

New Fluorinated Copolyimides with Pyridine Ring in the Main Chain

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ABSTRACT *The novel fluoro-containing aromatic diamines with pyridine ring in the main chain were synthesized. The fluorinated copolyimides, which derived from 4,4'-oxydiphthalic anhydride (ODPA), 4,4'-oxydianiline (ODA) and the diamines, were synthesized and characterized. Strong and flexible copolyimide films, which prepared by casting the poly(amic acid) solution and followed by thermal imidization, exhibit good thermal stability and mechanical properties. Moreover, the films also show a good transparency, which giving the UV-visible absorption cut-off at 340-360 nm. These properties make them potential application to microelectronic and optoelectronic fields.*

Keywords: Fluorinated diamines, Copolyimide, Pyridine, Thermal stability

INTRODUCTION

As an important polymer material, functional polyimides (PIs) have gained more and more attention in recent years due to their extensive application in microelectronic and optoelectronic industries as passivation coating or stress-relief layers for high density electronic packaging; interlayer dielectric material for multi-chip module (MCM); alignment films for liquid crystal display (LCD) as well as waveguide for optical filter communication^[1]. All of the applications are mainly attributed to the functionalization of the standard polyimide, which is known for good thermal stability and mechanical properties. One of the efficient methods for functionalization of standard polyimide is introducing the fluorine or fluoro-containing substitutes into the backbone or side chain of polyimide. The special physical and chemical characters of fluorine or fluoro-containing substitutes provide polyimide with many new features, such as, low dielectric constant, low moisture absorption, high transparency and high solubility^[2].

However, it doesn't always bring satisfied results when the fluorine was introduced into polyimides. For example, the excess fluorine content, especially when fluorine atoms located in the *ortho*-position of amine, will inevitably reduce the reactivity of diamine monomer due to the low polarizability and high electro-negativity of fluorine atoms, consequently result in the low molecular weight and poor mechanical property of the polyimides. Moreover, the introduction of fluorine sometimes will scarify the inherent qualities of the polyimides, such

as thermal stability and mechanical properties.

In the present work, a series of aromatic diamines with trifluoromethyl substituted phenyl in the side chain and pyridine ring in the main chain were synthesized. The trifluoromethyl group in the side chain is expected to affect the reactivity of amine located in the main chain. The pyridine ring in the main chain, which conjugated with benzene ring, is expected to maintain the good thermal stability and mechanical properties of the polyimides. The fluorinated copolyimides were synthesized from 4,4'-oxydiphthalic anhydride (ODPA), 4,4'-oxydianiline (ODA) and the diamines. The thermal and mechanical properties of the polyimides were investigated.

EXPERIMENTAL

Monomer Synthesis

4-[(4'-Trifluoromethylphenoxy)phenyl]-2,6-bis(4''-aminophenyl)pyridine (*p*-TFAP)

2.66g (100 mmol) of 4-(4'-trifluoromethyl)phenoxy benzaldehyde, 3.41 g (200 mmol) of *p*-nitroacetophenone, 10 g of ammonium acetate (130 mmol) and 30 ml of glacial acetic acid were added to a three-necked flask equipped with mechanical stirrer and a reflux condenser. The solution was refluxed with stirring for 3h. Then the yellow solid precipitated was filtered off and washed thoroughly with water to give a crude product of 4-[(4'-trifluoromethylphenoxy)phenyl]-2,6-bis(4''-aminophenyl)pyridine (*p*-TFNP). The product was purified by recrystallization in ethanol to give pale yellow crystals. Yield: 3.8 g (68.2%), m.p.: 248.1 °C. FT-IR (KBr, cm^{-1}): 1597.2, 1547.7, 1514.7, 1345.8, 1171.0, 1109.1, 857.1. $^1\text{H-NMR}$ (300 MHz, $\text{DMSO-}d_6$, ppm): 7.24-7.27 (d; 2H), 7.33-7.36 (d, 2H), 7.75-7.79 (d, 2H), 8.21-8.23 (d, 2H), 8.38-8.41 (m, 4H), 8.49 (m, 2H), 8.63-8.65 (d, 2H). Mass spectrometry (MS): [electron ionization (EI), m/e, percentage of relative intensity]: 557 (M^+ , 100). Analysis: Calc. for $\text{C}_{30}\text{H}_{18}\text{F}_3\text{N}_3\text{O}_5$: C, 64.64%; H, 3.25%; N, 7.53%. Found: C, 64.64%; H, 3.23%; N, 7.56%.

