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A simple attempt to change the solubility of polyimide by physical inclusion with β-cyclodextrin and its derivatives

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Abstract

Inclusion complex (IC) compounds such as 4,4′-oxydianiline (ODA) with β-cyclodextrin (β-CD), heptakis(2,6-di-*O*-methyl)-β-cyclodextrin (DM-β-CD) or heptakis(2,3,6-tri-*O*-methyl)-β-cyclodextrin (TM-β-CD) were newly prepared by a simple solution method using water or methanol. These ICs were reacted with 4,4′-hexafluoroisopropylidenediphthalic anhydride (6FDA) in *N*,*N*-dimethylacetamide (DMAc) to form a polyamic acid intermediate, which imidized thermally to novel pseudopolyimiderotaxanes (M_w: 8400–31 100, contents of β-CDs: 4.3–11.2%). Polymers were characterized by FTIR, ^{1}H NMR, and XRD. They showed good solubility in tetrahydrofuran, chloroform, methylene chloride, as well as polar aprotic solvents. All the β-CDs in the polymers were degraded under 380°C and polyimide moieties were stable up to 490°C in a N_2 stream. © 2001 Published by Elsevier Science Ltd.

Keywords: Polyimide; Beta-cyclodextrin; Inclusion complex

1. Introduction

Polyimides exhibit excellent electrical and high-temperature mechanical properties [1,2]. However, polyimides are often insoluble and intractable in their fully imidized form, thus presenting serious processing difficulties. Meanwhile, the inclusion of polymers by cyclodextrins (CDs) is of growing interest as it renders the possibility to change the physical and chemical properties of the polymers without the necessity of the analogous reaction. In general, there are two methods to obtain inclusion compounds of polymers: threading CD rings onto polymer chains and polymerization of the CD inclusion compound of a monomer [3–8]. In this article, as part of increasing the solubility and processability of intractable polyimides, we first introduced the ICs as a monomer for inclusion polyimide, and reported the preparation and characterization of novel pseudopolyimiderotaxanes containing β-CDs in the main chain, which started from ICs as monomers.

2. Experimental

2.1. Materials

All reagents were purchased from Aldrich, Acros, and TCI. 4,4′-Oxydianiline (ODA) and 4,4′-hexafluoroisopropylindenediphthalic anhydride (6FDA) were purified by vacuum sublimation. β-CD was used after recrystallization from water. Heptakis(2,6-di-*O*-methyl)-β-cyclodextrin (DM-β-CD) and heptakis(2,3,6-tri-*O*-methyl)-β-cyclodextrin (TM-β-CD) were prepared according to the literature methods [9,10]. *N*,*N*-Dimethylacetamide (DMAc) was refluxed with BaO, then distilled under reduced pressure, and stored over molecular sieves.

2.2. Instruments

^{1}H NMR spectra were obtained using a Varian VXR-300. IR spectra were recorded on a Nicolet Avatar 360 FTIR ESP. Melting points were measured on an Electrothermal IA9100 digital melting point apparatus. Gel permeation chromatography (GPC) was carried out using a Waters GPC system (a 600S controller, a 616 pump, a 717 Plus autosampler and a 410 differential refractometer), Ultrastyragel columns in series (Styragel HR-4, HR-3, HR-1 and HR-5E) and tetrahydrofuran (THF) as an eluent. Wide angle X-ray power diffractograms (WAXS) were measured with a Siemens S-5000 diffractometer with CuK_α (radiation wavelength: 1.54 Å, temperature of data collection: room temperature, collection range 2θ: 10–100). Thermogravimetric analysis (TGA) was conducted at a heating rate of 10°C min^{-1} and a nitrogen flow rate of 100 ml min^{-1} with a TA instrument SDT 2960 Simultaneous DSC–TGA.

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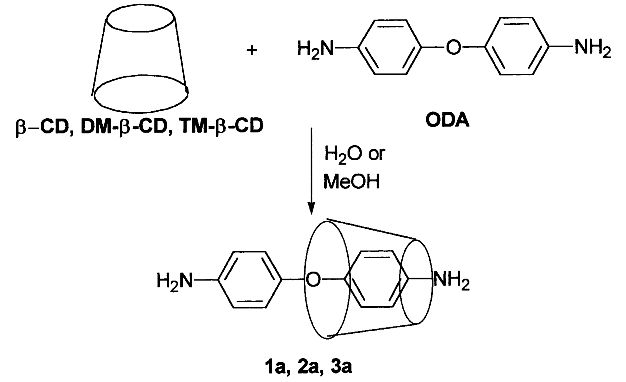


Scheme 1.

