

# Synthesis and characterization of soluble fluorenyl polyimides

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## Abstract

A series of cardo polyimides were prepared from cardo diamines containing different alkyl substituents and 4,4'-oxydiphthalic anhydride(ODPA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride(BTDA), 3,3',4,4'-biphenyl tetracarboxylic dianhydride(BPDA) and pyromellitic dianhydride(PMDA). The results show that the incorporation noncoplanar structure led by the introducing alkyl substituents on cardo diamine can improve the solubility of cardo polyimides in organic solvents. Most of cardo polyimides exhibited excellent solubility in common organic solvents such as m-cresol, chloroform, tetrahydrofuran(THF), N-methyl-2-pyrrolidinone(NMP), N,N-dimethylacetamide(DMAC) etc and intrinsic viscosity in N,N-dimethylacetamide(DMAC) ranged from 0.31-0.92dl/g.

Keywords: Cardo; fluorenyl polyimide; Solubility

## 1. Introduction

Polyimides containing a rigid backbone as a result of totally aromatic or heteroaromatic repeat units generally exhibit high thermal stability and good mechanical properties. However, they are generally insoluble and infusible in their fully imidized form, leading to processing difficulties; and this process of poly (amic acid) intermediate has several inherent problems such as emission of volatile byproducts (e.g., H<sub>2</sub>O) and storage instability etc. To overcome these problems, much research effort has been focused on synthesis of soluble and processable polyimides in fully imidized form without deterioration of their own excellent properties.

The introduction of "cardo" groups into polymers such as polyimides<sup>[1]</sup>, polyamides<sup>[2,3]</sup>, polyamideimides<sup>[4]</sup>, polyquinolines etc. can give them specific properties: (1)excellent heat resistance; (2)excellent solubility. Therefore, the introduction of "cardo" groups into the backbone of polymers is an effective approach for improving solubility and thereby processability of polyimides<sup>[1]</sup>. Because cardo polyimide contains a bulky bis-phenylfluorene moiety as the loop like moiety, they have high glass transition temperature while providing high solubility in different organic solvents.

In the present study, our objective is to investigate the effect of incorporation of different alkyl substituents on cardo diamine in the solubility and thermal stability of cardo polyimides. A series of cardo polyimides were synthesized and characterized based on ortho alkyl substituted cardo diamines such as 9,9-bis(4-aminophenyl)fluorene(BAFL), 9,9-bis (3-methyl-4-aminophenyl)fluorene(BAFL(2Me)) and 9,9-bis (3,5-diethyl-4-aminophenyl) fluorene (BAFL(4Me)) and different dianhydrides such as 4,4'-oxydiphthalic anhydride(ODPA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), 3,3',4,4'-biphenyl tetracarboxylic dianhydride(BPDA), pyromellitic dianhydride(PMDA). These polymers were characterized by Gel permeation chromatography (GPC), TGA, DMA etc.

## 2. Experimental section

### 2.1 Materials

9,9-bis(4-aminophenyl)fluorene, 9,9-bis(3-methyl-4-aminophenyl)fluorene and 9,9-bis(3,5-dimethyl-4-aminophenyl) fluorene was synthesized in our laboratory. 4,4'-oxydiphthalic anhydride(Shanghai Research Institute of synthetic resin), 3,3',4,4'-benzophenonetetracarboxylic dianhydride, 3,3',4,4'-biphenyltetracarboxylic dianhydride (Ube Industries, Ltd), pyromellitic dianhydride (Shanghai Research Institute of synthetic resin).

### 2.2 Polyimide synthesis

A typical polymerization procedure is as follows (Fig.1). Equivalent molar diamine and dianhydride was dissolved in dried m-cresol in 250ml four-necked flask fitted with a nitrogen inlet, a thermometer, a condenser and a mechanical stirrer. The reactive mixture was heated to reflux temperature under nitrogen atmosphere for 5h, and then the solution was precipitated in ethanol in a high speed blender. The product was filtrated and washed by excess ethanol, and was dried in a vacuum oven at 80°C /2hr and 200°C /5hr.

