Synthesis, Structure, and Ring-Opening Polymerization of Macrocyclic Aromatic Esters: A New Route to High-Performance Polyarylates

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ABSTRACT: A series of macrocyclic arylate dimers have been efficiently synthesized by an interfacial polycondensation of *o*-phthaloyl dichloride with bisphenols. A combination of GPC, FAB MS, and ^{1}H and ^{13}C NMR unambiguously confirmed the cyclic nature. Although single-crystal X-ray analysis of one such macrocycle reveals no severe strain on the cyclic structure, these macrocycles can undergo facile melt polymerization to give high molecular weight polyarylates.

Introduction

Polyarylates constitute an important class of engineering thermoplastics with excellent solvent resistance and thermal stability.[1,2] Linear polyarylates are traditionally obtained by solution polymerization of the phthalic dichloride and bisphenols or by polymerization in the melt (from activated monomers). Neither method is exempt from problems; when the former process is used, the problems derive from the generally low solubility of these polymers, which prevents the attainment of high molecular weights.[1,2] In the melt polymerization, the problems derive from the high melting points of these polymers and especially the very high melt viscosity, which combine to limit the application of these polymers in areas such as fiber impregnation and microscale fabrication. In recent years, the advantages of using cyclic polyarylate oligomers as precursors to high-performance linear polyarylates have been recognized.[3−7] While the yields of cyclic polyarylate oligomers reported by General Electric workers are often quite low. For example, the cyclic bisphenol A isophthalates were obtained in yields from 15% to 65% even in very low final concentrations. Substitution of the para-oriented terephthaloyl moiety for the meta gave even lower yields (<30% when only 10% para was used in synthesis of a mixed macrocycle). Another complication is that linear polyarylate oligomers were produced along with cyclics, and tedious separations were necessary. In our works, *o*-phthaloyl dichloride was employed instead of iso or terephthaloyl dichloride for two considerations: (1) *o*-phthaloyl dichloride may be more reactive than iso or terephthaloyl dichloride, hence a higher dilution condition may be achieved; (2) *o*-phthaloyl dichloride will provide a preferred conformation for cyclization. In this paper, we introduce a series of new macrocyclic arylate dimers, which were exclusively formed or predominantly formed in our procedure. Although single-crystal X-ray analyses of one such macrocycle reveal no severe strain in the cyclic structure, these compounds could undergo molten state polymerization to high molecular weight polyarylates.

Experimental Section

Materials and Instruments. *o*-Phthaloyl dichloride was redistilled before use. Other reagent-grade solvents and chemicals were used without further purification. GPC analyses were performed on a *Shimadzu* LC-4A apparatus equipped with a column of DuPont ZORBAX-PSM-60S, (25 cm × 0.62 cm diameter) and a UV detector using tetrahydrofuran (THF) as the eluent at a flow rate of 0.5 mL/min. The column was calibrated with a mixture of five polystyrene standards. Infrared spectra (KBr pellets and film) were recorded on a BIO-RAD FTS-7 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Varian Unity 400 spectrometer at 400 and 100 MHz, respectively. Samples were dissolved in $CDCl_3$ and chemical shifts were expressed in ppm using TMS as standard. FAB-MS spectra were performed on a VG-QUATTRO mass spectrometer using 3-nitrobenzyl alcohol as a matrix. Melting points were measured using a Mettler hot stage apparatus and a microscope. Single-crystal X-ray structure was determined using data obtained on a SIEMENS P4 4-Circle Diffractometer. The structure was resolved using the SHELXTL PLUS (Release 5.0).

Reactions of *o*-Phthaloyl Dichloride with Bisphenols. Into a 500 mL round-bottom flask equipped with a condenser and a thermometer were placed 250 mL methylene chloride, 70 mL distilled water, and 0.2 g cetyltrimethylammonium bromide. The mixture was preheated to 30 °C and then a 0.15 M methylene chloride solution of *o*-phthaloyl dichloride (50 mL) and a 0.15 M aqueous solution of bisphenol A or 4,4′-isopropylidenebis(2,6-dibromophenol) or phenolphthalein disodium salts (50 mL) in separate syringes were delivered into the mechanically stirred flask in an equimolar fashion over 5 h. The organic phase was separated and washed with distilled water three times and then evaporated to dryness. The reaction of *o*-phthaloyl dichloride with bisphenol A afforded 2.52 g cyclic dimer **3** (94% isolated yield, 100% yield by GPC). The reaction of *o*-phthaloyl dichloride with 4,4′-isopropylidenebis(2,6-dibromophenol) afforded 4.29 g white solid (85% yield) including 3.18 g cyclic dimer **4** (63% isolated yield, 71% yield by GPC). The reaction of *o*-phthaloyl dichloride with phenolphthalein afforded 2.99 g white solid (89% yield) including 2.22 g cyclic dimer **5** (66% isolated yield, 75% yield by GPC).