2.3. Complexation of ODA with β-CD **1a**

To a solution of β-CD (11.35 g, 10 mmol) in hot water, ODA (2 g, 10 mmol) was added portionwise with stirring. The reaction mixture was refluxed for 6 h and mixed vigorously with a mechanical stirrer. The insoluble ODA went into a solution, and the complex was crystallized on cooling to 4°C. The crystal was filtered, washed with cold water and then dried in vacuum. Yield: 90%, mp: >300°C, ^{1}H NMR (D_2O, ppm), ODA: $\delta = 6.62$ and 6.55 (d, 4H, aromatic CH), β-CD: $\delta = 4.85$ (d, 7H, H-1). IR (KBr, cm^{-1}), ODA: 1654 and 1503 (aromatic C=C), and 1227 (C–N).

2.4. Complexation of ODA with DM-β-CD **2a** and TM-β-CD **3a**

ODA (1 g, 5 mmol) and DM-β-CD (6.65 g, 5 mmol) or TM-β-CD (7.15 g, 5 mmol) was dissolved in MeOH at room temperature. After sufficient stirring, a transparent solution changed to a light brown or yellow solution. At that time, thin-layer chromatography analysis showed lower R_f value than ODA. The methanol was slowly removed in a warm cabinet to obtain a brown or a yellow solid as quantitative yield.

Compound **2a**. Mp: >300°C, ^{1}H NMR (D_2O, ppm), ODA: $\delta = 6.60$ and 6.51 (d, 4H, aromatic CH), DM-β-CD: $\delta = 4.99$ (d, 7H, H-1); 3.36 (s, 21H, OCH_3-2); 3.14 (s, 21H, OCH_3-6). IR (KBr, cm^{-1}), guest molecule: 1638 and 1503 (aromatic C=C), and 827 (aromatic C–H).

Compound **3a**. Mp: 70°C, ^{1}H NMR (D_2O, ppm), ODA: $\delta = 6.61$ (s, 8H, aromatic CH), TM-β-CD: $\delta = 5.10$ (d, 7H, H-1); 3.33 (s, 21H, OCH_3-2); 3.33 (s, 21H, OCH_3-3); 3.20 (s, 21H, OCH_3-6). IR (KBr, cm^{-1}), ODA: 3436 and 3357 (N–H), 1637 and 1502 (aromatic C=C), and 825 (aromatic C–H).

2.5. Synthesis of inclusion polyimides (pseudopolyimiderotaxanes)

A flame dried 25 ml round-bottom reaction flask fitted with a stirrer and a N_2 gas purge was used. To a solution of distilled DMAc (5 ml), **1a** (0.8 g, 0.5 mmol) was added. As soon as **1a** dissolved, 6FDA (0.22 g, 0.5 mmol) was added to a solution and effective stirring at room temperature for 2 h. A yellow viscous solution was heated and kept to 200°C for 6 h. Water was removed using a Dean-stark trap. The resulting viscous solution was poured into excess methanol and filtered. The precipitated polymer was washed several times with methanol and hot water, and then dried at 100°C for 24 h in a vacuum.

2.5.1. Polyimide **1** (**1a** + 6FDA)

^{1}H NMR (DMSO-d_6, ppm): $\delta = 8.20$ and 7.97 (d,2H, aromatic C–H), 7.76 (s, 2H, aromatic C–H), 7.50 and 7.25 (d, 4H, aromatic C–H); IR (KBr, cm^{-1}), polyimide: 1791, 1737 and 723 (C=O) 1379 (C–N) and 1500 (aromatic C=C).

2.5.2. Polyimide **2** (**2a** + 6FDA)

^{1}H NMR ($CDCl_3$, ppm): $\delta = 8.06$ and 7.90 (d,2H, aromatic C–H), 7.94 (s, 2H, aromatic C–H), 7.43 and 7.21 (d, 4H, aromatic C–H); IR (KBr, cm^{-1}), polyimide: 1791, 1729 and 727 (C=O) 1379 (C–N) and 1500 (aromatic C=C).