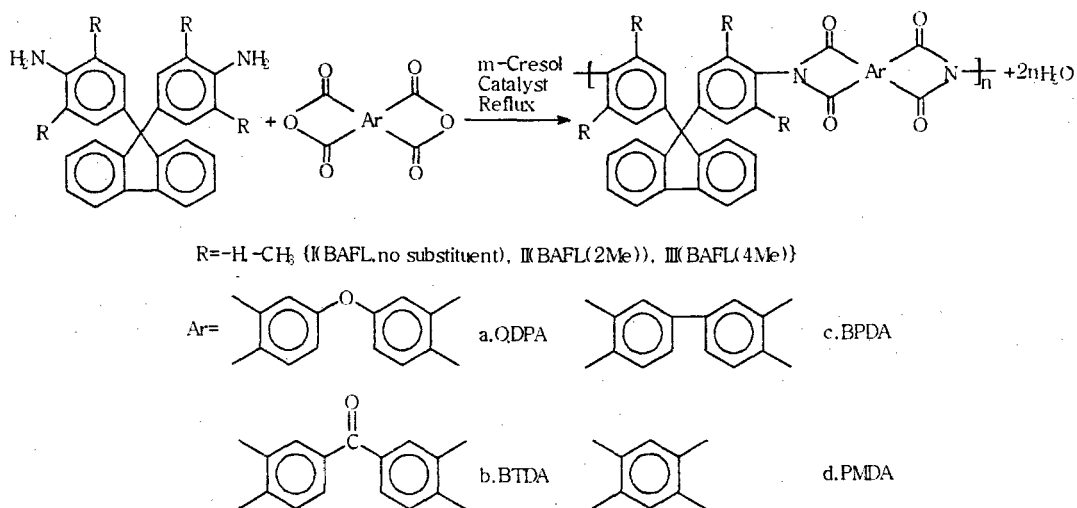


Fig. 1 Synthetic route of cardo polyimide

### 2.3 Measurements

Inherent viscosity measurements were made with 0.5% (w/v) solution of polymers in DMAc at 25±0.1°C using an Ubbelohde viscometer. Number average molecular weights (M<sub>n</sub>) and weight-average molecular weights (M<sub>w</sub>) by gel permeation chromatography (GPC) using a Waters 2414 instrument. The thermogravimetric analyses(TGA) were made with Perkin – Elmer 7 Series Thermal Analysis system. Experiments were carried out under N<sub>2</sub> atmosphere at a heating rate of 10°C /min. Dynamic Mechanical Analysis (DMA) was obtained using a Netzsch DMA242.

## 3. Result and discussion

### 3.1 Synthesis of polyimides

Soluble polyimides were synthesized by direct polymerization in m-cresol. Because these polyimides had a higher degree of polymerization and better organic solubility than those from the thermal cyclodehydration of PAAs in two steps<sup>[5]</sup> Polyimides Ia-Ic, IIa-IIc, IIIa-IIIc was prepared

by the method. But the polyimide Id, IId were insoluble in hot m-cresol, and were prepared by the classical two-step method and chemical imidization. Intrinsic viscosity in DMAc of the soluble polyimides ranged from 0.31 to 0.92 dl/g and Mns varied from 19000 to 52000 relative to polystyrene standards (Table 1).

**Table 1 Molecular weight and viscosity data for THF soluble polyimides synthesized**

Code	Polymer	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	$\eta^a$ (dl/g)
Ia	BAFL-ODPA	2.1	3.2	0.33
Ib	BAFL-BTDA	1.9	2.9	0.31
Ic	BAFL-BPDA	— <sup>b</sup>	—	0.85
Id	BAFL-PMDA	—	—	—
IIa	BAFL(2Me)-ODPA	4.0	5.9	0.55
IIb	BAFL(2Me)-BTDA	4.9	8.7	0.59
IIc	BAFL(2Me)-BPDA	5.2	9.2	0.92
IId	BAFL(2Me)-PMDA	—	—	—
IIIa	BAFL(4Me)-ODPA	2.6	4.4	0.34
IIIb	BAFL(4Me)-BTDA	2.7	4.7	0.40
IIIc	BAFL(4Me)-BPDA	3.2	5.7	0.58
IIId	BAFL(4Me)-PMDA	—	—	—

