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Ortho alkyl substituents effect on solubility and thermal properties of fluorenyl cardo polyimides

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Abstract

Five fluorenyl cardo diamines containing different alkyl substituents were synthesized and characterized. A series of fluorenyl cardo polyimides were prepared by polycondensation of these cardo diamines with 4,4′-oxydiphthalic anhydride (ODPA), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA), 3,3′,4,4′-biphenyl tetracarboylic dianhydride (BPDA) and pyromellitic dianhydride (PMDA). Most of fluorenyl 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 to 0.92 dl/g. T_g of polyimides based on ODPA decrease with the number and size of alkyl substituents on fluorenyl cardo diamine. The results show that the incorporation of noncoplanar structure led by the introducing alkyl substituents on fluorenyl cardo diamines improves the solubility of cardo polyimides in organic solvents without sacrificing thermal properties.

Keywords: Cardo; Fluorenyl polyimide; Solubility

1. Introduction

Polyimides are well known as high performance polymers for their excellent heat resistance, 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, 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_2O) 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 [4–12].

The introduction of fluorenyl ‘cardo’ groups into polymers such as polyimides [13–19], polyamides [20,21], polyquinolines [22] 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. Because cardo polyimide contains a bulky bisphenylfluorene 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 in fluorenyl cardo diamine on the solubility and thermal stability of cardo polyimides. A series of fluorenyl 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)), 9,9-bis(3-ethyl-4-aminophenyl) fluorene (BAFL(2Et)) and 9,9-bis(3,5-dimethyl-4-aminophenyl) fluorene (BAFL(4Me)), 9,9-bis(3,5-diethyl-4-aminophenyl)fluorene (BAFL(4Et) with different dianhydrides

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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). The solubility and thermal properties of the polyimides were investigated by Gel permeation chromatography (GPC), TGA, DMA etc.

2. Experimental section

2.1. Materials

9-Fluorenone (Shanghai coking and chemical corporation), aniline (Shanghai Lingfeng Chemical Reagent Co. Ltd), *O*-toluidine, 2-ethylaniline, 2,6-dimethylaniline, 2,6-diethylaniline (J & K Chemical Ltd). 4,4′-Oxydiphthalic anhydride (Shanghai Research Institute of synthetic resin), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride, 3,3′,4,4′-biphenyltetracarboylic dianhydride (Ube Industries, Ltd), pyromellitic dianhydride (Shanghai Research Institute of synthetic resin). *m*-Cresol and DMAc were dried in P2O5 for 2 days and distilled before use.

2.2. Monomer synthesis

2.2.1. 9,9-Bis(4-aminophenyl)fluorene [22]

In a 250 ml four-necked flask fitted with a nitrogen inlet, a themometer, a condenser and a mechanical stirrer, 40 g aniline hydrochloride, 80 g aniline, 18 g 9-fluorenone was added, the mixture was refluxed under nitrogen atmosphere for 5 h, then the warm reaction mixture was precipitated in 10 wt% hot potassium hydroxide solution. White powder was obtained after recrystallized in benzene. The product was dried in vacuo to give 21.4 g. Yield: 61.6%, mp = 236–238 °C (by WRS-1B digital melting point apparatus), IR (KBr) 3430, 3348, 1623 (NH_2) cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.5 (m, 4H, NH_2), 6.5–7.8 (m, 16H).

Anal. Calcd for $C_{25}H_{20}N_2$: C, 86.21%; H, 5.74%; N, 8.04%. Found: C, 85.68%; H, 5.78%; N, 7.93%.

2.2.2. 9,9-Bis(3-methyl-4-aminophenyl)fluorene

In a 250 ml four-necked flask fitted with a nitrogen inlet, a themometer, a condenser and a mechanical stirrer, 50 g *O*-toluidine hydrochloride, 80 g *O*-toluidine, 18 g 9-fluorenone was added, the mixture was refluxed under nitrogen atmosphere for 5 h, then the reactive mixture was cooled and precipitated in methanol. The product was washed with methanol and the white powder was gained and dried in vacuo to afford 26.5 g. Yield: 70.5%, mp = 232.2–233.2 °C (by WRS-1B digital melting point apparatus), IR (KBr) 3427, 3314, 1624 (NH_2) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.0 (m, 6H, $-CH_3$), 3.5 (m, 4H, NH_2), 6.5–7.8 (m, 14H).

