

New Heteroaromatic Polymers Containing Pyridine Moiety in the Main Chain

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ABSTRACT New heteroaromatic polymers, including polyimides (PIs) and polypyrrolone (PPys) have been synthesized from the new aromatic monomers containing pyridine moiety in the main chain, such as 2,6-bis(3',4'-dicarboxylphenyl)-4-phenylpyridine dianhydride (PyDA), 2,6-bis(3',4'-dicarboxylphenyl)-4-(3'-trifluoromethylphenyl) pyridine dianhydride (TFPyDA), 2,6-bis(3',4'-diaminophenyl)-4-phenylpyridine (PTPA), 2,6-bis(3',4'-diaminophenyl)-4-(4"-phenyl)phenyl pyridine (DPPA), 2,6-bis(3',4'-diaminophenyl)-4-(4"-fluorophenyl) pyridine (FPPA) and 2,6-bis(3',4'-diaminophenyl)-4-(3"-trifluoromethyl)phenyl pyridine (3FPA) and so on. The rigid pyridine ring and the strong conjugation interaction of the pyridine and phenyl ring endowed the polymers with good processability and maintained their inherent thermal properties at the same time.

Keywords: polyimide, polypyrrolone, dianhydride, tetraamine, thermal property

INTRODUCTION

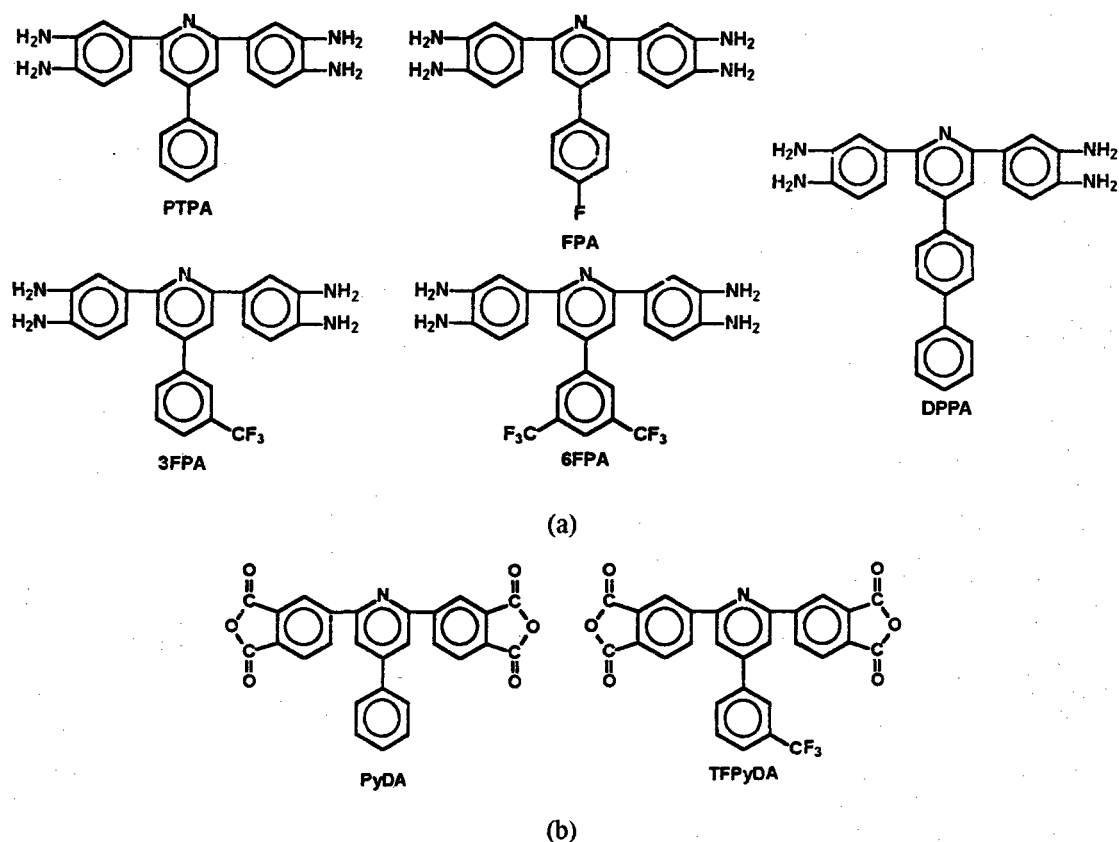
Heat-resistant polymers have been widely researched and developed in recent years for their potential applications in high temperature fields, such as aeronautical, mechanical, electrical, electronic and other areas^[1]. As the most promising thermal stable polymers, heteroaromatic polymer materials, such as polyimide (PI), poly(amide-imide) (PAI), polybenzimidazole (PBI), polybenzoxazole (PBO) and so on, gained considerable attention in recent years. The rigid molecular chains and strong interchain forces in the heteroaromatic polymers endow them with high thermal properties, but limit their processabilities at the same time. Therefore, many efforts have been concerned on improvement of their processabilities without scarifying their intrinsic good characteristics^[2]. Among the modifications, the introduction of bulky side groups to the molecular chains of the polymers has been thought to be one of the most promising ways^[3]. On the other hand, the introduction of heteroaromatic moiety is another effective method to achieve this aim^[4].

