# Synthesis and Characterization of Novel Aromatic Cyclic Oligoimides

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## Introduction

The formation of cyclic oligomers has been extensively studied, both theoretically and experimentally.[1] Recent reports have described the preparation of cyclic oligomers derived from aromatic carbonates[2], esters[3], amides[4], ether-ketones[5] and ether-imide[6] in fair to excellent yields. The synthesis of some of the materials mentioned above relied on the propensity of spirobiindane containing monomers to cause formation of cyclics. This paper describes the synthesis and characterization of novel cyclic oligoimides derived from mellophanic dianhydride(MPDA). In addition, cyclic dimer derived from MPDA and 4, 4'-Methylenedianiline (MDA) and cyclic trimer from MPDA and 4, 4'-oxydianiline (ODA) were separated by solvent extraction and characterized. Single crystal X-ray diffraction of cyclic dimer from MPDA/MDA reveals that it is complexed with 2 mole chloroform.

## Experimental

**Materials.** N,N-dimethylacetamide (DMAc) was purified by distillation over phosphorus pentoxide and stored over 4-Å molecular sieves. Acetic anhydride and triethlylamine (TEA) were used after distillation in the presence of magnesium and calcium hydride, respectively. Mellophanic dianhydride (MPDA) was synthesized by following a method described in the literature[7]. 4, 4'-Methylenedianiline(MDA) and 4, 4'-oxydianiline (ODA) were obtained from Shanghai Institute of Synthetic Resin and were purified by recrystallization from ethanol and vacuum sublimation prior to use, respectively.

**Instrumentation.** IR spectra were determined with a Bio-Rad Digilab Division

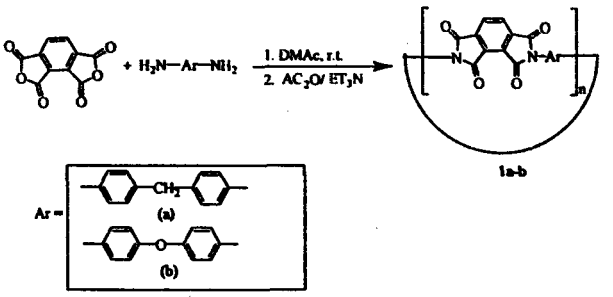
FTS-80 spectrometer. $^1H$ NMR spectra were recorded on a Varian Unity-400 spectrometer at 400 MHz, with tetramethylsilane (TMS) as an internal standard. Melting points were determined on a RY-1 melting point apparatus and were uncorrected unless otherwise stated. MALDI-TOF mass spectra were recorded on a LDI-1700 mass spectrometer with the instrument set in the positive reflection mode. 1,8,9-Anthracemetriol (dithranol) was used as the matrix and dimethyl sulfoxide (DMSO) was used as the solvent. Single crystal X-ray diffraction data were collected at 293(2) K on a Rigaku R-AXIS RAPID diffractometer ($\lambda$ = 0.710 73 Å ). The structure was solved by the direct method using the SHELXTL system and refined by a full matrix least squares on $F^2$ using all reflections.

**Synthesis of Cyclic oligomers and cyclic dimer of 1a.** The following experimental is a representative example of the procedure: A 500ml three neck round-bottom flask was charged with 120ml DMAc. A solution of MPDA (0.8581g, 3.9340mmol) in DMAc (40 ml ) and a solution of MDA (0.7800g, 3.9340mmol) in DMAc (40 ml ) were delivered into the mechanically stirred flask in an equimolar fashion over an 2h period. After the addition, the mixture was stirred for another 2h to ensure complete reaction. Then acetic anhydride ( 5ml ) and triethylamine (3ml ) were added. The temperature was gradually increased to 50℃. After 24h, the reaction solution was concentrated to 20ml under reduced pressure and poured into distilled water. The precipitate was filtered off, washed thoroughly with water and dried. After extraction in a Soxhlet extractor with 250ml chloroform, the solution was concentrated to 10ml and added to vigorously stirred methanol (100ml). The desired cyclic oligomers precipitated as a yellow solid in the methanol. The precipitate was filtered and dried in a vacuum oven (120℃) for 12h. The yield of cyclic oligomers was 0.40g (27% yield). The yellow cyclic dimer was obtained by recrystallization from chloroform (0.08g, 4% of total yield); IR (KBr): 1776, 1724, 1364, 724 $cm^{-1}$. A suitable crystal for X-ray diffraction for cyclic dimer of **1a** was obtained from chloroform solution by slow diffusion of hexane vaper.