Anal. Calcd for $C_{27}H_{24}N_2$: C, 86.17%; H, 6.38%; N, 7.45%. Found: C, 85.17%; H, 6.30%; N, 7.26%.

2.2.3. 9,9-Bis(3-ethyl-4-aminophenyl)fluorene

According to aforementioned method, the last product is a white powder. Yield: 64.7%, mp = 190–191 °C (by WRS-1B digital melting point apparatus),IR (KBr) 3427, 3314, 1624 (NH_2) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.1 (m, 4H, $-CH_2-$), 2.4 (m, 6H, $-CH_3$), 3.5 (m, 4H, NH_2), 6.5–7.8 (m, 14H).

Anal. Calcd for $C_{29}H_{28}N_2$: C, 86.14%; H, 6.93%; N, 6.93%. Found: C, 85.54%; H, 6.83%; N, 6.85%.

2.2.4. 9,9-Bis(3,5-dimethyl-4-aminophenyl)fluorene

According to aforementioned method, the last product is a pale yellow powder. Yield: 30%, mp = 320 °C (by DSC), IR (KBr) 3481, 3396, 1621 (NH_2) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.0 (m, 12H, $-CH_3$), 3.5 (m, 4H, NH_2), 6.5–7.8 (m, 12H).

Anal. Calcd for $C_{29}H_{28}N_2$: C, 86.14%; H, 6.93%; N, 6.93%. Found: C, 85.41%; H, 6.81%; N, 6.86%.

2.2.5. 9,9-Bis(3,5-diethyl-4-aminophenyl)fluorene

According to aforementioned method, the last product is a pale yellow powder. Yield: 20%, mp = 255 °C (by DSC),

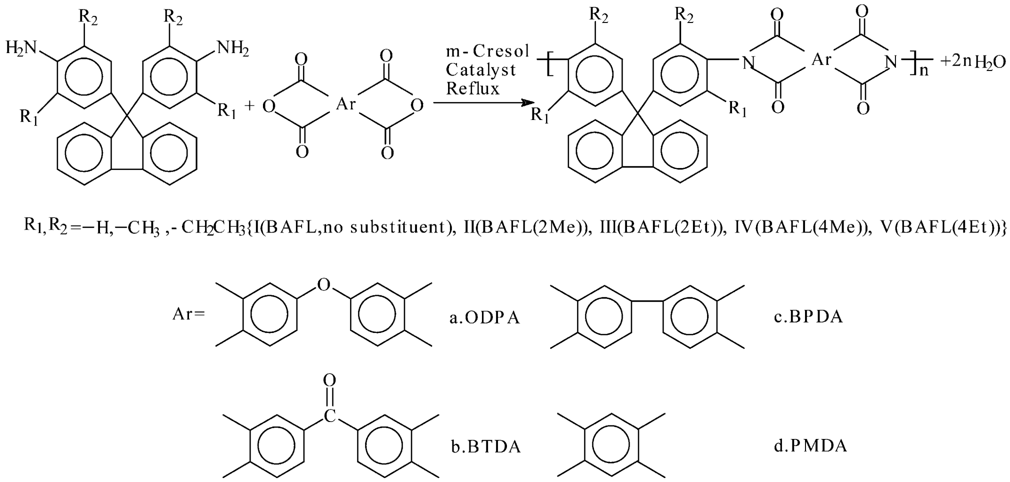

Fig. 1. Synthetic route of cardo polyimides.

IR (KBr) 3481, 3396, 1621 (NH_2) cm^{-1}. ^1H NMR ($CDCl_3$): δ 11.1 (m, 8H, –CH_2–), 2.4 (m, 12H, –CH_3), 3.5 (m, 4H, NH_2), 6.5–7.8 (m, 12H).

Anal. Calcd for $C_{33}H_{36}N_2$: C, 86.08%; H, 7.83%; N, 6.09%. Found: C, 85.79%; H, 7.68%; N, 6.01%.

2.3. Polyimide synthesis [23–25]

A typical polymerization procedure is as follows (Fig. 1). Equivalent molar diamine and dianhydride was dissolved in dried *m*-cresol in 250 ml four-necked flask fitted with a nitrogen inlet, a thermometer, a condenser and a mechanical stirrer. The reactive mixture was refluxed under nitrogen atmosphere for 5 h, 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/2 h and 200 °C/24 h.