Polyimides (PIs) and polypyrrolones (PPys) represent two of the most studied classes of heteroaromatic polymers for their excellent heat resistance and radiation resistance^[5-6]. In the fifth *China-Japan Seminar on Advanced Aromatic Polymers*, held in Changchun, China in 2002, we reported the aromatic polyimides derived from the diamine monomers containing pyridine moiety in the main chain^[7]. In this paper, a series of PIs and PPys were prepared from new monomers containing pyridine moiety in the main chain and phenyl-substituted groups in the side chains, for example, the dianhydride compounds, 2,6-bis(3',4'-dicarboxylphenyl)-4-phenylpyridine dianhydride (PyDA) and

2,6-bis(3,4-dicarboxylphenyl)-4-(3-trifluoromethylphenyl)pyridine dianhydride (TFPyDA); the tetraamine compounds, 2,6-bis(3',4'-diamino phenyl)-4-phenylpyridine (PTPA), 2,6-bis(3',4'-diamino phenyl)-4-(4"-phenyl) phenyl pyridine (DPPA), 2,6-bis(3',4'-diaminophenyl)-4-(4"-fluorophenyl) pyridine (FPPA) and 2,6-bis(3',4'-diaminophenyl) -4-(3"-trifluoromethyl)phenyl pyridine (3FPA). The synergistic effects of rigid pyridine ring and flexible phenyl side chains on the properties of the polymers were researched in detail.

