

Hee-Gweon Woo  
Hong Li  
*Editors*

# Advanced Functional Materials



ZHEJIANG UNIVERSITY PRESS  
浙江大学出版社



Springer

Hee-Gweon Woo  
Hong Li

# Advanced Functional Materials

With 109 figures



ZHEJIANG UNIVERSITY PRESS  
浙江大学出版社



Springer

## 图书在版编目(CIP)数据

先进功能材料 = Advanced Functional Materials:  
英文 / 禹熙权, 李弘编著. —杭州: 浙江大学出版社,  
2011.3

ISBN 978-7-308-08166-5

I. ①先… II. ①禹… ②李… III. ①功能材料—英  
文 IV. ①TB34

中国版本图书馆CIP数据核字(2010)第 233908 号

Not for sale outside Mainland of China

此书仅限中国大陆地区销售

## 先进功能材料

禹熙权 李 弘 编著

---

责任编辑 徐素君

文字编辑 李峰伟

封面设计 俞亚彤

出版发行 浙江大学出版社

网址: <http://www.zjupress.com>

Springer-Verlag GmbH

网址: <http://www.Springer.com>

排 版 杭州中大图文设计有限公司

印 刷 浙江印刷集团有限公司

开 本 710mm×1000mm 1/16

印 张 15

字 数 380 千

版 次 2011 年 3 月第 1 版 2011 年 3 月第 1 次印刷

书 号 ISBN 978-7-308-08166-5 (浙江大学出版社)

ISBN 978-3-642-19076-6 (Springer-Verlag GmbH)

定 价 108.00 元

---

版权所有 翻印必究 印装差错 负责调换

浙江大学出版社发行部邮购电话 (0571) 88925591

Hee-Gweon Woo  
Hong Li

## **Advanced Functional Materials**

---

## Preface

Humankind has achieved dramatic advancement of technology over the Stone Age, the Bronze Age, the Iron Age, the Plastic Age, and the Advanced Materials Age since their advent. Now we are living in the world of advanced materials including plastics, ceramics, renewable energy, sensors, etc. Literally we cannot live in daily life without using millions of products produced from the advanced technology. The developing rate of new technology is very fast. Global community really needs it for prosperity promotion.

There are great interests in six advanced technologies: nano-technology, bio-based technology, sensor technology, energy-based technology, high performance material-based technology, and fuel cell technology. During the past decades major progress in the synthesis, characterization, and applications of functional polymers has been accomplished along with the recent development of nanobioscience and environment technology. This monograph titled *Advanced Functional Materials* contains six chapters spanning from polymers to ceramics, sensor, and to fuel cell: high performance organic polymers, biodegradable organic polymers, inorganic polymers, ceramic composite formation, sensor, and fuel cell.

Chapter 1 deals with the synthesis and applications of high performance polymers including polyimides and other polymers. The high performance polymers are engineered for use in especially harsh environments with the virtue of a long life span, ease of maintenance and low cost of production. Standard common polymers (PE (polyethylene), PMMA (polymethyl methacrylate), PVC (polyvinyl chloride), etc.) have a thermal resistance below 100 °C and are less suitable for sliding/rolling surfaces. Examples of hard wearing high performance polymers, having a thermal resistance over 150 °C, are polyetheretherketon, polyethersulfon and polyimide. Engineering polymers are classified by a temperature resistance within 100 to 150 °C. The engineering polymers include polyamide, polycarbonate, polyoxymethylene, polyethylene terephthalate, ultra high molecular weight polyethylene, and polybutylene terephthalate. The authors hope to discuss polyimides with major emphasis since they are one of the most recent advanced materials of their kind while briefly describing other high performance organic polymers.

Chapter 2 discusses on the controlled synthesis of biodegradable organic polymers such as polylactic acid, polyglycolic acid and related copolymers. These polymers have found many significant applications in the field of biomedical science as drug-delivery carriers, resorbable sutures, artificial-tissue materials, and

so forth. The discussion is hence centered on the living and stereospecific or stereoselective ring-opening polymerization of lactides, particularly which uses low-toxic/non-toxic metal catalysts and metal-free organic catalysts/initiators to conduct the controlled polymerizations.

