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Generation of Cyclic Dimers during Formation of Poly(enaminonitriles)

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ABSTRACT: During the course of our efforts to determine the influence of the structure of bis(chlorodicyanovinyl) monomers and diamines on polymer properties it was found that certain diamines favor the formation of monodisperse cyclic oligomers.

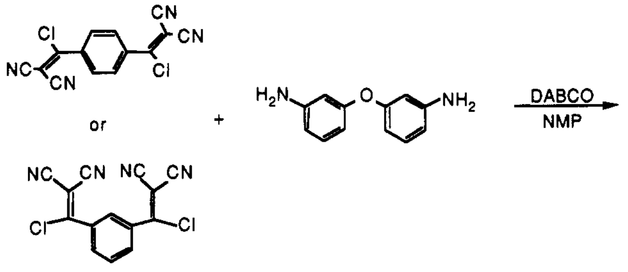
Introduction

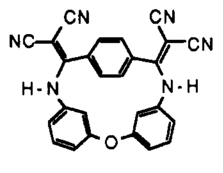
We have reported earlier that high molecular weight polymers were obtained from the polycondensation reactions of bis(chlorodicyanovinyl)benzenes with 4,4′-oxydianiline (4,4′-ODA) or many other diamines.[1–3] These polymers formed flexible, tough films which exhibited excellent thermal stability and good mechanical properties. It was of interest to try other ODA isomers, such as 3,3′-ODA, **3**, in the polymerizations to study the structural effects on the properties of the resulting polymers.

Results and Discussion

Surprisingly, it was found that the reaction of 2,2′-[1,4- or 1,3-phenylenebis(chloromethylidyne)]bispropanedinitrile (**1** or **2**) with diamine **3** (Scheme I) did not yield high polymer. When the reaction product was poured into acetone, it produced well-formed crystals. GPC chromatograms of both crude products showed very narrow, single peaks with an apparent average molecular weight of 950 using PS standards, suggesting the exclusive formation of a single molecular weight cyclic oligomer. Although preliminary molecular modeling calculations[4] indicated that an oligomer derived from two molecules of dichloride and diamine (tetramer) was the most stable cycle close to the molar mass indicated by GPC, the spectroscopic results (FAB-MS, IR, and ^{1}H and ^{13}C NMR) and, finally, the single-crystal X-ray diffraction analyses demonstrated that the products were cyclic dimers **4** or **5**. The single-crystal X-ray structure of cyclic dimer **4** is shown in Figure 1. Two acetone molecules per cyclic dimer were found to be incorporated as the solvent of crystallization.

Scheme I





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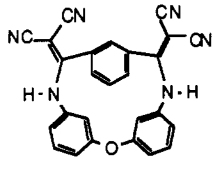

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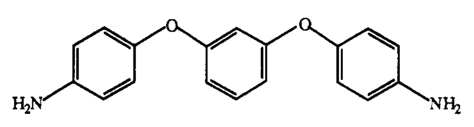
Clearly the difference in the nature of the products formed depends on the geometry of the diamine and its influence on the relative rates of cyclization and polymerization. Another diamine in which the amine groups are in a meta relationship to one another is *m*-bis(aminophenoxy)benzene (BAPB); **6**). When dichloride **1** is reacted with diamine **6**, large amounts of one cyclic oligomer (dimer) **7** are produced under the normal reaction conditions along with high molecular weight polymer.



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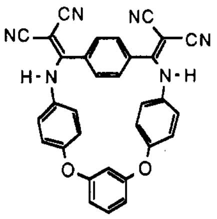

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The gel permeation chromatogram of the reaction product exhibited a bimodal distribution with a narrow, intense peak in the low molecular weight region and a broad peak at higher molecular weight. The narrow peak appeared at almost the same retention time at which the previously isolated cyclic dimers were observed. This low molecular weight portion (28%) could be separated simply by column chromatography. Again, the spectroscopic results (FAB-MS, IR, and ^{1}H and ^{13}C NMR) and, finally, the single-crystal X-ray diffraction analysis showed the product to be the cyclic dimer **7**. Figure 2 shows the single-crystal X-ray structure of compound **7**. 4-Methyl-4-hydroxy-2-pentanone (diacetone alcohol), a dimer of acetone, which is probably produced during the separation process using alumina, is incorporated in the crystal structure in a 1:2 (cyclic dimer:diacetone alcohol) ratio through hydrogen bonding. The cyclic compounds were found to be stable to over 400 °C by TGA. DSC of the cyclic dimers showed very sharp exothermic transitions