RESULTS AND DISCUSSIONS

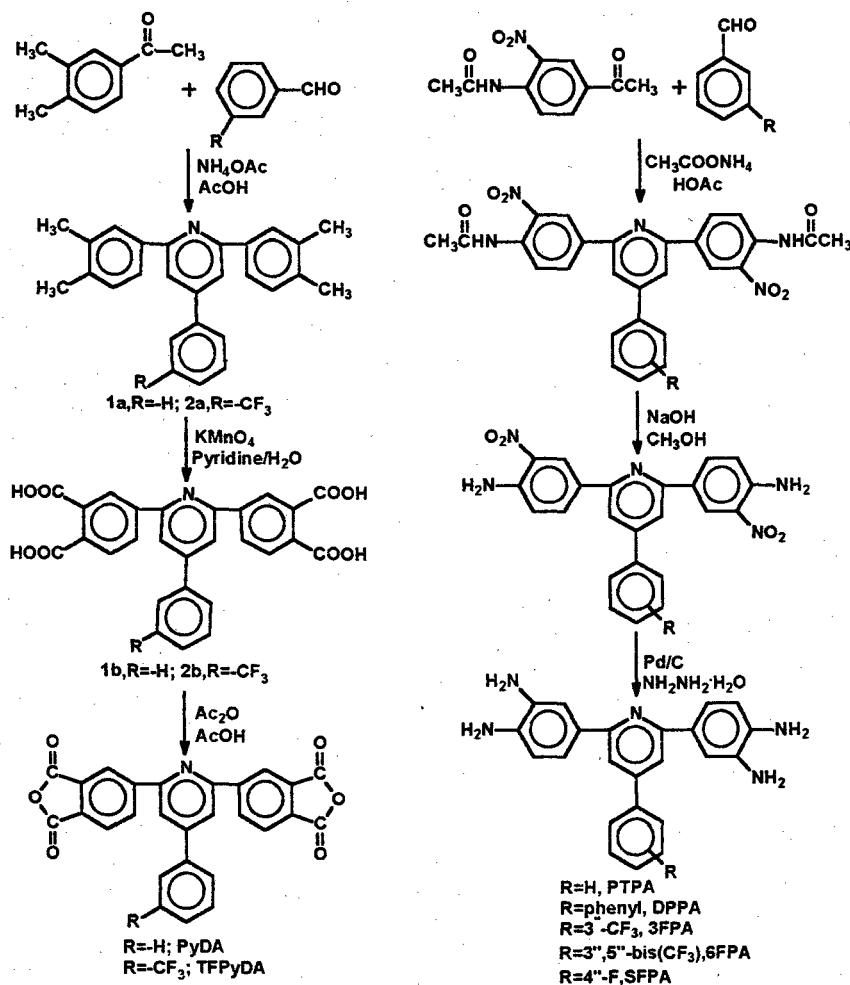
Synthesis of Monomers. The structures and abbreviations of the monomers are shown in Scheme 1 (a) and (b). The synthesis scheme for pyridine-bridged aromatic tetraamines and dianhydrides is shown in Scheme 2. For instance, the dianhydride monomers were prepared in three steps according to a well-developed method, modified Chichibabin's reaction^[8] of 3,4-dimethyl acetophenone and benzaldehyde compounds, followed by oxidization and dehydration. First, the pyridine-bridged aromatic tetra-methyl compounds, 2,6-bis(3,4-dimethylphenyl)-4-phenyl pyridine(1a, m.p.:206.9°C) or 2,6-bis(3,4-dimethylphenyl)-4-(3-trifluoromethyl phenyl)pyridine(2a, m.p.:152.7°C) was prepared from 3,4-dimethylacetophenone with benzaldehyde and *m*-trifluoromethyl benzaldehyde, respectively under the catalytic effects of ammonium acetate and glacial acetic acid. Then, the tetra-acid compounds 1b and 2b were obtained by oxidization of the corresponding tetra-methyl compounds with potassium