2.4. Measurements

IR spectra were recorded on a Nicolet 460, ^1H NMR spectra were obtained at 500 MHz using a Bruker Vance DSX-500 in $CDCl_3$ with tetramethylsilane as an internal standard. Elemental analysis was performed on a Vario EL III. Inherent viscosity measurements were made with 0.5% (w/v) solution of polymers in DMAc at 25 ± 0.1 °C using an Ubbelhode viscometer. Number average molecular weights (M_n) and weight-average molecular weights (M_w) by gel permeation chromatography (GPC) using a Waters 2414 instrument. The thermogravimetriy analyses (TGA) were made with Perkin–Elmer 7 Series Thermal Analysis system. Experiments were carried out under air and under N_2 atmosphere at a heating rate of 10 °C/min. Dynamic mechanical analysis (DMA) were obtained using a Netzsch DMA242. Melting point was measured by WRS-1B digital melting point apparatus. Computer simulation used SYBYL Molecular modeling from TRIPOS, Inc. (versions 6.9).

3. Result and discussion

3.1. Synthesis of polyimides

Polyimides Ia–Ic, IIa–IId, IIIa–IIId, IVa–IVd, Va were synthesized by one step 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. However, the polyimide Id was insoluble in hot *m*-cresol, and was prepared by two-step method and chemical imidization. Intrinsic viscosity in DMAc of the polyimides ranged from 0.31 to 0.92 dl/g and M_ns varied from 19,000 to 52,000 (Table 1). Particularly, it is found that M_n of polyimides based on BAFL(2Me) and BAFL(2Et) is higher than other polyimides. It could be contributed to the high activity of BAFL(2Me) and BAFL(2Et) owing to the electron donating of alkyl group. The activity of cardo diamine is influenced by introduction of *ortho* alkyl substituted group. As we know, alkyl group could increase the activity due to its electron donating effect and super conjugated effect, meanwhile, could decrease its activity of diamine due to steric hindrance effect. Therefore, the activity of BAFL(2Me) and BAFL(2Et) are higher than that of BAFL(4Me) and BAFL(4Et). BAFL(4Me) and BAFL(4Et) have four *ortho* substituted groups, the influence of steric hindrance effect is great, so the activity of diamines is lower, specially, low molecular weight of polyimides were obtained for BAFL(4Et).

Table 1
Molecular weight and viscosity data for THF soluble polyimides

Code	Polymer	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	η[a] (dl/g)
Ia	BAFL–ODPA	2.1	3.2	0.33
Ib	BAFL–BTDA	1.9	2.9	0.31
Ic	BAFL–BPDA	–[b]	–	0.89[c]
Id	BAFL–PMDA	–	–	–
IIa	BAFL(2Me)–ODPA	4.0	6.2	0.55
IIb	BAFL(2Me)–BTDA	4.9	8.7	0.59
IIc	BAFL(2Me)–BPDA	5.2	9.2	0.92[c]
IId	BAFL(2Me)–PMDA	7.3	15.6	1.00
IIIa	BAFL(2Et)–ODPA	4.4	7.0	0.50
IIIb	BAFL(2Et)–BTDA	5.6	9.9	0.61
IIIc	BAFL(2Et)–BPDA	5.9	11.1	0.85
IIId	BAFL(2Et)–PMDA	4.5	9.3	0.66
IVa	BAFL(4Me)–ODPA	2.2	3.5	0.34
IVb	BAFL(4Me)–BTDA	2.7	4.7	0.40
IVc	BAFL(4Me)–BPDA	3.2	5.7	0.58[c]
IVd	BAFL(4Me)–PMDA	–	–	–
Va	BAFL(4Et)–ODPA	0.63	1.2	–

[a] Intrinsic viscosities measured in DMAc at 25 °C.

[b] Insoluble in THF.

[c] Intrinsic viscosities measured in NMP at 25 °C because of insoluble in DMAc.

Table 2
Solubility of polyimides

Polyimide	NMP	DMAc	*m*-Cresol	$CHCl_3$	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	S	S	S	S	S
BAFL(2Et)–ODPA	S	S	S	S	S
BAFL(2Et)–BTDA	S	S	S	S	S
BAFL(2Et)–BPDA	S	S	S	S	S
BAFL(2Et)–PMDA	S	S	S	S	S
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
BAFL(4Et)–ODPA	S	S	S	S	S

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

3.2. Organo-solublity

As shown in Table 2, most of cardo polyimides being prepared from fluorenyl cardo diamines and ODPA, BTDA, BPDA and 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 fluorenyl cardo diamine can significantly improve the solubility of cardo polyimides in organic solvents. For example, BAFL(2Me)–PMDA can dissolve in NMP, DMAc, *m*-cresol, $CHCl_3$ and THF, BAFL(4Me)–PMDA can also dissolve in hot *m*-cresol, NMP and chloroform. BAFL(2Me)–BPDA is insoluble in DMAc, while BAFL(2Et)–BPDA is soluble, it can be attributed to the bigger size of ethyl substituent than that of methyl substituent. The bigger substituents make the polyimide more noncoplanar structure than that of smaller substituent by bond rotation.

