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Poly(aryl prehnitimide)s

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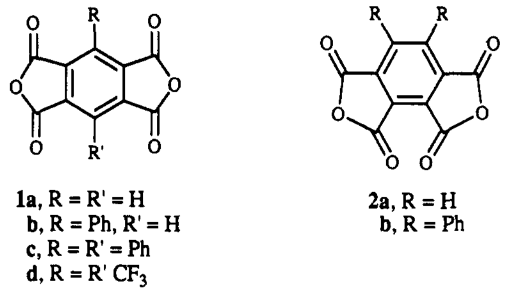
Aromatic poly(pyromellitimide)s as one of the most important classes of high-performance polymers have excellent electrical and mechanical properties and are known for their good chemical resistance. Due to their high solvent resistance or poor solubility, they are routinely synthesized via the two-step polymerization process, involving the formation of soluble poly(amic acid) precursors and subsequent thermal or chemical imidization.[1] The thermal solid-phase imidization often produces infusible and insoluble aromatic polyimides with poorly defined molecular architectures. This process limits poly(pyromellitimide)s (e.g., Kapton) for uses as thin films and coatings, since the fabrication of desirable, defect-free, large parts is hampered by the evolution of the water of imidization. The poly(amic acid) precursors are also known to undergo a redistribution reaction which can affect molecular weight distribution of polyimides.[2] In order to overcome these limitations, much effort has been focused on the development of aromatic poly(pyromellitimide)s that can be made in the imide form by melt or/and solution polymerization. Structural modifications are carried out on the diamine and dianhydride monomers. A wide variety of flexible bridging units are incorporated into the diamine monomers that impart mobility to the otherwise rigid polymer backbone.[1a] Among many aromatic diamines, 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl stands out for its ability to impart solubility and maintain the rigidity and high strength of the polyimide.[3] Recently, considerable research has been centered on structural modification of pyromellitic dianhydride (PMDA, **1a**) by introducing pendant groups, aiming at increasing the solubility of poly(pyromellitimide)s without substantially decreasing the rigidity of these polyimide backbones. Thus, phenylated pyromellitic dianhydrides **1b**,**c** and trifluoromethyl-substituted dianhydride **1d** (Figure 1) were synthesized and polymerized with aromatic diamines.[4] It was found that polyimides based on diphenylpyromellitic dianhydride **1c** with aromatic diamines containing flexible ether or methylene linkages, meta-catenation, or cardo linkages were organosoluble and could be synthesized by a one-step solution polymerization. But poly(pyromellitimide)s derived from **1b**–**d** with rigid diamines such as *p*-phenylenediamine and 4,4′-diaminobiphenyl still remained insoluble in common organic solvents and had to be made via poly(amic acid) precursors. Seemingly, the symmetry of a nearly planar pyromellitimide structure dominates the overall solubility of rodlike aromatic poly(pyromellitimide)s, and the slightly twisted, pendant phenyl group on PMDA can only contribute to the solubility to a certain extent.

It is generally recognized that a branched, asymmetric molecule tends to be more soluble than its linear, symmetric isomer. For example, the solubilities of polyimides derived from isomeric 3,3′-, 3,4′-, and 4,4′-oxydiphthalic anhydrides (ODPA) can be dramatically affected by the catenation patterns. The more asymmetric polyimide (ca. from 3,4′-ODPA) is more soluble than the less asymmetric one (ca. from 4,4′-ODPA).[5] Prehnitic dianhydride (**2a**)[6] is a structural isomer of PMDA and has a nonlinear functionality. Aromatic polyimides based on **2a** are still unknown, except for an ill-defined, water-soluble copolymer derived from **1a** and **2a** with 3,3′-diaminodiphenyl ether described in a patent.[7] In light of the effect of the catenation pattern on the solubility of polyimide, another structural modification of PMDA would be the alternation of the anhydride position. Since, to our best knowledge, no reports on the synthesis of **2b** have appeared in the literature to date, it is appropriate to synthesize diphenylprehnitic dianhydride (**2b**) and a series of polyimides based on this new monomer. Of particular interests were to investigate the effect of the bent but still rigid dianhydride functionality on the solubility and other properties of poly(aryl prehnitimide)s.



