessing groups with high molar refractions and low molar volumes would exhibit high refractive index (21). Thus, PPQs might exhibit high refractive index values due to their high contents of the high-molar-refraction aromatic components. Recently, high-refractive-index (high-*n*) polymers have attracted much attention in advanced optoelectronic fields (22–26). However, to our best knowledge, few reports have discussed the refractive indices of PPQs in the literature. The in-plane ($n_{\mathrm{TE}}$), out-of-plane ($n_{\mathrm{TM}}$), and average refractive indices ($n_{\mathrm{av}}$) results along with the calculation results of birefringences ($\Delta n$) are presented in Table 2. All the PPQ films have higher $n_{\mathrm{TE}}$ values than $n_{\mathrm{TM}}$ values, indicating that they have positive birefringences and the molecular chains are preferentially aligned in the film plane.

PPQ-II$_a$ exhibited an extreme high $n_{av}$ value of 1.7739 at 632.8 nm, which is among the highest values of organic polymers reported in the literature (27). This high value is mainly attributed to the high aromatic contents and relatively rigid molecular skeleton of the polymer. When an additional ether linkage was introduced (PPQ-III$_b$), the $n_{av}$ decreased from 1.7739 to 1.7355 due to the expanded molecular packing density. Similarly, when the bulky methyl substituents were incorporated, the $n_{av}$ values of PPQ-III$_a$ and PPQ-III$_b$ continually decreased.

All the PPQ films showed birefringences of 0.0002–0.0007. Such small values can be attributed to the low degree of molecular orientation of the polymers due to the existence of flexible ether linkages in the molecular chains (28).

## 4 Conclusions

To increase the $T_g$ values and solubility of ether-bridged PPQs without forfeiting their thermal stability, a novel tetraketone monomer (III) containing multi-methyl-substituted backbone was synthesized. The PPQs derived from III showed $T_g$ values higher than 280°C and good solubility in polar aprotic solvents and some low-boiling-point solvents. Meanwhile, the thermal and mechanical properties of the PPQ-III films were slightly deteriorated. Conversely, the optical transparency of the films was enhanced due to the bulky molecular packing caused by the methyl substituents. In particular, PPQ-III$_b$ demonstrated good combined properties, including a $T_{5\%}$ of 479°C, $T_g$ of 287°C, $n_{av}$ of 1.6998, and $\Delta n$ of 0.0003; hence, it might be a good candidate for high-tech applications.

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