

Review

A MOLECULAR APPROACH TO THE SYNTHESIS OF NOVEL POLYIMIDES*

Zhi-yuan Wang**

Department of Chemistry, Carleton University, 1125 Colonel by Drive, Ottawa, Canada K1S 5B6

Abstract In the past ten years there has been a flurry of activity in the synthesis of new specialty polymers, largely as a result of the increased need for high technology materials. Interest is mainly shown in two distinct categories of polymers: a) polymers which are used in very small quantities to fulfill critical needs as a part of device systems, and b) high-performance engineering polymers which significantly extend their mechanical and thermal properties for structural applications. Polyimides and their unparalleled versatility have captured the attention and imagination of scientists and engineers. This article describes some of the recent work done by the author's group on the rational design at the molecular level and the synthesis of polyimides that have unusual structures and novel properties.

Keywords Polyimides, Poly(aryl prehnitimide)s, AB-type monomer, Solid-state polymerization

INTRODUCTION

Aromatic polyimides represent one of the most important classes of high-performance polymers and are generally divided into two types, addition and condensation polyimides. Addition polyimides are exemplified by bismaleimides, norbornene-terminated oligoimides such as the NASA's PMR-15 and ethynyl-terminated oligoimides such as the Thermid® series produced by the National Starch and Chemical Corp., U.S.A. In spite of their brittleness, cured addition polyimide resins are used as the composite matrices in applications such as printed circuit boards and structural composites. Composites are receiving considerable attention for several diverse applications, particularly in airplanes, automobiles, trains, and off-shore oil-drilling platforms.

Condensation polyimides can be prepared from a variety of relatively inexpensive monomers such as aromatic dianhydrides and aromatic or aliphatic diamines. Due to the availability of a large number of monomers, many polyimides can be tailor-made to have desirable glass transition or crystalline melt temperature, toughness, modulus, melt viscosity, coefficient of thermal expansion, and other properties. This versatility has permitted the development of various commercial products from condensation polyimides such as those shown in Fig. 1, including adhesives, composite matrices, coatings, films, fibers, foams, moldings, and membranes. For example, the most widely used polyimide, commercially known as Kapton® film and produced from pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline, exhibits many attractive features such as very high tensile strength (172.4 MPa), high tensile modulus (2.96 GPa), and outstanding thermal stability (4.4% weight loss after 500 h at 300°C in air)^[1].

Although the first synthesis of an aromatic polyimide was reported in 1908^[2], it was not until

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** Corresponding author: Zhi-yuan Wang (王植源), E-mail: wangw@ccs.carleton.ca

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the late 1950s that high molecular weight polyimides were prepared^[3-5]. Polycondensation of an aromatic dianhydride and a diamine is a common method for the synthesis of polyimides. The polymerization can be done in a one-step process or a two-step process via a poly(amic acid).

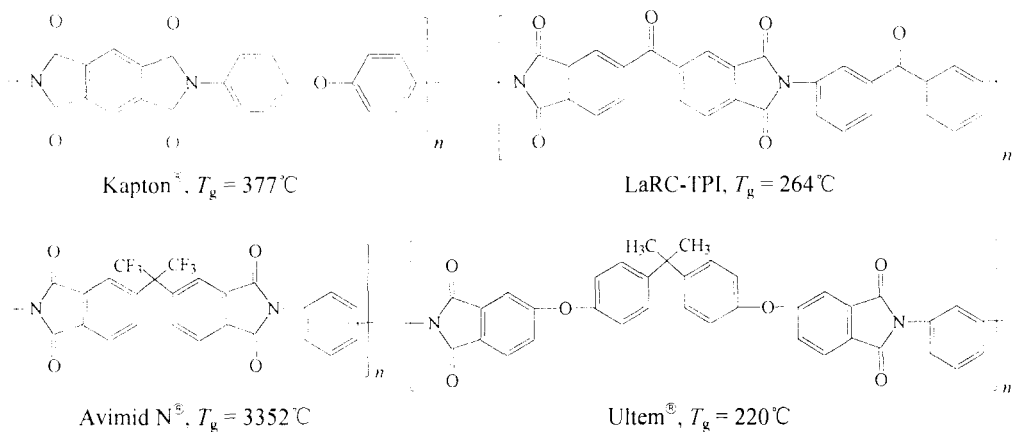


Fig. 1 Chemical structures of some commercial polyimides

For intractable aromatic polyimides, such as most polypyromellitimides derived from PMDA, one-step polymerization is not possible due to rapid loss of the molecular mobility and solubility of the resulting polyimide with relatively low molecular weight. The formation of the poly(amic acid) is a must and is usually carried out in a polar aprotic solvent, such as *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), or *N*-methylpyrrolidinone (NMP) at 15 to 75°C^[6-9]. The poly(amic acid) is then thermally imidized to yield the polyimide. Low melting poly(ether imide)s can be obtained by melt polymerization^[10] and soluble polyimides can be prepared by a one-step solution process in a high boiling organic solvent, such as *m*-cresol and *p*-chlorophenol, at elevated temperatures^[11-13]. In this case, it is necessary to keep the reaction medium homogenous and to remove the water generated from imidization during polymerization. The one-step solution process becomes more and more important, as it can produce soluble polyimides in bulk.

STRUCTURAL MODIFICATIONS OF POLYIMIDES AT THE MOLECULAR LEVEL

Aromatic polyimides already have various applications as mentioned above, in part owing to their high thermal stability, solvent resistance and good mechanical properties. Nevertheless, academic and industrial researchers continue to develop and to improve synthetic methods, and also to change and control the properties of polyimides through structural modifications.

The fabrication of a polymeric material requires that polymers be either molten below their decomposition temperatures for a molding extrusion process, or soluble in an organic solvent for a casting process. However, due to their inertness to organic solvents and heat resistance, many aromatic polyimides have poor processability.

Although the structure-solubility relationships of polyimides are not fully understood, the effects of chemical structure on the properties of polyimides have been extensively studied. The results revealed that certain structural features, such as the chain rigidity and strong interactions between polymer chains and crystallinity, are responsible for high softening/melting temperatures and insolubility. The interactions between polyimide chains are induced by the electronic polarization and the crystalline interaction^[14], which can result in tight packing between the polymer chains and increase the melting temperature and the insolubility of the polymer. For example, polypyromellitimide derived from *p*-phenylenediamine and PMDA has a *T_g* of 702°C and a *T_m* of

1027°C by calculation^[15]. These values could not be confirmed experimentally since they are above the decomposition temperature of the polyimide.

In order to fabricate an insoluble rigid-rod aromatic polyimide, it is necessary to process it in the form of its soluble poly(amic acid) precursor, which is subsequently thermally imidized. However, one of the problems associated with the poly(amic acid) is its short storage life. During the storage period, the molecular weight of the poly(amic acid) decreases gradually, which can significantly affect the properties of the final product. Furthermore, this two-step process limits the application of polyimides in the form of thin films and coatings. The fabrication of large and thick parts using this method is complicated by the release of water during imidization. It should also be noted that the thermal properties of aromatic polyimides, such as high T_g and thermal stability, are usually inversely related to the solubility and the ease of processing. That is, if the solubility of the polyimide increases, its T_g and thermal stability decrease.