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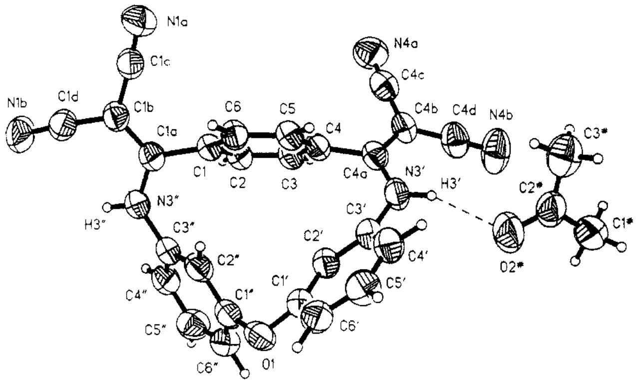


Figure 1. Crystal structure of compound 4.

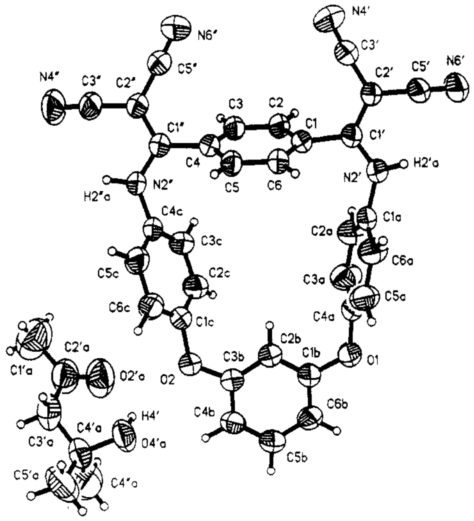
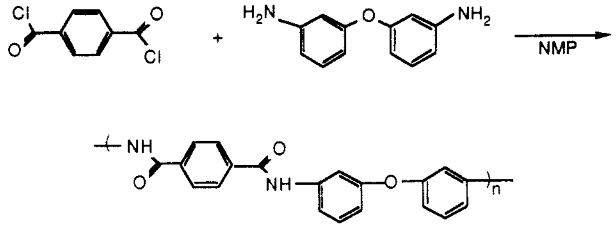


Figure 2. Crystal structure of compound 7.

Scheme II



at temperatures of 438, 395, and 442 °C, respectively, which suggests the occurrence of some type of chemical reaction or rearrangement (probably intermolecular). Because of the conformational restriction, the intramolecular cyclization reaction[1] that is observed for linear molecules is hardly expected to occur in these cyclic compounds. Further support for the intermolecular nature of this process is seen in the fact that all the cyclic compounds retain about 75% of their weight when heated to 900 °C (10 °C/min) under N_2. It may be concluded from these observations that some cross-linking reaction is occurring which prevents volatilization of the residue.

For comparison, terephthaloyl chloride was reacted with 3,3′-ODA under similar conditions to those used for the reaction of monomer 1 with the same diamine. In this case, a relatively high molecular weight polymer with an inherent viscosity of 0.60 dL/g (0.5 g/dL of DMAC, 25 °C) was obtained (Scheme II).

A clear, flexible film was cast from a DMAC solution. A glass transition was observed (DSC) at around 210 °C, and a broad endotherm (probably a melting transition) was observed at around 380 °C. A second scan only showed the glass transition. Under nitrogen, the polymer was stable up to 400 °C and 55 wt % of the initial weight remained at 900 °C (TGA).

