

Synthesis and Properties of Polyamide-imides Containing Fluorenyl Cardo Structure

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ABSTRACT: A series of alternating polyamide-imides (PAIs) with fluorenyl cardo having inherent viscosities of 0.38–0.88 dL/g was synthesized by one-pot polycondensation of cardo diamines, trimellitic anhydride, and various aromatic diamines including *p*-phenylene diamine, *m*-phenylene diamine, 4,4'-oxydianiline, 3,4'-oxydianiline, 2,2-bis[4-(4-aminophenoxy)phenyl]propane, 2,2-bis[4-(3-amino phenoxy)phenyl]propane using triphenyl phosphite as condensing agents. Most of the polymers were readily soluble in a variety of organic solvents, such as *N*-methyl-2-pyrrolidin-one, *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide, dimethyl sulfoxide, pyridine, and tetrahydrofuran, etc. PAIs exhibited better solubility when

alkyl substituents were incorporated. Moreover, the effects of the linkage of imide/amide on the properties of PAIs were also discussed. The glass-transition temperatures of these polymers were recorded between 235 and 448°C by DSC and 10% weight loss temperature of all polymers exceed 450°C in air. The films of the resulting PAIs could be cast from their DMAc solutions. These films had a tensile strength in the range of 43–111 MPa, and an elongation at break in the range of 1.5–7.1%. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2494–2501, 2007

Key words: cardo; fluorenyl polyamide-imide; solubility; properties

INTRODUCTION

Aromatic polyimides are well known as high performance polymers for their superior resistance to spontaneous pyrolysis and oxidative degradation, electrical insulating properties, and mechanical characteristics; so they are widely used in fields of electrical materials, adhesives, and composite fiber and film materials.^{1–3} However, they are generally insoluble and infusible in their fully imidized form; it makes them generally difficult to fabricate; and imidization of poly(amic acid) intermediate has several inherent problems such as emission of volatile byproducts (e.g., H₂O) and storage instability etc.

Polymers containing at least one element in the repeating unit that is induced in the cyclic side group have become the subject of many investigations. These polymers were termed Cardo polymers from the Latin “Cardo” (a loop), since such groups can be considered as loops at the backbone of the macromolecule⁴ (Scheme 1).

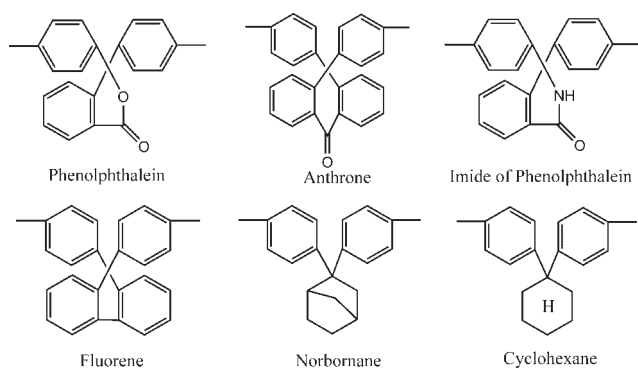
The polymer was termed fluorenyl cardo polymer containing fluorenyl structure in the backbone (Scheme 1). The introduction of fluorenyl “cardo”

groups into polymers such as polyimides,^{4–11} polyamides,^{12,13} polyamide-imide (PAI),^{14–16} polyquinolines¹⁷ etc. can endow with 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. However, according to our previous study,¹⁰ their mechanical properties were poor owing to a rigid bulky bisphenylfluorene moiety on the cardo polyimide backbone, which led the film to be brittle.

PAIs, as a family, have deserved particular attention as they are probably the class of copolyimides that most closely resemble the thermal properties of aromatic polyimides. Furthermore, the inclusion of an amide group into the polyimide backbone increases its processability, solubility, and moldability, but thermal property was slightly decreased. Liaw et al.^{18–20} and Yang and coworkers^{21–23} have done many eximious works about soluble PAIs by the direct polycondensation of diimide-dicarboxylic acid and various in *N*-methyl-2-pyrrolidinone (NMP) using triphenyl phosphite as condensing agents.