a. Intrinsic viscosities measured in DMAc at 25°C;

b. —: insoluble in THF

### 3.2 Organo-solubility

As shown in Table 2, most of cardo polyimides being prepared from cardo diamines and ODPA, BTDA, BPDA or PMDA exhibited excellent solubility in common organic solvents such as m-cresol, chloroform, THF, NMP, DMAc etc. The results show that the incorporation noncoplanar structure led by the introducing alkyl substituents on cardo diamine can significantly improve the solubility of cardo polyimides in organic solvents. For example, BAFL(4Me)-PMDA can even dissolve in hot m-cresol, NMP and chloroform.

**Table 2 Solubility<sup>a</sup> Of Polyimides**

Polyimide	NMP	DMAc	m-Cresol	CHCl <sub>3</sub>	THF
BAFL-ODPA	S	S	S	S	S
BAFL-BTDA	S	S	S	S	S
BAFL-BPDA	S	Ins	S	S	Ins
BAFL-PMDA	Ins	Ins	Ins	Ins	Ins
BAFL(2Me)-ODPA	S	S	S	S	S
BAFL(2Me)-BTDA	S	S	S	S	S
BAFL(2Me)-BPDA	S	Ins	S	S	S
BAFL(2Me)-PMDA	Ins	Ins	Ins	Ins	Ins
BAFL(4Me)-ODPA	S	S	S	S	S
BAFL(4Me)-BTDA	S	S	S	S	S
BAFL(4Me)-BPDA	S	Ins	S	S	S
BAFL(4Me)-PMDA	*S	G	*S	*S	Ins

a. Solubility: S, soluble at room temperature; Ins, insoluble; \*S, soluble on heating; G, gel.

### 3.3 Thermal and thermo-oxidative stability

To discuss thermal and thermo-oxidative stability, the onset temperature corresponding to 5%, 10% and 15% weight loss of this system was measured by TGA in dry nitrogen (Table 3). All polyimides show good thermal and thermo-oxidative stability, powder samples of these polyimides undergo 5% weight loss between 430°C and 554°C in nitrogen at a heating rate of 10°C/min. Incorporation of ortho alkyl substituents resulted in the descend of thermal stability, but the 5% weight loss temperature still exceed 400°C.

**Table 3 Thermal stability of polyimides**

Polyimide	TGA wt. loss(°C)		
	5%	10%	15%
BAFL-ODPA	554	582	593
BAFL-BTDA	553	586	598
BAFL-BPDA	532	588	597
BAFL-PMDA	553	580	590
BAFL(2Me)-ODPA	483	514	537
BAFL(2Me)-BTDA	470	509	535
BAFL(2Me)-BPDA	476	519	532
BAFL(2Me)-PMDA	472	511	542
BAFL(4Me)-ODPA	430	473	493
BAFL(4Me)-BTDA	454	480	498
BAFL(4Me)-BPDA	466	487	503
BAFL(4Me)-PMDA	529	564	579

Moreover, the T<sub>g</sub> value of ODPA-type Cardo polyimide ranges for 307 to 368°C measured by using a Netzsch DMA242. This indicated that cardo polyimides show good thermal and thermo-oxidative stability. The increase of number of alkyl substituents on cardo diamine resulted the decrease of T<sub>g</sub>, which results was unexpected, the reason need to be researched further.

### 4. Conclusion

Cardo polyimides were prepared from cardo diamines and ODPA, BTDA, BPDA or PMDA, and characterized by Gel permeation chromatography(GPC), TGA, DMA etc. The incorporation noncoplanar structure led by the introducing alkyl substituents on cardo diamine can improve the solubility of cardo polyimides in organic solvents without sacrificing thermal properties..