The mixture of *p*-TFNP (5.57 g, 10 mmol), ethanol (150 ml) and 0.24 g of Pd/C was added to a three-necked flask. Then hydrazine monohydrate (15 ml) was added dropwise during 1.5h at 75-80 °C. The reaction mixture was refluxed for 24h followed by filtered to remove Pd/C. The *p*-TFAP, white crystals precipitated from the filtrate, was washed with water and then dried in vacuum overnight. Yield: 4.43 g (89.0%), m.p.: 175.0 °C (DSC). FT-IR (KBr, cm^{-1}): 3401.3, 3331.1, 1329.7, 1602.0, 1503.4, 1326.7, 1246.9, 1176.6, 830.5. $^1\text{H-NMR}$ (300 MHz, $\text{DMSO-}d_6$, ppm): 5.43 (s, 4H), 6.68-6.70 (d, 4H), 7.22-7.25 (m, 2H), 7.27-7.30 (m, 2H), 7.77-7.80 (m; 2H), 7.81 (s, 2H), 8.01-8.04 (d, 4H), 8.07 (s, 4H). Mass spectrometry (MS): [electron ionization (EI), m/e, percentage of relative intensity]: 497(M^+ , 100). Analysis: Calc. for $\text{C}_{30}\text{H}_{22}\text{F}_3\text{N}_3\text{O}$: C, 72.42%; H, 4.46%; N, 8.44%. Found: C, 72.37%; H, 4.48%; N,

8.44%.

The other diamine monomers, 4-[(4'-trifluoromethyl)phenyl]-2,6-bis(4''-amino phenyl)pyridine (*p*-TFP), 4-[(4'-trifluoromethyl)phenyl]-2,6-bis(3''-aminophenyl)pyridine (*m*-TFP), 4-[3',5'-bis(trifluoromethyl)phenyl]-2,6-bis(4''-aminophenyl)pyridine (*p*-DTFP), 4-[3',5'-bis(trifluoromethyl)phenyl]-2,6-bis(3''-aminophenyl)pyridine (*m*-DTFP) and 4-[(4'-trifluoromethylphenoxy)phenyl]-2,6-bis(3''-aminophenyl)pyridine (*m*-TFAP) were synthesized according to the same method as described above.

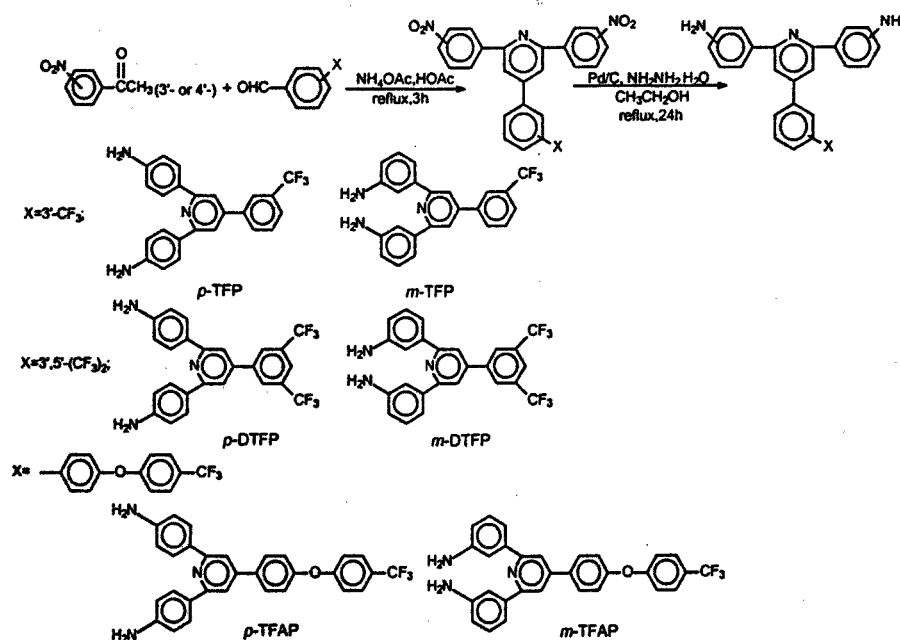
Polymer Synthesis

In a typical experiment, ODA (3.10 g, 10 mmol) was added to a stirred solution of ODA (1.00 g, 5 mmol) and *p*-TFAP (2.49 g, 5 mmol) in NMP (25 ml). The mixture was stirred at room temperature for 24h in argon to yield a viscous poly(amic acid) solution. Polyimide was obtained by thermal imidization of the poly(amic acid) solution. in the following procedure: 80 °C/2h, 150 °C/1h, 250 °C/1h. PI-5 film, derived from ODA, ODA and *p*-TFAP (ODPA/ODA/TFAP) was pale yellow in color. FT-IR (film, cm⁻¹): 1775, 1720(ν_{C=O}), 1385 (ν_{C=N}).

