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Synthesis and Polymerization of 2,15-Diaza-1,16-dioxo[16]paracyclophane

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Introduction

Cyclic amides (lactams) are well-known precursors to polyamides. Their chemistry and polymerization have been well characterized.[1] Less often studied are the cyclic diamides. However, the cyclic dimer of caprolactam has been well characterized as it is a byproduct of nylon 6 formation.[2] This material can be polymerized to nylon 6, although not as readily as caprolactam. Many other cyclic oligoamides are known in the literature, usually as byproducts of polymerization.[3]

Recent work has demonstrated the utility of using cyclic oligomers as precursors for a variety of high T_g, amorphous polymers, such as polycarbonates, polyarylates, poly(ether ketones), and polysulfones.[4] Cyclic oligomers provide low-viscosity precursors that can be polymerized rapidly in situ with suitable catalysts to give high molecular weight polymeric structures. A related process is the anionic polymerization of caprolactam done in molds as monomer casting[5] or reaction injection molding (nylon RIM).[6] These processes provide the means to form highly complicated and large parts without the tremendous pressures necessary for injection molding. The advantage of these processes is, however, based on the facts that (a) the monomer is low melting and (b) the polymer is high melting and highly crystalline. Hence, the polymerization can be conducted below the melting point of the polymer to permit direct fabrication of the part.

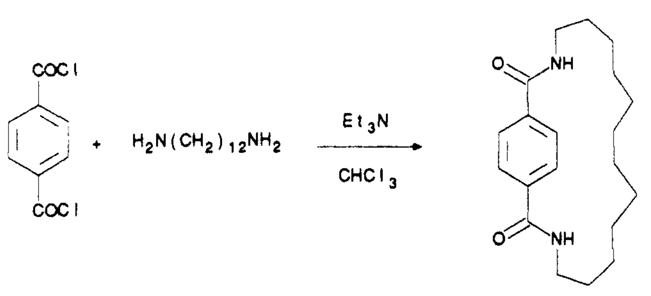
As more demanding uses for thermoplastics are being developed, newer resins with higher use temperatures are being investigated. One such polyamide is poly(dodecamethyleneterephthalamide) (nylon 12T). This material has a higher melting temperature[7] than conventional nylons which would allow its use in more demanding thermal environments.

It was of interest to see if a cyclic precursor of this polymer could be formed and whether it could be polymerized to give high molecular weight material with properties identical to those of the conventionally prepared material.

Although the cyclic monomer of nylon 12T has not been reported, several related compounds have been.[8] These authors reported on a variety of cyclic diamides including the cyclic monomers for nylon 8T and 6T. The polymerization of these compounds was not investigated. Also, due to the limited instrumentation available at that time, no description of the structure of these compounds was possible.

Results and Discussion

We prepared the cyclic diamide of 1,12-dodecanediamine and terephthaloyl chloride in a similar manner to that described above. The reaction was run at very high dilution to minimize the production of linear oligomers or polymer. A surprisingly high yield (>50%) of the cyclic diamide was isolated. A small amount of the cyclic tetramide was also present.



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Solution-state ^1H and ^{13}C NMR of this compound in DMSO reveals that this compound exists in two distinct conformations in the solution state, one symmetrical and one unsymmetrical. Interestingly, in tetrachloroethane (TCE) solution only the unsymmetrical conformation is seen at room temperature. However, at elevated temperature (ca. 100 °C), this converts to the symmetrical structure. When the solution is cooled, the compound returns to the unsymmetrical form. Similar changes are seen in the solid-state NMR. A second paper will discuss the structures of the different conformations present in both solution and the solid state.[9]

Another interesting feature of the solution-state ^1H NMR is a resonance at 0.6 ppm in the unsymmetrical conformation. This high-field resonance is probably due to shielding from the aromatic ring current, implying that this segment of the methylene chain is directly over the aromatic ring. At higher temperature the resonance disappears as the material converts to the symmetrical structure. To confirm that this is indeed a single compound, a small amount of the cyclic diamide was reacted with trifluoroacetic anhydride to give the bis(trifluoroacetimide). Solution-state NMR of this compound showed only one set of resonances, consistent with the proposed structure.