Considering the common problems associated with the aromatic polyimides, it is therefore desirable and also challenging to design and synthesize the polyimides that have good solubility and at the same time are able to retain high temperature properties. The following approaches are currently used for structural modifications: 1) introduction of a flexible unit, 2) introduction of a large pendant group, 3) introduction of a large kink and a non-planarity, and 4) disruption of symmetry and recurring regularity through copolymerization.

These modifications are all conducted at the molecular level or at the "monomer" stage, involving the design and synthesis of new diamine and dianhydride monomers, and the manipulation of the monomer ratios in polycondensation.

Being the smallest and most rigid dianhydride, PMDA has recently been subjected to structural modification, aimed at increasing the solubility of poly(pyromellitimide)s without substantially decreasing the rigidity. In a PMDA molecule only the 3,6-positions are available for functionalization. Conceivably, substitutions of PMDA at the 3,6-positions would produce a series of new monomers. PMDA has been modified by introducing phenyl^[16, 17], trifluoromethyl^[18], trifluoromethoxy^[19], 3-trifluoromethylphenyl and 4-trifluoromethylphenyl^[20] groups at the 3,6-positions (Fig. 2). It was found that polyimides based on diphenylpyromellitic dianhydride (PMDA-b) with aromatic diamines containing flexible ether or methylene linkages, *meta*-catenation, or cardo linkages were organo-soluble and could be synthesized using one-step solution polymerization. Poly(pyromellitimide)s derived from the 3,6-substituted PMDA with rigid diamines such as *p*-phenylenediamine and 4,4'-diaminobiphenyl remained insoluble in common organic solvents and were prepared via their poly(amic acid) precursors.

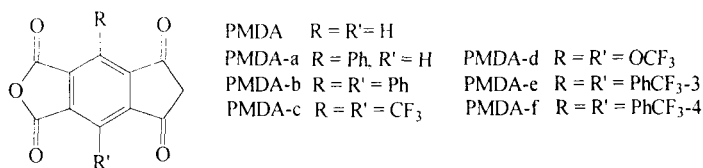


Fig. 2 Structures of PMDA and 3,6-substituted PMDA

POLY(ARYL PREHNITIMIDE)S: A NOVEL POLYIMIDE HAVING A BENT UNIT

Although the above four common approaches to structural modifications of aromatic polyimides have been recognized, there are still other possible routes to modify the structures of polyimides at the molecular level. By reviewing all known aromatic dianhydride monomers, two facts come to the surface. First, two anhydride groups are apart from each other by at least one atom (e.g. PMDA). Thus, adjusting the position of the two anhydride groups in PMDA, namely, moving one

anhydride group in close proximity to the other should be another structural alternation that would result in a polyimide with a rigid zigzag shape. Secondly, the AB-type monomer having an amine and an anhydride in the same molecule is not commercially available, which makes one wonder about the synthetic viability and potential use of such an AB monomer. The following describes some of the recent work done in the author's group, addressing these two issues.

Rational Design

Since the polyimide synthesized from diphenylpyromellitic dianhydride (PMDA-b, Fig. 2) and rigid *p*-phenylenediamine was still insoluble in common organic solvents, one can assume that the linearity of the planar pyromellitimide structure dominates the overall solubility of rod-like aromatic poly(pyromellitimide)s. The pendant phenyl groups on PMDA-b can enhance the solubility only to a certain extent. Therefore, the structural design should be centered on how to break the linearity of the diimide. By moving two cyclic imide rings side by side, a series of polyimides having a repeating unit featuring a non-linear but still planar diimide moiety can be realized (Fig. 3). The nonlinear diimide unit in the polymer backbone should still be rigid because of the fused heterocyclic imide rings. This bent diimide could allow the polyimides to retain its high-temperature performance, while increasing the solubility by reducing the interchain interaction due to its zigzag shape. The pendant phenyl groups should have a larger twist angle than that in PMDA-b, because the steric hindrance between the two aromatic rings in the *o*-terphenyl unit is larger than that in the "*p*-terphenyl" unit for the latter case. The pendant phenyl groups should impart thermal stability to the polyimides. The required monomer, diphenylprehnitic dianhydride (DPPDA) or 5,6-diphenylbenzene-1,2,3,4-tetracarboxylic dianhydride, is a structural isomer of PMDA-b.

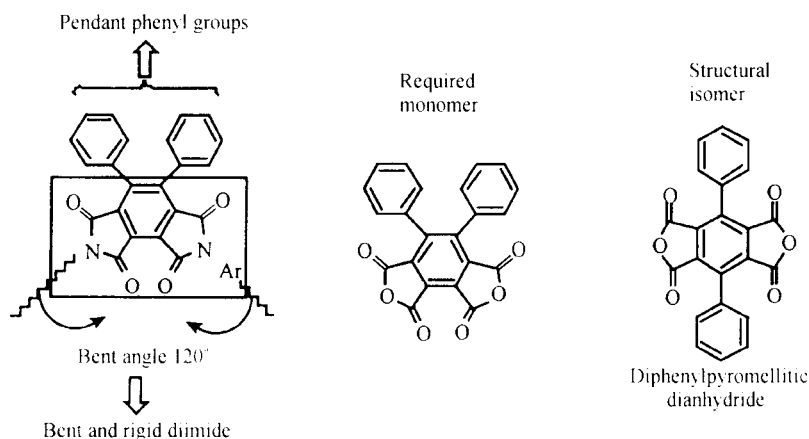


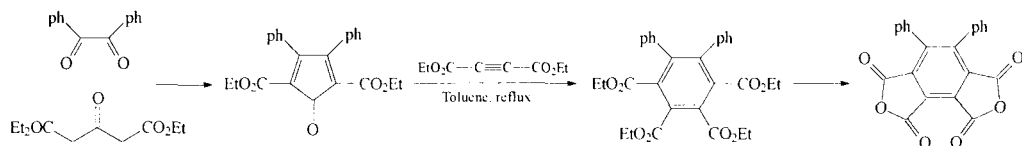
Fig. 3 Proposed bent polyimides and the required dianhydride monomer

Benzene-1,2,3,4-tetracarboxylic dianhydride or so-called prehnitic dianhydride^[21, 22] is a structural isomer of PMDA (Prehnitic acid: 1,2,3,4-benzenetetracarboxylic acid. The names given to the 1,2,3,4- and 1,2,3,5-isomers are confused in the literature; the name prehnitic acid appears preferable for the former compound because it indicates the source from oxidation of a tetramethylbenzene with the accepted name prehnitene. See Ref. [21] and [22]). Aromatic polyimides based on prehnitic dianhydride are still unknown, except for an ill-defined, water-soluble copolymer derived from PMDA and prehnitic dianhydride with 3,3'-diaminodiphenyl ether described in a patent^[23].

Monomer and Polyimide Syntheses

Diphenylprehnitic dianhydride (DPPDA) was readily synthesized from diethyl 1,3-acetone-

dicarboxylate, benzil and diethyl acetylenedicarboxylate in high yields (Scheme 1)^[24, 25]. The dianhydride could be purified by sublimation *in vacuo* or by recrystallization from chlorobenzene and could be stored in a dry container over months without any deterioration. The versatility of synthetic route and availability of many diaryl 1,2-diones and polycyclic ortho-quinones such as acenaphthenequinone and phenanthrenequinone allow an easy access to a wide range of other substituted prehnitic dianhydrides.