PI-1 (ODPA/ODA/*p*-TFP), PI-2 (ODPA/ODA/*m*-TFP), PI-3 (ODPA/ODA/*p*-DTFP), PI-4 (ODPA/ODA/*m*-DTFP) and PI-6 (ODPA/ODA/*m*-TFAP) were prepared by the same method as described above.

RESULTS AND DISCUSSION

Monomers The chemical structures and abbreviations of the fluorine-containing aromatic diamines are shown in Scheme 1.



Scheme 1 Synthesis of monomers

All the diamines were prepared by reducing the corresponding nitro-compounds, which synthesized from nitroacetophenone and the corresponding fluoro-containing aldehyde by the modified Chichibabin reaction [3]. The FT-IR spectra of *p*-TFAP, *m*-TFAP and the corresponding dinitro compounds are shown in Figure 1. The IR spectra for *p*-TFNP and *m*-TFNP show the absorption due to N-H stretching vibration of amino at *ca.* 3401 and 3331 cm^{-1} . No absorptions due to the N-H stretching vibration of diamines (*ca.* 1597 and 1345 cm^{-1}) were observed. The characteristic absorption of pyridine, appearing at *ca.* 3337 ($\nu_{\text{C-H}}$), 1602 ($\nu_{\text{C-C}}$) and 830 ($\nu_{\text{C-H}}$) cm^{-1} was also apparently observed, which indicated the successful synthesis of the monomers. The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of the monomers are shown in Figure 2. The $^1\text{H-NMR}$ spectrum of *p*-TFAP showed the peaks due to protons in pyridine ring (H_3) and