Cyclic Dimer 3 Based on *o*-Phthaloyl Dichloride and Bisphenol A. Mp: 302−304 °C. MS (FAB): *m/e* 717 (M^{+1}, 100), 702 ($M^{+1}-CH_3$, 70). IR (KBr): 2964.5 ($-CH_3$), 1746.2, 1734.8 (C═O), 1600.9, 1505.7 (aromatic C═C), 1271.0, 1248.4, 1207.1, 1170.6 (COC) cm^{-1}. ^{1}H NMR ($CDCl_3$): 7.97 (m, H_a, J = 5.6Hz), 7.69 (m, H_b, J

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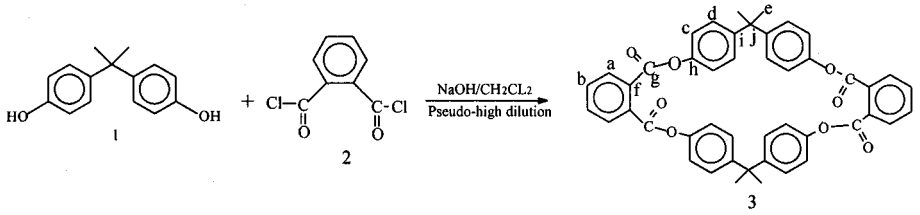
Scheme 1



= 5.6Hz), 7.20 (d, H_d, J = 8.8Hz), 7.08 (d, H_c, J = 8.8Hz), 1.67 (s, CH_3). ^{13}C NMR ($CDCl_3$): 166.01 (carbonyl carbons), 148.58, 148.12, 131.63 (substituted aromatic), 131.70, 129.52, 127.92, 120.82 (unsubstituted aromatic), 42.61(quaternary carbon), 31.04 (methyl groups).

Cyclic Dimer 4 Based on *o*-Phthaloyl Dichloride and 4,4′-Isopropylidenebis(2,6-dibromophenol). Mp: 384−386 °C. MS (FAB): *m/e* 1348 (M^{+1}), 1333 ($M^{+1}-CH_3$). IR (KBr): 2968.3($-CH_3$), 1775.4, 1757.4 (C═O), 1584.2, 1549.7, 1546.0, 1388.8 (aromatic C═C), 1235.1, 1215.6, (COC) cm^{-1}. ^1H NMR ($CDCl_3$): 8.25 (m, H_a, J = 5.6Hz), 7.76 (m, H_b, J = 5.6Hz), 7.34 (s, H_d), 1.68 (s, CH_3). ^{13}C NMR ($CDCl_3$): 162.39 (carbonyl carbons), 149.60, 144.44, 130.88, 117.84 (substituted aromatic), 132.09, 130.97, 130.47 (unsubstituted aromatic), 42.49 (quaternary carbon), 30.10 (methyl groups).

Cyclic Dimer 5 Based on *o*-Phthaloyl Dichloride and Phenolphthalein. Mp: 333.6−335.4 °C. MS (FAB): *m/e* 897(M^{+1}). IR (KBr): 1772.6, 1749.4 (C═O), 1599.1, 1506.2 (aromatic C═C), 1266.4, 1206.3, 1168.0 (COC) cm^{-1}. ^1H NMR ($CDCl_3$): 7.98 (d, 2H), 7.96 (m, 4H), 7.74 (t, 2H), 7.69 (m, 4H), 7.60 (m, 4H), 7.38 (m, 8H), 7.21 (m, 8H). ^{13}C NMR ($CDCl_3$): 169.36, 165.69 (carbonyl carbons), 151.40, 150.82, 138.50, 131.28, 125.35 (substituted aromatic), 134.43, 131.97, 129.66, 129.47, 128.52, 126.17, 124.14, 121.62 (unsubstituted aromatic), 90.69 (quaternary carbons).