In the present study, the objective is to synthesize fluorenyl cardo PAIs by one-pot polycondensation and investigate the effect of incorporation of alkyl substituents on fluorenyl cardo diamines on the solubility and thermal stability of cardo PAIs. Moreover, the effect of incorporation of amide-bond and

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Scheme 1 Schematic diagram of different Cardo groups.

the effect of linking structure of cardo in polymeric backbone on the properties of PAIs were also discussed. A series of fluorenyl cardo PAIs were synthesized and characterized based on cardo diamines such as 9,9-bis(4-aminophenyl)fluorene (BAFL), 9,9-bis(3-methyl-4-aminophenyl)fluorene (BAFL(2Me)), 9,9-bis(3-ethyl-4-aminophenyl)fluorene (BAFL(2Et)), trimellitic anhydride, and various diamines such as *p*-phenylenediamine, *m*-phenylenediamine, 4,4'-oxydianiline, 3,4'-oxydianiline, 2,2-bis[4-(4-aminophenoxy)phenyl]propane, 2,2-bis[4-(3-aminophenoxy)phenyl]propane. The solubility, thermal properties, and mechanical properties of the PAIs were investigated by TGA, DSC, etc.

EXPERIMENTAL SECTION

Reagents and solvents

9,9-Bis(4-aminophenyl)fluorene (BAFL), 9,9-bis(3-methyl-4-aminophenyl)fluorene (BAFL(2Me)), 9,9-bis(3-ethyl-4-aminophenyl)fluorene (BAFL(2Et)), 4,4'-oxydianiline, 3,4'-oxydianiline, 2,2-bis[4-(4-aminophenoxy)phenyl]propane, 2,2-bis[4-(3-aminophenoxy)phenyl]propane (Shanghai Research Institute of Synthetic Resins, Shanghai, China), trimellitic anhydride (Lancaster), *p*-phenylenediamine, *m*-phenylenediamine (Sinopharm Chemical Reagent, Shanghai, China), NMP, and DMAc were dried in CaH₂ for 2 days and distilled before use.

Polyamide-imide synthesis

In a four-necked flask with a nitrogen inlet, a thermometer, a Dean-Stark trap, and a mechanical stirrer, cardo diamines and double molar trimellitic anhydride were dissolved in dried *N*-methyl-2-pyrrolidinone (NMP) and xylene. The reactive mixture was refluxed at 160°C under nitrogen atmosphere for a period of time and water was entirely eliminated by using a Dean-Stark water separator, then xylene was also eliminated by using a Dean-Stark water separator to make the reaction temperature exceed to 180°C. The reaction was carried out 5 h to ensure the completion of imidization. Then the reaction was

cooled to room temperature and equivalent molar diamine, and condensing agents including triphenyl phosphate, pyridine, and CaCl₂ were directly added into the flask at constant stirring. The solution was stirred for about 3 h at 145°C and a brown viscous solution was obtained. Then, the viscous solution was precipitated in methanol in a high speed blender. The PAI powder was filtrated and washed by excess methanol and water; then it was dried in a vacuum oven at 200°C for 12 h. In this case, the resulting PAI has head-to-head structure. To discuss the effect of linkage of amide-imide on the properties of PAI, the PAIs of tail-to-tail structure were also synthesized by altering the feeding order of diamines different from the above one (Scheme 2).

Preparation of polyamide-imide films

A solution was made by the dissolution of about 3 g of the PAI in 17 mL DMAc at 80°C to afford an ~15 wt % solution. The clear solution was poured on 45 cm × 45 cm plate glass, which was placed in a 100°C oven for 3 h for evaporation of the solvent, then dried at 130°C for 2 h, 160°C for 2 h, 180°C for 2 h, and 200°C for 2 h. The flexible PAI films with 50–60 μm thickness were then stripped from the glass substrate.