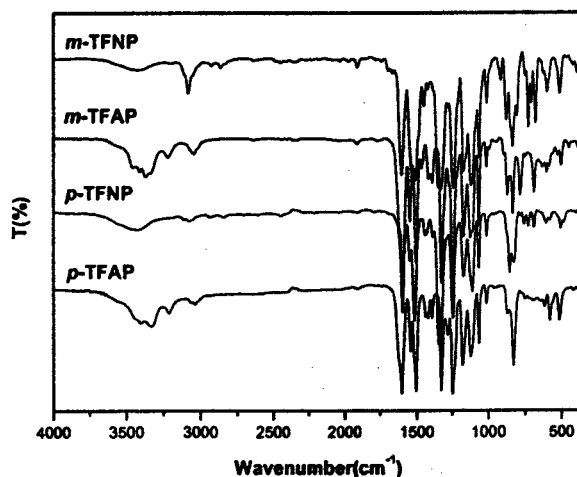


Figure 1 FT-IR spectra of the monomers

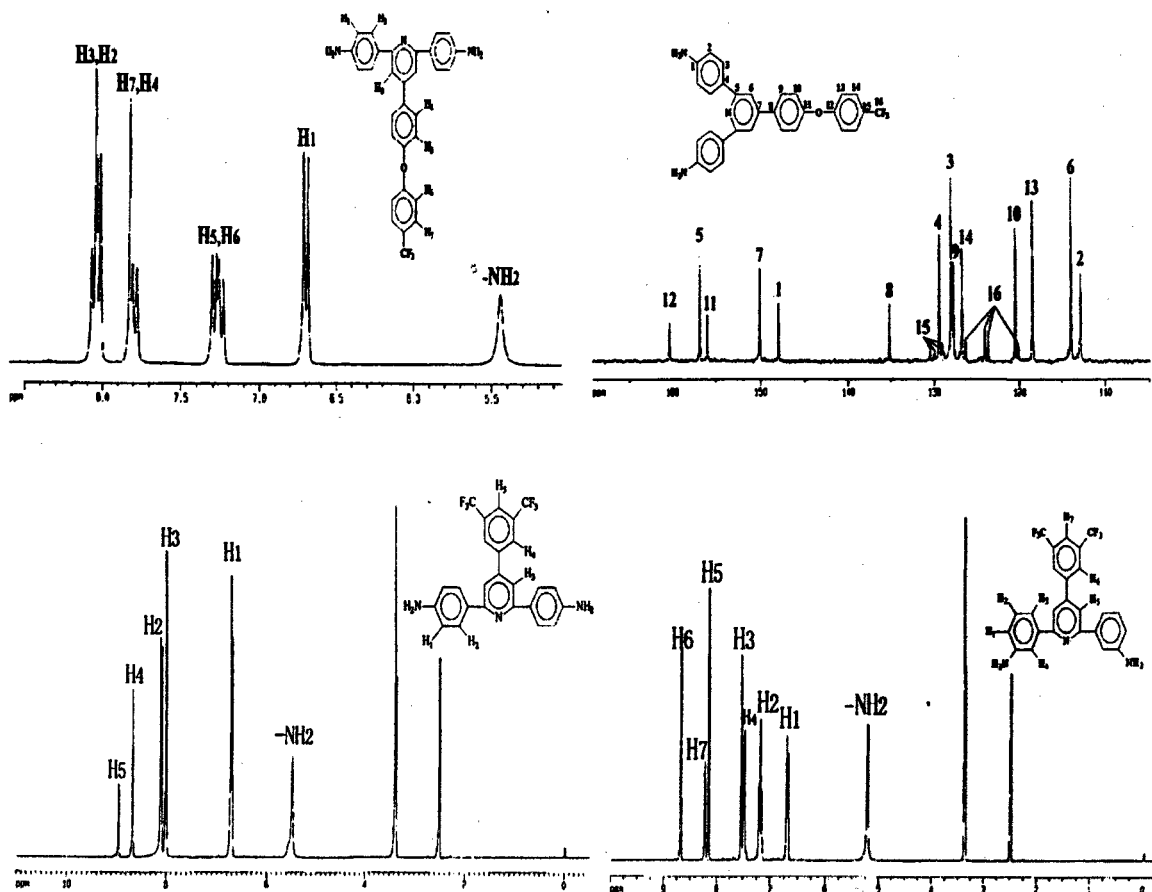
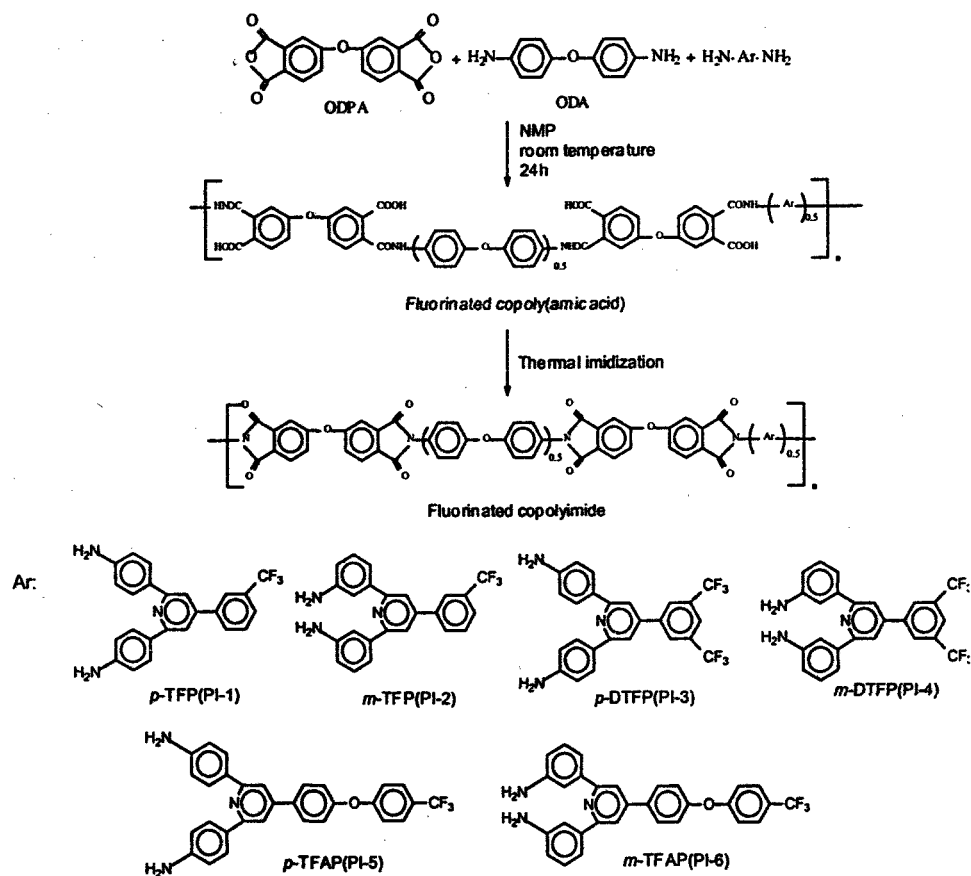