Scheme 1 Structures and abbreviations of the monomers

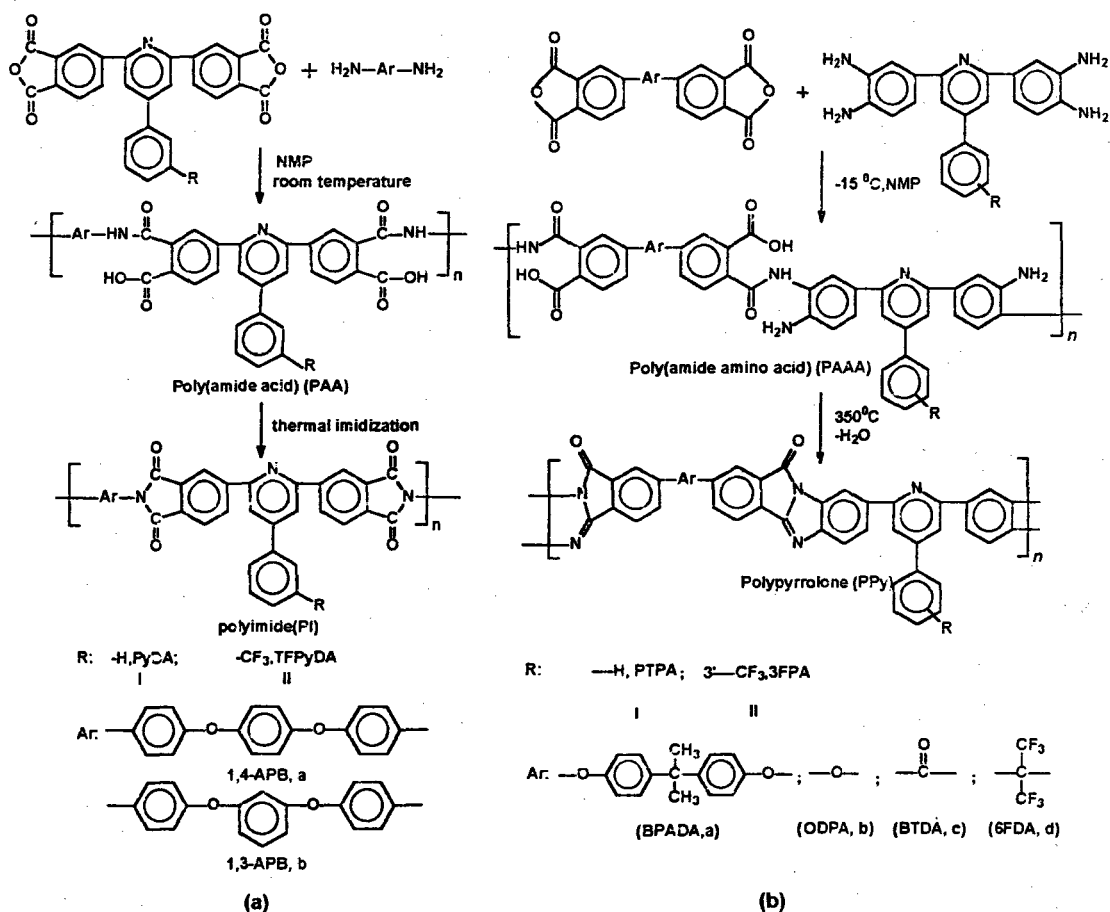
(a) tetraamine; (b) dianhydrides

permanganate and the pyridine catalyst. Finally, the two dianhydrides PyDA (m.p.:387.3^oC) and TFPyDA (m.p.:328.9^oC) were prepared by dehydration of the tetra-acid with acetic anhydride and acetic acid. The tetraamine PTPA was prepared by reducing the corresponding nitro-compound, which was synthesized by the reaction of 3-nitro-4-acetamidoacetophenone with benzaldehyde using the same pathway as reported by the modified Chichibabin's reaction. The other aromatic tetraamines were synthesized according to the same procedure.



Scheme 2 Synthesis of the new monomers

Synthesis and Properties of polyimides. Polyimides I and II were prepared by thermal imidization of the PAA precursors, which were synthesized from the dianhydrides PyDA or TFPyDA and two aromatic diamines, 1,4-bis(4-aminophenoxy)benzene(1,4-APB) and 1,3-bis(4-aminophenoxy)benzene(1,3-APB), respectively (Scheme 3a). The structures of the polymers were identified by FT-IR and elemental analysis. The flexible and tough polyimide films exhibited high thermal stability and the decomposition onset temperatures of the film were higher than 560^oC, and the 5% and 10% weight lost temperatures of the films were in the range of 574-595^oC and 606-622^oC, respectively (Figure 1). The films also exhibited high T_g (255-299^oC) determined by DSC measurement (Figure 2). Furthermore, the films showed good mechanical properties, low moisture absorption, low color intensity and good



