

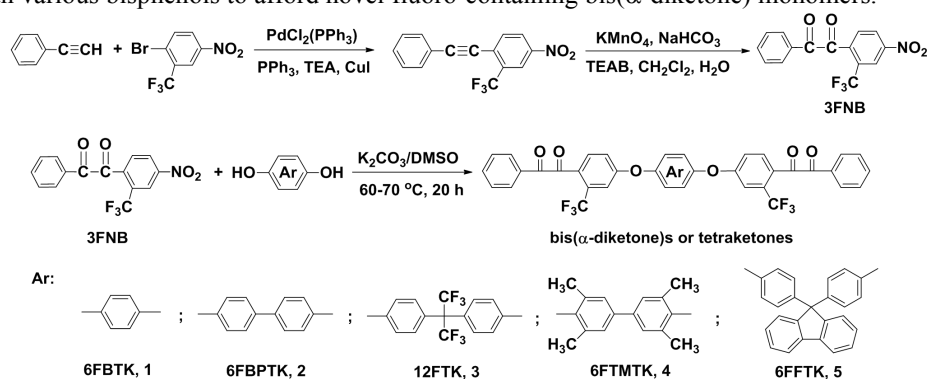
Fluorinated Polyphenylquinoxalines: novel heteroaromatic polymers with high thermal resistance and excellent hydrolysis stability

Hong-jiang Ni (倪洪江)¹, Guang-qiang Fang², Jin-gang Liu (刘金刚)^{1*}, Shi-yong Yang¹

¹Laboratory of Advanced Polymer Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P. R. China, ² State Key Laboratory of Metal Matrix Composites, School of Materials Science and Engineering, Shanghai Jiaotong University, Shanghai 200240, P. R. China. E-mail: liujg@iccas.ac.cn

Polyphenylquinoxalines (PPQs) are characterized by the phenyl-substituted quinoxaline rings in their structures. Ever since their first report in 1967, PPQs have been investigated as a class of high performance thermoplastic heteroaromatic polymers [1]. The highly conjugated quinoxaline rings and lateral phenyl substituents in PPQs endows the polymers many favorable properties, including high thermal and thermooxidative stability, good solubility in organic solvents and relatively low dielectric constants, and excellent hydrolysis stability. Especially, the extraordinary hydrolytic resistance of PPQs in either neutral water (PH value: ~7.0) or in strong alkaline solution (PH value>13.0) attract great attention from the researchers and engineers. This specific feature is the advantage that the other high temperature polymers, such as polyimide do not possess. Thus, PPQs have found potential applications as functional membranes or structural components in specific high-tech fields [2]. However, PPQs have not been widely studied and commercialized like their heteroaromatic polymer analogues. This is mainly due to their high cost caused by the very limited commercial available starting monomers, including bis(α -diketone)s and bis(o-diamine)s.

In the present work, based on our previous work on functional PPQs^[3-5], a series of fluorinated PPQs have been synthesized from the newly-developed trifluoromethyl-containing aromatic bis(α -diketone) monomers. Introduction of $-\text{CF}_3$ substituents in PPQs is to enhance the hydrolysis stability of the PPQs by virtue of the hydrophobic nature of fluorine groups. The effects of $-\text{CF}_3$ substituents on the thermal and hydrolysis properties were investigated. **Scheme 1** showed the synthesis pathway of fluorinated bis(α -diketone) monomers, including 1,4-bis(4-phenylglyoxaloyl-3-trifluoromethylphenoxy)benzene (6FBTK), 4,4'-bis(4-phenylglyoxaloyl-3-trifluoromethylphenoxy)biphenyl (6FBPTK), 2,2'-bis[4-(4-phenylglyoxaloyl-3-trifluoromethylphenoxy)phenyl]hexafluoropropane (12FTK), 4,4'-bis(4-phenylglyoxaloyl-3-trifluoromethylphenoxy)-3,3',5,5'-tetramethylbiphenyl (6FTMTK), and 9,9-bis[4-(4-phenylglyoxaloyl-3-trifluoromethylphenoxy)phenyl]fluorene (6FFTK). First, the starting material, 4-nitro-2-trifluoromethylbenzil (3FNB) was synthesized via a two-step procedure. The nitro in 3FNB was activated by both of the electron-withdrawing benzil and trifluoromethyl groups. Thus, it can easily undergo displacement reactions with various bisphenols to afford novel fluoro-containing bis(α -diketone) monomers.