Figure 2 $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of the monomers

ortho to pyridine ring (H_2) at the farthest downfield of the spectrum. The peaks due to proton in trifluoromethyl-substituted phenyl moiety (H_7) appeared at the second farthest downfield of the spectrum, which according to the strong electron-withdrawing trifluoromethyl group. In all circumstances, the protons ortho to amine group showed at the farthest upfield of the spectrum. In ^{13}C -NMR spectrum of *p*-TFAP, C_{16} and C_{15} showed clear quartet absorption at 120-126 ppm and 129-132 ppm, respectively, which probably due to the $^2J_{\text{C-F}}$ and $^3J_{\text{C-F}}$ coupling of the carbons with fluorine atoms in the diamine.

Polymer Synthesis Copolyimides were prepared by thermal imidization of poly(amic acid)s, which prepared by reacting of ODPA with ODA and the corresponding fluorine-



Scheme 2 Synthesis of copolyimides

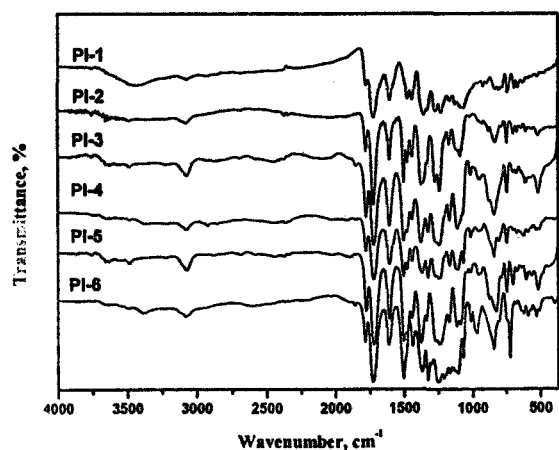


Figure 3 FT-IR spectra of copolyimides

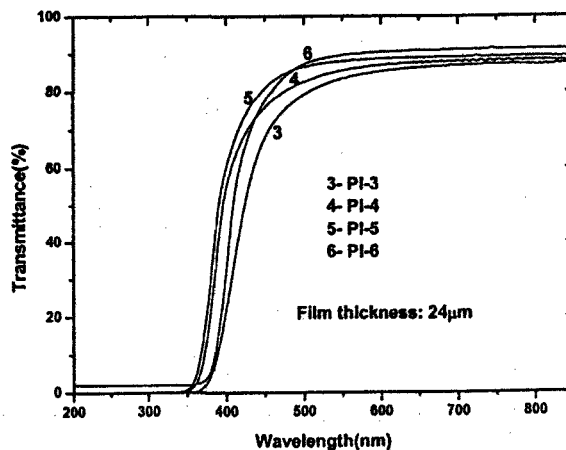


Figure 4 UV-visible spectra of copolyimides

containing diamines, respectively (Scheme 2). The inherent viscosities of the poly(amic acid)s, which determined by Ubbelohde-viscometer with 0.5 g dl⁻¹ NMP solution at 30 °C, are ranged in 0.79-1.32 dl/g (Table 1). Strong and flexible films could be prepared by casting poly(amic acid) solutions, followed by thermally baking with the following procedure: 80 °C/3h, 180 °C /1h and 250 °C/1h. The FT-IR spectra of the polyimides are shown in Figure 3. The absorptions at about 1780 and 1720 cm⁻¹, assigned to the asymmetric and symmetric C=O stretching vibrations of imide groups, were observed in all of the polymers. Moreover, the absorption assigned to the C-N stretching vibration of imide groups were also observed at about 1380 cm⁻¹. Figure 4 depicts the UV-visible spectra of the polyimides. It is observed that the cut-off wavelengths are located at 340-360 nm, moreover, the transmittance at 450 nm is nearly 80%, suggesting the high transparency in visible light region. The high transparency is attributed to the presence of the trifluoromethyl groups in polymer backbones.