Chapter 3 describes the high functional inorganic polymers containing main group 13 – 16 elements in the polymer backbone chain. Polymers can be largely divided into two categories: organic polymers and inorganic polymers. Organic polymers tend to lose their advantageous material properties (light weight, flexibility, fabricability, elasticity, mechanical strength, conductivity, optoelectricity, etc.) in the presence of oxygen, ozone, corrosion, ultraviolet radiation or at extreme high/low temperatures. Nonetheless, most organic polymers used heavily and widely in modern daily life, hardly decompose in the natural environment and burn releasing toxic chemicals as well, creating serious environmental pollution. Furthermore, the availability of raw materials for organic polymers, whose backbone chains consist mainly of carbon atoms linked together or separated by heteroatoms, such as oxygen or nitrogen, is limited by the anticipated shortage of natural petroleum/coal resources. Therefore, research on the design, synthesis, characterization and applications of inorganic polymers, inorganic-organic hybrid polymers or organometallic polymers is needed to avoid these problems. Inorganic polymers have main group non-metallic or sub-metallic elements (Si, Ge, Sn, B, P, N, O, S, etc.), main group metals (Mg, Al, etc.) or transition metals (i.e., d-block or f-block elements) within the polymers. Main group metal-based and transition metal-containing inorganic polymers have been extensively reviewed by many authors and are not covered here because they are beyond the scope of this article, due to the limit of space and interest. Main group non-metallic or sub-metallic inorganic polymers are composed of mainly boron (polyboranes, polyborazines, polycarboranes, etc.), silicon/germanium/tin (polysilanes, polysilane-co-germane, polycarbosilanes, polysiloxanes, polysilathianes, polysilazanes, polygermanes, polystannanes, etc.), phosphorous (polyphosphazenes, etc.) and sulfur (polysulfur, polysulfur nitrides, etc.) atoms, which do not originate from petroleum/coal resources.

Chapter 4 covers the preparation of various ceramic composites using various hybrid preceramic polymeric precursors, including super-resistant Si-C-B-N, electrically conducting  $\text{MoSi}_2/\text{SiC}$ , superhard Ti-B-N and highly thermally conducting Al-B-N nanocomposites, thermally insulating Al-Cr-phosphates. Moreover, some application examples of preceramic polymers are introduced to demonstrate their utility in structural ceramic materials as an alternative preparative route to the conventional powder sintering process, such as ceramic matrix composites and ceramic film. In addition, the authors summarize the recent development of porous SiC materials from templated preceramic polymers and the fabrication of small and complicated ceramic features using near net shape processing techniques, such as lithography.

Chapter 5 discusses chemical and biological sensors based on porous silicon nanomaterials. It was not until 1990, when L. T. Canham first reported efficient, tunable, room temperature luminescence in the visible range from porous silicon,

that interest in the field grew exponentially. From this point on, a large number of academic and industrial researchers from all over the world began to study the porous silicon pore structure, light emission mechanism, surface chemistry, and feasibility for optoelectronic applications. The many favorable characteristics and the vast interest in porous silicon have given rise to a variety of new applications, such as light emitting devices, multilayer structure, solar energy conversion, chemical and biological sensors, drug delivery application, ultrasound generators, microengineering, astrophysics, signal processing and nuclear science.

Chapter 6 covers a critical prospective on the recent advances in microbial fuel cell (MFC) with an emphasis on the performances of MFC, materials, operational factors and applications of MFCs in the future. The article includes the following: MFC designs, characterizations and performance, the recent advances in MFC configurations and performances, the microbial metabolism and parameters defining the performance of MFC, electricity producing bacterial communities, the primary mechanism for electron transfer of electricigens to electrodes, the characteristics of electrochemically active bacteria in a mediator-less system, microbial physiology and engineering approaches regarding Benthic Unattended Generators for powering remote-sensing or monitoring devices, the inherent constraints of MFCs and suggestions for MFC performance improvement, the anodic electron transfer mechanisms in electrochemically active bacteria, improved cathode reactions and the application of new electrode materials.

As matter of fact, this book is oriented to give general and specific knowledge to the readers working in the field of material science and engineering, not to the casual readers. Nonetheless we hope that the readers can expand their knowledge while enjoying the book with relaxing and fruitful mind. We left some space for the readers' imagination.