1a, R = R' = H
b, R = Ph, R' = H
c, R = R' = Ph
d, R = R' CF_3

2a, R = H
b, R = Ph

Figure 1.

Diphenylprehnitic dianhydride (**2b**) was readily synthesized in three steps from diethyl 1,3-acetonedicarboxylate, benzil, and diethyl acetylenedicarboxylate in high yields (Scheme 1). The Diels–Alder reaction of the cyclone **3**, which was easily prepared from 1,3-acetonedicarboxylate and benzil according to a known procedure,[8] and diethyl acetylenedicarboxylate afforded the tetraester **4** in 95% yield. Hydrolysis with an excess of potassium hydroxide in boiling ethylene glycol and subsequent acidification gave the corresponding tetraacid **5b**, which was then dehydrated at about 250 °C under vacuum to produce the dianhydride **2b**.[9] An alternative approach involved the Diels–Alder reaction with inexpensive maleic anhydride, followed by aromatization with bromine, hydrolysis, and dehydration. The highly pure monomer was obtained by recrystallization from chlorobenzene or by sublimation under vacuum. Its structure was unambiguously confirmed by FTIR, ^1H and ^{13}C NMR, and high-resolution mass spectrometries.

The hydrolysis of ethyl 5,6-diphenyl-1,2,3,4-benzenetetracarboxylate (**4**) under different conditions provided useful information on the relative reactivity of two different carbonyl groups. If the hydrolysis was done in aqueous ethanol even with 10 equiv of potassium hydroxide, the regioisomer **5a** was obtained quantitatively. The ^{13}C NMR spectrum of **4** showed two peaks at chemical shifts of 166.0 and 167.0 ppm, assigned to two different esters' sp^2 carbons at C-1,4 and C-2,3 positions, respectively. Such a small difference in chemical shifts suggests that all four ester groups have a similar reactivity toward a nucleophile in consideration of only the electronic effect.[10] The remarkable inertness of the ester at C-1,4 positions toward nucleophilic attack in the base hydrolysis is obviously caused by the steric hindrance provided by two pendant phenyl rings. Since both base hydrolysis and imide formation are reactions of the nucleophilic displacement type, the amine nucleophile in polymerization should preferably attack the less hindered carbonyl groups at C-2 and C-3 rather than the two carbonyls adjacent to the phenyl groups.