Melt Polymerization of Cyclic Dimer 3. Cyclic dimer **3** (2.00 g, 2.79 mmol) and terabutylammonium tetraphenylborate (5 mL of 0.56 mmol solution of methylene chloride) were combined in 10 mL methylene chloride. The methylene chloride was then evaporated and the solid mixture was dried overnight at 100 °C in a vacuum oven. The solid was transferred to a test tube, and polymerization was carried out at 310 °C in a nitrogen atmosphere for 40 min. The resulting polymer had an $\eta_{sp/c}$ of 0.48 dL/g (0.34% in chloroform at 25 °C), and a M_w of 96 000, and a M_n of 51 000. IR (film): 2968.8($-CH_3$), 1765.3−1731.8 (C═O), 1597.6, 1579.3, 1504.5 (aromatic C═C), 1275.0−1160.0 (COC) cm^{-1}. ^{13}C NMR ($CDCl_3$): 165.82 (carbonyl), 148.62, 148.09, 131.68 (substituted aromatic), 131.72, 129.46, 127.87, 120.86 (unsubstituted aromatic), 42.52 (quaternary carbons), 30.93 (methyl groups). The polymerization of cyclic dimer **5** was carried out at 340 °C by similar procedure. The resulting polymer had an $\eta_{sp/c}$ of 0.38 dL/g (0.34% in chloroform at 25 °C), and a M_w of 68 000, and a M_n of 37 000. IR (film): 1775.9−1731.1 (C═O), 1597.3, 1503.5, 1465.4 (aromatic C═C), 1273.0, 1255.8, 1203.0, 1165.4 (COC) cm^{-1}. ^{13}C NMR ($CDCl_3$): 169.36, 165.46 (carbonyls), 151.41, 150.79, 138.39, 131.33, 125.25 (substituted aromatic), 134.51, 131.97, 129.68, 129.55, 128.44, 126.10, 124.12, 121.63 (unsubstituted aromatic), 90.70 (quaternary carbons).

Results and Discussion

Tyuzyo et al. once reported an isolation of cyclic dimer from the crude products obtained by the interfacial polycondensation of *o*-phthaloyl dichloride with bisphenol A.[8] However, when we repeated the experiment, but made use of pseudo-high-dilution principle,[9] evaporation of the organic phase to dryness afforded a white product **3**. (See Scheme 1) Surprisingly, GPC chromatography of the crude product showed a very narrow, single peak suggesting the exclusive formation of a single molecular weight product. The spectroscopic results (FABMS, FTIR, and ^1H and ^{13}C NMR) and finally single-crystal X-ray diffraction analyses demonstrated that the product was cyclic dimer **3**. The single-crystal X-ray structure of compound **3** is shown in Figure 1 and the packing diagram is shown in Figure 2. The phenyl rings in cyclic compound **3** are rigidly planar with very small deviations from the planarity (root mean square deviations from the planarity of the phenyl planes are 0.005, 0.007, and 0.005 Å, respectively). Other possible contributors to the ring strain should be the distortions at the turning points of the molecular polygons, expressed in phenyl−C(═O)−O, (O═)C−O−phenyl bond angles and phenyl−C−phenyl bond angles. However, in cyclic compound **3**, these bond angles are almost equal to the idealized values,[10−12] except the bond angle of $C_{18}-O_4-C_{17}$(═O) varies more than any other from 118.6(3)° of $C_{10}-O_1-C_7$ to 122.0-(3)° (idealized: 118.8° [10]), which is presumably to relieve the ring strain. All these data suggest that cyclic compound **3** was constructed without severe internal strain. Since the creation of the pseudo-high-dilution condition may favor the formation of smaller ring size cyclic oligomers as a result of dilution beyond a critical concentration as suggested by Jacobson and Stockmayer,[13] the strain-free cyclic compound **3** was exclusively formed in the interfacial polycondensation of *o*-phthaloyl dichloride with bisphenol A (final concentration was 0.025 M).

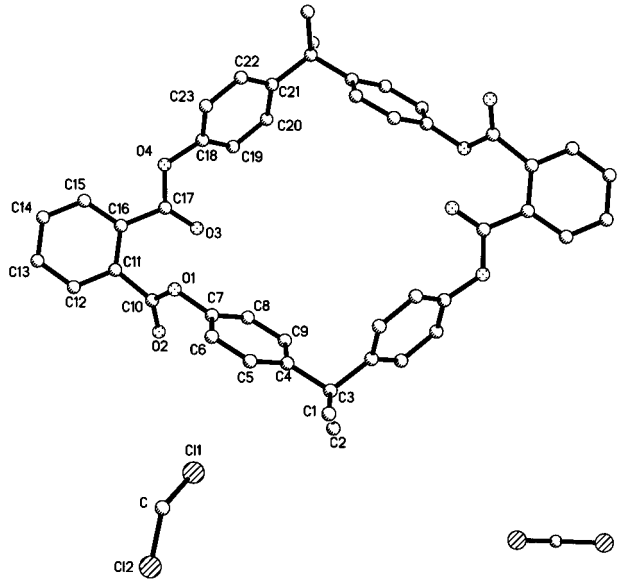


Figure 1. The X-ray structure of cyclic dimer **3**.