2.5.3. Polyimide **3** (**3a** + 6FDA)

^{1}H NMR ($CDCl_3$, ppm): $\delta = 8.06$ and 7.90 (d,2H, aromatic C–H), 7.94 (s, 2H, aromatic C–H), 7.43 and 7.21 (d, 4H, aromatic C–H); IR (KBr, cm^{-1}), polyimide: 1791, 1733 and 723 (C=O) 1376 (C–N) and 1500 (aromatic C=C).

3. Results and discussion

As shown in Scheme 1, inclusion compound (**1a**) of ODA and β-CD was obtained by dissolving ODA in hot water. Other inclusion compounds (**2a** and **3a**) from ODA and modified β-CDs were isolated by removing the methanol after the identification of product by thin layer chromatograph (TLC). This TLC analysis showed lower R_f value than ODA. All the ICs were soluble in water, which indicated the complexation of the hydrophobic guest molecule by β-CD and its derivatives. In addition, **2a** and **3a** were soluble in chloroform, but ODA was not soluble. All the ICs were characterized by physical property, ^{1}H NMR and IR.

In ^{1}H NMR spectra (Figs. 1 and 2) of β-CD and ICs, most protons of ICs were shifted to upfield slightly: the signal of **1a** ($\delta_{3C\text{–}H} = 3.66$, $\delta_{5C\text{–}H} = 3.65$) and the signal of **2a** ($\delta_{3C\text{–}H} = 3.42$, $\delta_{5C\text{–}H} = 3.48$) were shifted from the corresponding signals of CDs ($\delta_{3C\text{–}H} = 3.78$, $\delta_{5C\text{–}H} = 3.68$ for β-CD, $\delta_{3C\text{–}H} = 3.80$, $\delta_{5C\text{–}H} = 3.73$ for DM-β-CD) [11–13]. It is interesting that 3C–H and 5C–H were oriented towards the interior of the cavity, and therefore, changes in its signal provide information on the inclusion process.

As shown in Scheme 2, the polymerization of ICs and 6FDA was performed by a thermal solution method to avoid side reactions followed by chemical imidization in the presence of host molecules. These compounds were

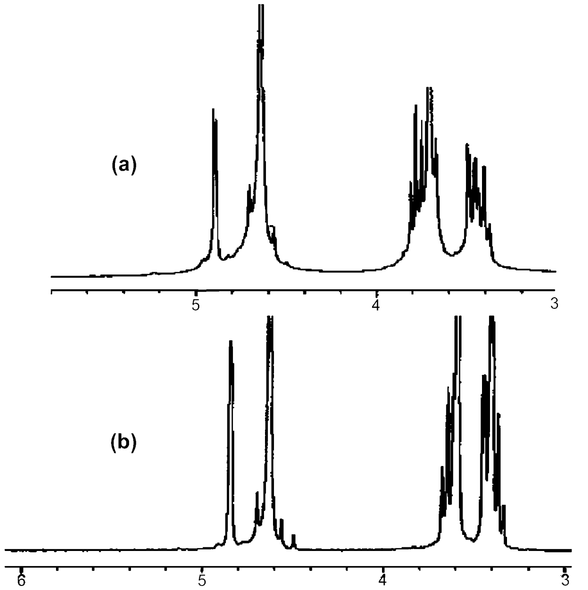


Fig. 1. ^{1}H NMR spectra of (a) β-CD and (b) **1a** in D_2O.

characterized by ^{1}H NMR and FTIR (Figs. 3 and 4). Both β-CD-free polyimide (CD-free PI) and inclusion polyimides possessed the characteristic imide absorptions in the regions 715–725 (bending of C=O), 1375–1379 (C–N stretch), 1724–1740 (symmetrical stretch, C=O) and 1787–1791 cm^{-1} (asymmetrical stretch, C=O) [1,2], 3200–3650 and about 2930–2980 cm^{-1} in the spectra of the inclusion polyimides were due to OH and aliphatic CH absorptions.

Table 1 showed the results of pseudopolyimiderotaxanes. Weight-average molecular weights of inclusion polyimides were in the range of 8400–31 100, which were restricted by a thermal solution imidization method [14]. Low yield and molecular weight of polyimide **2** were caused by low solubility of **2a** at room temperature in DMAc. But the film formation of all the inclusion polyimides on the glass substrates was very good. After thermal decomposition of polyimiderotaxanes, the film of showed transparent and good conditions.