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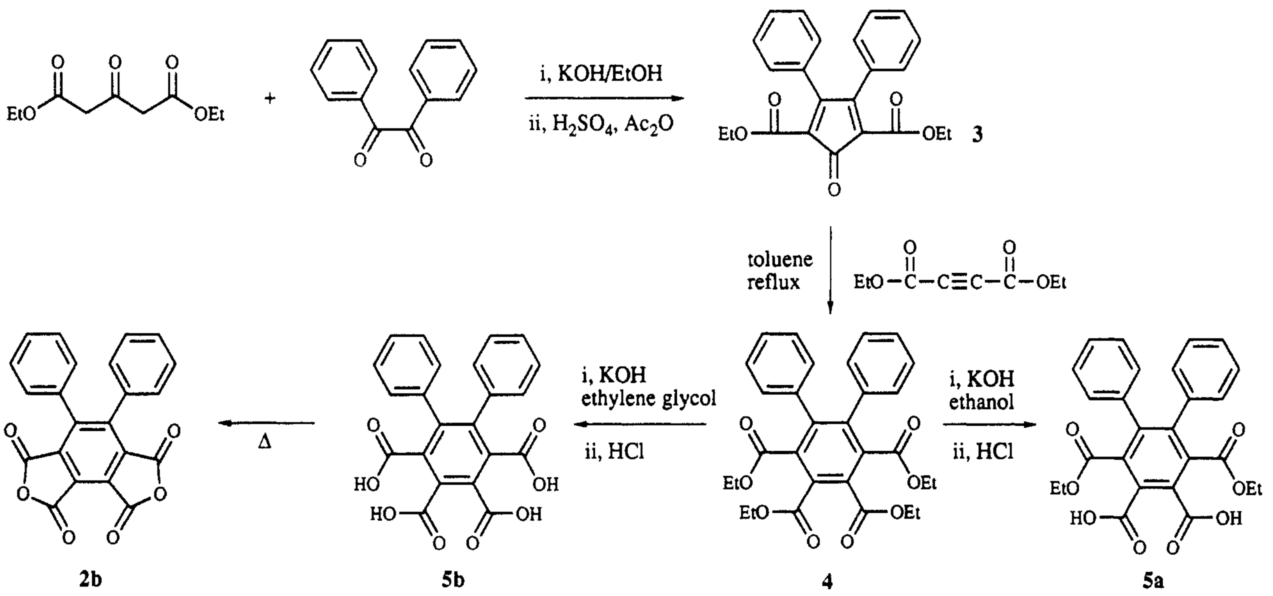
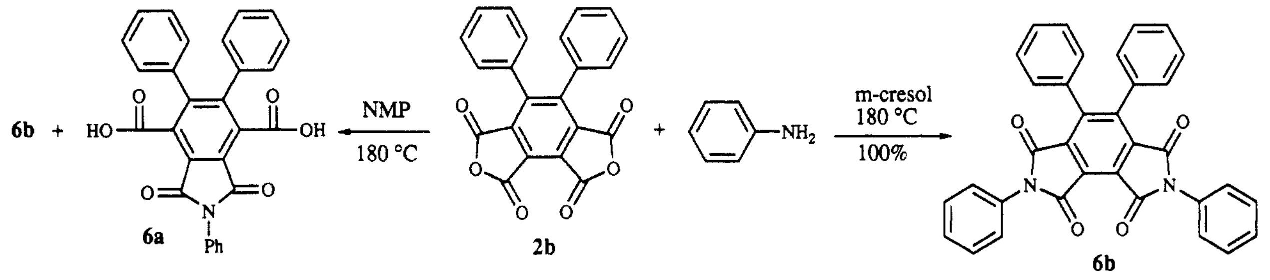
Scheme 1. Synthesis of Diphenylprehnitic Dianhydride (2b)



Scheme 2. Model Reactions of the Dianhydride 2b and Aniline



Unlike PMDA and other commercially available dianhydrides, the polymerization of dianhydride **2b** may present a potential problem associated with competitive monoimide (e.g., **6a**) versus diimide (e.g., **6b**) formation. The formation of the monoimide would cause either incomplete polymerization or cross-linking. The model reaction of the dianhydride **2b** with aniline was first carried out in *N*-methylpyrrolidinone (NMP) and gave a mixture of **6a**, **6b**, and other unidentified compounds. When the same reaction was done in *m*-cresol, the desired diimide **6b** was obtained in quantitative yield (Scheme 2).[11] This solvent effect can be attributed to the facts that water is miscible with NMP but not with *m*-cresol, and the resulting water during the reaction in NMP can effectively interfere with imidization or hydrolize the amic acid intermediate. A recent kinetic study on solution imidization suggests that both formation and cleavage of the amic acid are present and complete imidization via relinking of partially degraded products and further cyclization of the reproduced amic acid is possible at 180 °C.[12] However, prolonged heating at about 180 °C in NMP did not change the ratio of **6a** and **6b**.

On the basis of the results from model reactions, one-step polymerizations of the dianhydride **2b** with various aromatic diamines **7a–e** were then carried out in *m*-cresol in the presence of a catalytic amount of isoquinoline at 200 °C (Scheme 3). Water formed during the imidization was continuously removed with a stream of nitrogen. Depending on the chain rigidity and the solution concentration, either homogeneous solutions or clear gels could be obtained. Further dilution down to 2–3% solution concentration was needed to prevent gelation for the polymers **8a** and **8d**. But no precipitation of oligomers occurred during all polymerizations. High molecular weight polyimides were readily formed, except for the polymer **8d** due to relatively low reactivity of the diamine **7d**. In Table 1 intrinsic viscosities, solubilities, and thermal properties are compiled for different polyimides **8a–e**.