Finally, the editors of the book would like to appreciate their coworkers for the dedicated contribution described in the respective chapter. We should particularly thank Prof. Xiaojia Chen, vice president of Zhejiang University Press for inviting us to compile the book.

Hee-Gweon Woo  
Gwangju, the Republic of Korea

Hong Li  
Tianjin, P.R. China  
January, 2011

---

# Contents

<b>1 Polyimides and High Performance Organic Polymers.....</b>	<b>1</b>
1.1 Introduction.....	1
1.2 Aromatic Polyimides.....	2
1.2.1 Polyimides .....	3
1.2.2 Classification.....	4
1.2.3 Aromatic Polyimides.....	5
1.2.4 Synthesis of Aromatic Polyimides.....	6
1.2.5 Properties of Aromatic Polyimides.....	7
1.2.6 Applications for Aromatic Polyimides.....	8
1.3 Aliphatic Polyimides.....	9
1.3.1 Monomers for Fully Aliphatic Polyimides .....	10
1.3.2 Synthesis of Fully Aliphatic Polyimides.....	11
1.3.3 Structural Confirmation of Fully Aliphatic Polyimides.....	12
1.3.4 Properties of Fully Aliphatic Polyimides.....	14
1.4 Polyimides for Organic Light-Emitting Devices and Flexible Substrates.....	17
1.4.1 Semi-conducting Polyimides .....	17
1.4.2 Polyimides as Plastic Substrate for the Flexible OLED.....	19
1.5 Polyimide-Based Nanohybrids.....	20
1.6 Other General High Performance Polymers.....	22
1.6.1 Polyetheretherketon (PEEK) .....	22
1.6.2 Polysulphone (PSU) .....	23
1.6.3 Polysulfides.....	25
1.6.4 Polycarbonates (PC) .....	26
1.6.5 Polyamides (PA) .....	27
1.6.6 Poly(Butylene Terephthalate) (PBT) .....	29
1.6.7 Poly(Phenylene Oxides) .....	29
1.6.8 Polynorbornene (PNB) .....	30
1.7 Summary.....	31
References.....	32
<b>2 Advanced Biodegradable Organic Polymers.....</b>	<b>37</b>
2.1 Introduction.....	37
2.2 Synthesis of Biodegradable Polymers by Polycondensation.....	38
2.2.1 General Polycondensation Technique.....	39



2.2.2	Post Polycondensation Technique.....	40
2.2.3	Chain-Extension Technique.....	41
2.2.4	Enzyme-Catalyzed Polycondensation.....	42
2.3	Synthesis of Biodegradable Polymers by Ring-Opening Polymerization.....	42
2.3.1	Monomers.....	42
2.3.2	Polymerization with Metal Catalysts.....	43
2.3.3	Polymerization Using Metal-Free Organic Catalysts.....	55
2.3.4	Enzyme-Catalyzed Ring-Opening Polymerization.....	60
2.4	Concluding Remarks.....	61
	References.....	61
<b>3</b>	<b>High Functional Inorganic Polymers Containing Main Group 13 - 16 Elements in the Polymer Backbone Chain.....</b>	<b>65</b>
3.1	Introduction.....	65
3.2	Group 14 Inorganic Polymers: Polysilanes, Polygermanes, Polystannanes, and their Copolymers.....	66
3.2.1	Dehydrocatenation of Group 14 Hydrides to Polymers.....	67
3.2.2	Redistributive Catenation of Group 14 Hydrides to Polymers.....	77
3.2.3	Exhaustive Hydrosilylation, Hydrogermylation and Hydrostannylation of Group 14 Hydrides on Vinyl Derivatives.....	85
3.2.4	Formation of Polysilane-Metal Nanoparticle Composites.....	89
3.3	Group 13 Inorganic Polymers: Polyborazines.....	89
3.4	Group 15 Inorganic Polymers: Polyphosphazenes.....	91
3.5	Group 16 Inorganic Polymers: Polysulfur and Poly(sulfur nitride).....	92
3.6	Summary.....	93
	References.....	93
<b>4</b>	<b>Preparation and Applications of Ceramic Composite Phases from Inorganic Polymers.....</b>	<b>103</b>
4.1	Introduction.....	103
4.2	Preparation of Composite Phases from Inorganic Polymers.....	105
4.2.1	Si-C-B-N Ceramics via Hydroboration from Borazine Derivatives and Trivinylcyclotrisilazane.....	105
4.2.2	SiC/MoSi <sub>2</sub> Ceramic Composites Prepared by Polymer Pyrolysis.....	111
4.2.3	Ti-B-N Composite from a Hybrid Precursor of Polyborazine and TiH <sub>2</sub> .....	117
4.2.4	Al-B-N Nanocomposite from Polyborazine and Al Metal.....	120
4.2.5	Al-Cr-Phosphates as Low Temperature Curable Binders.....	124
4.3	Applications of Preceramic Polymers.....	130
4.3.1	Preparation of Carbon Fiber Reinforced BN Matrix Composite.....	130
4.3.2	BN Film by Spin-Coating Process of a Polymeric Precursor.....	137
4.3.3	Fabrication of SiC-Based Ceramic Microstructures.....	140
4.4	Summary.....	150
	References.....	152