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# 可溶性苄基聚酰亚胺的合成和表征

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## 摘要

利用不同烷基取代的 Cardo 二胺分别与 4,4'-氧双邻苯二甲酸酐 (ODPA)、3,3',4,4'-四羧基二苯甲酮二酐 (BTDA)、3,3',4,4'-联苯四羧酸二酐 (BPDA) 和均苯四甲酸二酐 (PMDA) 反应, 制备得到了一系列 Cardo 聚酰亚胺。实验结果表明, 通过在 Cardo 二胺上引入非共平面的烷基取代基能提高 Cardo 聚酰亚胺在有机溶剂中的溶解性。实验得到的大部分 Cardo 聚酰亚胺溶于间甲酚、氯仿、四氢呋喃 (THF)、N-甲基吡咯烷酮 (NMP) 和 N,N-二甲基乙酰胺 (DMAc) 等有机溶剂, DMAc 中的特性粘度范围为 0.31—0.92dl/g。

关键词: Cardo; 苄基聚酰亚胺; 可溶性

## 1、引言

含有刚性主链的全芳族或芳杂环聚酰亚胺具有高的热稳定性和良好的机械性能, 但是它们在酰亚胺化后通常是不溶不熔, 加工困难; 利用聚酰亚胺酸中间体路线又存在加工过程中产生挥发性小分子 (如水) 和储存稳定性差等问题。为克服这些问题, 合成可溶性聚酰亚胺引起了更多关注。

在聚酰亚胺<sup>[1]</sup>、聚酰胺<sup>[2,3]</sup>、聚酰胺酰亚胺<sup>[4]</sup>和聚喹啉等聚合物中引入 Cardo 基团能赋予这些聚合物特殊性能: (1) 优异的耐热性; (2) 优异的溶解性。因此, 在聚酰亚胺主链上引入 Cardo 基团是提高聚酰亚胺溶解性和加工性能的有效途径<sup>[1]</sup>。这是因为 Cardo 聚酰亚胺含有大的双苯基苄基侧环, 所以能够在保持高玻璃化转变温度的同时提高聚合物在有机溶剂中的溶解性。

在本研究中, 我们的目的是研究在 Cardo 二胺上引入不同的烷基取代基对 Cardo 聚酰亚胺的溶解性和热稳定性的影响。基于邻位烷基取代的 Cardo 二胺, 如 9,9'-双(4-氨基苯基)苄、9,9'-双(3-甲基-4-氨基苯基)苄和 9,9'-双(3,5-二甲基-4-氨基苯基)苄, 和不同二酐, 如 4,4'-氧双邻苯二甲酸酐 (ODPA)、3,3',4,4'-四羧基二苯甲酮二酐 (BTDA)、3,3',4,4'-联苯四羧酸二酐 (BPDA) 和均苯四甲酸二酐 (PMDA), 的一系列聚酰亚胺被合成。这些聚酰亚胺被使用 GPC、TGA、DMA 等方法表征。

## 2、实验部分

### 2.1 原料

9,9'-双(4-氨基苯基)苄、9,9'-双(3-甲基-4-氨基苯基)苄和 9,9'-双(3,5-二甲基-4-氨基苯基)苄: 自制。4,4'-氧双邻苯二甲酸酐 (ODPA)、均苯四甲酸二酐 (PMDA): 上海市合成树脂研究所。3,3',4,4'-四羧基二苯甲酮二酐 (BTDA)、3,3',4,4'-联苯四羧酸二酐 (BPDA): 日本宇部。

### 2.2 聚酰亚胺合成

典型的合成路线如下 (图 1): 在带有氮气导管, 温度计, 冷凝管和搅拌桨的 250ml 四口烧瓶中, 等摩尔的二胺和二酐溶解在间甲酚中, 反应混合物加热回流 5 小时, 高速搅拌下倒入大量乙醇中沉淀。产品过滤, 大量乙醇洗涤, 在真空烘箱中 80°C/2hr, 200°C/5hr 干燥。