Scheme 3. Synthesis of Polyimides

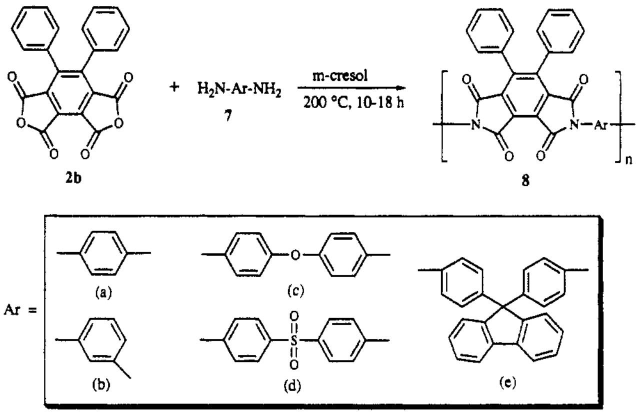


Table 1. Characteristics of Polymers 8

polymer 8	[η][a]	TGA[b] (°C)	solubility[c] TCE	DMF	DMSO	DMAc	NMP	*m*-cresol
a	0.95	560	+	+	+	+	+	+
b	0.40	526	+	+	+	+	+	+
c	1.01	438	+	+	+	+	+	+
d	0.26	533	–	±	+	±	+	+
e	0.50	554	+	+	+	+	+	+

[a] Intrinsic viscosity in NMP at 30 °C. [b] 5% weight loss in nitrogen, obtained on a TA TGA 51 and a Seiko TG/DTA 220 at a heating rate of 10 °C/min. [c] Key: +, fully soluble; ±, partially soluble; –, insoluble at room temperature.

All polyimides gave intrinsic viscosities ranging from 0.26 to 1.01 dL/g in NMP at 30 °C. These intrinsic viscosities are relatively lower than those of rigid-rod polymers that usually have intrinsic viscosities above 2.0 dL/g. Nevertheless, transparent, "fingernail creasable" films can be cast from their NMP solutions, except for **8d**, indicating reasonably high molecular weights and some degree of toughness.

The structures of the synthesized polyimides were characterized by FTIR and high-field ^{1}H and ^{13}C NMR spectrometries. By comparing IR spectra of the monomer **2b**, model compound **6b**, and polymers, the complete imidization in polymerization was confirmed. The IR spectrum of the dianhydride **2b** displayed two carbonyl peaks at 1855 and 1792 cm^{-1}. For the diimide **6b**, two carbonyl peaks shifted to 1771 and 1730 cm^{-1} where the polymers showed two peaks as well. The ^{13}C NMR spectrum of the polymer **8a** displayed two distinguishable lines at 162.0 and 164.4 ppm for carbonyl carbons, which matched well with two peaks in the spectrum of the structurally similar diimide **6b**.[11]

In comparison with poly(aryl pyromellitimide)s, the solubilities of polyimides **8** are significantly improved. All polyimides are soluble in NMP, dimethyl sulfoxide (DMSO), and *m*-cresol at ambient temperatures. Furthermore, except for the polymer **8d**, they are all soluble in other common organic solvents such as 1,1,2,2-tetrachloroethane (TCE), *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), and pyridine. It is worth notice that the rodlike polyimide **8a** derived from *p*-phenylenediamine is very soluble in all solvents mentioned above at ambient temperatures and can be readily produced in high molecular weight via a one-step polymerization process without precipitation and gelation. In sharp contrast, no high molecular weight polymers can be prepared from *p*-phenylenediamine and the dianhydrides **1** by direct solution polymerization. Although they can be produced via soluble poly(amic acid) precursors, these rigid-rod polymers are insoluble in common organic solvents like TCE, DMF, DMSO, and pyridine.[4a] Evidently, the significant improvement in solubility is attributed to the unique structural features of polymer: the bent diimide functionality and twisted pendant phenyl groups.