<b>5 Chemical and Biological Sensors Based on Porous Silicon Nanomaterials.....</b>	<b>157</b>
5.1 Introduction.....	157
5.2 Interferometric Sensors Based on Porous Silicon Nanomaterials.....	158
5.2.1 Fabrication of Porous Silicon.....	158
5.2.2 Chemical Sensing Application of Porous Silicon.....	173
5.2.3 Biological Sensing Application of Porous Silicon.....	183
5.3 Summary.....	189
References.....	190
<b>6 Microbial Fuel Cells as the Real Source of Sustainable Energy.....</b>	<b>195</b>
6.1 Introduction.....	195
6.2 Configurations and Designs of Microbial Fuel Cells.....	196
6.2.1 MFC Components.....	196
6.2.2 Two-Chambered MFCs.....	197
6.2.3 Single-Chambered MFCs.....	198
6.2.4 Up-Flow Mode MFCs.....	199
6.2.5 Stacked MFCs.....	200
6.3 Electrode Materials and Catalysts.....	201
6.3.1 Electrode Materials.....	201
6.3.2 Cathodic Catalysts.....	202
6.4 Performance of Microbial Fuel Cells.....	204
6.4.1 Parameters Defining the Performance of MFCs.....	204
6.4.2 Effects of Conditions When Operating MFCs.....	206
6.5 Metabolism in Microbial Fuel Cells.....	212
6.6 Applications.....	213
6.7 Summary.....	215
References.....	215
<b>Index.....</b>	<b>221</b>

---

# Polyimides and High Performance Organic Polymers

**Chang-Sik Ha\*, Anu Stella Mathews**

Department of Polymer Science and Engineering, Pusan National University,  
Pusan 609-735, the Republic of Korea

Tel.: +82-51-510-2407; Fax: +82-51-514-4331

\*E-mail: csha@pnu.edu

## 1.1 Introduction

The amazing scope of wartime applications accelerated the development and growth of polymers to meet the diverse needs of special materials in different fields of activity.<sup>[1,2]</sup> Polyurethanes were developed in 1937, polyepoxides in 1947 and acrylonitrile-butadiene-styrene (ABS) terpolymer in 1948.<sup>[3,4]</sup> The discovery of the Zeigler-Natta catalyst in the 1950s brought about the development of linear polyethylene and stereoregular polypropylene.<sup>[4]</sup> Thereafter, the emergence of polyacetal, polyethylene terephthalate, polycarbonate, and many new copolymers, was noted. Commercial requirements paved the way for the development of highly temperature-resistant materials, which include polyphenylene oxides, polysulphones, polyimides, poly(amide-imide)s and polybenzimidazoles. These high performance polymers to which standard metal engineering equations can be applied are widely commercialized now. Polymers with properties of strength, heat-resistance or flame-resistance or chemical-resistance that far exceed those of more conventional polymers are termed "High Performance Polymers". They are capable of sustaining high loads and stresses and are dimensionally stable.<sup>[5-7]</sup>