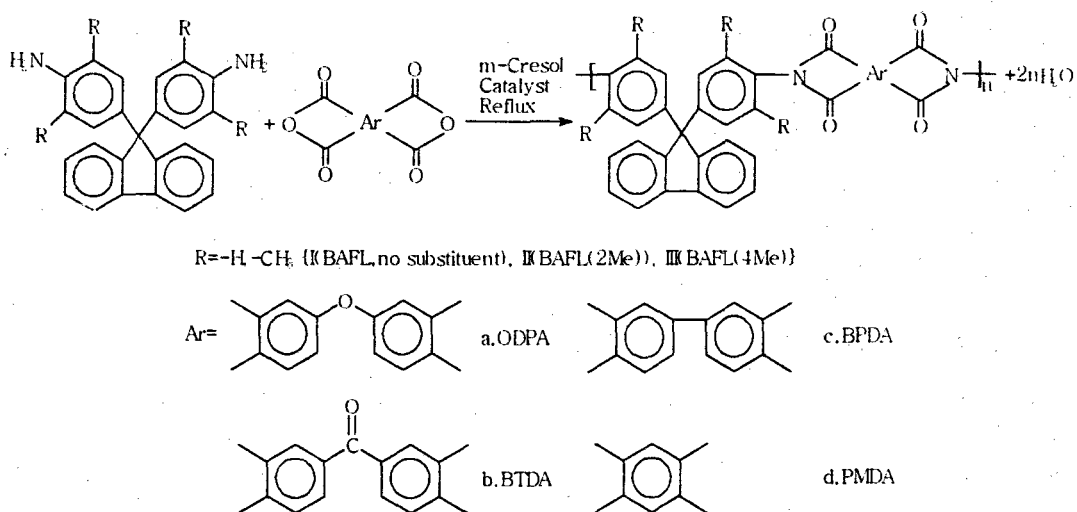


图 1 Cardo 聚酰亚胺的合成路线

### 2.3 测试

特性粘度为 25±0.1°C 下, 0.5% (w/v) 聚合物 DMAc 溶液使用乌氏粘度计测定。数均分子量 (Mn) 和重均分子量 (Mw) 采用 Waters 2414 型凝胶渗透色谱仪测定。TGA 用 Perkin-Elmer 7 Series Thermal Analysis system 在干燥氮气, 10°C/min 升温速率下测定。DMA 用 Netzsch DMA242 测定。

## 3、结果与讨论

### 3.1 聚酰亚胺合成

可溶性聚酰亚胺在间甲酚中直接聚合得到。因为这些聚酰亚胺比那些通过聚酰胺酸和热环化的两步法得到的聚酰亚胺具有更高的聚合度和更好的溶解性<sup>[5]</sup>。聚酰亚胺 Ia-Ic, IIa-IIc, IIIa-IIIc 使用一步法制备, 但聚酰亚胺 Id, IId 由于不溶于热的间甲酚, 使用两步法化学亚胺化制备。得到的可溶性聚酰亚胺的特性粘度范围是 0.31—0.92dl/g, 数均分子量在 19000 到 52000 间 (见表 1)。

表 1 四氢呋喃可溶的聚酰亚胺的分子量和粘度数据

Code	Polymer	Mn×10 <sup>-4</sup>	Mw×10 <sup>-4</sup>	η <sup>a</sup> (dl/g)
Ia	BAFL-ODPA	2.1	3.2	0.33
Ib	BAFL-BTDA	1.9	2.9	0.31
Ic	BAFL-BPDA	— <sup>b</sup>	—	0.85
Id	BAFL-PMDA	—	—	—
IIa	BAFL(2Me)-ODPA	4.0	5.9	0.55
IIb	BAFL(2Me)-BTDA	4.9	8.7	0.59
IIc	BAFL(2Me)-BPDA	5.2	9.2	0.92
IId	BAFL(2Me)-PMDA	.....	.....	—
IIIa	BAFL(4Me)-ODPA	2.6	4.4	0.34
IIIb	BAFL(4Me)-BTDA	2.7	4.7	0.40
IIIc	BAFL(4Me)-BPDA	3.2	5.7	0.58
IIId	BAFL(4Me)-PMDA	.....	.....	—