Thermal Properties and Mechanical Properties The thermal properties of the polyimides, including onset decomposition temperature (T_d), temperature at 10% weight loss ($T_{10\%}$) and the glass transition temperature T_g , were detected. The results are shown in Table 1. The polyimides give T_d of 547-599 °C, T_g of 249-288 °C (Figure 5) and residual weights of 56%-72% at 700 °C in nitrogen, which indicated the good thermal resistance. The mechanical properties of polyimide films (6.35×127 mm) were tested at 25 °C with an instron instrument. The polyimide films have tensile strengths of 102.4-138.4 MPa, elongation at break of 9-18%, and tensile modulus of 0.77-1.17 GPa, which demonstrated that the films have good mechanical properties.

Table 1 Thermal properties and mechanical properties of polyimides

| PAA | η_{inh} (dL/g) | PI | T_g (°C) | T_d^a (°C) | $T_{10\%}^b$ (°C) | Rw ^c (%) | E_B^d (%) | T_S^d (MPa) | Y_M^d (GPa) |
|------|------------------------|------|---------------|-----------------|----------------------|------------------------|----------------|------------------|------------------|
| PA-1 | 0.79 | PI-1 | 271.3 | 548.5 | 596.9 | 70 | 10 | 116.8 | 1.17 |
| PA-2 | 0.96 | PI-2 | 255.9 | 576.2 | 611.7 | 69 | 11 | 113.4 | 1.03 |
| PA-3 | 0.84 | PI-3 | 282.1 | 568.9 | 602.1 | 72 | 9 | 102.4 | 1.14 |
| PA-4 | 0.92 | PI-4 | 249.5 | 599.6 | 621.2 | 68 | 11 | 103.4 | 0.94 |
| PA-5 | 1.25 | PI-5 | 288.9 | 547.0 | 562.2 | 57 | 16 | 137.8 | 0.84 |
| PA-6 | 1.32 | PI-6 | 272.4 | 568.7 | 588.9 | 56 | 18 | 138.4 | 0.77 |

a) T_d : Onset decomposition temperature;

b) $T_{10\%}$: Temperatures at 10% weight loss;

c) Residual weight retention (Rw %) at 700 °C;

d) E_B : Elongation at Breakage; T_S : Tensile Strength; Y_M : Young's Modulus

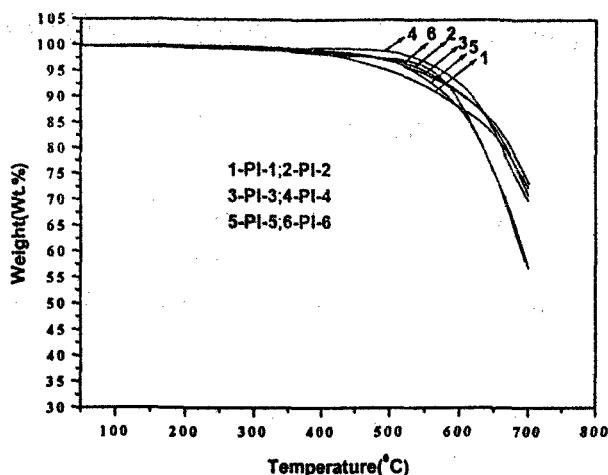


Figure 5 TGA curves of copolyimides (N_2 , heating rate: 20 °C)

CONCLUSIONS New fluoro-containing diamines with pyridine ring in the main chain were synthesized and characterized. A series of fluorinated copolyimides derived from ODPA, ODA and the diamines were prepared by two-step procedure. The strong and flexible polyimide films exhibited good thermal and mechanical properties. The films also showed a good transparency in visible light region.

REFERENCES

1. M. K. Ghosh, K. L. Mittal, editors. Polyimide: fundamental and applications, New York: Marcel Dekker, 1996.
2. H. W. Zhou, J. G. Liu, Z. G. Qian, S. Y. Zhang, S. Y. Yang, *J. Polym. Sci., Part A: Polym. Chem.*, 2001,39,2404-2413
3. K. Xie, J. G. Liu, H. W. Zhou, S. Y. Zhang, S. Y. Yang, *Polymer*, 2001,42, 7267-7274
4. Weiss. M, *J. Am. Chem. Soc.*, 1952,74,200-202