Scheme 1 Synthesis of diphenylprehnitic dianhydride

The crystal structure of DPPDA (Fig. 4) shows that the tricyclic part of benzenetetra-carboxylic dianhydride is almost flat. Dihedral angles (62.5° and 69.6°) between the pendant phenyl rings and the central benzene core are relatively larger than that (49.8°) between the two phenyls, revealing that the three benzene rings are highly twisted. The bulky phenyl groups push two carbonyls at 1,4-positions away, causing a slight distortion of the phthalic anhydride rings. The length of the C(7)–C(8) bond (0.1495 nm) is slightly longer than that of the C(9)–C(10) bond (0.1481 nm), indicating that carbonyls at 2,3-positions of DPPDA should be slightly more reactive than the other two at 1,4-positions without considering a steric hindrance caused by the two phenyl rings. The bond angles of C(3)–C(10)–C(9) and C(10)–C(7)–C(8) are 133.4° and 108.0° , respectively, both about $12\sim13^\circ$ off from 120° , which suggests that the bent angle between two imide groups is about 122° .

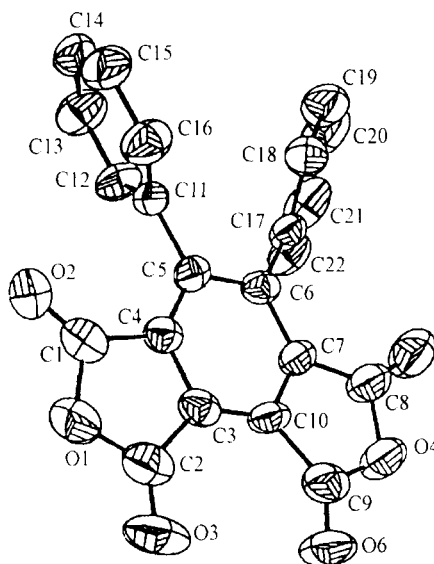


Fig. 4 Crystal structure of diphenylperhnitic dianhydried

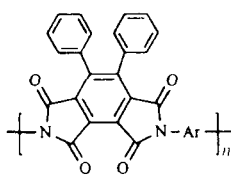
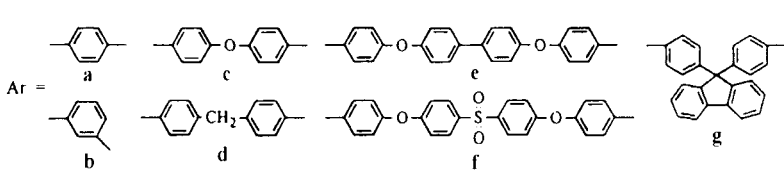
One-step polymerizations with various aromatic diamines were best carried out in *m*-cresol in the presence of a small amount of isoquinoline at 200°C . The water formed from imidization was removed together with a small amount of *m*-cresol with a stream of nitrogen. Depending on the diamine used, the solution concentration varies from 5% to 18%. With rigid or/and linear diamines

like *p*-phenylenediamine and 4,4'-oxydianiline, the polymerization concentration must be kept low in order to prevent gel formation. For flexible or bent diamines, especially for *m*-phenylenediamine, the solution concentration should be maintained as high as possible to suppress the formation of cyclic oligomers. High molecular weight polyimides can be readily obtained with aromatic diamines in about 18 h, except for less reactive 4,4'-diaminophenylsulfone.

Characterization

By comparison, poly(aryl prehnitimide)s have much more improved solubilities than poly(aryl pyromellitimide)s. Except for polyprehnitimide **e**, they are readily soluble in many common organic solvents at ambient temperatures such as TCE, DMAc, NMP, DMSO, and DMF, *m*-cresol, and even pyridine (Table 1). Polyprehnitimide **b** is exceptionally soluble in chloroform and THF, presumably owing to the zigzag shape of its backbone. It should be noted that great solubility in certain organic solvents (e.g., THF, DMF and DMSO) which are miscible with water enables these polyimides to be fabricated easily as asymmetric membranes. Furthermore, the rod-like polyprehnitimide **a** derived from *p*-phenylenediamine is remarkably soluble at ambient temperatures and can be readily produced in high molecular weight via a one-step polymerization process without precipitation and gelation. In contrast, the polyimides derived from PMDA or substituted PMDA and *p*-phenylenediamine could not be prepared by one-step solution polymerization and displayed limited solubility in common organic solvents. Evidently, the significant improvement in solubility for poly(aryl prehnitimide)s is attributed to the unique bent diimide and twisted pendant phenyl groups. Although it was soluble in *m*-cresol during polymerization, polyprehnitimide **e** could not be re-dissolved completely in the same solvent.

Table 1. Solubilities of poly(aryl prehnitimide)s*

									
									
Ar	CHCl ₃	TCE	DMF	DMSO	DMAc	NMP	<i>m</i> -Cresol	THF	Pyridine
a	-	+	-	+	+	+	+	-	+
b	+	+	-	+	+	+	+	+	+
c	-	+	+	+	+	+	+	-	+
d	±	+	+	+	+	+	+	-	+
e	-	-	-	-	-	-	±	-	-
f	±	+	+	+	+	+	+	-	+
g	-	+	+	+	+	+	+	-	+

* Measured at room temperature. Key: +, fully soluble; ±, partially soluble; -, insoluble.

Intrinsic viscosities of all poly(aryl prehnitimide)s ranged from 0.45 to 1.81 dL/g (Table 2). The formation of transparent, creasable films from polymers indicates that these polyimides have high molecular weights and some degree of toughness. Poly(aryl prehnitimide)s appeared to have relatively low solution viscosities and low molecular weights measured by GPC relative to polystyrenes, due to the bent diimide structure. For example, polyprehnitimides **b** ($[\eta] = 0.50$ dL/g) and **f** ($[\eta] = 0.77$ dL/g) have the number-average molecular weights of 21700 and 51000, respectively.

Polyprehnitimides **b**, **c**, **e**, **f** showed distinct high T_g ranging from 362 to 437°C. The T_g of polymers **a** and **g** were not detectable by DSC. The T_g of some poly(aryl prehnitimide)s could also be determined from the E'' or $\tan\delta$ values obtained from TMA in stress-strain mode. Except for polyprehnitimides **e** and **g** that could not form tough films for TMA measurement, these polyimides

have T_g values (E'') ranging from 340 to 443 °C. As expected, the highest T_g was obtained for the most rigid polyprehnitiimide **a**. The most flexible polymer **f** has the lowest T_g of 340 °C. Increasing the chain stiffness or decreasing the number of bridging bonds in the diamines shifts the T_g to a higher value, as seen for polyimides **e** (362 °C) and **c** (402 °C). Ultimately, polyprehnitiimides **a** and **b** derived from rigid phenylenediamines have T_g values over 440 °C. The solvent cast films for polyprehnitiimides **a–e**, **f** were clear, flexible and tough. Young's moduli (E') measured for polymers **a–e**, **f** ranged from 2.07 GPa to 3.94 GPa (Table 2). High E' values (> 3.0 GPa) were observed for polymers **a**, **c** and **f**. Polyprehnitiimide **b** has a relatively low Young's modulus (2.07 GPa), probably due to its zigzag-like structure.