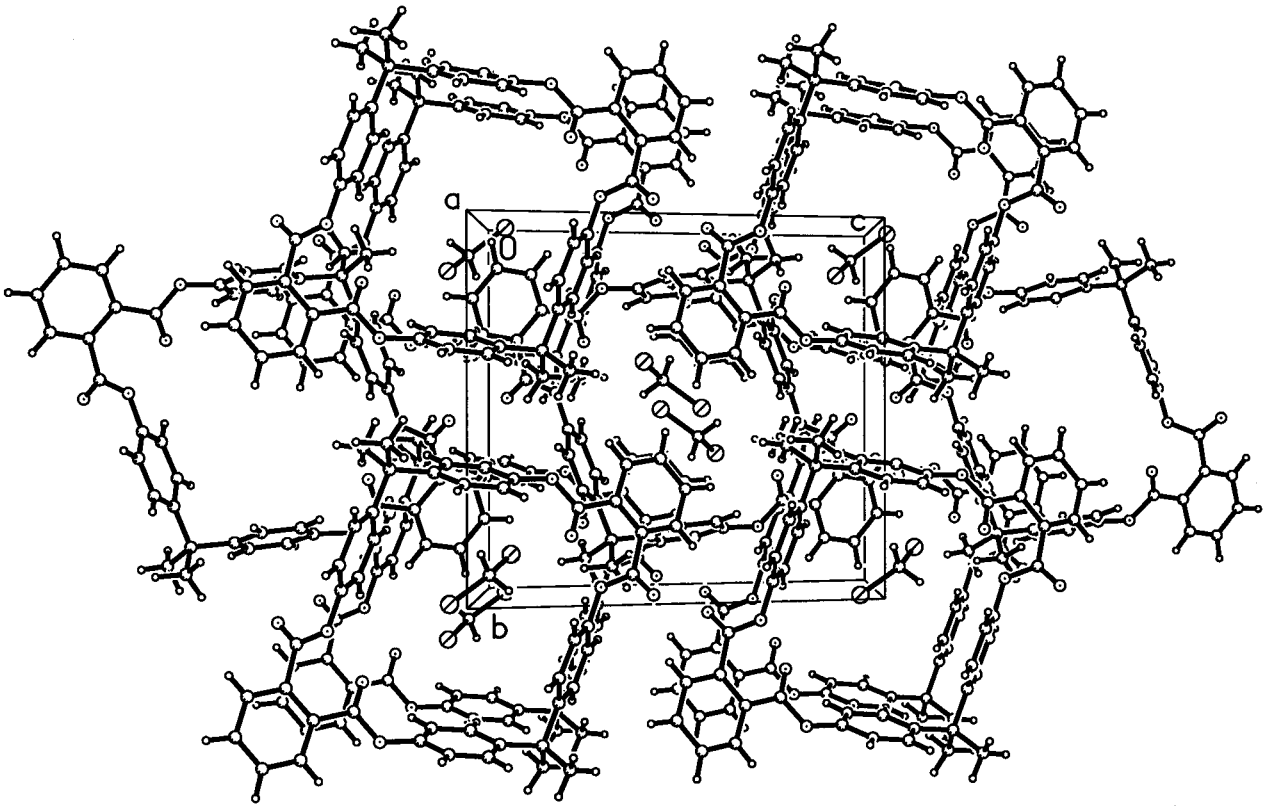
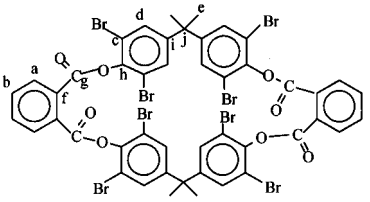


Figure 2. The packing diagram of cyclic dimer **3**.

The cyclic dimer **4** and **5** have also been synthesized in the same conditions, but they were produced as a



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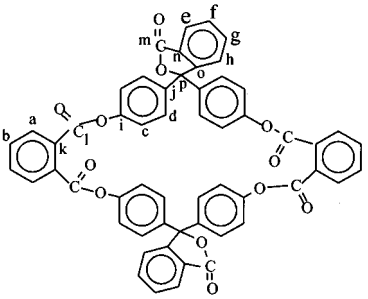

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main product (cyclic dimer made up more than 70% of the crude product determined by GPC) along with a small amount of higher molecular weight cyclics (cyclic trimer and tetramer were observed in FAB−MS spectra) or polymer. Preliminary X-ray data indicated that cyclic dimer **4** is also a less strained macrocycle. The relative insolubility of cyclic dimer **4** and **5** compared with their higher molecular weight cyclics and polymers, allows straightforward isolation of the macrocycles. The crude materials may be purified by recrystallization from methylene chloride or THF. The cyclic dimer **4** was obtained in 63% isolated yield (71% yield by GPC), and cyclic dimer **5** was obtained in 66% isolated yield (75% yield by GPC).