Scheme 3 Synthesis of the polyimide (a) and polypyrrolone (b)

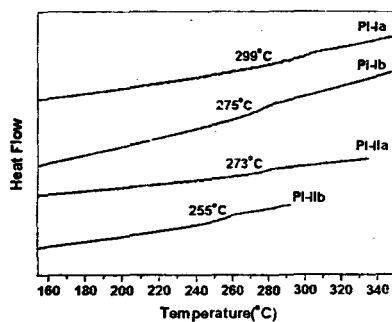
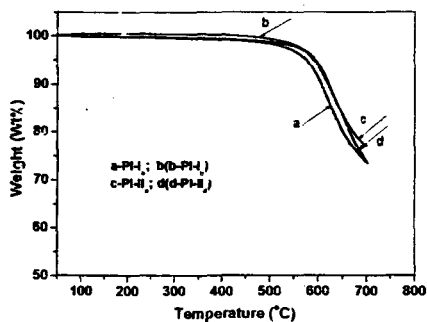


Figure 1 TGA curves of aromatic polyimides Figure 2 DSC curves of aromatic polyimides

dielectric properties. The good combined properties of the polymers could be attributed to the coordinate effects of the rigid pyridine ring and the bulky phenyl side chains.

Synthesis and Properties of polypyrrolones. Polypyrrolones I and II were prepared by thermal cyclization of poly(amide amino acid)s (PAAAs), which were prepared by polycondensation of aromatic dianhydrides with the aromatic tetraamines in NMP at low temperature (Scheme 3b). The reaction was strongly affected by the stoichiometry, adding sequence and adding interval of the monomers. For example, the reaction mixture easily gelled during the reaction when dianhydride was overfed or the adding interval was too short. Therefore, an exact stoichiometry of the dianhydride and the tetraamine and a long addition interval was necessary in the synthesis of the PAAA solution. It was

found that the [dianhydride]/[tetraamine] mole ratio close to 1.00 was required to yield a PAAA solution with reasonable viscosity which could produce a strong and flexible polymer film by casting the polymer solution on a glass substrate followed by thermal curing at temperatures up to 350°C.

The thermal properties, including onset decomposition temperature (T_d), temperature at 10% ($T_{10\%}$) weight loss, residual weight ratio at 750°C (R_w) and the glass transition temperature (T_g) were shown in Figure 3. The T_d s ranged from 482-541 °C for PTPA-based polymers and 492-579°C for 3FPA-based ones, respectively. The $T_{10\%}$ temperatures, which were usually defined as the criterion of the thermal stability for high-temperature polymers, were all higher than 550 °C. In general, the polymer thermal stabilities decreased depending on the aromatic dianhydrides employed in the following order: ODPa > BTDA > BPADA > 6FDA; As for the same aromatic dianhydride, the polypyrrolone decreased in their thermal stability depending on the aromatic tetraamines employed in the following order of PTPA > 3FPA. ODPa-based polypyrrolones exhibited the best thermal stability. For instance, PPy-I_b derived from ODPa and PTPA exhibited T_d of 521 °C, $T_{5\%}$ of 579 °C and $T_{10\%}$ of 652 °C. The excellent thermal stabilities of the polymers could be interpreted by the stable multiaromatic conjugated structures in the polymer backbones. More interesting, the ODPa-based polypyrrolones could maintain nearly 80% of their original weights when heating to 750°C in nitrogen. For instance, PPy-I_b and PPy-II_c showed R_w s of 84% and 73%, respectively.