Table 2. Characterization of poly(aryl prehnitiimide)s

Ar	$[\eta]^a$ (dL/g)	T_g^b (°C)	T_g^b (°C)	T_d^c (°C)	T_d^c (°C)	E' ^d (GPa)	Film ^e
		DSC	TMA	N ₂	air		
a	0.95	N/O ^f	443	560	524	3.14	Clear, tough, flexible
b	0.50	437	424	553	523	2.07	Clear, tough, flexible
c	1.01	420	402	514	491	3.94	Clear, tough, flexible
d	1.81	421	395	507	449	2.85	Clear, tough, flexible
e	0.95 ^g	362	– ^h	483	480	–	Brittle
f	0.77	366	340	529	489	3.14	Clear, tough, flexible
g	0.45	N/O	–	554	516	–	Clear, flexible

a) Intrinsic viscosity measured in NMP at 30 °C; b) Except for **d** measured by DSC at a heating rate of 10 °C/min, the rest were obtained from DSC in oscillation mode at a heating rate of 3 °C/min; c) 5% weight loss at a heating rate of 10 °C/min; d) Young's modulus measured from TMA; e) Cast from TCE; f) N/O: Not observed; g) in *o*-chlorophenol at 30 °C; h) Not measured

Like many aromatic polyimides and poly(aryl pyromellitimide)s, all poly(aryl prehnitiimide)s displayed excellent thermal stability. The onset temperatures for 5% weight loss in nitrogen were in the range of 483 to 560 °C, as assessed by TGA (Table 2). In air, these temperatures were lower, in the range of 449 to 524 °C. The excellent thermostability of polyprehnitiimide **a** is particularly noteworthy, for its 5% weight loss at 560 °C in nitrogen and 524 °C in air. It should be mentioned that, since these polyimides are not end-capped and have different molecular weights, their molecular weights and the nature of the end group should have a direct impact on the thermal and thermooxidative stability. For example, the degradation for the uncapped polyprehnitiimide **b** began at about 485 °C in air and catastrophic decomposition appeared at about 555 °C. When it was heated in air at 400 °C, this polymer lost 10% of weight in about 14 h with a degradation rate of 0.0705 mg/h, then decomposed more rapidly at the rate of 0.196 mg/h.

Rigid Alternating Copolyimides Containing a Bent Unit

Copolymerization of two different dianhydrides or two different diamines is also a common practice to improve solubility and achieve a combination of desired properties^[26]. However, if two dianhydrides or two diamines have quite different reactivities, a short block of homopolymer may form first. Such oligoimides like oligo(*p*-phenylene pyromellitimide) may be insoluble in the polymerization solvent, which would prevent further chain growth. In fact, it is difficult to achieve a high content (ca. over 50%) of pyromellitimide by direct solution copolymerization of PMDA and a dianhydride comonomer even with a flexible diamine such as 4,4'-oxydianiline or 4,4'-methylenedianiline^[27]. It would be more difficult to obtain a high molecular weight soluble 1:1 copolyimide by direct random copolymerization of PMDA with another rigid dianhydride and stiff *p*-phenylenediamine.

Among all soluble poly(aryl prehnitiimide)s, the one (**a**, Table 1) without a bridging unit derived from DPPDA and *p*-phenylenediamine was notably soluble in DMF, DMAc, TCE, and pyridine. Such a remarkably high solubility can be attributed to the unique 122°-bent functionality

in DPPDA. Subsequently, an attempt was made to render the soluble feature offered by DPPDA to rather insoluble rigid-rod poly(*p*-phenylene pyromellitimide) through random copolymerization^[28]. But the premature polymer precipitated from the reaction mixture of DPPDA and PMDA in a 1:1 ratio with *p*-phenylenediamine in *m*-cresol. It was found that PMDA reacted faster than DPPDA to yield an insoluble oligopyromellitimide. To improve the solubility by shortening the pyromellitimide block, the sequential addition was employed by first reacting *p*-phenylenediamine with DPPDA in a 2:1 molar ratio and then by slowly introducing PMDA. The resulting copolymer remained soluble in *m*-cresol during polymerization but was still insoluble in TCE, DMAc, or NMP. Obviously, this sequential copolymerization could not produce the alternating copolyimide without defect or short block. Preston *et al.* have shown that using bent aromatic diamines can improve the processability of stiff-chain polyimides^[29]. It is therefore appropriate to further investigate the effects of the alternating structure and the bent prehnitimide unit on the solubility of rigid copolyimides.

The required diamine, DPPDA-DA (Fig. 5), was synthesized by the reduction of dinitro precursor derived from DPPDA and 4-nitroaniline and fully characterized by spectroscopic means and chemical analysis^[30]. Polymerizations of this diamine with PMDA and NDA, respectively, were carried out in *m*-cresol at 200°C. The solution concentration was best kept at 2% in order to prevent gelation.

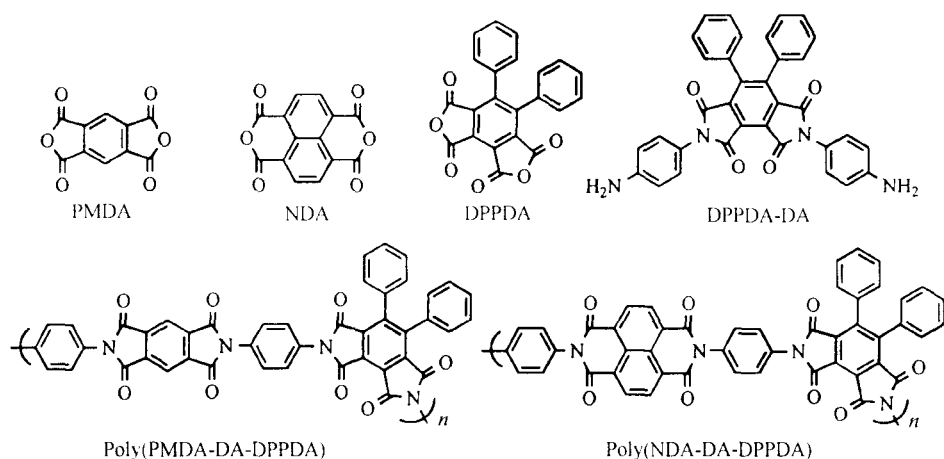


Fig. 5 Diamine and dianhydrides for making perfectly alternating copolyimides

The alternating diad structures of poly(PMDA-DA-DPPDA) and poly(NDA-DA-DPPDA) were confirmed by IR and NMR. Three model bisimides representing all three possible diads were prepared from *p*-phenylenediamine, phthalic anhydride, and 1,8-naphthalic anhydride, and used to aid the structural elucidation. Intrinsic viscosities of the “as-prepared” poly(PMDA-DA-DPPDA) and poly(NDA-DA-DPPDA) were 0.57 and 0.89 dL/g (Table 3), relatively lower than those for typical rigid-rod polyimides. But creasible tough films could be cast from the reaction solution for both polymers, indicating the formation of high molecular weight polymers. Relatively low viscosity can be attributed to the bent diimide structure and incomplete imidization. Thermogravimetry of both “as-prepared” polyimides showed the loss of water occurring at 280–300°C. After being treated at 300°C for a short time (10 min) to effect complete imidization, the powdered copolyimides showed no weight loss up to 450°C. As expected, solution viscosity increased to 1.04 and 1.20 dL/g for poly(PMDA-DA-DPPDA) and poly(NDA-DA-DPPDA), respectively (Table 3).