For any applications, the prime importance is given to three factors: life span, maintenance and cost.<sup>[7]</sup> In this regard, high performance polymers are engineered for use in especially harsh environments with the virtue of a long life span, ease of

maintenance and low cost of production. These merits have accelerated the application of these polymers. Standard polymers have a thermal resistance  $<100\text{ }^{\circ}\text{C}$  and are less suitable for sliding/rolling surfaces. Examples of these polymers include high density polyethylene (HDPE), low density polyethylene (LDPE), poly(methyl methacrylate) (PMMA), and poly(vinyl chloride) (PVC). They have low melting points and therefore cannot operate at elevated temperature and the majority of these polymers decompose or readily oxidize at high temperatures. The current demand is for polymers which retain useful properties for a long period at higher temperature with high thermo-oxidative stability, i.e., they should withstand degraded properties over long periods at high temperature in the air. High performance polymers show high temperature-resistance and high mechanical strength. Examples of hard-wearing high performance polymers, having a thermal resistance  $>150\text{ }^{\circ}\text{C}$ , are polyetheretherketon (PEEK), polyethersulfon (PES) and polyimide (PI). Engineering polymers are classified by a temperature resistance within  $100\text{ to }150\text{ }^{\circ}\text{C}$ . The engineering polymers include polyamide (PA), polycarbonate (PC), polyoxymethylene (POM), poly(ethylene terephthalate) (PET), ultra high molecular weight polyethylene (UHMWPE), and poly(butylene terephthalate) (PBT). One basic factor which determines the stability is the strength of the bonds which join different groups in the backbone. For instance, a polymer chain with Si-O bonds would be more stable than one with C-C bonds, due to the higher bond energy of Si-O. A phenylene unit in the backbone also shows more stability than a chain with an alkenylene backbone owing to the stiffness and deformation-resistance of the phenylene ring. Based on the above arguments, several high performance polymers are synthesized and successfully applied. Firstly, we wish to discuss polyimides since they are one of the most recent advanced materials of their kind. Then we will briefly describe other high performance polymers.

A considerable amount of research work is being carried out into the development of high performance polymers and to improve their efficiency. The main stimulus has come from the development and characterization of new materials for space exploration. Construction of a spacecraft or a satellite, for instance, needs materials that can withstand high surface temperature, are light weight and have high dimensional stability. Modern military and civil aircraft use a high percentage of such polymers. Conventional materials like metals, glass and ceramics are being fast replaced. Polymers also find applications in the microelectronics and optoelectronics industries. In the next section we wish to discuss more advances of polyimides among the high performance polymers mentioned above.

## 1.2 Aromatic Polyimides

In this section, we will introduce polyimides and their classification, as well as synthesis, properties and applications of aromatic polyimides.

### 1.2.1 Polyimides

Polyimides (PIs) are a new generation of polymers with inherently rigid chains and of high commercial importance.<sup>[8]</sup> PIs possess excellent thermal, mechanical and electrical properties and thus have found immense applications in many technologies, ranging from microelectronics to high temperature matrices and adhesives for gas separation membranes.<sup>[9-24]</sup> These materials are prepared by incorporating highly stable and rigid heterocyclic ring systems into the polymer chain. PIs are available for use as plastics, films, laminating resins, insulating coatings and high temperature structural adhesives. Thermal stability of polyimides is attributed to the presence of an inert imide ring and high interchain interaction, i.e., high cohesion among the polymer chains. A representative structure of a polyimide is shown in Fig. 1.1.