Scheme 1 Synthesis of fluorinated bis(α -diketone)s

The detail structure characterization for the newly-developed bis(α -diketone)s is as follows. **6FBTK**: yellow solid. Melting point: 172°C (DSC peak temperature). ¹H NMR (600 MHz, DMSO-*d*₆): δ 7.96 (*d*, *J*=8.2 Hz, 4H), 7.88 (*d*, *J*=8.8 Hz, 2H), 7.81 (*t*, *J*=7.4 Hz, 2H), 7.65 (*t*, *J*=8.0 Hz, 4H), 7.62 (*d*, *J*=2.7 Hz, 2H), 7.39 (*s*, 4H), 7.30 (*dd*, *J*=8.8, 2.7 Hz, 2H). ¹³C NMR (151 MHz, DMSO-*d*₆): δ 192.3, 191.8, 161.6, 151.2, 136.1, 135.5, 132.0,

129.9, 130.1 (q , $J=32.9$ Hz), 129.4, 126.2, 122.8, 122.7 (q , $J=274.4$), 119.6, 117.1 (q , $J=5.7$ Hz). Elemental analysis: $C_{36}H_{20}F_6O_6$, Calculated: C, 65.26%; H, 3.04%; Found: C, 65.11%; H, 3.39%. **6FBPTK**: brown solid. Melting point: 124 °C (DSC peak temperature). 1H NMR (600 MHz, DMSO- d_6): δ 7.98 (d , $J=7.3$ Hz, 4H), 7.91 (d , $J=8.7$ Hz, 2H), 7.86-7.77 (m , 6H), 7.68-7.60 (m , 6H), 7.37-7.29 (m , 6H). ^{13}C NMR (151 MHz, DMSO- d_6): δ 192.2, 191.8, 161.3, 153.6, 136.5, 136.0, 135.4, 132.0, 130.0 (q , $J=33.2$ Hz), 129.4, 128.8, 126.3, 122.7 (q , $J=274.4$ Hz), 120.9, 119.8, 117.2 (q , $J=5.2$ Hz). Elemental analysis: $C_{42}H_{24}F_6O_6$, Calculated: C, 68.30%; H, 3.28%; Found: C, 67.11%; H, 3.32%. **6FTMTK**: yellow solid. Melting point: 96n°C (DSC peak temperature). 1H NMR (600 MHz, DMSO- d_6): δ 7.97 (d , $J=7.7$ Hz, 4H), 7.88 (d , $J=8.8$ Hz, 2H), 7.80 (t , $J=7.4$ Hz, 2H), 7.64 (t , $J=7.7$ Hz, 4H), 7.58 (s , 4H), 7.54 (s , 2H), 7.04 (d , $J=8.8$ Hz, 2H). ^{13}C NMR (151 MHz, DMSO- d_6): δ 192.5, 191.7, 161.0, 148.9, 137.2, 136.7, 135.5, 132.0, 130.8, 130.4 (q , $J=32.9$ Hz), 129.9, 129.4, 127.7, 125.5, 122.8 (q , $J=274.4$ Hz), 117.1, 115.3 (q , $J=6.2$ Hz), 15.9. Elemental analysis: $C_{46}H_{32}F_6O_6$, Calculated: C, 69.52%, H, 4.06%; Found: C, 69.63%, H, 4.26%. **12FTK**: brown solid. Melting point: none; a glass transition like temperature region was observed at round 144°C. 1H NMR (600 MHz, DMSO- d_6): δ 7.98 (d , $J=7.1$ Hz, 4H), 7.92 (d , $J=8.2$ Hz, 2H), 7.81 (t , $J=7.4$ Hz, 2H), 7.71 (d , $J=2.7$ Hz, 2H), 7.65 (t , $J=8.0$ Hz, 4H), 7.47 (d , $J=8.8$ Hz, 4H), 7.38 (dd , $J=8.8, 2.7$ Hz, 2H), 7.33 (d , $J=9.3$ Hz, 4H). ^{13}C NMR (151 MHz, DMSO- d_6): δ 192.0, 191.8, 160.2, 155.2, 135.8, 135.4, 131.9, 130.1 (q , $J=33.3$ Hz), 129.9, 129.4, 128.7, 127.2, 123.9 (q , $J=286.5$ Hz), 122.7 (q , $J=274.4$ Hz), 120.81, 119.93, 118.20 (q , $J=5.9$ Hz), 64.95-61.74 (m). Elemental analysis: $C_{45}H_{24}F_{12}O_6$, Calculated: C, 60.82%, H, 2.72%; Found: C, 60.61%, H, 2.83%. **6FFTK**: brown wax-like solid. 1H NMR (600 MHz, DMSO): δ 7.95 (d , $J=8.1$ Hz, 6H), 7.84 (d , $J=8.7$ Hz, 2H), 7.79 (t , $J=7.4$ Hz, 2H), 7.63 (t , $J=7.8$ Hz, 4H), 7.59 (d , $J=2.4$ Hz, 2H), 7.48 (d , $J=7.7$ Hz, 2H), 7.42 (t , $J=7.4$ Hz, 2H), 7.34 (t , $J=7.4$ Hz, 2H), 7.24 (d , $J=8.8$ Hz, 4H), 7.20 (dd , $J=8.7, 2.3$ Hz, 2H), 7.13 (d , $J=8.8$ Hz, 4H). ^{13}C NMR (151 MHz, DMSO): δ 192.3, 191.8, 161.3, 152.8, 150.2, 142.6, 139.5, 136.1, 135.4, 132.0, 130.0 (d , $J=32.6$ Hz), 129.9 (q , $J=8.0$ Hz), 129.7, 129.4, 128.1, 128.0, 126.1, 125.9, 122.7 (q , $J=273.3$ Hz), 120.7, 119.6, 117.4 (q , $J=6.0$ Hz), 64.00. Elemental analysis: $C_{55}H_{32}F_6O_6$, Calculated: C, 73.17%; H, 3.57%; Found: C, 73.39%; H, 3.77%. **Fig.1** showed the typical two-dimensional 1H - ^{13}C heteronuclear single-quantum coherence (HSQC) spectrum for 6FBTK. The absorptions of the protons cohered well with those of the corresponding carbon signals, indicating the successful preparation of the target compound.