Poly(PMDA-DA-DPPDA) and poly(NDA-DA-DPPDA) are remarkably soluble in organic solvents like DMF, DMAc, NMP, and *m*-cresol (Table 3). The significant improvement in

solubility, as compared to the copolyimide produced by sequential copolymerization, is evidently attributed to the bent prehnitimide unit and the perfect alternate sequence. Regular insertion of the bent unit into the rigid-rod backbone effectively prevents the polymer chains from close packing, to form a long-range ordered structure. The pendant phenyl rings attached to the central benzene core also contribute to the reduction of strong interchain interactions. It is worthwhile noting that poly-(NDA-DA-DPPDA) containing the naphthalimide moiety was more soluble than poly(PMDA-DA-DPPDA) in TCE. It was also noted that the polymers became slightly less soluble after being thermally treated in solid powder form. The minor decrease in solubility was primarily due to the completion of imidization, rather than the increase in crystallinity or cross-linking.

Table 3. Characterization of poly(PMDA-DA-DPPDA) and poly(NDA-DA-DPPDA)

Copolyimide	Viscosity (dL/g) ^b	T_d (°C) in N ₂ ^c	T_d (°C) in air ^c	Solubility ^d					
				TCE	DMF	DMAc	NMP	<i>m</i> -Cresol	Pyridine
PMDA-DA-DPPDA	0.57	365	356	–	+	+	+	+	+
(cured) ^a	1.04	530	424	–	+	±	+	+	±
NDA-DA-DPPDA	0.89	505	403	+	+	+	+	+	+
(cured)	1.20	530	416	+	+	+	+	+	±

a) Powered "as-prepared" polyimides were heated at 300°C for 10 min; b) intrinsic viscosity in NMP at 30°C; c) onset temperature for 5% weight loss, obtained on a Seiko TG 220 at a heating rate of 10°C/min; d) room temperature; Key: +, fully soluble; ±, partially soluble; –, insoluble.

Neither of the T_g and crystalline melting endotherms was detected for poly(PMDA-DA-DPPDA) and poly(NDA-DA-DPPDA) by differential scanning calorimetry. Young's moduli determined by thermomechanical analysis for both "as-prepared" polymers were in the vicinity of 3 GPa. After thermal treatment at 300°C for 10 min, Young's modulus of poly(NDA-DA-DPPDA) dropped from 3.3 to 1.6 GPa. The decrease of Young's modulus is indicative of the increased stiffness of the polymer backbone as a result of complete imidization.

AMINO-ANHYDRIDES: A NEW AB-TYPE MONOMER FOR POLYIMIDES

Unlike many condensation polymers that can be made from a bifunctional monomer, very few amino-anhydride monomers and their corresponding AB-type polyimides are known and well characterized. This result is mainly attributed to the ease of self condensation between the amine and the anhydride. Two known amino-anhydrides, 4-aminophthalic anhydride^[31, 32] and 4-aminonaphthalic anhydride, were obtained by reduction of the corresponding nitro precursors (Fig. 6) (It is available from Aldrich Chemical Co. and can be recrystallized from nitrobenzene as moisture-sensitive orange needles with *m.p.* > 350°C. *Beil.*, 18(2): 469). But the former was difficult to isolate as a pure monomer, due to rapid oligomerization during drying or heating prior to melting. As a result, 4-aminophthalic anhydride and its derivatives were difficult to polymerize to high molecular weight polyimides^[33]. 4-Aminonaphthalic anhydride is stable during isolation and purification, but polycondensation of this amino-anhydride is likely to yield an insoluble rigid-rod polyimide.

The AB-type polyimides have been made by two-step polymerization of an amino-dicarboxylic acid (A, Fig. 6) and a mono-ester of amino-dicarboxylic acid (B, Fig. 6). Both monomers can be isolated and purified because they are more stable than the corresponding amino-anhydrides. However, polymerization of the amino-diester C in *m*-cresol or neat afforded a low molecular weight polyimide with an inherent viscosity of 0.13 dL/g^[34], presumably because of the low reactivity of the ester group.

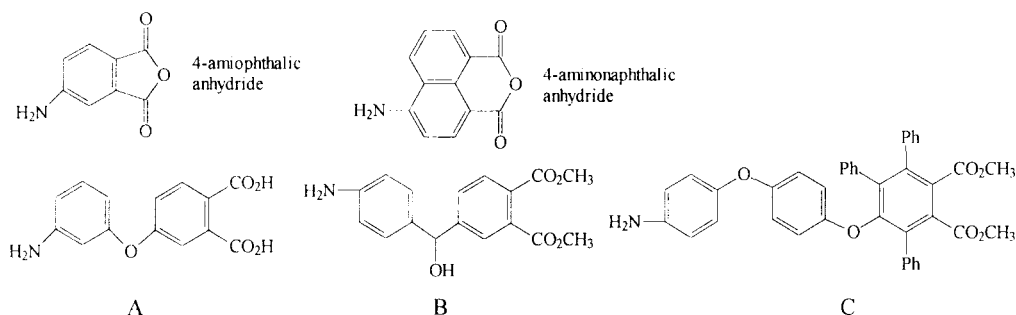


Fig. 6 Known amino-anhydrides and other AB-type monomers

From a synthetic point of view, by using an amino-anhydride monomer, one can avoid the strict stoichiometric control needed in polycondensation, with obvious advantages in the production and processing of polyimides. However, such an AB monomer has to be stable and unreactive at ambient temperatures so that purification is possible and yet, on the other hand, it must be sufficiently reactive at elevated temperatures to make polymerization to high molecular weight possible. These two requirements seem to be in stark contrast to one another. In the conventional practice of making polyimides derived from a dianhydride and a diamine monomer, it is necessary to weigh the two monomers precisely with a 1:1 mole ratio in order to obtain a high molecular weight polymer. Also, a dianhydride is usually very moisture-sensitive, and can be hydrolyzed to the corresponding carboxylic acid, resulting in the stoichiometry of two monomers being off and giving a polyimide with low molecular weight. Since an AB monomer bears two reactive groups in one molecule, it always maintains a stoichiometric balance, ensuring a high molecular weight for the polymer.

Monomer Design and Synthesis

Our original objective was to design a monomer that allows the introduction of a [5]helicene unit into a polyimide. Helicenes are chiral molecules that can be best described as exclusively carbon-containing polycyclic aromatic compounds. Their helical conformations result from the overlapping of terminal aromatic rings and therefore form a pair of conformational enantiomers. Upon resolution of these enantiomers, helicenes can show high optical rotations ($[\alpha]_D^{25}$) of the order of $1,000^\circ$ to $10,000^\circ$ ^[35, 36]. Considering the unique features of [5]helicene, it is desirable to incorporate a helicene unit into a macromolecule. First of all, the polycyclic aromatic structure of a helicene would result in a rigid, thermally stable polymer with good mechanical properties. Secondly, the non-planar monomeric units would offer the possibility of improving solubility. Additionally, the high optical rotations plus the extended array of π -systems from the helicene structure might result in an optically active polymer with a very large optical rotation.