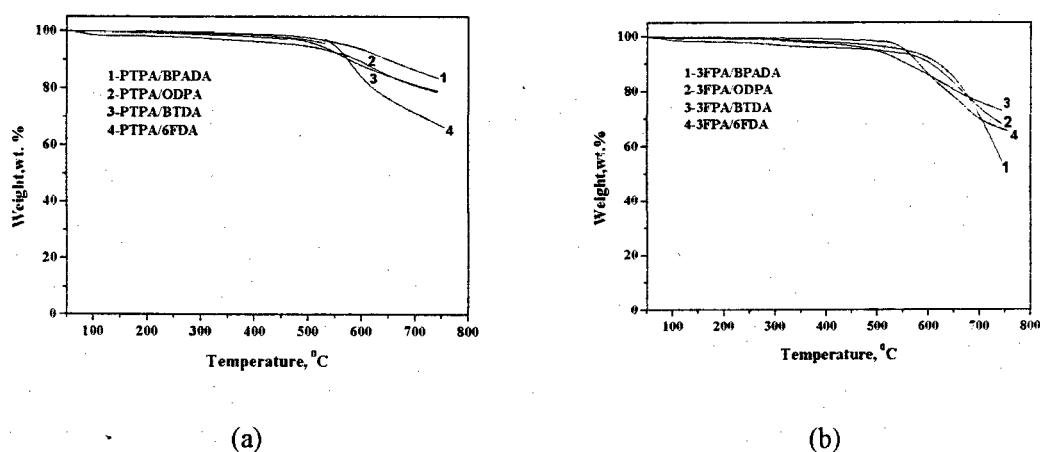


Figure 3 TGA curves of the PPys. (a) PTPA-based PPys; (b) 3FPA-based PPys

The T_g s of the PPy films determined by DSC were higher than 300°C. For instance, the 3FPA-based polymers showed T_g of 300~382°C, which decreased with the sequence of BTDA > 6FDA > ODPa > BPADA. (Figure 4). The high T_g was mainly attributed to the strong inter- and intramolecular interactions in the polymer backbone.

The hydrolytic resistance of the PPy films was investigated. Experimental results demonstrated that polypyrrolones possessed good hydrolysis resistance in alkaline aqueous solution (Table 1). Although aromatic polyimides possess great combined physical and chemical properties including high thermal stability, high mechanical property and high environmental stability, their hydrolysis resistance.

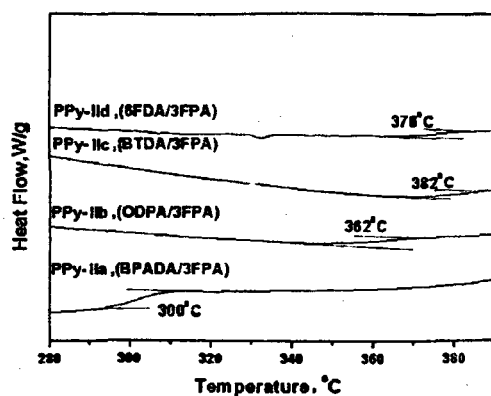


Figure 4 DSC curves of the 3FPA-based PPys (in air, heating rate: 10°C/min)

especially in alkaline aqueous solution, were generally poor due to the inherent chemical structures in the polymer backbones, i.e. imide bonds were easily broken by the OH⁻ attack to be decomposed. It was reported that Kapton[®] film would be completely hydrolyzed after boiling in hydrazine to produce two initial monomers, pyromellitic anhydride (PMDA) and 4,4'-oxydianiline (ODA) quantitatively.

As seen from Table 1, polypyrrolone films cured at 350°C could stand 12–18 h in the 10% boiling alkaline solution before hydrolysis was initially observed. After boiling in 10% aqueous sodium hydroxide for 7 days, the polypyrrolone films could retain most of their original shapes and toughness. TGA result indicated (Figure 5) that PPy-I_a showed acceptable thermal resistance even after boiling in 10% NaOH solution for 7 days, the R_w at 750°C was 63%, higher than that of PPy-I_a film cured up to 300°C (52%) although lower than that of PPy-I_a film cured under 350°C (82%), which demonstrating that the thermal-stable chemical structures still remained in the polymer backbones. In addition, the PPy films cured at 300°C showed inferior hydrolysis stability to that of the PPy films cured at 350°C, which proved from another point that the final curing temperature of 350°C was necessary to ensure the properties of the PPy films. The excellent alkaline hydrolysis resistance for polypyrrolones could be probably attributed to the fused multiaromatic structures.