Furthermore, Table 2 displays that solubility of fluorenyl cardo polyimides in organic solvents was related to the number of introducing alkyl substituents on fluorenyl cardo diamines. Cardo polyimides based on BAFL(2Me) and BAFL(2Et) have the best solubility due to the noncoplanar structure of imide unit, even polyimides based on PMDA (BAFL–PMDA(2Me) and BAFL–PMDA(2Et)) can also dissolve in organic solvents. However, it was found that the further increase of the number of *ortho* alkyl substituents on BAFL did not improve the solubility of the polyimides.

To discuss the relationship between solubility and alkyl substituents on cardo diamine, the bond rotation angle ω between between imide ring and phenylene ring was obtaind by computer modeling It is shown that dihedral angle ω is least in cardo polyimides based on BAFL, the dihedral angle ω increase with the number of substituents on BAFL, while the dihedral angle ω' between phenylene ring and fluorenyl ring changes slightly. The chemical structure and bond rotation angle of five fluorenyl cardo diamines are shown in Fig. 2 and Table 3. The introducing substitute groups result in an increase in the dihedral angle ω between imide ring and phenylene ring. The coplanar structure is broken because the bond rotation weakens the conjugation of main chain, therefore, the introduction nocoplanar structure improve the solubility of these polyimides. Moreover, the dihedral angle ω of the polyimides based on BAFL(4Me) and BAFL(4Et) is larger than that based on BAFL(2Me) and BAFL(2Et), but the solubility of the former is less than that of the later. It suggests probably that the solubility of cardo polyimides also related to the dihedral angle ω' between phenylene ring and fluorenyl ring except dihedral angle ω

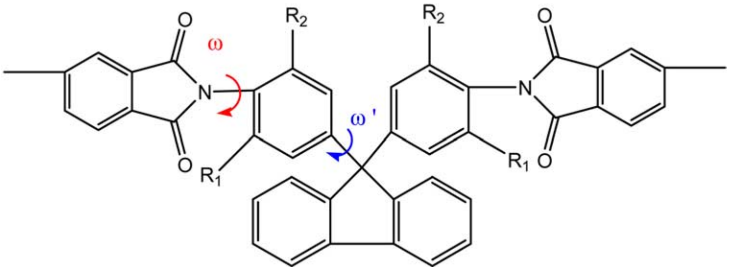

Fig. 2. Schematic diagram of bond rotation of cardo polyimides.

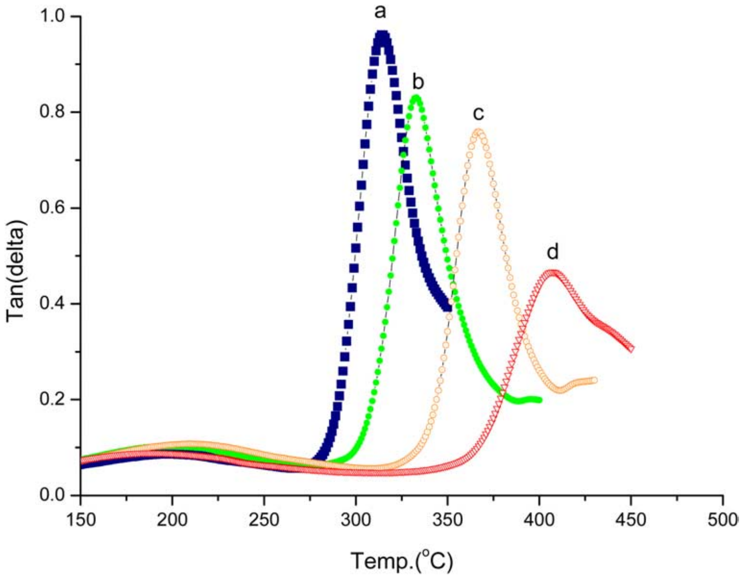

Fig. 3. Dynamic mechanical spectra for cardo polyimides of BAFL(2Et) at 5.0 Hz. (a) BAFL(2Et)–ODPA; (b) BAFL(2Et)–BTDA; (c) BAFL(2Et)–BPDA; (d) BAFL(2Et)–PMDA.