Frimer *et al.* recently reported the synthesis of a difunctional helicene, [5]helicene-5,6,9,10-tetracarboxylic dianhydride (Fig. 7), which involved a photochemical cyclization^[37]. It was further demonstrated that a soluble, high molecular weight polyimide could be made by solution polymerization of this [5]helicene dianhydride and 3,3'-(hexafluoroisopropylidene)dianiline^[38]. The polyimides based on this novel dianhydride were found to have higher long-term thermal stability than PMR-15 thermosetting resin.

Clearly, the construction of the helicene core is a crucial step in any large scale production of a [5]helicene-based monomer, which should preferably be done by a non-photochemical process. 5,6,9,10-Tetrahydro[5]helicene-7,8-dicarboxylic anhydride (Scheme 2) is known^[39,40] and can be readily prepared in large scale in high yield from readily available starting materials using a conventional chemical process. Given that this [5]helicene unit is functionalized with an anhydride

group, an imide can be readily formed, making a polyimide a logical choice for a first attempt to incorporate a helicene unit into a macromolecule. Granted, we were somewhat surprised, but certainly pleased to learn that the amino-anhydride monomers could be readily obtained^[41].

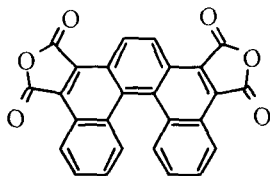
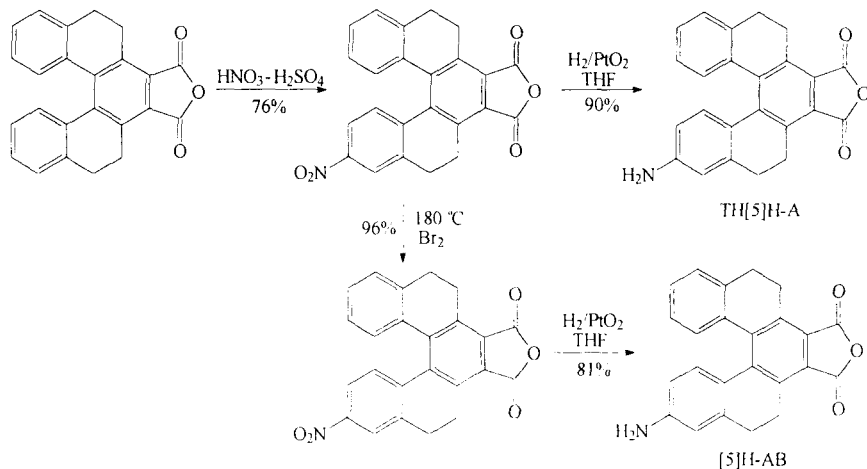


Fig. 7 [5]Helicene-5,6,9,10-tetracarboxylic dianhydride



Scheme 2 A route to AB-type amino-anhydride monomers

Since tetrahydro[5]helicene anhydride was readily prepared from α -tetralone and maleic anhydride in three steps, subsequent mononitration of this C_2 -symmetric anhydride became the key to our procedure. Selective mononitration was found to be best carried out in a mixture of acetic acid and chloroform using 70% nitric acid and concentrated sulfuric acid as a nitrating agent (Scheme 2). Under such reaction conditions, the pure nitro-anhydride could be obtained in 76% yield after a simple workup. Reduction of the nitro group by hydrogenation using PtO_2 in THF afforded the amino-anhydride (TH[5]H-AB) which could be purified by a short-column flash chromatography. The [5]helicene-based monomer ([5]H-AB) was obtained from the corresponding nitro-anhydride which was derived from its unsaturated precursor upon aromatization by treatment with elemental bromine in refluxing *o*-dichlorobenzene (Scheme 2).

Unlike 3- and 4-aminophthalic anhydrides which do not show any melting points by gradual heating, TH[5]H-AB and [5]H-AB displayed sharp melting points, 181.8°C by DSC or 181–183°C for the former and 331.7°C by DSC for the latter. At temperatures higher than their melting points the condensation reaction took place rapidly to yield water and oligoimides. Both TH[5]H-AB and [5]H-AB monomers could be stored in a dry container over months without any deterioration. They are stable in refluxing chloroform and TCE but become reactive in polar solvents such as DMSO, DMAc and NMP at elevated temperatures. [5]H-AB could be sublimed under vacuum at ca. 200°C without any self condensation. Structures of TH[5]H-AB and [5]H-AB were confirmed by spectroscopic means (IR, NMR, MS). The structure of TH[5]H-AB was also confirmed by a single crystal X-ray diffraction analysis (Fig. 8). The crystal structure shows that the two terminal benzene rings are non-coplanar with an interplanar angle of 50.9°. The amino and anhydride

groups are connected by a conjugated biphenyl moiety to form a “push-and-pull” system.

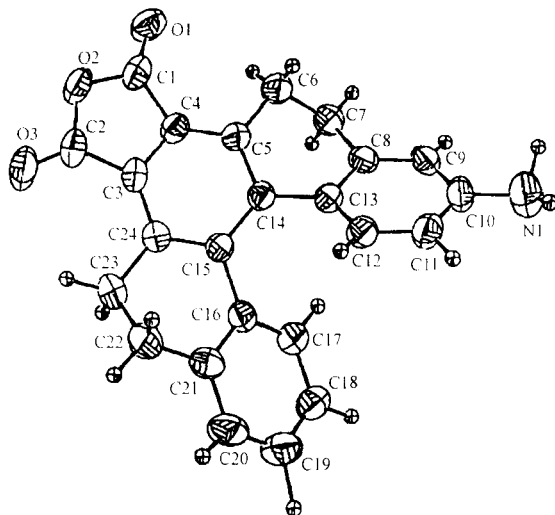


Fig. 8 The crystal structure of TH[5]H-AB

Synthesis of PolyTH[5]H-AB

One-step polymerization of TH[5]H-AB was carried out in *m*-cresol at 6% solid contents in the presence of a small amount of isoquinoline at 200 °C^[42–44]. High molecular weight polyTH[5]H-AB (Fig. 9) could be readily obtained in 18 h. Prolonged polymerization would cause gelation. Complete imidization was confirmed by the presence of two carbonyl bands at 1764 and 1712 cm^{−1} for the imide group in the IR spectrum. PolyTH[5]H-AB was readily soluble in TCE and showed limited solubility in chloroform and NMP at ambient temperatures. It was more soluble in chlorinated hydrocarbon solvents like chloroform and TCE than polar solvents such as DMAc, DMF and DMSO. This might be due to the high carbon-hydrogen content of tetrahydro[5]helicene unit and low imide component. It had a weight-average molecular weight of 188,000 measured by GPC relative to standard polystyrene and a polydispersity index of 2.23. Intrinsic viscosity was 0.84 dL/g in TCE at 30 °C.

The T_g could not be detected by DSC or DMA up to 450 °C, indicative of the high rigidity of the polymer backbone. Despite the presence of aliphatic moieties, polyTH[5]H-AB displayed good thermal stability. The onset temperature for 5% weight loss in nitrogen was at 499 °C, as assessed by TGA. In air, the onset temperature was 455 °C, still comparable to most of the polyimides reported. A clear, flexible and tough film could be cast from the TCE solution of polyTH[5]H-AB. Young's modulus of the non-oriented, amorphous film was measured to be 2.91 GPa at 25 °C and 2.36 GPa at 200 °C using DMA in tensile stress-strain mode.