**Synthesis of Cyclic oligomers and cyclic trimer of 1b.** The same procedure was used as for **1a**, but with monomer MPDA (0.9388g, 0.43mmol) and ODA (0.8618g, 0.43mmol) as starting materials. The yield of cyclic oligomers was 0.30g (18% yield). The yellow cyclic trimer was obtained by recrystallization from chloroform (0.05g, 3% of total yield); IR (KBr): 1775, 1726, 1369, 724 $cm^{-1}$.

## Results and Discussions

When two step solution polymerization of MPDA with ODA or MDA was carried out in DMAc at room temperature, precipitations occurred during amic acid stage indicating the formation of oligomers. So all the polymerizations were carried out to obtain oligoimides under pseudo high dilution conditions (**Scheme 1**).




**Scheme 1.** Synthesis of Cyclic oligomers

Cyclic oligomers **1a** and **1b** were then obtained by solvent extraction with chloroform in about 20% yield. MALDI-TOF-MS spectra indicated that oligomers **1a** and **1b** consist principally of macrocycles with repeating units of 2-7. A typical spectrum of MALDI of **1b** is shown in **Figure 1**. By using 1,8,9-dithranol as matrix and DMSO as solvent, a relatively clean positive spectrum with excellent signal to noise ratio was obtained for the reaction product. The MALDI-TOF-MS spectrum gives the correct protonated molecular ion peaks for the desired cyclic oligomers from dimer (n=2) to pentamer (n=5). The expanded scale of the MS spectrum of **1b** shows three signals for each oligomer. For example, signals for the trimer are located at 1147, 1169 and 1185 Da. The signal at 1147 Da corresponds to the protonated molecular ion peak, that at 1169 Da is due to the adduct of the trimer with a sodium cation, while at 1185 Da is due to the adduct of the trimer with a potassium cation. Furthermore, according to the relative abundance, cyclic trimer is the main product in **Figure 1 (i)**, however, after the polyamic acid solutions were stayed at room temperature for two weeks, the main product is cyclic dimer (**Figure 1 (ii)**). It is indicated that the tendency to form cyclic amide acid of trimer is stronger than that of dimer at the beginning, and the former is slowly transformed to the latter at room temperature. It is obvious a equilibrium between cyclic amide acid of trimer and that of dimer is existed, and the former is the product of kinetic control, the latter is of thermodynamic control.

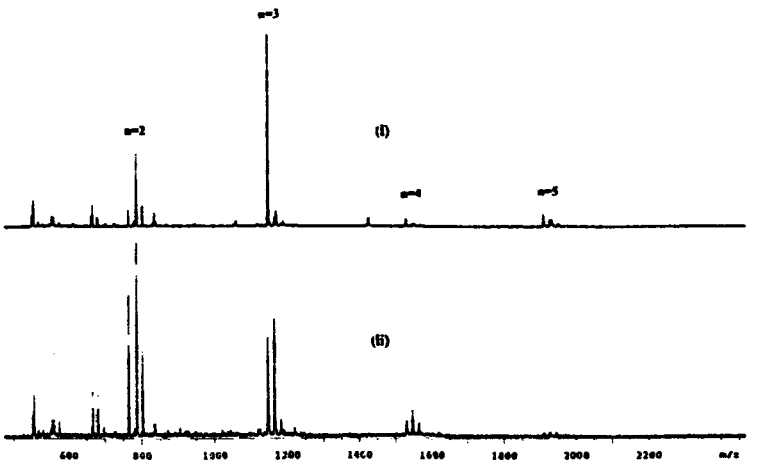



**Figure 1.** MALDI-TOF-MS spectra for cyclic oligomers **1b** obtained from MPDA/ODA: (i) chemical cyclodehydration was conducted immediately after the formation of the poly(amic) acid solutions; (ii) chemical cyclodehydration was conducted after the poly(amic) acid solutions were stayed at room temperature for two weeks.