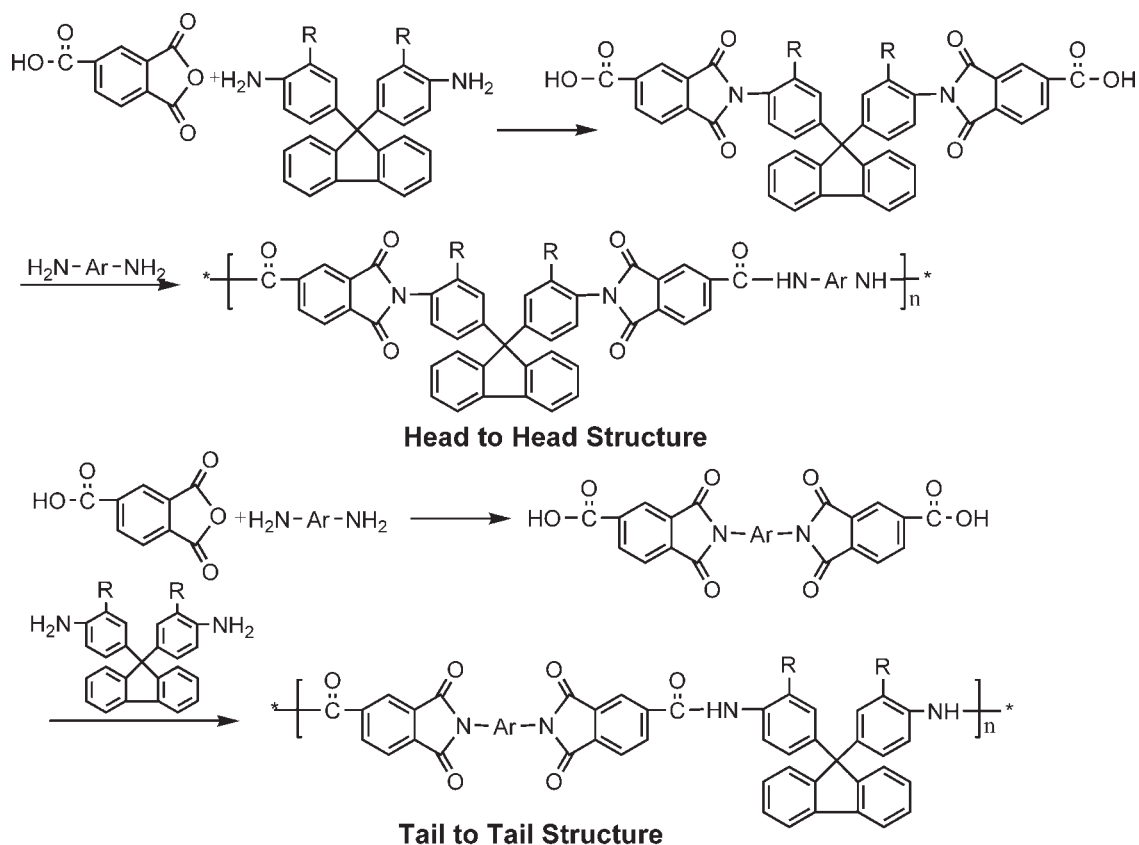
Measurements

IR spectra were recorded on a Nicolet 460. Inherent viscosity measurements were made with 0.5% (w/v) solution of polymers in DMAc at (25 ± 0.1)°C using an Ubbelohde viscometer. The thermogravimetry analyses (TGA) were made with TA TGA Q50. Experiments were carried out under air and under N₂ atmosphere at a heating rate of 20°C/min. Differential scanning calorimetry (DSC) was carried out using TA DSC Q10 under N₂ atmosphere at a heating rate of 20°C/min. Tensile properties were determined from stress-strain curves obtained with a LLOYD-LF according to GB13022. Computer simulation used Chem3D Ultra molecular modeling from CambridgeSoft Corporation (Version 9.0).

RESULTS AND DISCUSSION

Synthesis of polyamide-imides

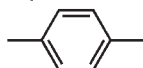
A series of alternating PAIs with fluorenyl Cardo (Ia–IIIId) was synthesized by one-pot direct polycondensation without isolating diimide-dicarboxylic acid intermediates, cardo diamines, trimellitic anhydride, and various diamines in NMP using triphenyl phosphite as condensing agents. Intrinsic viscosity of the PAIs ranged from 0.38 to 0.88 dL/g in DMAc. The structure of PAIs was confirmed by IR. For



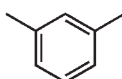
R=H(I), CH₃(II), CH₂CH₃(III)

Various diamine structure (Ar=a-f)

