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Synthesis and Characterization of Soluble Cardo Poly(ester-imide)s Derived from 9,9-Bis[4-(3,4-dicarboxybenzoyloxy)phenyl]fluorene

Zhiqiang Hu, Chunhua Zhang, and Shanjun Li

ABSTRACT

A novel fluorenyl cardo dianhydride-9,9-bis[4-(3,4-dicarboxybenzoyloxy)phenyl]fluorene (BDPF) was synthesized and characterized. A series of fluorenyl cardo poly(ester-imide)s (FCPEIs) were prepared by the polycondensation of BDPF with m-phenylene diamine, 4,4'-oxydianiline (4,4'-ODA), 3,4'-oxydianiline (3,4'-ODA), 2,2-bis[4-(4-amino-phenoxy)phenyl]propane, 2,2-bis[4-(4-amino-phenoxy)phenyl]hexafluoropropane, and 1,6-hexamethylenediamine. Most of the FCPEIs exhibited excellent solubility in common organic solvents such as 1,2-dichlorobenzene (o-DCB), chloroform, tetrahydrofuran, N,N-dimethylacetamide (DMAc), dimethyl sulfoxide, N-methyl-2-pyrrolidinone, etc. Intrinsic viscosities of FCPEIs in DMAc, for instance, ranged from 0.29–0.52 dL/g. The glass transition temperature of these polymers was between 199°C and 283°C by differential scanning calorimetry, and the 5% weight loss temperature of all polymers exceeded 400°C in air.

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cardo polymers; fluorenyl polymers; polyimides; poly(ester-imide)s; solubility; thermal properties

Introduction

Polyimides are well known as high-performance polymers for their excellent heat resistance, electrical insulating properties, and mechanical characteristics, so these are widely used in the fields of electrical materials, adhesives, and composite fiber and as film materials.[1–3] However, these are generally insoluble and infusible in their fully imidized form, leading to processing difficulties; in addition, the process using a poly(amic acid) intermediate has several inherent problems such as emission of volatile byproducts (e.g. H₂O), storage instability, etc. To overcome these problems, much research effort has been focused on the synthesis of soluble and processable polyimides in fully imidized form without deterioration of their own excellent properties.[4–12]

Poly(ester-imide)s (PEIs) are a class of thermally stable polymers having a wide use, mainly in the electrical industry. Generally, PEIs have been divided into two species: partly aromatic PEIs, and wholly aromatic PEIs. Partly aromatic PEIs generally have the properties of liquid crystals with a low $T_g$ of about 100–150°C because of the aliphatic structure in their
main chains. Aromatic PEIs have a high $T_g (>200^\circ C)$ but are generally insoluble in organic solvents.

Polymers containing at least one part of the repeating unit that incorporates a cyclic side group have become the subject of many investigations. These polymers have been termed as cardo polymers from the Latin “cardo” (a loop), since such groups can be considered as loops in the backbone of a macromolecule.\textsuperscript{[13]} The polymers used here are termed as fluorenyl cardo polymers, containing the fluorenyl structure in the backbone (Scheme 1). The introduction of fluorenyl “cardo” groups into polymers, such as polyimides,\textsuperscript{[13–19]} polyamides,\textsuperscript{[20,21]} polyquinolines,\textsuperscript{[22]} etc., can endow them with specific properties, such as excellent heat resistance and excellent solubility.

In our previous paper, we described the successful preparation of a series of polyimides, poly(amide-imide)s and bismaleimides\textsuperscript{[23–25]} containing fluorenyl cardo structure. The results showed that these polymers exhibited excellent solubility in common organic solvents, and high thermal stability. In the present study, our objective was to investigate the synthesis and properties of cardo PEIs derived from 9,9-bis[4-(3,4-dicarboxybenzoyloxy)phenyl]fluorene (BDPF). A series of fluorenyl cardo poly(ester-imide)s (FCPEIs) were prepared by polycondensation of BDPF with m-phenylene diamine (m-PDA), 4,4’-oxydianiline (ODA), 3,4’-ODA, 2,2-bis[4-(4-amino-phenoxy)phenyl]propane (BAPP), 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (BDAF), and 1,6-hexamethylenediamine (HAD). The solubility and thermal properties of FCPEIs were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