Cyclic dimer derived from MPDA/MDA and cyclic trimer from MPDA/ODA were obtained by solvent extraction and recrystallization with chloroform from oligomers **1a** and **1b**, respectively. Their cyclic nature was unambiguously confirmed by MALDI-TOF-MS, NMR and FT-IR. From IR spectra, the characteristic absorption boands of the imide ring appeared near 1780 (asym C=O stretching), 1720 (sym C=O stretching), 1380 (C-N stretching), and 725 $cm^{-1}$ (imide ring deformation), while the characteristic amide peak at about 1665 $cm^{-1}$ had disappeared, indicating cyclic oligomers had been fully imidized. The $^1H$ NMR and MALDI-TOF-MS spectra of cyclic dimer of **1a** are illustrated in **Figure 2** and **Figure 3**, respectively. **Figure 3** shows the correct three signals for cyclic dimer of **1a** at 761, 783 and 799 Da, corresponding to the protonated molecular ion peak, the adduct of the dimer with a sodium cation, the adduct of the dimer with a potassium cation, respectively. The $^1H$ NMR and MALDI-TOF-MS spectra of cyclic trimer of **1b** are illustrated in **Figure 4** and **Figure 5**, respectively. **Figure 5** shows the correct signal for cyclic trimer of **1b** at 1146 Da, corresponding to the molecular ion peak of the trimer. The $^1H$ NMR spectra in **Figure 2** and **Figure 4** are also consistent with their cyclic structures. To obtain the decisive evidence of the cyclic structure, the single crystal X-ray structure of dimer from MPDA/MDA was determined, as is shown in **Figure 6**. X-ray analysis indicates that the macrocyclic dimer is complexed with 2 mole chloroform.