a. 特性粘度在 25°C, DMAc 中测定;

b. —表示在 THF 中不溶。

### 3.2 溶解性

如表 2 所示, 大部分由 Cardo 二胺和 ODPA、BTDA、BPDA、PMDA 制备得到的 Cardo 聚酰亚胺在通常的有机溶剂, 如间甲酚、氯仿、四氢呋喃 (THF)、N-甲基吡咯烷酮 (NMP) 和 N,N-二甲基乙酰胺 (DMAc), 具有优良的溶解性。结果表明, 非共平面的烷基取代基的引入能有效提高 Cardo 聚酰亚胺的溶解性。比如, BAFL(4Me)-PMDA 甚至能溶于热的间甲酚, 氯仿和 NMP。

表 2 聚酰亚胺的溶解性<sup>a</sup>

Polyimide	NMP	DMAc	m-Cresol	CHCl <sub>3</sub>	THF
BAFL-ODPA	S	S	S	S	S
BAFL-BTDA	S	S	S	S	S
BAFL-BPDA	S	Ins	S	S	Ins
BAFL-PMDA	Ins	Ins	Ins	Ins	Ins
BAFL(2Me)-ODPA	S	S	S	S	S
BAFL(2Me)-BTDA	S	S	S	S	S
BAFL(2Me)-BPDA	S	Ins	S	S	S
BAFL(2Me)-PMDA	Ins	Ins	Ins	Ins	Ins
BAFL(4Me)-ODPA	S	S	S	S	S
BAFL(4Me)-BTDA	S	S	S	S	S
BAFL(4Me)-BPDA	S	Ins	S	S	S
BAFL(4Me)-PMDA	*S	G	*S	*S	Ins

a. 溶解性: S, 室温可溶; Ins, 不溶; \*S, 加热可溶; G, 凝胶。

### 3.3 热和热氧化稳定性

为讨论热和热氧化稳定性, 5%, 10%和 15%热失重的温度利用 TGA 在干燥氮气下测定 (表 3)。所有得到的聚酰亚胺展示了良好的热和热氧化稳定性, Cardo 聚酰亚胺粉状样品的 5%热失重温度在 430°C 到 544°C 之间。引入烷基取代基可能导致热稳定性下降, 但热失重温度依然大于 400°C。

表 3 聚酰亚胺的热稳定性

Polyimide	TGA wt. loss(°C)		
	5%	10%	15%
BAFL-ODPA	554	582	593
BAFL-BTDA	553	586	598
BAFL-BPDA	532	588	597
BAFL-PMDA	553	580	590
BAFL(2Me)-ODPA	483	514	537
BAFL(2Me)-BTDA	470	509	535
BAFL(2Me)-BPDA	476	519	532
BAFL(2Me)-PMDA	472	511	542
BAFL(4Me)-ODPA	430	473	493
BAFL(4Me)-BTDA	454	480	498
BAFL(4Me)-BPDA	466	487	503
BAFL(4Me)-PMDA	529	564	579

此外, 使用 Netzsch DMA242 测定的 ODPA 型 Cardo 聚酰亚胺的 Tg 值在 307 °C 到 368 °C 之间。这也表明 Cardo 聚酰亚胺具有良好的热和热氧化稳定性。烷基引入数量的增加导致 Tg 的下降, 原因需要进一步研究。

#### 4、结论

利用 Cardo 二胺与 ODPA、BTDA、BPDA、PMDA 反应制备得到了 Cardo 聚酰亚胺, 并通过 GPC、TGA、DMA 等进行了表征。通过在 Cardo 二胺上引入非共平面的烷基取代基能在不降低热性能的同时提高 Cardo 型聚酰亚胺在有机溶剂中的溶解性。

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