**Experimental**

**Reagents and solvents**

The reagents and their sources were as follows: 9-Fluorenone (Shanghai Coking and Chemical Corp., China); phenol, HAD, thionyl chloride, methanesulfonic acid, acetic anhydride, methylene dichloride, 1,2-dichlorobenzene (o-DCB), tetrahydrofuran (THF), dimethylformamide (DMF), and N-methyl-2-pyrrolidinone (NMP) (Shanghai Lingfeng Chemical Reagent Co. Ltd., China); N,N-dimethylacetamide (DMAc) (Zhejiang Jiangshan Chemical Co. Ltd., China); dimethyl sulfoxide (DMSO); and chloroform (CHCl$_3$) (Shanghai Yonghua

![Scheme 1. Schematic diagrams of the different cardo groups.](image-url)
Special Reagent Factory, China); 3-Mercapto propionic acid and trimellitic anhydride (Lancaster Synthesis Inc., UK); 3,4'-ODA, 4,4'-ODA BAPP, and BDAF (Shanghai Research Institute of Synthetic Resins, China); m-PDA (Sinopharm Chemical Reagent Co. Ltd., China); Pyridine (Shanghai Chemical Reagent Co. Ltd., China); triethyl amine (Shanghai Yongsheng Reagent Factory, China). DMAc, NMP, pyridine, and triethyl amine were dried in CaH₂ for two days, and distilled before use.

Measurements

Fourier transform–infrared (FT-IR) spectra were recorded on a Nicolet 460 spectrometer (Nicolet, USA) using KBr pellets. ¹H-NMR and ¹³C-NMR spectra were obtained at 500 MHz using a Bruker Avance DRX-400 (Bruker BioSpin GmbH, Germany) in DMSO-d₆ with tetramethylsilane as an internal standard. Elemental analysis was performed on a Vario EL III (Elementar Analysensysteme GmbH, Germany). Inherent viscosity measurements were made with 0.5% (w/v) solutions of the polymers in NMP at 25±0.1°C using an Ubbelhode viscometer. The TGA was made with a TGA-Q50 (TA Instruments, USA). Experiments were carried out in air and under N₂ atmosphere at a heating rate of 10°C/min. The glass transition temperatures were measured using a DSC Q10 (TA Instruments, USA) in N₂ atmosphere at a heating rate of 20°C/min. Melting points were measured by a WRS-1B digital melting point apparatus (Shanghai Precision & Scientific Instrument Co. Ltd., China) or the DSC Q10.

Monomer syntheses

9,9-bis(4-hydroxyphenyl)fluorene (BHPF). In a 250-mL four-necked flask fitted with nitrogen inlet, thermometer, condenser, and mechanical stirrer, 37.7-g phenol, 0.25-g 3-mercapto propionic acid, 36.0-g 9-fluorenone, and 150-mL methylene dichloride were added; then 15-mL methanesulfonic acid was added drop-wise at ambient temperature. The mixture was refluxed under nitrogen atmosphere for 5 h; then it was cooled to ambient temperature, crystallized, filtered, and washed with methylene dichloride. The obtained product was dried in vacuo to yield a white powder (45.0 g, yield = 65%, and mp = 225.5–225.6°C by WRS-1B digital melting point apparatus) (Scheme 2).

The FT-IR spectrum of BHPF (Fig. 1) exhibited characteristic absorption peaks: 3479 cm⁻¹ (the phenolic hydroxyl group stretching vibration), 3031 cm⁻¹ (phenyl rings, C-H

Scheme 2. Synthesis route of 9,9-bis(4-hydroxyphenyl)fluorene (BHPF).
stretching vibration), 1608 cm\(^{-1}\), 1508 cm\(^{-1}\), and 1444 cm\(^{-1}\) (phenyl rings, C-C, and C=C stretching vibration).

\(^1\)H-Nuclear Magnetic Resonance (NMR) and \(^{13}\)C-NMR spectra of BHPF are presented in Figs. 2 and 3. The spectra were consistent with its structure.