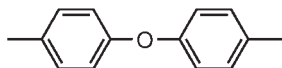
a. p-phenylenediamine (PDA)



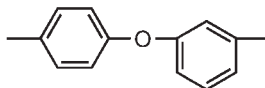
b. m-phenylenediamine(MDA)



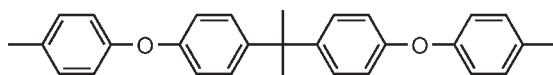
c. 4,4'-oxydianiline(4,4'-ODA)



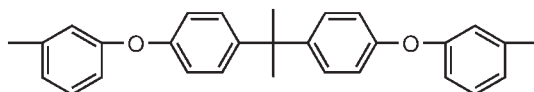
d. 3,4'-oxydianiline(3,4'-ODA)



e. 2,2-bis[4-(4-aminophenoxy)phenyl]propane(BAPP)



f. 2,2-bis[4-(3-aminophenoxy)phenyl]propane(mBAPP)



Scheme 2 Synthesis route used to prepare the head-to-head and tail-to-tail structure of fluorenyl cardo polyamide-imides.

example, polymer Ic exhibited the characteristic absorptions: 3400 cm^{-1} (N—H, amide groups), 1779 cm^{-1} , 1718 cm^{-1} (C=O, imide group), 1669 cm^{-1} (C=O, amide group), 1372 cm^{-1} (C—N, imide

group), 727 cm^{-1} (C=O, bending, imide deformation) in Figure 1. Moreover, IR spectra of other PAIs revealed that the characteristic absorptions of imide groups appeared around 1780, 1720, and 1370 cm^{-1} ,

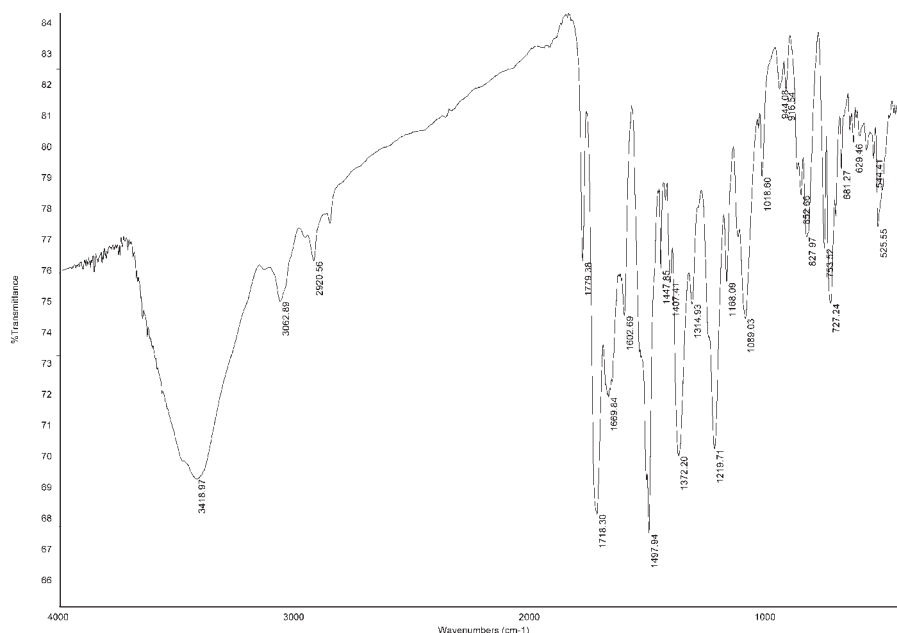


Figure 1 FT-IR spectra of Polymer Ic (BAFL-4,4'-ODA).

and those of the amide group appeared around 3400 and 1670 cm^{-1} .

Organosolubility of polyamide-imides

As shown in Table I, most of cardo PAIs being prepared from fluorenyl cardo diamines and other vari-

ous aromatic diamines exhibited excellent solubility in common organic solvents such as NMP, DMAc, DMF, DMSO, pyridine, THF, etc.