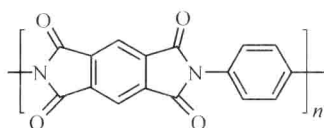


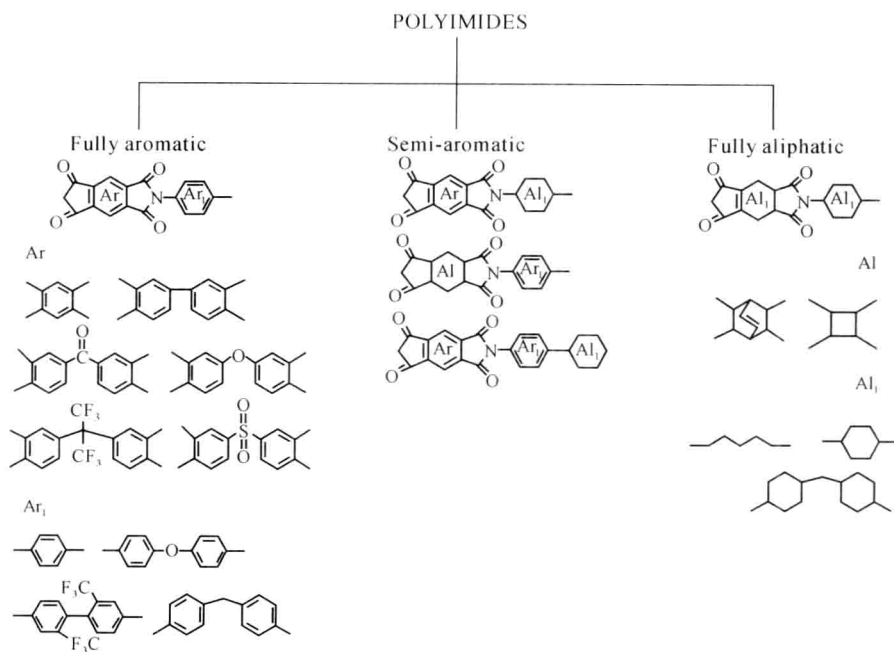
Fig. 1.1. Representative structure of aromatic polyimide

The first synthesis of a polyimide from 4-aminophthalic acid was performed by Bogert and Renshaw in 1908.<sup>[25]</sup> However, a high-molecular weight aromatic polyimide was first synthesized in 1955 by Edwards and Robinson.<sup>[26]</sup> Poly(4,4'-oxydiphenylene pyromellitimide) (PMDA-ODA PI), widely known as Kapton<sup>®</sup> which can remain stable in a wide range of temperatures from  $-269$  to  $400$  °C, was first commercialized in the early 1960s.<sup>[27]</sup> Kapton<sup>®</sup> film is used in, among other things, flexible printed circuits (flexible electronics) and spacesuits. Kapton<sup>®</sup> insulated wiring has been widely used in civil and military avionics (electrical wiring for aircraft) because of its very light weight compared to other insulator types, as well as possessing good insulating and temperature characteristics. The NASA Jet Propulsion Laboratory has considered Kapton<sup>®</sup> as a good plastic support for solar sails because of its long duration in the space environment.<sup>[28]</sup> Kapton<sup>®</sup> is also used to monitor the flux on X-ray sources. A number of PIs have been synthesized and investigated extensively in aspects of structure and property relationships and applications after the success with Kapton<sup>®</sup>.<sup>[29]</sup> PIs are known to be thermally stable due to their heterocyclic imide rings on the backbone, and the thermal stability is further significantly improved by incorporating aromatic rings on the backbone and/or side groups. In addition to such high thermal stability, the nature of the chemical structure consisting of rigid imide and aromatic rings always provides excellent mechanical and dielectric properties as well as high chemical resistance. Beyond these advantageous properties, a variety of functionalities (for example, photo reactivity, molecular recognition ability, nonlinear optical responsibility, light emitting ability, and so on) can be added into the backbone and/or side groups of PIs, depending on their application demands.<sup>[30-41]</sup>

Due to these advantageous properties as well as the functionalities, PIs have found diverse applications in the microelectronics, flat panel display, aerospace and chemical and environmental industries as flexible circuitry carriers, stress buffers, inter dielectric layers, passivation layers, liquid crystal alignment layers, varnishing resins, fibers, matrix materials, and gas and chemical separation membranes.<sup>[42-48]</sup>