**Figure 1.** FT-IR spectra of BHPF.

**Figure 2.** \(^1\)H-NMR spectrum of BHPF.
1H-NMR.DMSO-d6: δ 9.32 ppm m.2H.OH. δ 6.64−7.89 ppm m.16H aromatic ring (xH, x represents the number of H in the same chemical environment in the groups listed in BHPF).

13C-NMR.DMSO-d6: δ 156.54 ppm C11. δ 152.37 ppm C1. δ 140.02 ppm C6. δ 136.70 ppm C8. δ 129.38 ppm C9. δ 128.33 ppm C3. δ 157.96 ppm C4. δ 126.62 ppm C2. δ 121.00 ppm C5. δ 115.54 ppm C10. δ 64.32 ppm C7 (Cy, y represents the serial number of carbon atoms in the chemical formula).

The results of elemental analysis were in good agreement with the calculated values. Analysis calculated for C25H20O2: C 85.69%; H 5.18%. Found: C 85.67%; H 5.30%.

9,9-bis[4-(3,4-dicarboxybenzoyloxy)phenyl]fluorene (BDPF). 28.8-g trimellitic anhydride and excess thionyl chloride were added to a 250-mL four-necked flask fitted with nitrogen inlet, thermometer, condenser, and mechanical stirrer. The mixture was refluxed under nitrogen atmosphere until the solution was clear and transparent; then the excess thionyl chloride was separated by distillation in vacuum and 20-mL anhydrous THF was added. A solution of 26.3-g (0.075 mol) BHPF in THF/pyridine (v/v D1:1) was added drop-wise with constant stirring, and the mixture was refluxed for 2 h. After being cooled, the product was filtered, washed with water, and dried in vacuo. The crude BDPF product was obtained as a yellowish powder (50.2 g, yield = 95.8%) (Scheme 3).

For purification, the aforementioned crude product was dissolved in 160-mL acetic anhydride and refluxed for 3 h. Then the solution was cooled to ambient temperature, crystallized, filtered, and washed with toluene. An off-white solid was obtained and dried in vacuo to yield a purified BDPF product (29.4 g, yield based on BHPF = 56.1%, mp = 292°C by DSC).
The FT-IR spectrum of BDPF (Fig. 4) indicated absorption peaks at 1846 and 1782 cm\(^{-1}\), assigned to the C=O stretch of dianhydride, and 1736 cm\(^{-1}\) assigned to the C=O stretch of ester bonds.

\(^1\)H-NMR and \(^{13}\)C-NMR spectra of BDPF are presented in Figs. 5 and 6. The spectra were consistent with its structure.

**Scheme 3.** Synthesis route of 9,9-bis[4-(3,4-dicarboxybenzoxyloxy)phenyl]fluorene (BDPF).

The FT-IR spectrum of BDPF (Fig. 4) indicated absorption peaks at 1846 and 1782 cm\(^{-1}\), assigned to the C=O stretch of dianhydride, and 1736 cm\(^{-1}\) assigned to the C=O stretch of ester bonds.

\(^1\)H-NMR and \(^{13}\)C-NMR spectra of BDPF are presented in Figs. 5 and 6. The spectra were consistent with its structure.
Figure 5. $^1$H-NMR spectrum of BDPF.

Figure 6. $^{13}$C-NMR spectrum of BDPF.
The $^1$H-NMR. DMSO-d$_6$: δ 7.03–8.57 ppm m. 22H aromatic ring.

$^{13}$C-NMR. DMSO-d$_6$: δ 162.68 ppm C12. δ 162.33 ppm C20. δ 162.23 ppm C19. δ 150.11 ppm C11. δ 149.10 ppm C8. δ 143.46 ppm C1. δ 139.47 ppm C6. δ 136.89 ppm C18. δ 135.68 ppm C13. δ 135.24 ppm C16. δ 131.99 ppm C15. δ 128.75 ppm C9. δ 128.05 ppm

Scheme 4. Schematic diagram of fluorenyl poly (ester-imide)s.
C14. δ 127.92 ppm C17. δ 125.97 ppm C2. δ 125.81 ppm C5. δ 125.71 ppm C3. δ 121.60 ppm C10. δ 120.65 ppm C4. δ 64.13 ppm C7.