In Table I, it shows that the incorporation of noncoplanar structure led by the introducing of alkyl substituents on fluorenyl cardo diamine can significantly improve the solubility of cardo PAIs in organic sol-

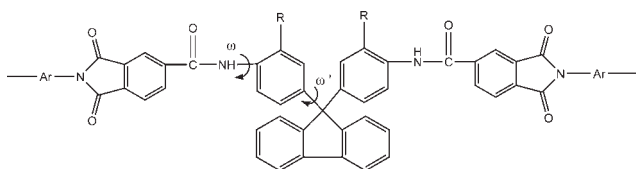
TABLE I
Organosolubility^{a,c} and Inherent Viscosity^b of Polyamide-imides

Code	Polymer	NMP	DMAc	DMF	Py	THF	DMSO	η (dL/g)
Ia	BAFL-PDA	S	S	S	S	Ins	S	0.85
aI	PDA-BAFL	S	S	S	S	Ins	S	0.69
Ib	BAFL-MDA	S	S	S	S	Ins	S	0.63
bI	MDA-BAFL	S	S	S	S	Ins	S	0.55
Ic	BAFL-4,4'-ODA	S	S	S	S	Ins	S	0.88
cI	4,4'-ODA-BAFL	S	S	S	S	Ins	S	0.79
I d	BAFL-3,4'-ODA	S	S	S	S	SW	S	0.67
dI	3,4'-ODA-BAFL	S	S	S	S	SW	S	0.62
Ie	BAFL-BAPP	S	S	S	S	PS	S	0.62
eI	BAPP-BAFL	S	S	S	S	SW	S	0.72
If	BAFL-mBAPP	S	S	S	S	SW	S	0.55
fI	mBAPP-BAFL	S	S	S	S	S	S	0.44
IIa	BAFL(2Me)-PDA	S	S	S	S	SW	S	0.54
IIb	BAFL(2Me)-MDA	S	S	S	S	PS	S	0.56
IIc	BAFL(2Me)-4,4'-ODA	S	S	S	S	PS	S	0.73
IId	BAFL(2Me)-3,4'-ODA	S	S	S	S	PS	S	0.52
IIf	BAFL(2Me)-BAPP	S	S	S	S	S	S	0.57
IIIf	BAFL(2Me)-mBAPP	S	S	S	S	S	S	0.64
IIIa	BAFL(2Et)-PDA	S	S	S	S	PS	S	0.52
IIIb	BAFL(2Et)-MDA	S	S	S	S	S	S	0.39
IIIc	BAFL(2Et)-4,4'-ODA	S	S	S	S	S	S	0.49
III d	BAFL(2Et)-3,4'-ODA	S	S	S	S	S	S	0.38

^a S, soluble; PS, partly soluble; SW, swelling; Ins, insoluble.

^b Intrinsic viscosities measured with 0.5% (w/v) solution of polymers in DMAc at $(25 \pm 0.1)^\circ\text{C}$ using an Ubbelohde viscometer.

^c The concentration of polymer solution for solubility testing is 5% (w/w).



Scheme 3 Schematic diagram of bond rotation of cardo polyamide-imides.

vents. For example, BAFL-4,4'-ODA and BAFL-3,4'-ODA are insoluble or swelling in THF, but BAFL(2Me)-4,4'-ODA and BAFL(2Me)-3,4'-ODA can partly dissolve, furthermore, BAFL(2Et)-4,4'-ODA and BAFL(2Et)-3,4'-ODA can entirely dissolve in THF. BAFL-BAPP and BAFL-mBAPP have a bad solubility in THF, but BAFL(2Me)-BAPP and BAFL(2Me)-mBAPP exhibit an excellent solubility in THF. It can be attributed to the incorporation of methyl or ethyl substituent on the polymeric backbone according to our previous study.¹⁰ To discuss the relationship between solubility and alkyl substituents on cardo diamine, the bond rotation angle ω between imide ring and phenylene ring was obtained by computer modeling. The chemical structure and bond rotation angle of fluorenyl cardo diamines are shown in Scheme 3, Figure 2, and Table II. It is shown that dihedral angle ω is least in cardo PAIs based on BAFL; the dihedral angle ω increases with the size of substituents on BAFL, while the dihedral angle ω' between phenylene ring and fluorenyl ring changes slightly. The introduction of substitute groups on BAFL results in the breakage of the coplanar structure, because the bond rotation weakens the conjugation of main chain with an increase of the dihedral angle ω between imide ring and phenylene ring. Therefore, the introduction of noncoplanar structure improves the solubility of these polymers. Moreover, the Cardo PAIs with the larger ω' have the better solubility than that with the smaller ω' , because the dihedral angle ω' between phenylene ring and fluorenyl ring could affect the rotation of the bond between