Table 1 Hydrolytic resistant property in alkaline aqueous solution of the PPy films

PPy	t_{d300}^a (h)	t_{w300}^b (h)	t_{d350}^c (h)	t_{w350}^d (h)
Ia	10	48	18	>168(7 days)
Ib	12	32	17	>168(7 days)
Ic	11	40	18	>168(7 days)
IIa	10	52	16	>168(7 days)
IIb	11	46	13	>168(7 days)
IIc	9	48	12	>168(7 days)

a Initial hydrolyzing time of 300°C-curing PPys; *b* Wholly hydrolyzing time of 300°C-curing PPys; *c* Initial hydrolyzing time of 350°C-curing PPys; *d* Wholly hydrolyzing time of 350°C-curing PPys;

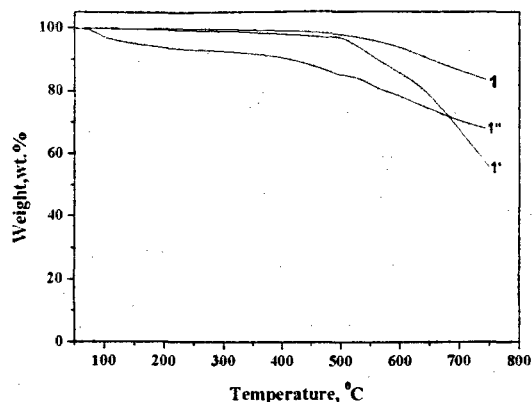


Figure 9 TGA curves of PPy-I_a with different final curing temperatures

- 1) PPy-I_a cured at 350 °C; 1') PPy-I_a cured at 300 °C curing; 1'') PPy-I_a cured at 350 °C, followed by boiling in 10% aqueous NaOH solution for 7 days

CONCLUSIONS

A series of new polyimides and polypyrrolones have been synthesized from pyridine-bridged aromatic monomers, including dianhydrides, PyDA and TFPyDA; tetraamine, PTPA and 3FPA. Experimental results indicated that both the polymers showed good processability and at the same time, high thermal stabilities and mechanical properties. Strong and flexible polymer films could be obtained by casting their precursor solution on glass substrate, followed by thermal dehydrating at elevated temperatures. The PPy films exhibited excellent alkaline hydrolytic resistance, which retained the shapes and toughness even after being boiled in 10% sodium hydroxide solution for 7 days.

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主链含有吡啶环的新型芳杂环高分子

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摘要 采用主链含有吡啶单元的新型芳香族单体, 如二酐单体 2,6-双(3',4'-二羧基苯基)-4-苯基吡啶二酐(PyDA)、2,6-双(3',4'-二羧基苯基)-4-(3-三氟甲基苯基)吡啶二酐(TFPyDA); 四胺单体 2,6-双(3',4'-二氨基苯基)-4-苯基吡啶(PTPA)、2,6-双(3',4'-二氨基苯基)-4-(4-苯基)苯基吡啶(DPPA)、2,6-双(3',4'-二氨基苯基)-4-(4-氟苯基)吡啶(FPPA)与 2,6-双(3',4'-二氨基苯基)-4-(3-三氟甲基苯基)吡啶(3FPA)制备了新型芳杂环高分子聚酰亚胺(PI)和聚吡啶(PPy)。刚性吡啶环、吡啶环与苯环间的强烈相互作用以及侧链的庞大侧基赋予了这些聚合物材料良好的加工性能, 同时保持了这些材料固有的耐热性能。

关键词 聚酰亚胺; 聚吡啶; 二酐; 四胺; 热性能