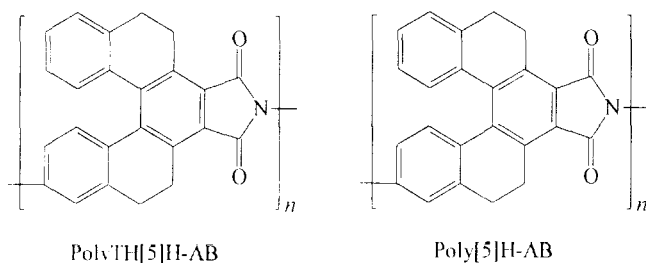


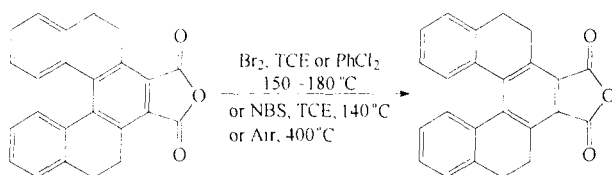
Fig. 9 AB-type polyimides

Synthesis of Poly[5]H-AB

Solution polymerization of [5]H-AB monomer was attempted in *m*-cresol (2% concentration) at 200 °C, but only an insoluble oligomer was formed. Oligo[5]H-AB was not soluble in any organic solvents and concentrated sulfuric acid. The IR spectrum of oligo[5]H-AB showed the imido carbonyl bands at 1767 and 1716 cm⁻¹.

Due to poor solubility, rigid polymers often cannot be obtained in high molecular weight by one-step solution polymerization. The precipitation of oligomers or ill-defined materials is often the case for this type of polymer. In order to overcome this problem, a precursor strategy can be used which involves the synthesis of a soluble polymer precursor followed by polymer transformation to yield the final rigid polymer. The transformations have been achieved for several classes of polymers by means of photochemical process^[45], thermal curing^[46], or chemical processes^[47-49]. Among these methods, a chemical transformation offers more versatility, because many reactive groups are known to be able to be converted chemically into a cyclic functionality. In our case, although poly[5]H-AB cannot be made by one-step solution polycondensation from [5]H-AB, it could conceivably be obtained from polyTH[5]H-AB by polymer transformation.

As a model reaction, tetrahydro[5]helicene anhydride was converted quantitatively into [5]helicene anhydride upon treatment with elemental bromine at elevated temperatures (Scheme 3). This aromatization reaction was best carried out by adding bromine to the substrate in hot TCE or *o*-dichlorobenzene at temperatures of 150–180 °C. If the reaction is run at lower temperatures or from room temperature to high temperature, the desired product is obtained in low yield along with brominated by-products. A plausible explanation for this aromatization reaction is that at high temperature bromine is homolytically cleaved to generate a bromine radical which abstracts a hydrogen radical at the benzylic position. Another bromine radical adds to the benzylic carbon and HBr then is eliminated spontaneously at high temperatures to form a carbon-carbon double bond. The radical mechanism was further confirmed by using *N*-bromosuccinimide (NBS) as the bromine radical source. The aromatization reaction was completed at 140 °C in 1 h (Scheme 3). The product was spectroscopically identical to the one made by aromatization with elemental bromine. Finally, aromatization can also easily be done by heating in air at 400 °C.



Scheme 3 Model aromatization reactions

Based on this model reaction, polyTH[5]H-AB was subjected to aromatization using bromine to yield poly[5]H-AB. Thus, upon addition of bromine into a refluxing TCE solution of polyTH[5]H-AB, yellow poly[5]H-AB precipitated out immediately. The polymer transformation was also performed on the solid film. The free-standing thin film of polyTH[5]H-AB was treated with bromine vapor at high temperature (ca. 260 °C) and converted into poly[5]H-AB without thermal or chemical degradation. Completion of the chemical transformation or aromatization was unambiguously confirmed by FTIR. The aliphatic C-H bands were clearly seen close to the lower wave-number side of the 3000 cm⁻¹ for polyTH[5]H-AB and were completely vanished in the IR spectrum of poly[5]H-AB. The spectra of the powdered oligo[5]H-AB and the film of poly[5]H-AB were almost superimposable.

Due to the presence of the helicene moiety, the film of poly[5]H-AB had a higher thermal

stability than that of the precursor polyTH[5]H-AB, with the onset temperature for 5% weight loss at 537°C in nitrogen and 485°C in air. The tensile modulus (6.34 GPa at 25°C) of the film of poly[5]H-AB was much higher than that (2.91 GPa) of polyTH[5]H-AB and remained high (5.48 GPa) even at 200°C. The high rigidity of [5]helicene-based polyimide is certainly responsible for its high tensile modulus. No T_g for poly[5]H-AB could be detected by DSC or TMA up to 500°C.

To the best of our knowledge, this is the first case of an AB-type amino-anhydride monomer that can be obtained in high purity and polymerized to the corresponding polyimide with high molecular weight. Therefore, it is highly possible that other interesting aromatic amino-anhydrides could be designed, synthesized and polymerized. Although the origin of the stability of our amino-anhydrides is still under investigation, the potential applications of amino-anhydride monomers, on the basis of the different reactivity of the amine and anhydride functionalities, can be envisaged. For example, it could be utilized as an end-capping agent to synthesize well-defined oligomers, useful for making the segmented polyimides. A variety of copolyimides and polysulfones containing tetrahydro[5]helicene and [5]helicene units have been prepared^[50, 51].

Solid-State Polymerization

Conventional condensation polyimides are made exclusively from a dianhydride and a diamine (AA + BB) by one-step solution polymerization or by a two-step process involving solution polymerization and solid state curing. Seemingly, one-step solid state polymerization of an AB-type amino anhydride monomer would be an attractive, solvent-free route to polyimide materials. However, no attempts have been undertaken to synthesize polyimide from an AB-type amino anhydride monomer, presumably because common wisdom dictates that such a monomer is unstable and forms a poly(amic acid) at ambient temperatures. We recently succeeded in solid-state polymerization of TH[5]H-AB or 3-amino-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride, to produce a polyimide thin film.

Thin films can be formed by spin coating TH[5]H-AB from THF solution onto either silicon wafer or Pyrex[®] glass (TH[5]H-AB(100±2 mg) was dissolved in 0.50 mL of THF. Two drops of this solution was deposited onto the surface of silicon wafers or Pyrex[®] glass plates by spin coating). Thermal treatment of the deposited film under argon atmosphere, using a typical temperature profile (monomer films were heated to 350°C over 1 h, maintained at that temperature for 4 to 18 h then heated to 450°C, maintained at that temperature for 15 min then cooled to room temperature), induces the monomer to first form oligoimides at 350°C. Final thermal treatment at 450°C above the glass transition temperature of the oligoimides (the glass transition temperature (T_g) for the oligomer derived from TH[5]H-AB is 435°C by DSC) is necessary to effect complete transformation to high molecular weight polyTH[5]H-AB. Heating to this temperature may seem extreme; nonetheless polyTH[5]H-AB is stable up to a temperature of 490°C under inert atmosphere. It should be noted that the solid-state polymerization is not a melt process since the appearance of oligoimides can be confirmed with no visible signs of melting. A melting point observed by DSC was only for powdered samples of TH[5]H-AB rather than a spin-cast film.