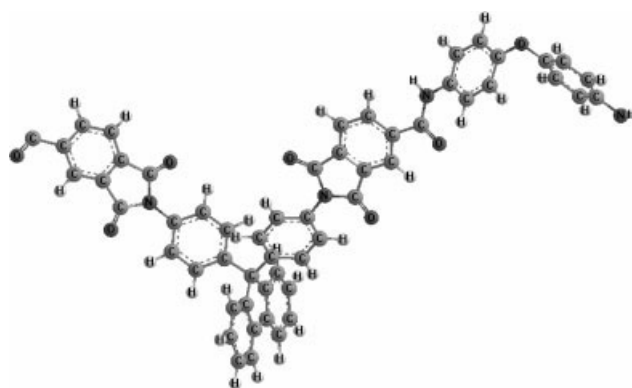


Figure 2 3D structure modeling of cardo polyamide-imide (BAFL-4,4'-ODA).

TABLE II
Bond Rotation Degree of Cardo Polyamide-imides

Diamine	ω	ω'
BAFL(R=H)	21.83	64.65
BAFL(2Me)(R=CH ₃)	31.68	65.81
BAFL(2Et)(R=CH ₂ CH ₃)	35.24	66.96

imide ring and phenylene ring and weakening extend of the conjugation of main chain.

Meanwhile, it was found that the solubility of cardo PAIs increases with increasing of the distance among the imide-rings, isomer of aromatic diamine also improve its solubility in organic solvents, but the effects of the linkage of imide/amide on the solubility of cardo PAIs is not obvious.

T_g and thermal stability of PAIs

The thermal properties of the PAIs were evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (Figs. 3 and 4, and Table III). T_g of the PAIs increases with the increase of rigidity of other diamines (BAFL-PDA (448°C) > BAFL-MDA (412°C) > BAFL-4,4'-ODA (374°C) > BAFL-BAPP (318°C) > BAFL-3,4'-ODA (292°C) > BAFL-mBAPP (244°C) and PDA-BAFL (414°C) > MDA-BAFL (384°C) > 4,4'-ODA-BAFL (371°C) > BAPP-BAFL (320°C) > 3,4'-ODA-BAFL (300°C) > mBAPP-BAFL(235°C)). T_g of PAIs with head-to-head structure is higher than those with tail-to-tail structure when diamine is very rigid such as PDA or MDA, but the difference is not obvious with the increase of flexibility of diamines. It demonstrates that the fluorenyl cardo imide linkage would cause significant influence on T_g of PAIs when the rigid diamine incorporates into the amide linkage of polymers backbone.

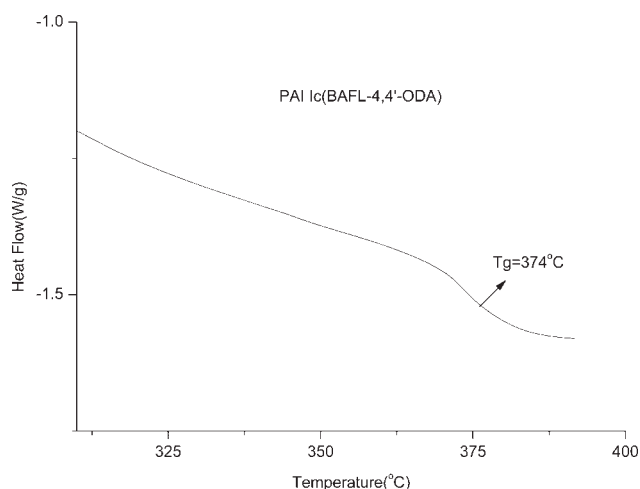


Figure 3 DSC traces of polyamide-imide Ic(BAFL-4,4'-ODA).