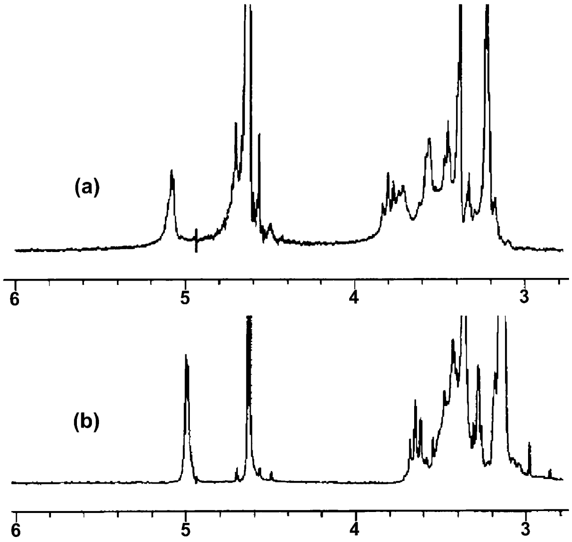
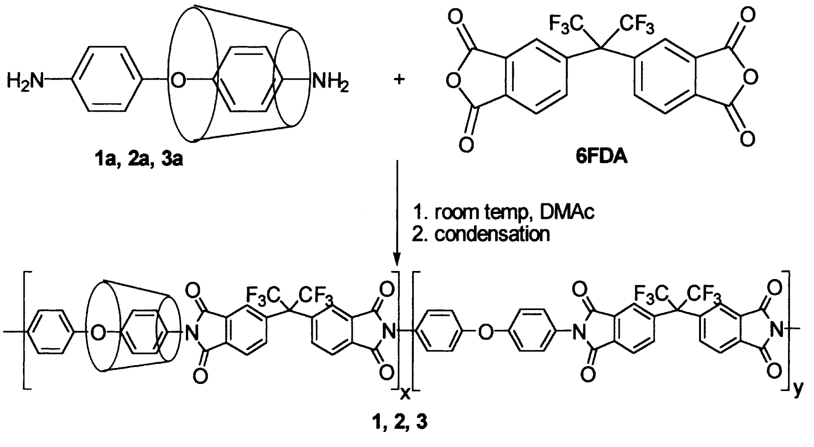


Fig. 2. ^{1}H NMR spectra of (a) DM-β-CD and (b) **1b** in D_2O.

The ^{1}H NMR spectra (Fig. 3) of CD-free PI and **1** contained the signals of both CD and polyimide chain. The β-CDs contents (mol%) in the inclusion polyimides were determined by the ^{1}H NMR analysis of two protons at 7.25 ppm in a 6FDA group and seven protons at 4.85 ppm in C(1) of β-CD. The β-CDs wt% of polyimides were also determined (TGA curve in Fig. 2). It showed the thermal behaviors of the polyimides (CD-free PI, **1**, **2**, and **3**) in which first decomposed curve were in charge of β-CDs wt% of polyimides. Therefore, we could convert from the β-CD mol% to β-CD wt% of the β-CD inclusion polyimide using Eq. (1), as follows:

$$\beta\text{-CDs (wt\% in polyimide)} = \left(M_{\beta\text{-}CDs} \times \frac{X}{100}\right) \times \left[M_{\beta\text{-}CDs} \times \frac{X}{100} + (M_{ODA} + M_{6FDA} - 2M_{H_2O})\right]^{-1} \times 100 \qquad (1)$$



Scheme 2.

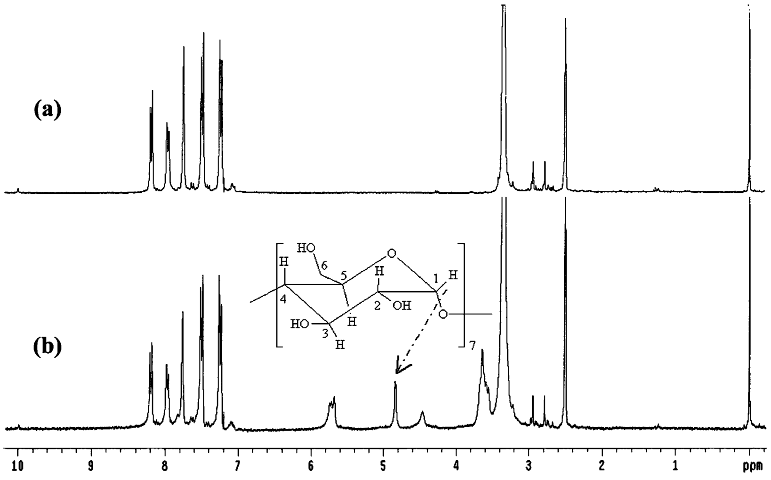


Fig. 3. ^{1}H NMR spectrum of (a) CD-free PI and (b) **1** in DMSO-d_6.