## 1.2.2 Classification

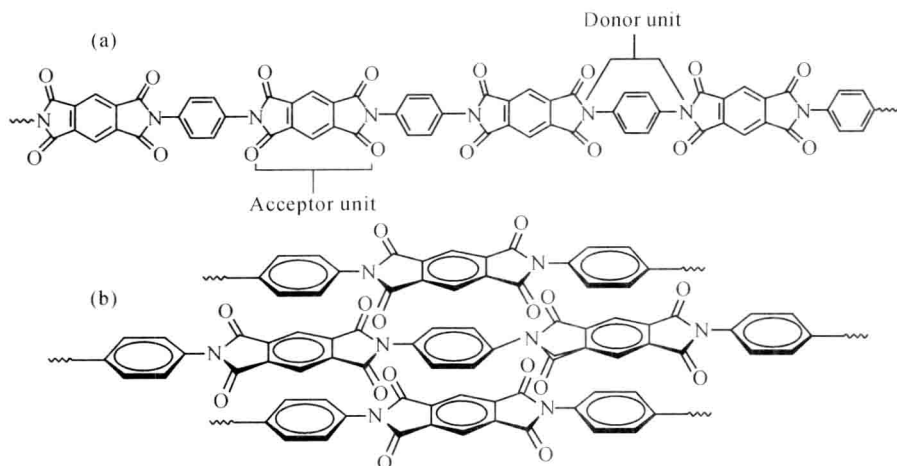
According to the monomers from which polyimides are derived, they can be broadly classified as fully aromatic polyimides, semi-aromatic polyimides and fully aliphatic polyimides (Fig. 1.2).<sup>[8]</sup> Aromatic polyimides are derived from an aromatic dianhydride and diamine. Semi-aromatic ones contain any one of the monomer aromatics: i.e., either the dianhydride or diamine is aromatic and the other part is aliphatic. Finally, the third category consists of the polymers formed as a result of the combination of aliphatic dianhydride and diamine.



**Fig. 1.2.** Classification of polyimides into three broad categories, depending upon the chemical structure of the backbone (Adapted from Ref. 8. Copyright (2007), with permission from the Polymer Society of Korea)

### 1.2.3 Aromatic Polyimides

Aromatic polyimides (PIs) are typical of most commercial polyimides, such as Ultem from G.E. and DuPont's Kapton<sup>®</sup>. These polymers have such incredible mechanical and thermal properties that they are used in place of metals and glass in many high performance applications in the electronics, automotive, and even the aerospace industries. These properties come from strong intermolecular forces between the polymer chains. A polymer which contains a charge transfer complex consists of two different types of monomers, a donor and an acceptor (Fig. 1.3).<sup>[49]</sup> The donor has plenty of electrons to go around because of its nitrogen groups and the acceptor with its carbonyl group draws away its electron density. So the donor lends some of its electrons to the acceptor, holding them tightly together. Thus, the polymer chains will stack together like strips of paper, with donors and acceptors paired up due to the formation of a charge transfer complex between adjacent units in the polymer chain as shown in Fig. 1.3(b). This charge transfer complex holds the chains together very tightly, not allowing them to move around very much. When things cannot move around on the molecular level, they cannot move around in the whole material. This is the reason why polyimides are so robust. The charge transfer complex is so strong that it sometimes becomes necessary to make the polymer a little softer, leading it to be processable. Aromatic polyimides synthesized from only aromatic monomers are often insoluble in their fully imidized form, thus having a low processability. In addition, as most of the aromatic polyimides absorb visible light intensely, they cannot be used in areas where colorlessness is an important requirement. It is well known that the origin of coloration in aromatic polyimides is caused by the inter- and intra-molecular charge transfer(CT) interactions between the five membered ring of the imide group and the aromatic ring, as explained above in Fig. 1.3. The high dielectric constant also arising from these interactions is also a demerit of aromatic polyimides. Despite its excellent properties, low processability, high dielectric constant and light or dark yellow coloration hinders its successful application in optoelectric materials and high-speed multilayer printed wiring boards. Efforts to suppress the CT interactions have included the use of siloxane,<sup>[50]</sup> sulfonyl,<sup>[51]</sup> fluorinated<sup>[52]</sup> and aliphatic<sup>[53]</sup> moieties. Among these, aliphatic structures display a lower dielectric constant and higher transparencies which result from their lower molecular density and polarity and low probability of undergoing inter or intra-molecular charge transfer. Thus, incorporation of aliphatic units to enhance the desired properties was applied widely.