The cyclic compounds prepared can be converted to high molecular weight polymer through ring-opening polymerization via an ester exchange reaction.[5] Melt polymerizations have been performed on cyclic dimer **3** and **5** with 0.1% tetrabutylammonium tetraphenylborate as an initiator. Both compounds underwent molten state polymerization within 40 min at 310 and 340 °C, respectively, to give high molecular weight polymers. Only about 5% cyclics were found in the final product, but chain−chain equilibrium occurred very rapidly leading to average dispersity near 2.0. Cyclic dimer **3** gave polymer with a reduced viscosity of 0.48 dL/g (0.34% in chloroform at 25 °C), and an M_w of 96 000 and an M_n of 51 000. Cyclic compound **5** gave polymer with a reduced viscosity of 0.38 dL/g (0.34% in chloroform at 25 °C), and an M_w of 68 000 and an M_n of 37 000 (by GPC using polystyrene standards). The structures of both polymers have been fully confirmed by IR and ^{13}C NMR, and all are consistent with the corresponding cyclics. A GPC trace of cyclic compound **3** and resulting polymer is shown in Figure 3. The resulting polymers are tough and transparent, soluble in many common solvents, such as methylene chloride, chloroform and THF. Both polymers, unlike their cyclic dimers, are amorphous by differential scanning calorimetry, showing a glass transition (onset) at 148.0 °C for polymer **3** and at 230.7 °C for polymer **5**. Polymer **3** has a 5% weight loss at 358 °C, and polymer **5** has a 5% weight loss at 388 °C in the nitrogen atmosphere. Polymerization does not occur in the absence of an initiator even at 320−340 °C.

Because of the large ring size and lack of ring strain in the above macrocycles, the polymerization reactions should be essentially thermoneutral.[14] The fact that these macrocycles can undergo the molten state polymerization indicates the unusual situation where the cyclic oligomers are less structurally ordered than the linear polymers. At the temperatures of polymeriza-

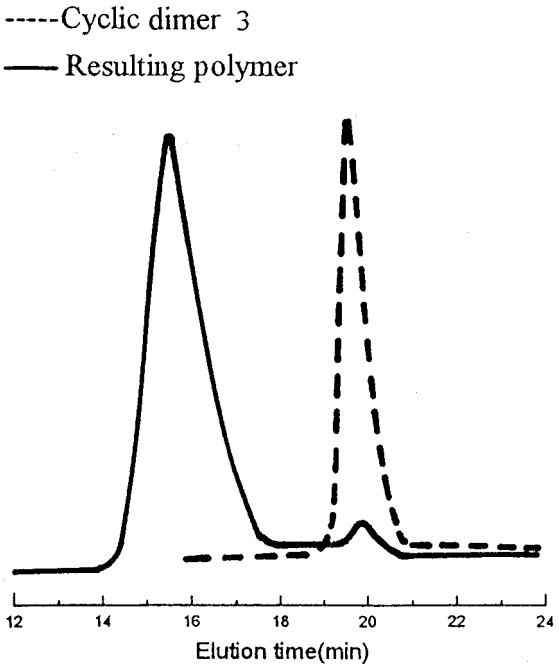

Figure 3. The GPC trace of cyclic dimer **3** and the resulting polymer.

tions (310−340 °C), the more thermally relaxed linear chains must have an essentially smaller system entropy than that of the structurally disordered cyclics and hence an entropically driven polymerization processes. Dynamic simulation of the polymerization reaction is in progress.

Conclusion

An efficient synthesis of cyclic aromatic ester dimers containing phthalic moiety via the interfacial polycondensation route has been described. The formation of a cyclic dimer may be caused by the existence of a preferred conformation of the adduct which favors ring formation under the given conditions. Detailed structural characterization of these novel compounds by FAB−MS, ^{1}H and ^{13}C NMR, GPC, and single-crystal X-ray diffraction confirmed the cyclic nature. Melt polymerization of these macrocycles gave high molecular weight polyarylates.

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Supporting Information Available: Figures showing ^{1}H and ^{13}C NMR spectra and tables of crystallographic data, atomic parameters, bond lengths and angles, torsion angles, and anisotropic temperature factors (10 pages). Ordering information is given on any current masthead page.

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