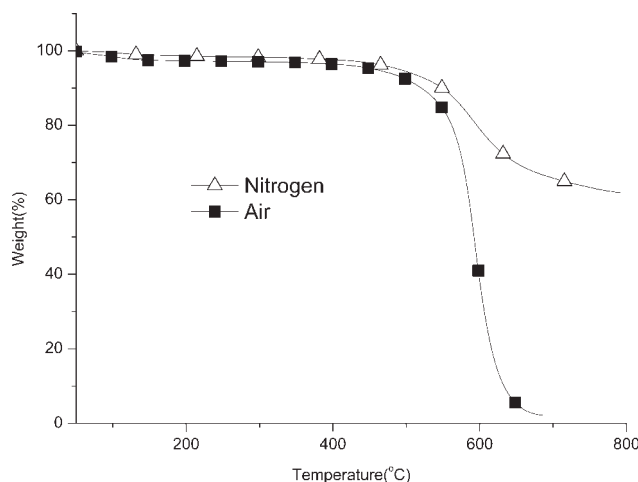


Figure 4 TGA curves of polymer Ic (BAFL-4,4'-ODA) under air and nitrogen atmosphere.

In addition, as shown in Table III, all PAIs with para diamine have higher T_g than those with meta diamine. Moreover, to discuss thermal stability, the onset temperature corresponding to 10% weight loss of the PAIs was measured by TGA under air and under nitrogen, respectively (Fig. 4 and Table III). All polyimides show good thermal stability, powder samples of these PAIs undergo 10% weight loss in the range of 457–545°C in air at a heating rate of 20°C/min and char yields of 50–64% at 800°C under nitrogen atmosphere. Thermal stability of PAIs

decrease with the increase of the size of alkyl substituents (T10 (in air): BAFL-4,4'-ODA (510°C) > BAFL(2Me)-4,4'-ODA (483°C) > BAFL(2Et)-4,4'-ODA (465°C)). Moreover, PAIs with head-to-head linkages structure of cardo in PAIs backbone behave relatively better thermal stability than those with tail-to-tail linking structure.

Mechanical properties of PAIs film

Mechanical properties of the PAI films were measured, the results of tensile strength, elongation at break, and tensile modulus are summarized in Table IV. The polymer films had tensile strength of 43–111 MPa, elongation to break of 1.5–7.1%, tensile modulus of about 3.0 GPa, indicating that they are strong and hard materials. According to our previous study, mechanical properties of the brittle film obtained by casting the solution of polyimide (BAFL-ODPA) and copolyimides (BAFL(0.5)-ODA(0.5)-PMDA(1)) could not be measured, thus, it indicates that the incorporation of an amide group into the polyimide backbone improves its mechanical properties without sacrificing thermal properties.

CONCLUSION

The article reports that the effects of the size of introducing alkyl substituents on fluorenyl cardo diamines on solubility and thermal properties of cardo

TABLE III
 T_g and Thermal Stability of PAIs

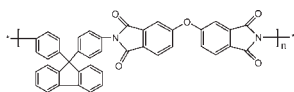
Code	Polymer	T_{max} (°C)		T_{10} (°C)		T_g (°C)	Y_c (%)
		Air	N ₂	Air	N ₂		
Ia	BAFL-PDA	593	587	535	545	448	64
aI	PDA-BAFL	593	599	515	528	414	59
Ib	BAFL-MDA	592	591	531	549	412	63
bI	MDA-BAFL	589	477, 596	527	531	384	61
Ic	BAFL-4,4'-ODA	593	592	510	548	374	61
cI	4,4'-ODA-BAFL	598	601	530	545	371	61
Id	BAFL-3,4'-ODA	597	593	545	555	292	63
dI	3,4'-ODA-BAFL	595	467, 617	524	540	300	61
Ie	BAFL-BAPP	591, 639	544, 585	522	522	318	62
eI	BAPP-BAFL	479, 593	535, 587	499	485	320	59
If	BAFL-mBAPP	598, 649	545, 584	531	521	244	63
fI	mBAPP-BAFL	470, 585	532, 585	495	512	235	55
IIa	BAFL(2Me)-PDA	546, 571	576	493	523	–	56
IIb	BAFL(2Me)-MDA	574	540, 577	496	515	379	55
IIc	BAFL(2Me)-4,4'-ODA	573	579	483	533	382	63
IId	BAFL(2Me)-3,4'-ODA	548	526	480	508	330	54
IIe	BAFL(2Me)-BAPP	453, 574	516	467	504	335	59
IIf	BAFL(2Me)-mBAPP	420, 569	524	474	507	299	56
IIIa	BAFL(2Et)-PDA	552	522, 637	457	494	361	50
IIIb	BAFL(2Et)-MDA	562	520	471	486	336	55
IIIc	BAFL(2Et)-4,4'-ODA	565	509	465	494	326	53
IIId	BAFL(2Et)-3,4'-ODA	565	504	467	495	303	58