The results of elemental analysis were in good agreement with the calculated values. Analysis calculated for C_{43}H_{22}O_{10}: C 73.92%; H 3.17%. Found C 73.62%; H 3.45%.

**Synthesis of PEIs**

A typical two-step polymerization procedure is as follows. In a 250-mL four-necked flask fitted with nitrogen inlet, thermometer, condenser, and mechanical stirrer with an ice bath, one of the chosen diamines was dissolved in dried DMAc and an equivalent molar amount of dianhydride BDPF was added. The reactive mixture was stirred for 8 h. Then a mixture of acetic anhydride/triethyl amine (v/v = 4:1) was added and stirred for 2 h at an ambient temperature and at 80°C for 1 h. Then the reaction solution was precipitated in methanol in a high-speed blender. The product was filtered and washed with excess methanol and water, and dried in a vacuum oven at 80°C for 2 h and at 200°C for 12 h. The PEI powder was obtained (Scheme 4).

**Result and discussion**

**Synthesis of PEIs**

All PEIs were prepared by the two-step method described above, followed by chemical imidization. The intrinsic viscosity in DMAc of poly(ester amic acid)s ranged from 0.29 to 0.52 dL/g (Table 1). However, these values of intrinsic viscosities of all poly(ester amic acid)s were low. This, we suggest, should be attributed to the influence of steric hindrance caused by rigid and bulky bisphenylfluorene moieties and the ester bonds of BDPF, so the activity of dianhydride was lower, and only low molecular weights of FCPEIs were obtained.

The FCPEIs were characterized by FT-IR. The FT-IR spectrum of PESI-2, as an example, is presented in Fig. 7. The PESI-2 exhibited the following characteristic absorptions of a PEI: 1781 cm\(^{-1}\) (C=O asymmetric stretch, imide carbonyl group), 1720 cm\(^{-1}\) (C=O symmetric stretch, imide carbonyl group), 1499 cm\(^{-1}\) (phenyl rings, C-C stretching vibration), 1375 cm\(^{-1}\) (C-N stretch, imide group), 1239 cm\(^{-1}\) (aromatic ether stretching), and 722 cm\(^{-1}\) (imide ring deformation).

**Table 1.** The organo-solubility of poly(ester-imide)s\(^{a}\).

<table>
<thead>
<tr>
<th>Code</th>
<th>Poly(ester-imide)</th>
<th>(\eta) (dL/g)</th>
<th>o-DCB</th>
<th>DMAc</th>
<th>THF</th>
<th>CHCl(_3)</th>
<th>DMSO</th>
<th>NMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>PESI-1</td>
<td>MDA-BDPF</td>
<td>0.29</td>
<td>G</td>
<td>S</td>
<td>G</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>PESI-2</td>
<td>4,4'-ODA-BDPF</td>
<td>0.43</td>
<td>G</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>PESI-3</td>
<td>3,4'-ODA-BDPF</td>
<td>0.44</td>
<td>G</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>PESI-4</td>
<td>HAD-BDPF</td>
<td>0.31</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>PESI-5</td>
<td>BAPP-BDPF</td>
<td>0.49</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>PESI-6</td>
<td>BDAF-BDPF</td>
<td>0.52</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
</tbody>
</table>

\(^{a}\)Solubility at room temperature: S, soluble at room temperature; Ins, insoluble; S', soluble on heating; G, gel.
Organo-solubility

As shown in Table 1, most of the FCPEIs prepared from BDPF and m-PDA, 4,4′-ODA, 3,4′-ODA, BAPP, BDAF, and HAD exhibited excellent solubility in common organic solvents such as CHCl₃, DMAc, DMSO, and NMP, with some of these soluble only in hot solvent (S°). For instance, m-PDA–BDPF could dissolve only in hot NMP, DMAc, CHCl₃, and DMSO.