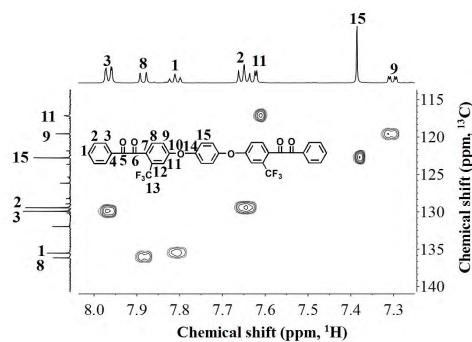


Fig. 1 1H - ^{13}C HSQC spectrum of 6FBTK

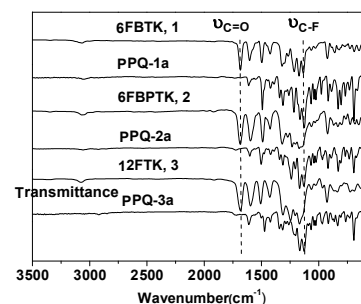


Fig. 2 FT IR spectra of bis(a-diketone)s and PPQs

The prepared 6FBTK (1), 6FBPTK (2), and 12FTK with polymerizable grade purities were reacted with bis(o-diamine)s, including 3,3'-diaminobenzidine (a) and 3,3',4,4'-tetraaminodiphenylether (b) to afford fluorinated PPQs (PPQ-1a~b from 6FBTK, PPQ-2a~b from 6FBPTK, and PPQ-3a~b from 12FTK), as shown in **Scheme 2**. The prepared PPQ resins were soluble in *N*-methyl-2-pyrrolidinone (NMP) and flexible and tough PPQ films were cast from the PPQ/NMP solutions. **Fig. 2** compares the FT IR spectra of monomers and the PPQs. The characteristic absorptions of carbonyl in the bis(a-diketone)s located at 1684 cm^{-1} disappear in the spectra of PPQs, indicating the successful conversion from the monomers to polymers. Meanwhile, the characteristic absorption bands due to C-F bonds in $-CF_3$ groups at 1134 cm^{-1} are observed in both of the monomers and PPQs.

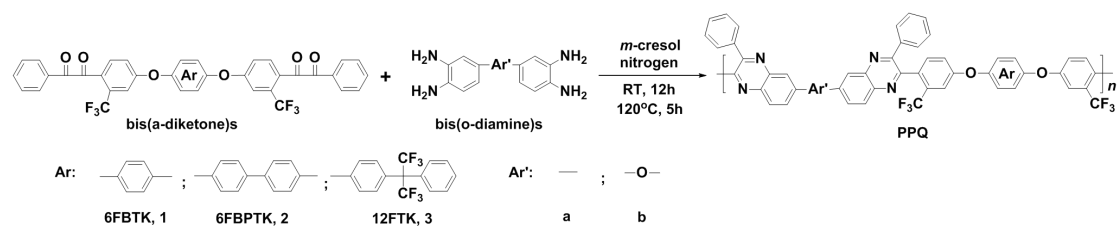
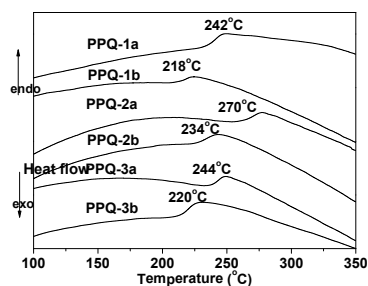
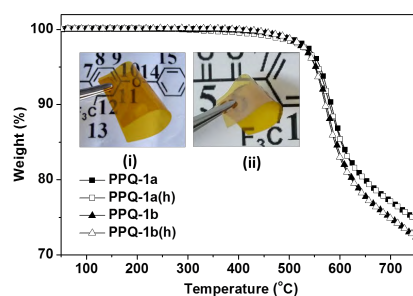
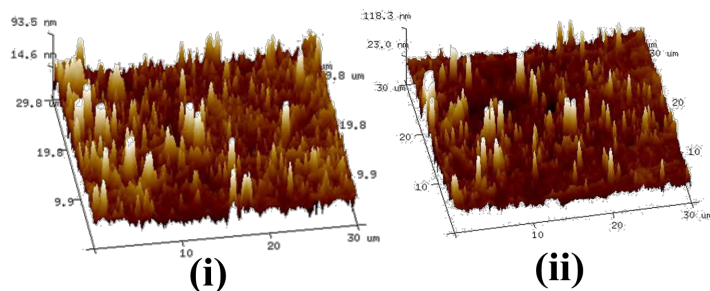