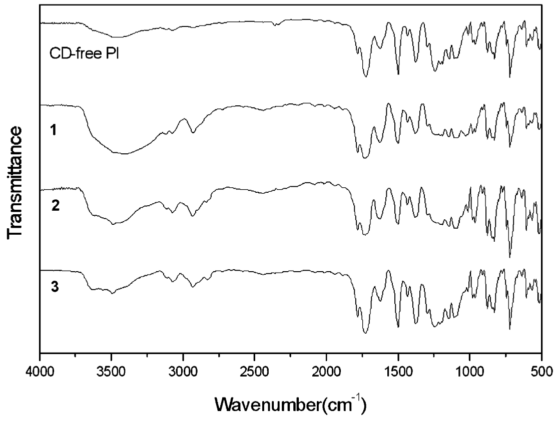


Fig. 4. IR spectra of the CD-free polyimide and pseudopolyimiderotaxanes.

where X is β-CDs mol% in NMR of polyimide, $M_{\beta\text{-CD}}$, M_{ODA}, M_{6FDA} and M_{H_2O} are molecular weight of each molecule, respectively. All the inclusion polyimides showed low CD contents of 4.3–11.2 mol%. It is considered as the result of the exclusion of the guest molecule (ODA) during the polymerization reaction. Hence, the protons of the aromatic portion in the polymer were little affected by the β-CD because of low contents of β-CD (11.2 mol%). The signals of β-CD portion in the polyimide **1** were broadened in comparison with the monomer **1a**, which were general in the inclusion polymers [15–18]. As represented in Table 1, the results converted from β-CDs mol% to β-CDs wt%, were almost same with the weight loss of β-CDs wt% of TGA curves. Meanwhile, the polymerization of ODA and 6FDA was performed in the presence of β-CD and its derivatives in polar aprotic solvents; there was no β-CD inclusion in the resulting polyimides.

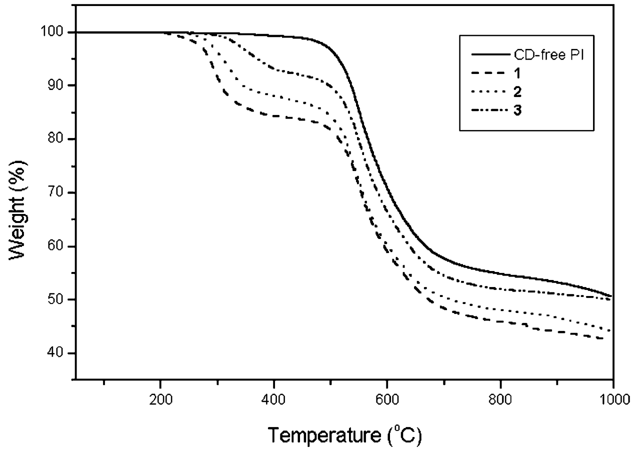


Fig. 5. TGA thermograms of CD-free PI and pseudopolyimiderotaxanes.

The thermal behaviors of the polymers under a nitrogen stream were shown in Fig. 5. As expected (the β-CDs were decomposed through 240–400°C) [19], β-CD, DM-β-CD and TM-β-CD began to decompose at 220, 245 and 280°C, respectively. All of the β-CD portions in the inclusion polyimides were degraded under 400°C and polyimide moieties were stable up to 490°C in a N_2 stream. Decomposition of CD-free PI started at 497°C, same as other inclusion polyimides. It is interesting to note that the residue (char) of **3** is 50.1 wt%, which is little different from the CD-free PI (50.7%), though it contains 9.1 wt% of TM-β-CD. The amount of thermally stable residue depends on the substituents of β-CD [19].