The stepwise transformation from TH[5]H-AB to polyTH[5]H-AB can be confirmed on silicon wafer using FTIR spectroscopy, by monitoring the disappearance of the anhydride's carbonyl stretching at 1827 and 1761 cm⁻¹ and the appearance of the imide's carbonyl peaks at 1764 and 1713 cm⁻¹. After treatment at 350°C the presence of both anhydride and imide functionality can be clearly seen. Furthermore GPC analysis indicated that there was only low molecular weight polymer formed ($n = 1\sim5$) at 350°C. Heating to 450°C resulted in the complete disappearance of the anhydride peaks. The films of TH[5]H-AB and oligoTH[5]H-AB were completely soluble in many solvents (e.g., chloroform) and can easily be peeled off from the silicon surface. However, the final film of polyTH[5]H-AB was remarkably scratch resistant and was completely resistant to common organic solvents such as boiling 1,1',2,2'-tetrachloroethane for

days.

Upon examination of the surface topology, the spin-cast film of TH[5]H-AB (Fig. 10a) is coherent and shows no sign of powdering but several topographical features can be seen. However, the film of polyTH[5]H-AB (Fig. 10b) is free of defects on its surface and of nearly uniform thickness and does not show any signs of stress fractures.

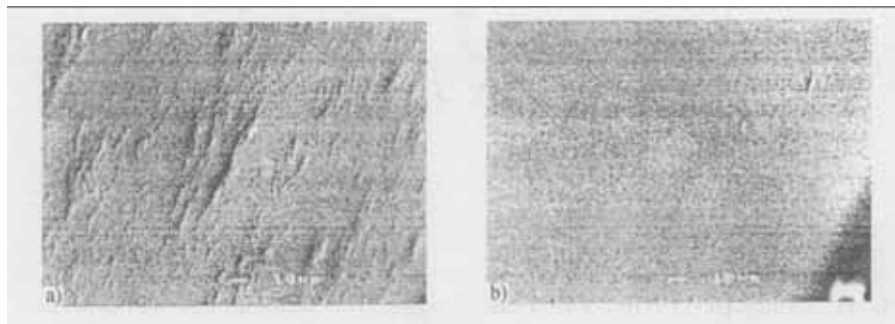


Fig. 10 Electron micrographs of a) TH[5]H-AB as deposited on silicon wafer; b) polyTH[5]H-AB after thermal treatment to 450°C. Both were taken at 60° inclination from the surface.

The presented method for polyimide thin film formation has several advantages over traditional solution processes. Spin coating has proved to be an effective way to deposit thin films of TH[5]H-AB onto the surface of the substrate and has allowed for the control of the film thickness simply based on the amount of monomer deposited on the substrate. The use of volatile THF leaves the cast monomer films nearly free of solvent, thus making the film formation a nearly dry process (self-assembled films contained less than 10% of THF by weight, as analyzed by thermo-gravimetry). In contrast, one-step solution polymerization is usually done in toxic *m*-cresol; whereas the precursor poly(amic acid) solutions typically contain 80% by weight of the amide solvents such as 1-methyl-2-pyrrolidinone.

In comparison with other cases of solid state polymerization, our system is uniquely different. Imai *et al.* were able to produce both aromatic and aromatic/aliphatic polyimides by thermal treatment of nylon salt-type monomers in the solid state^[52–56]. Furthermore, vapor deposition techniques have been used to form thin and ultra-thin polyimide (e.g. Kapton) films^[57–60]. This process requires the use of a specialized apparatus and is limited in general utility because only a few diamine and dianhydride monomers can be used^[61]. Given that the molecular structure of TH[5]H-AB bears no resemblance to any of the above examples of monomers that undergo solid state polymerization, it must have unique features of its own that afford this ability.

The ability of TH[5]H-AB to undergo a solid-state polymerization is two-fold. Firstly, it is stable to self-polymerization at room temperature, making isolation and manipulation possible. Yet, the monomer becomes activated to polycondensation at elevated temperatures. Secondly, this monomer has a tendency to self-assemble through the formation of a hydrogen-bonding entity between its amino and its anhydride functionalities. The X-ray diffraction analysis shows the amino and anhydride functionalities of TH[5]H-AB form a six-membered hydrogen-bonding entity (Fig. 11), resulting in the formation of an extended array of self-assembled monomers across multiple unit cells. The anhydride carbonyl involved in the hydrogen-bonding entity is the one that is *para* to the amino group across the biphenyl moiety. The distance between the oxygen and hydrogen atoms making up the hydrogen-bonding entity is approximately 0.25 nm (Hydrogen positions are calculated). Such a regularity and breadth of molecular arrangement suggest that there is a method to its assembly (The length and width of TH[5]H-AB indicated in Fig. 11 are the atom to atom distances and not the distances as would be projected onto the graphite surface).

Therefore, the polymerization at elevated temperature must then be an outcome of the collapse of this hydrogen-bonding entity and the formation of an imide bond.

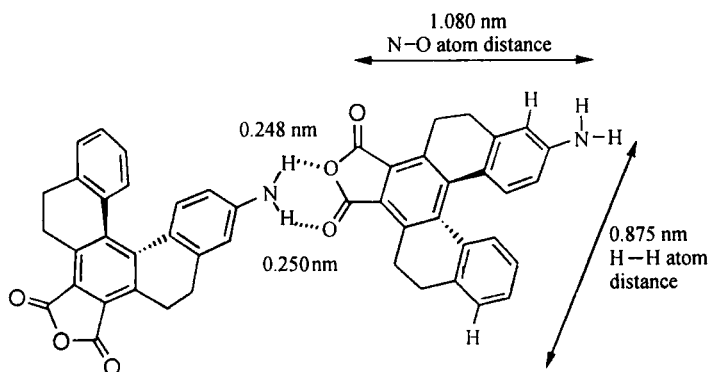


Fig. 11 Arrangement of TH[5]H-AB within its single crystal with relevant distances marked

CONCLUDING REMARKS

Man-made polymers have historically been the most important of the contributions of chemistry to materials science. But it seems unlikely that there will be many new commodity polymers introduced in the future. A new commodity polymer would have to provide fundamentally new properties or significantly lowered cost for existing properties to justify its introduction; neither possibility seems likely. However, functional and “smart” polymers, and new processes for existing monomers and polymers will be important. These specialty polymers are value-added materials, and their high performance and low-volume demand justify the cost. A current challenge to the synthetic polymer chemists is the design and preparation of polymers with exceptional properties. To this end, both diamine and dianhydride monomers are utilized as an ideal “carrier” which carry the desired structural features and physical properties. For example, the high T_g and thermal stability offered by polyimide have been utilized in the design of NLO polyimides, aiming at improving the signal stability^[62]. It is the author’s belief that “novel properties come from materials with novel structures”.

Acknowledgment I wish to express my warmest thanks to my colleagues who have made possible the work I have described here: Jian Ping Gao, also a dear friend of mine since our study at Peking University during the memorable period of 1978~1982, Yu Qi and Timothy P. Bender, two very able graduate students. My sincere thanks also go to my chemistry mentors at Peking University and McGill University, who taught and prepared me to explore an exciting, mysterious world of chemistry. I am particularly grateful to my mentor, Dr. Allan S. Hay, for his constant guidance during my postdoctoral study at McGill University and my present research at Carleton University.

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