The solubilities, we suggest, can be attributed to the rigid bulky, bisphenylfluorene moiety of BDPF dianhydride, leading to a decrease in intermolecular forces. Moreover, the flexible linkages of diamines, such as ether bonds (—O—) and isopropyl groups (—C(CH₃)₂—), could lead to the weakening of conjugation effect of main chain, increase in the conformational entropy of the molecule, and lead to the reduction of free energy of solution. Thus, as a result, the solubility of FCPEIs was improved significantly compared with a typical PEI.

\( T_g \) and thermal stability

The glass transition temperatures of FCPEIs were evaluated by DSC (Table 2). Fig. 8 shows the heating scan of PESI-6 as an example. The \( T_g \) of FCPEIs increased with

Table 2. \( T_g \) of the poly (ester-imide)s.

<table>
<thead>
<tr>
<th>Code</th>
<th>Polymer</th>
<th>( T_g ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PESI-1</td>
<td>MDA–BDPF</td>
<td>283</td>
</tr>
<tr>
<td>PESI-2</td>
<td>4,4′-ODA–BDPF</td>
<td>257</td>
</tr>
<tr>
<td>PESI-3</td>
<td>3,4′-ODA–BDPF</td>
<td>247</td>
</tr>
<tr>
<td>PESI-4</td>
<td>HAD–BDPF</td>
<td>199</td>
</tr>
<tr>
<td>PESI-6</td>
<td>BAPP–BDPF</td>
<td>237</td>
</tr>
<tr>
<td>PESI-7</td>
<td>BDAF–BDPF</td>
<td>254</td>
</tr>
</tbody>
</table>

Figure 7. FT-IR spectra of PESI-2 (4,4′-ODA–BDPF).
increase in the rigidity of diamines: HAD–BDPF (199°C) < BAPP–BDPF (237°C) < 3,4'-ODA–BDPF (247°C) < BDAF–BDPF (254°C) < 4,4'-ODA–BDPF (257°C) < m-PDA–BDPF (283°C). Furthermore, the PEIs based on fluorinated diamines had a higher $T_g$, such as BDAF–BDPF (254°C) > BAPP–BDPF (237°C). The reason could be attributed to the form of hydrogen bonds and the steric hindrance induced by the larger size of –CF₃ than –CH₃; this led to increase of $T_g$ in the fluorinated polyimide.

To characterize thermal stability, the onset temperatures corresponding to 5, 10, and 15% weight loss of FCPEIs were measured by TGA in air and under nitrogen (Fig. 9 and Table 3). All FCPEIs showed good thermal stability; powder samples of these PEIs underwent 5% weight loss between 416°C and 431°C, 10% weight loss between 442°C...
and 472°C, and 15% weight loss between 453°C and 494°C in air at a heating rate of 10°C/min. The char yield of FCPEIs was 19–50% at 800°C under nitrogen atmosphere. Since aromatic rings are the basic building blocks from which char is formed, the char yield increased with the aromatic content of FCPEIs: HAD–BDPF (19%) < BAPP–BDPF (35%) < 3,4′-ODA–BDPF (42%) < 4,4′-ODA–BDPF (43%) < m-PDA–BDPF (48%) < BDAF–BDPF (50%). Therefore, the higher the aromatic content of a polymer, the higher the char yield.[26] Furthermore, BDAF–BDPF had a higher char yield than BAPP–BDPF; this can be ascribed to the presence of high fluorine contents in the polymer backbone. The temperatures of maximum rates of decomposition (\(T_{\text{max}}\)) of FCPEIs were reached in a range of 475–489°C in air and 480–536°C in nitrogen. In conclusion, all FCPEIs exhibited good thermal stability.

### Conclusions

The present work reports the synthesis and characterization of a novel fluorenyl cardo dihydrachloride containing ester bond – BDPF and its PEIs (FCPEIs). Intrinsic viscosities of FCPEIs in DMAC ranged from 0.29 to 0.52 dL/g. Most of the FCPEIs exhibited excellent solubility in common organic solvents such as o-DCB, CHCl₃, THF, DMAc, DMSO, and NMP. These FCPEIs also exhibited good thermal stability, the glass transition temperature was between 199°C and 283°C by DSC, and 5% weight loss temperature of all polymers exceeded 400°C in air. We suggest that these could be used for high temperature resistant coatings, impregnating resins, and adhesives.

### References