The formation of cyclic oligomers in polymerization reactions is a relatively widespread phenomenon and has been frequently observed in the preparation of condensation polymers or in the ring-opening polymerization of heterocyclic monomers.[5] Cyclic oligomers are formed under a variety of experimental conditions, which are often deliberately chosen to avoid polymer formation. This is the case for the well-known "high dilution method" of Ruggli and Ziegler,[6] which was devised to minimize the amount of polymer formed when molecules carrying very reactive end groups are cyclized. It is very unusual, however, to observe the formation of a cyclic dimer as the exclusive product from the normal reaction conditions for solution polymerization as were used in the system described herein. It seems that the exclusive formation of cyclic dimer in these systems is due to the existence of a preferred conformation of the initial AB adduct which favors cyclization to form stable cyclic molecules. The fact that terephthaloyl chloride and 3,3′-ODA apparently only form a high molecular weight polymer may indicate that a conformation which favors dimer formation is not readily attainable. In the case of the more flexible *m*-BAPB, the number of dimers which can attain a conformation favoring cyclization is apparently a smaller fraction of the available conformations and polymerization competes with cyclization. Molecular modeling studies aimed at elucidating this point are currently in progress.

Conclusion

In summary, it has been observed that cyclic oligomers (dimers) are produced as the exclusive reaction product under the normal reaction conditions for condensation polymerization involving bis(chlorodicyanovinyl)benzenes with 3,3′-ODA. The formation of a single cyclic oligomer was also observed with these dichlorides and a different meta-substituted diamine, *m*-BAPB. However, the cyclic oligomer in this instance was formed along with high molecular weight, linear polymer. 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.

Experimental Section

A. Chemicals and Instruments. 2,2′-[1,4- or 1,3-Phenylenebis(chloromethylidyne)]bispropanedinitrile (1 or 2) were prepared according to the procedure previously reported.[1] *N*-Methylpyrrolidone (NMP) and dimethylacetamide (DMAC) were dried and fractionally distilled over barium oxide. 1,4-Diazabicyclo[2.2.2]octane (DABCO) was purified by sublimation. 3,3′-Oxydianiline (3,3′-ODA) and (3,3′-bis(4-aminophenoxy)benzene (*m*-BAPB; Mitsui Toatsu) were purified by recrystallization and sublimation.

Infrared (IR) spectra were recorded on a Perkin-Elmer Model 1800 Fourier transform infrared spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian XL-200 spectrometer operating at 200 MHz for ^1H and 50.3 MHz for ^{13}C spectra. Mass spectra (MS) were obtained with a Hewlett-Packard Model 5987 integrated gas chromatograph–mass spectrometer. Fast atom bombardment mass spectra (FAB-MS) were obtained on a VG 70E mass spectrometer at the Polaroid Corp., Cambridge, MA. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on Perkin-Elmer System 7 instruments interfaced with a Perkin-Elmer Model 7500 computer. Single-crystal X-ray structures were determined using data obtained on a Siemens R3mIV diffractometer. The structures were resolved using the SHELXTL *PLUS* (Release 4.21/V) computer program. Gel permeation chomotography was conducted with a Waters Maxima 820 highpressure liquid chromatograph equipped with a Waters Ultrastyragel linear GPC column with THF as the eluting solvent (flow rate, 1 mL/min). The column was calibrated with polystyrene standards.

B. Reactions of Bis(chlorodicyanovinyl)benzenes with Diamines. A typical procedure that was developed for the preparation of poly(enaminonitriles) was used as reported.[1] 3,3′-ODA or *m*-BAPB was reacted with an equimolar amount of bis(chlorodicyanovinyl)benzene monomer in the presence of DABCO as the acid acceptor in NMP under nitrogen. The reaction mixture was stirred at 80 °C for 24 h before precipitation into a large amount of water. The precipitate was filtered, washed with methanol and water, and dried in vacuum to give a light tan powder in good yields (90–95%).

3,15-Diaza-2,16-(dicyanomethylidene)-9-oxatetracyclo-[15.2.2.1^{4,8}.1^{10,14}]tricosa-1(20),4,6,8(23),10,12,14(22)-nonaene (4). No melting (sharp exotherm at 438 °C by DSC). MS (FAB): *m/e* 427 (M^{+1}, 14) 307 (100) 289 (60). UV (THF): λ_{max} 331, 278.5 226 nm. IR (KBr): 3245 (NH), 2221 (CN), 1616, 1578 (s) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 11.22 (s, 2 H, NH), 7.45 (s, 4 H, aromatic protons from bischloro monomer), 7.37 (t, 2 H), 7.13 (d, 2 H), 6.88 (d, 2 H), 5.54 (s, 2 H). ^{13}C NMR (DMSO-d_6): δ 168.0 (vinyl C–N), 155.7 (aromatic C–O), 139.3, 133.1, 130.5, 119.9, 117.3, 116.0, 114.5, 114.4, 54.2 (*C*–CN).