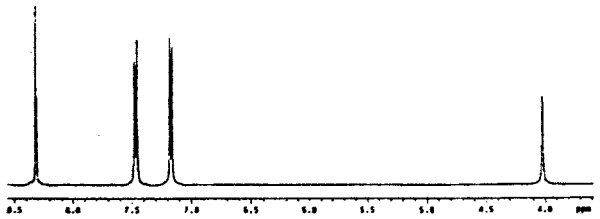


**Figure 2.** $^1H$ NMR spectra (400 MHz) of cyclic dimer of **1a** in DMSO-$d_6$.

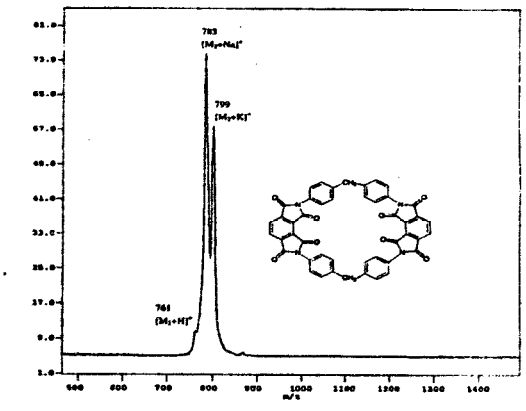



**Figure 3.** MALDI-TOF-MS spectrum for cyclic dimer of **1a**

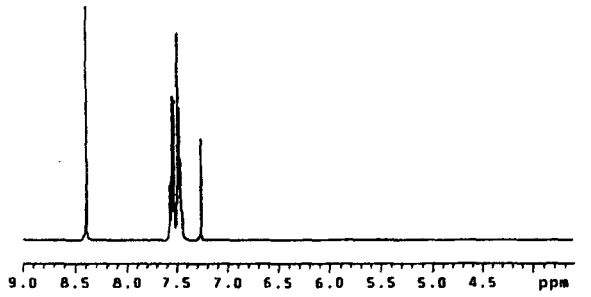



**Figure 4.** $^1H$ NMR spectra (400 MHz) of cyclic dimer of **1b** in $CDCl_3$.

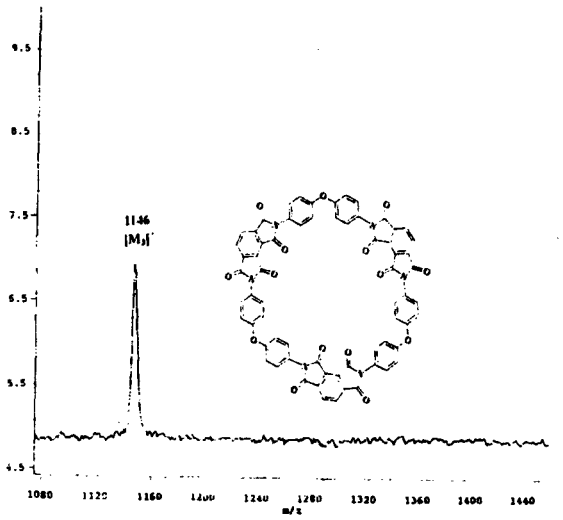



**Figure 5.** MALDI-TOF-MS spectrum for cyclic dimer of **1a**

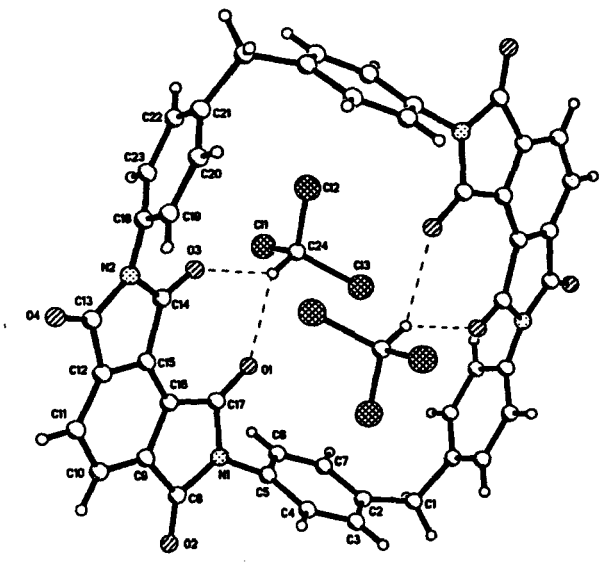


**Figure 6.** The crystal structure of cyclic dimer of **3a** for $C_{46}H_{24}O_8N_4 \cdot 2CHCl_3 \cdot 6H_2O$, showing the intramolecular hydrogen bonds in one dimer ($H_2O$ molecules are omitted for clarity ).

The imidization of cyclic oligoamic acid was run in DMAc using standard chemical techniques. Interestingly, the tendency to form cyclic compounds was so great that even in very concentrated solutions (solid content 20% by weight), some cyclic formation was still observed. The high propensity of the monomer dianhydride to form cyclic oligomers is presumably due to the rigidity of the dianhydride monomer coupled with the orientation angle of the ortho dianhydride functionalities. This structural rigidity and orientation increases the probability of an end-to-end encounter and thereby facilitates cyclic formation.

## Conclusions

Macrocyclic aromatic oligoimides were synthesized by polymerization of mellophanic dianhydride (MPDA) with 4, 4'-Methylenedianiline (MDA) or 4, 4'-oxydianiline (ODA) using standard two-step process under a pseudo-high-dilation condition. Cyclic dimer derived from MPDA and MDA and cyclic trimer from MPDA and ODA were isolated by solvent extraction and characterized. In addition, a equilibrium between cyclic amide acid of trimer from MPDA/ODA and that of dimer is existed, and the former is the product of kinetic control, the latter is of thermodynamic control. The tendency to formation cyclic oligomers for MPDA was also discussed.

## Acknowledgements.

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