Fig. 3 depicted the differential scanning calorimetry (DSC) curves of PPQ films and the glass transition temperatures (T_g) are listed in **Table 1**. The T_g values of PPQ films are in the range of 218- 270 °C. For the same bis(α -diketone) monomer, the T_g values decreased in the order of PPQ-a>PPQ-b due to the flexible ether linkages in 3,3',4,4'-tetraaminodiphenylether. The hydrolysis stability of the PPQ films was evaluated by boiling the free-standing PPQ films in aqueous sodium hydroxide (NaOH) solution (20 wt%) for 7 days. Then, the PPQ films were thoroughly cleaned with deionized water and thermogravimetric analysis (TGA) was performed to evaluate the properties of the films. **Fig. 4** compares the TGA curves of the PPQ films before and after hydrolysis. The appearances of the films were inserted in the figure. It can be observed that the film color did not exhibit apparent change. In addition, the hydrolyzed PPQ films maintained their original microstate. The surface roughness (R_a) values determined by the atomic force microscope (AFM) for PPQ-1a film are shown in **Fig. 5**. The R_a values of the film remained unchanged after hydrolysis. The thermal properties of the films are also retained. For instance, the 5% weight loss temperature of PPQ-1a(h) film ("h" stands for hydrolysis) was 556 °C, which was only 5 °C lower than that of the pristine PPQ-1a film (561 °C). This indicates that the thermal-stable skeleton structures of PPQ-1a were maintained even after boiling in concentrated alkaline solution. All the results were summarized in Table 1.


Fig. 3 DSC curves of PPQ films

Fig. 4 TGA curves for PPQ films before (i) and after hydrolysis (ii)

Fig. 5 AFM images for PPQ-1a film before (i) and after hydrolysis (ii)

 R_a (i)=13 nm, R_a (ii)=13 nm

Table 1. Thermal and hydrolysis properties of PPQ films

polymers	T_g^a (°C, DSC)	$T_{5\%}^b$ (°C)	$T'_{5\%}{}^b$ (°C)	R_{w700}^c (%)
PPQ-1a	242	561	556	77
PPQ-1b	218	552	551	75

PPQ-2a	270	558	559	79
PPQ-2b	234	553	552	77
PPQ-3a	244	548	545	71
PPQ-3b	220	544	542	69

^a T_g : glass transition temperatures; $T_{5\%}$: 5% weight loss temperature; $T'_{5\%}$: 5% weight loss temperature for PPQs after boiling in 20 wt% aqueous NaOH solution for 7 days. R_{w700} : residual weight ratio at 700 °C.

In summary, the present fluorinated PPQ films exhibited excellent hydrolysis stability and thermal properties. The good combined properties make the films good candidates as various membranes for fuel cell fabrications or other high-tech applications. It would be discussed in detail in the future.

Acknowledgment

Financial support from the *National Nature Science Foundation of China* (51173118) is gratefully acknowledged.

References

- [1] Hergenrother P M, Levine H H. Phenyl-substituted polyquinoxalines. *J Polym Sci Part A-1*, 1967, 5: 1453-1466.
- [2] Rabilloud G. High performance polymers. 2. Polyphenylquinoxaline and polyimides: chemistry and applications. Paris: Editions Technip, 1999.
- [3] Cheng Li, Zhuo Li, Jin-gang Liu, Hai-xia Yang and Shi-yong Yang, Fluorene-bridged polyphenylquinoxalines with high solubility and good thermal stability: synthesis and properties, *Chin. J. Polym. Sci.*, 2010, 28: 971-980.
- [4] Cheng Li, Zhuo Li, Jin-gang Liu, Hai-xia Yang, Shi-yong Yang, Multi-methyl-substituted Polyphenylquinoxalines with High Solubility and High Glass Transition Temperatures: Synthesis and Characterization, *J. Macromol. Sci., Part A: Pure Appl Chem*, 2010, 47, 248-253.
- [5] Cheng Li, Zhuo Li, Jin-gang Liu, Xiao-juan Zhao, Hai-xia Yang, Shi-yong Yang, Synthesis and characterization of organo-soluble thioether-bridged polyphenylquinoxalines with ultra-high refractive indices and low birefringences, *Polymer*, 2010, 51: 3851-3858.