3,15-Diaza-2,16-(dicyanomethylidene)-9-oxatetracyclo-[15.3.1.1^{22}.1^{23}]tricosa-1(20),4,6,8(23),10,12,14(22)-nonaene (5). Mp 385 °C (DSC, melting is followed by a sharp exothermic transition). MS (FAB): *m/e* 427 (M^{+1}, 37) 307 (100) 289 (60). UV (THF): λ_{max} 325.5, 248, 210 nm. IR (KBr): 3220 (br, NH), 2219 (CN), 1570 (s), 1448, 1413 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 11.2 (s, 2 H, NH), 7.65 (s, 1 H), 7.48 (m, 3 H), 7.37 (t, 2 H), 7.19 (d, 2 H), 6.84 (d, 2 H), 5.52 (s, 2 H). ^{13}C NMR (DMSO-d_6): δ 167.7 (vinyl C–O), 155.7 (aromatic C–O), 139.0, 132.3, 131.6, 130.7, 130.0, 129.4, 119.2, 116.1, 115.6, 114.7, 114.4, 56.3 (*C*–CN).

C. 3,19-Diaza-8,14-dioxa-2,20-(dicyanomethylidene)pentacyclo[19.2.2.2^{4,7}.2^{5,8}.1^{9,13}]triaconta-1(23),4,6,29(30),9,11,13-(28),15,17,26(27)-dodecaene (7). No melting (sharp exotherm at 442 °C by DSC). IR (KBr): 3239 (NH), 2218 (CN), 1595, 1567, 1505, 1271 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 9.94 (s, 2 H, NH), 7.7 (s, 4 H, aromatic H from bischloro monomer), 7.41 (t, 1 H), 7.07 (d, 4 H), 6.95 (d, 4 H), 6.86 (dd, 2 H), 6.12 (s, 1 H). ^{13}C NMR (DMSO-d_6): δ 167.0 (vinyl C–N), [158.0, 153.8] (aromatic C–O), 133.7, 133.5, 131.4, 130.5, 126.1, 119.6, 114.6, 114.2, 113.2, 57.5 (*C*–CN).

D. Poly(iminocarbonyl-1,4-phenylenecarbonylimino-1,3-phenyleneoxy-1,3-phenylene). 3,3′-ODA (0.4343 g, 2.17 mmol) was dissolved in 15 mL of NMP in a three-necked flask equipped with a nitrogen inlet and outlet, a condenser, and a magnetic stirrer. To this solution was added terephthaloyl chloride (0.4404 g, 2.17 mmol). The homogeneous mixture became viscous gradually. After stirring about 30 min at room temperature DABCO (0.50 g, 4.46 mmol) in 5 mL of NMP was added slowly. The clear solution turned milky and very viscous immediately. The reaction was warmed to 60 °C and stirred for 8 h before precipitation into water in a high-speed blender. A white, fibrous precipitate was collected, washed with water and alcohol, and then dried in vacuo over P_2O_5 at 120 °C for 48 h to afford 0.68 g (95%) of polymer with an inherent viscosity of 0.60 dL/g at 25 °C in DMAC (concentration, 0.5 g/dL). A flexible film was cast from DMAC solution. T_g (film, DSC): 215 °C. IR (film): 3306 (NH), 3068 (aromatic H), 1658 (C=O), 1600, 1538, 1488, 1436, 1268, 1182, 1158 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 10.42 (2 H, NH), 8.0 (4 H), 7.54 (m, 4 H), 7.33 (t, 2 H), 6.80 (2 H). ^{13}C NMR (DMSO-d_6): δ 164.8 (C=O), 156.8 (aromatic C–O), 140.5, 137.3, 129.9, 127.6, 115.4, 114.2, 110.6.

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Supplementary Material Available: X-ray structure determination summaries for compounds 4 and 7 (26 pages). Ordering information is given on any current masthead page.

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