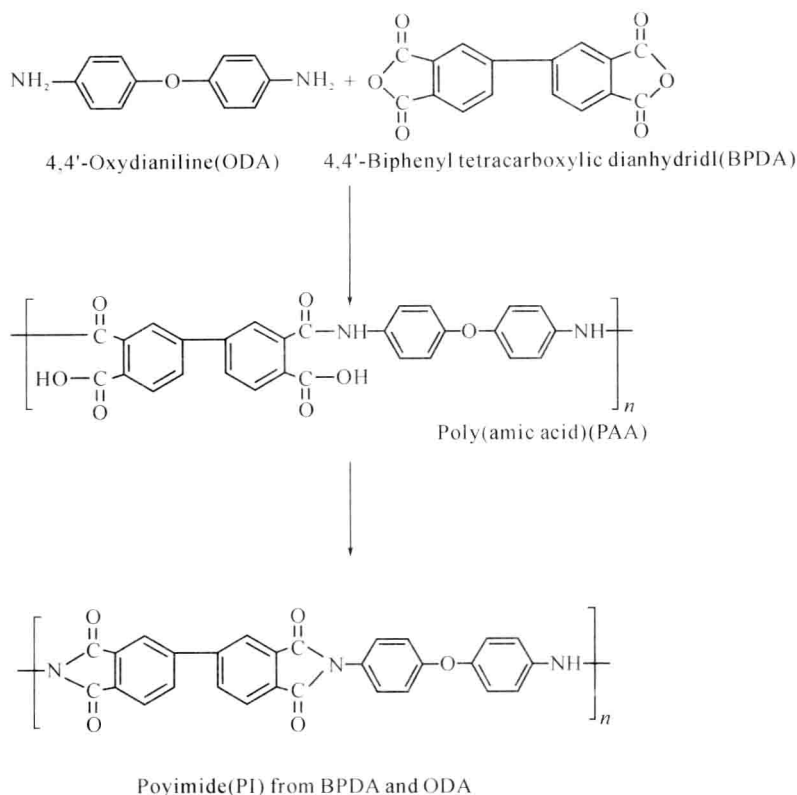


**Fig. 1.3.** Donor-acceptor system prevailing in PIs and the resulting interchain locking. (a) Nitrogen atoms having a higher electron density than the carbonyl groups lend some of their electrons to the acceptor while carbonyl groups draw electron density away from the acceptor unit; (b) Interchain interlocking of PI backbones. Polyimides may stack like this allowing the carbonyl of the acceptor on one chain to interact with the nitrogens of the donor on the adjacent chains (Modified from Ref. 49)

### 1.2.4 Synthesis of Aromatic Polyimides

Aromatic polyimides are generally prepared through a two-step procedure by the ring opening polyaddition of aromatic polyimides to aromatic tetracarboxylic dianhydrides in *N*-methyl pyrrolidone (NMP) or *N,N*-dimethyl acetamide (DMAc) solution giving soluble polyamic acid. The polyamic acid thus formed is imidized into polyimides by thermal cyclodehydration. The polyimides thus formed are insoluble in their fully imidized form. The multi-step process makes the materials applicable in the state of soluble polymeric intermediate. The schematic representation of two-step synthesis of the polyimide is given in Scheme 1.1.<sup>[22]</sup> Direct preparation of polyimides without the isolation of polyamic acid at elevated temperature is another route of synthesis. This is widely known as one step synthesis since it does not have an intermediate stage.





**Scheme 1.1.** Schematic representation of two-step synthesis of aromatic polyimides, where 3,3'-4,4'-biphenyl tetracarboxylic dianhydride (BPDA)-4,4'-oxydianiline (ODA) poly(amic acid) (PAA) precursor is thermally imidized to BPDA-ODA PI (Adapted from Ref. 22. Copyright (2003), with permission from Elsevier)

### 1.2.5 Properties of Aromatic Polyimides

Polyimide parts and laminates can serve continuously in air at 260 °C; the service temperature for intermittent exposure can range from cryogenic to as high as 482 °C. Glass-fiber reinforced versions retain over 70% of their flexural strength and modulus at 249 °C. Creep is almost nonexistent, even at high temperatures and deformation under load (28 MPa) is less than 0.05% at room temperature for 24 h.<sup>[49]</sup> These materials have good wear resistance and low coefficients of friction, both of which are further improved by polytetrafluoroethylene (PTFE) fillers. Self-lubricating parts containing graphite powders have flexural strengths above 69 MPa, which are considerably higher than those of typical thermoplastic bearing compounds. Electrical properties of PI moldings are outstanding over a wide range of temperature and humidity conditions. Polyimide parts are unaffected by