The glass transition temperature (T_g's) of the polymers **8** were not detectable by differential scanning calorimetry (DSC). Similarly, the T_g's of arylated and unsubstituted aromatic poly(pyromellitimide)s were also reported to be very weak, not well-defined, and difficult to detect.[4a] In addition, none of polymers **8** showed melting points on DSC below 600 °C. The polymers displayed good thermal stabilities, in spite of their bent diimide structure. The onset temperature for 5% weight loss in nitrogen was in the range of 438–560 °C (Table 1), as assessed by thermogravimetric analysis. The thermal stability of the wholly aromatic polymer **8a** was particularly noteworthy, for its 5% weight loss at 560 °C. Thus, according to preliminary DSC and TGA data, these polyimides appear to be amorphous or have a very low degree of crystallinity.

Our results demonstrated that changing the substitution pattern of the anhydride groups on a core benzene ring can greatly affect the solubility of the resulting polyimides. The versatility of the synthetic route and availability of many diaryl-1,2-diones and cyclic *o*-quinones such as acenaphthenequinone and phenanthrenequinone allow easy access to a wide range of substituted prehnitic dianhydrides. Future work will be focused on the syntheses of copolymers derived from the dianhydrides **1a** and **2b** and the characterizations of mechanical properties of these polyimides.

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(9) (a) Diethyl acetylenedicarboxylate (18.4 g, 10.8 mmol) was added to a solution of the cyclone **3** (33.9 g, 90.2 mmol) in toluene (120 mL) at room temperature. The reaction mixture was heated at reflux overnight. After removal of toluene, the product, ethyl 5,6-diphenyl-1,2,3,4-benzenetetracarboxylate (**4**), was washed with diethyl ether and then recrystallized from cyclohexane as white crystalline solids: 44.4 g (95%); mp 143–144 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.12 (6 H, m), 6.95 (4 H, m), 4.34 (4 H, q, J = 7.2 Hz), 3.92 (4 H, q, J = 6.8 Hz), 1.34 (6 H, t, J = 7.2 Hz), 0.85 (6 H, t, J = 7.2 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 166.95, 165.96, 142.18, 136.92, 135.52, 130.37, 129.62, 127.56, 127.48, 62.26, 61.58, 13.85, 13.41. (b) In a 250-mL, round-bottomed flask equipped with a condenser were placed the tetraester **4** (3.5 g) and KOH (5.6 g), ethylene glycol (80 mL), and water (20 mL). The mixture was heated at reflux (oil bath temperature 200–220 °C) overnight. After cooling to about 100 °C, the reaction mixture was poured in acetone (100 mL). The white precipitate was collected by filtration and then dissolved in water (100 mL). The aqueous solution was acidified with concentrated HCl, and the resulting white solids, the acid **5b**, was collected on the filter funnel (2.3 g, 86%). The crude tetraacid was heated in a sublimator under vacuum (0.25 mmHg) at 200 °C. The sublimed dianhydride **2b** as yellow crystals was obtained: 1.7 g (82%); mp 235–256 °C; IR (KBr, cm^{-1}) 1847.1, 1784.2; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34 (6 H,

m), 7.06 (4 H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.46, 146.82, 150.26, 135.05, 131.23, 129.66, 129.46, 129.42, 129.41, 128.27, 127.68. HRMS. Calcd for $C_{22}H_{10}O_6$: 370.0467. Found: 370.0467.

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(11) Mp 290.0–290.5 °C; FTIR (KBr, cm^{-1}) 1771 and 1730; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (m, 10 H), 7.25 (m, 6 H), 7.10 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.94, 162.44, 147.15, 133.60, 133.13, 131.19, 129.64, 129.03, 128.85, 128.52, 128.46, 127.93, 127.71, 126.58. HRMS. Calcd for $C_{34}H_{20}N_2O_4$: 520.1424. Found: 520.1402.

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