(Table 3). The cardo polyimides 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 imide ring and phenylene ring and weakening extend of the conjugation of main chain.

3.3. T_g and thermo-oxidative stability

The T_g value of ODPA-type cardo polyimdes measured by using a Netzsch DMA242 at 5 Hz. T_g of polyimides based on ODPA decrease with the number of alkyl substituents on fluorenyl cardo diamine (BAFL (373 °C) > BAFL(2Me) (364 °C)–BAFL(4Me) (367 °C)), and with increase of the size of alkyl substituents (BAFL(2Me) (364 °C) > BAFL(2Et) (314 °C)). In addition, as shown in Table 3 and Fig. 3, T_g of the polyimides based on BAFL(2Et) increase with rigid increase of dianhydrides (PMDA (407 °C) > BPDA (366 °C) > BTDA (332 °C) > ODPA (314 °C)) The results demonstrate further coplanar of PI chain is distorted with the increase of the number of alkyl substituent on cardo diamines.

Moreover, 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 under air and under nitrogen (Table 4). All polyimides show good thermal and thermo-oxidative stability, powder samples of theses polyimides undergo 5% weight loss between 433 and 562 °C in air 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.

4. Conclusion

The article studies that the effects of the number and size of introducing alkyl substituents on fluorenyl cardo diamines on solubility and thermal properties of cardo polyimies. Intrinsic viscosity in DMAc of the polyimides ranged from 0.31 to 0.92 dl/g. The solubility in organic solvents and thermal properties of fluorenyl cardo polyimides was related to the number and size of introducing alkyl substituents on fluorenyl cardo diamines. Incorporation of *ortho* alkyl substituents resulted in the descend of thermal stability, but the 5% weight loss temperature still exceed 400 °C. T_g of polyimides based on ODPA decrease with the number and size of alkyl substituents on fluorenyl cardo diamine. T_g of the polyimides based on BAFL(2Et) increase with rigid increase of dianhydrides (PMDA > BPDA > BTDA > ODPA).The results indicate that The

Table 3
Bond rotation degree of cardo polyimides

Diamine	ω	ω'
BAFL ($R_1=R_2=H$)	47.32	74.89
BAFL(2Me) ($R_1=H$, $R_2=CH_3$)	58.88	77.64
BAFL(2Et) ($R_1=H$, $R_2=CH_2CH_3$)	71.28	76.24
BAFL(4Me) ($R_1=CH_3$, $R_2=CH_3$)	76.58	73.66
BAFL(4Et) ($R_1=CH_2CH_3$, $R_2=CH_2CH_3$)	87.33	75.33

Table 4
T_g and thermal stability of polyimides

Polyimide	TGA weight loss (°C)						T_g (°C)
	5%		10%		15%		
	Air	N_2	Air	N_2	Air	N_2	
BAFL–ODPA	451	571	541	590	567	608	373
BAFL–BTDA	522	564	561	586	574	603	–
BAFL–BPDA	562	590	588	607	597	622	–
BAFL–PMDA	553	595	580	618	590	638	–
BAFL(2Me)–ODPA	483	543	514	561	537	586	364
BAFL(2Me)–BTDA	470	540	509	566	535	586	–
BAFL(2Me)–BPDA	476	576	519	594	532	610	–
BAFL(2Me)–PMDA	487	563	508	580	525	594	–
BAFL(2Et)–ODPA	433	514	479	540	517	570	314
BAFL(2Et)–BTDA	446	508	492	550	524	586	332
BAFL(2Et)–BPDA	461	543	492	561	517	578	366
BAFL(2Et)–PMDA	455	523	481	543	505	561	407
BAFL(4Me)–ODPA	459	494	480	531	497	554	367
BAFL(4Me)–BTDA	454	534	480	567	498	591	–
BAFL(4Me)–BPDA	466	531	487	567	503	592	–
BAFL(4Me)–PMDA	529	560	564	581	579	604	–

incorporation noncoplanar structure led by the introducing alkyl substituents on fluorenyl cardo diamine can improve the solubility of cardo polyimides in organic solvents without sacrificing thermal properties.

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