The solubility of the pseudopolyimiderotaxanes was qualitatively studied and the results are listed in Table 2. β-CD-free PI was soluble at room temperature in polar aprotic solvents such as NMP, DMSO, DMF and insoluble in common organic solvents. But polyimides **1**, **2** and **3** were soluble in THF, dioxane as well as polar aprotic solvents, particularly polyimides **2** and **3** were even soluble in chloroform, dichloromethane at room temperature. These solubility changes in the inclusion polyimides were due to the presence of β-CDs having good solubility [7,8,20]. In accordance with these results, DM-β-CD and TM-β-CD

Table 1
Results of pseudoimiderotaxanes

Inclusion polyimide	Type	Yield (%)	β-CD content[a] (calculated wt% from NMR data)	β-CD content (founded wt% from TGA curve)	M_n ($\times 10^{-3}$)	M_w ($\times 10^{-3}$)[b]	Film formation[c]
1	β-CD	90	11.2 (17.28)	16.07	9.2	24.6	Good
2	DM-β-CD	71	7.8 (14.57)	12.44	4.0	8.4	Good
3	TM-β-CD	88	4.3 (9.1)	7.92	12.0	31.1	Good

[a] Mol% of the β-CD, DM-β-CD and TM-β-CD contained in the polyimides, respectively.

[b] Determined by GPC using THF as the eluent and polystyrene standards.

[c] All the films were spin-coated in the solution state using by a volatile solvent, THF.

Table 2
Solubilities of pseudoimiderotaxanes. Samples: powdery pseudoimiderotaxanes. + + : soluble, − − : insoluble at room temperature. Abbreviations: NMP, *N*-methyl-2-pyrrolidone; DMSO, dimethylsulfoxide; DMF, dimethylformamide; THF, tetrahydrofuran; EA, ethyl acetate

	NMP	DMSO	DMF	*m*-Cresol	THF	Dioxane	$CHCl_3$	CH_2Cl_2	Acetone	EA
CD-free PI	++	++	++	++	−−	−−	−−	−−	−−	−−
1	++	++	++	++	++	++	−−	−−	−−	−−
2	++	++	++	++	++	++	++	++	−−	−−
3	++	++	++	++	++	++	++	++	−−	−−

were more soluble than β-CD in organic solvents such as chloroform and dichloromethane. Therefore, introduction of β-CD into the polyimide chain to form pseudopolyrotaxanes would alter their solubility, which can overcome the drawback of wholly aromatic polyimides.

XRD data of inclusion polyimides showed no difference from that of CD-free PI (Fig. 6). The polyimides revealed a recognizable peak at around $2\theta = 17.5°$. Therefore, it was considered that low contents of β-CDs in the inclusion polyimides neither help the separation of the polymer chain–chain interactions nor form crystalline complex with polymers [21–24].

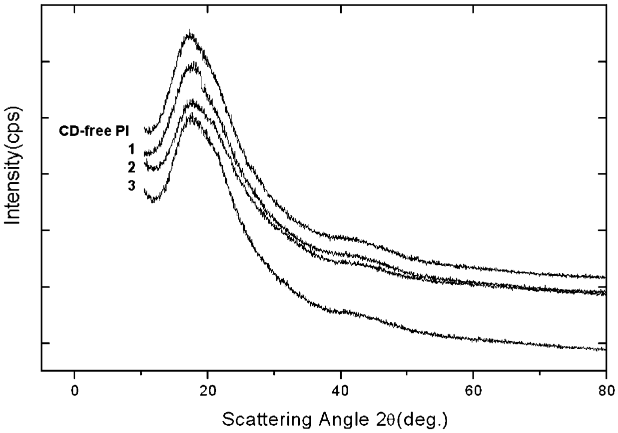


Fig. 6. Wide angle X-ray diffraction diagram of CD-free PI and pseudo-polyimiderotaxanes.

4. Conclusions

A specific inclusion compound (ICs) of ODA and β-CD, DM-β-CD and TM-β-CD were designed in order to develop aromatic polyimides with the desirable organo-solubility. The polymerization of ICs with aromatic dianhydride was carried out in DMAc. As a result, novel inclusion polyimides were prepared and these showed a good thermal stability and a high solubility to common solvents, THF, chloroform, methylene chlroride as well as polar aprotic solvents. These solubility changes in the inclusion polyimides were due to the presence of cyclodextrins having good solubility. Therefore, introduction of cyclodextrins into the polyimide chain to form pseudopolyrotaxanes would alter their solubility, which could overcome the drawback of wholly aromatic polyimides.

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