T_{max} , the maximum decomposition temperature; T_{10} , TGA 10% weight loss (°C); Y_c , the char yield at 800°C.

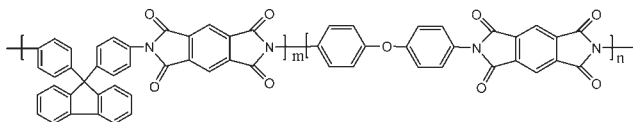
TABLE IV
Mechanical Properties of the PAIs Films

Code	Polymer	Tensile strength (MPa)	Elongation to break (%)	Tensile modulus (GPa)	Film quality
Ia	BAFL-PDA	92	3.2	3.4	Flexible
aI	PDA-BAFL	81	2.7	3.3	Flexible
Ib	BAFL-MDA	99	4.4	3.5	Flexible
bI	MDA-BAFL	66	2.0	3.2	Flexible
0Ic	BAFL-4,4'-ODA	90	7.1	–	Flexible
cI	4,4'-ODA-BAFL	91	3.9	–	Flexible
Id	BAFL-3,4'-ODA	71	4.7	–	Flexible
dI	3,4'-ODA-BAFL	83	4.4	–	Flexible
Ie	BAFL-BAPP	97	7.1	–	Flexible
eI	BAPP-BAFL	71	7.0	–	Flexible
If	BAFL-mBAPP	64	3.0	–	Flexible
fI	mBAPP-BAFL	84	4.1	2.8	Flexible
IIa	BAFL(2Me)-PDA	107	2.2	3.5	Flexible
IIb	BAFL(2Me)-MDA	67	2.9	2.9	Flexible
IIc	BAFL(2Me)-4,4'-ODA	111	4.3	–	Flexible
IId	BAFL(2Me)-3,4'-ODA	108	4.6	–	Flexible
IIe	BAFL(2Me)-BAPP	107	4.4	3.3	Flexible
IIf	BAFL(2Me)-mBAPP	81	3.6	3.2	Flexible
IIIc	BAFL(2Et)-4,4'-ODA	43	1.5	3.1	Brittle
Ref-1	BAFL-ODPA	–	–	–	Brittle
Ref-2	BAFL-4,4'-ODA-PMDA	–	–	–	Brittle

Ref-1:



Ref-2:



PAIs. Moreover, the effect of incorporation of amide-bond and the effect of linkage structure of cardo (head to head or tail to tail) in the polymeric backbone on the properties of PAIs were also discussed. Most of the polymers were readily soluble in aprotic polar solvents such as NMP, DMAc, and DMF, as well as in less polar solvents such as DMSO, pyridine, tetrahydrofuran, etc. The PAIs exhibited better solubility when alkyl substituents were incorporated. Inherent viscosities of these PAIs in DMAc ranged from 0.38 to 0.88 dL/g. The glass transition temperatures of PAIs were in the range of 235–448°C by DSC and 10% weight loss temperature of all polymers exceed 450°C in air. The polymer films had a tensile strength in the range of 43–111 MPa, an elongation at break in the range of 1.5–7.1%. The results indicate that the fluorenyl cardo PAIs obtained display high T_g , good thermal stability, and mechanical properties. Moreover, the fluorenyl cardo imide linkage would cause significant influence on T_g of PAIs when the rigid diamine incorporates into the amide

linkage of polymers backbone. In addition, PAIs with head-to-head linkage structure of cardo in PAIs backbone have relatively better thermal stability than those with tail-to-tail linking structure, but the effects of the linkage of imide/amide on the solubility of cardo PAIs is not obvious.

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