During a DSC analysis of the cyclic diamide it was found that at temperatures above its melting temperature (273 °C) this material rapidly polymerizes (<5 min). A sample of the diamide was heated to 300 °C for 40 min under a nitrogen atmosphere. The polymer was purified by dissolution and precipitation to give an 86% yield of high molecular weight polymer (reduced viscosity of 1.81 in sulfuric acid). This polymer is identical with material prepared by conventional melt polymerization of 1,12-dodecanediamine and terephthalic acid, as characterized by DSC and NMR. It is interesting that the compound polymerizes spontaneously in the melt without the addition of a catalyst. The cyclic dimer of caprolactam polyermizes only sluggishly without an added catalyst.[2b] The primary route of polymerization in the case of the caprolactam dimer involves transamidation to form caprolactam and polymerization of the caprolactam. The high polymerization rate of cyclic diamide 1 may reflect the higher ring strain in this molecule. To eliminate the effects of possible impurities, a sublimed sample of the cyclic diamide was heated to 320 °C in a differential scanning calorimeter, held at that temperature for 20 min, cooled, and rescanned. The second scan showed melting endotherms characteristic of the polyamide, indicating polymerization.

This system represents an interesting alternative to classical melt polycondensation, although a practical synthesis of the cyclic diamide would be needed to make this route economical.

Experimental Section

Terephthaloyl chloride was supplied by Aldrich Chemical Co. (Milwaukee, WI) and sublimed before use. The 1,12-dode-

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canediamine was supplied by DuPont Chemicals (Wilmington, DE) and sublimed before use. Chloroform was freshly distilled from phosphorus pentoxide. A dual syringe pump, Model 22, from Harvard Apparatus (South Natick, MA) was used for the simultaneous addition of monomers. All other compounds were used as received.

Preparation of 2,15-Diaza-1,16-dioxo[16]paracyclophane. A solution of 2.00 g (9.98 mmol) of freshly sublimed 1,12-dodecanediamine in 45 mL of chloroform was taken up in a 50-mL gastight syringe. A solution of 2.03 g (10.0 mmol) of terephthaloyl chloride in 45 mL of chloroform was taken up in a second syringe. A dual-syringe pump was used to add these solutions to a 2-L, three-neck flask containing 3.0 mL (21.5 mmol) of triethylamine in 800 mL of chloroform. The two solutions were added simultaneously at 10 mL/h. A white precipitate slowly formed during the course of the addition. The reaction mixture was allowed to stir at room temperature overnight.

The resulting mixture was filtered and the filtrate washed with water, 10% potassium carbonate, and water, dried ($MgSO_4$), and reduced to give a white solid.

The filtered solid was extracted overnight with hot chloroform in a Soxhlet extraction apparatus. The resulting chloroform solution was combined with the above residue and reduced to give 2.38 g (85% yield) of an off-white solid.

The combined fractions were recrystallized from chloroform to give 1.71 g (52% yield) of a white solid: mp 272–273 °C; ^{1}H NMR (400 MHz, TCE) δ 7.8 (m, 2 H), 7.5 (m, 2 H), 6.6 (br s, 1 H), 6.2 (br s, 1 H), 3.5 (s, 2 H), 3.0 (s, 2 H), 1.6–0.6 (m, 20 H); MS *m/z* (relative intensity) 330 (M^+, 100%), 273 (12%), 104 (15%). Anal. Calcd for $C_{30}H_{30}N_2O_2$: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.63; H, 9.23; N, 8.31.

Trifluoroacetylation of 2,15-Diaza-1,16-dioxo[16]paracyclophane. A solution of the cyclic diamide (0.11 g, 0.33 mmol) in 10 mL of dry chloroform was treated with 1 mL of trifluoroacetic anhydride. This solution was stirred overnight at room temperature. The solvent and excess reagent were removed under reduced pressure to give a white solid: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.9 (s, 4 H), 3.8 (t, 4 H), 1.7 (quin, 4 H), 1.4–0.9 (m, 20 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 173, 161 (quart), 137, 130, 116 (quart), 48, 28.6, 28.5, 28.0, 27.8, 25.8.

Polymerization of 2,15-Diaza-1,16-dioxo[16]paracyclophane. A polymerization tube was charged with 0.49 g (1.48 mmol) of the cyclic diamide, vacuum-purged with nitrogen (3×), and placed in a 300 °C oil bath for 40 min. The reaction mass was allowed to cool, and the resulting plug of polymer was dissolved in concentrated sulfuric acid. This solution was filtered and precipiated into water. The resulting precipitate was washed with 10% potassium carbonate solution and then with water. This off-white solid was dried overnight (110 °C, vacuum) to give 0.42 g (86% yield) of a polymer with a reduced viscosity of 1.81 in sulfuric acid.

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Registry No. 1, 143076-54-4; 1 (homopolymer), 143076-55-5; 1 (SRU), 26009-07-4; $ClCOC_6H_4$-*p*-COCl, 100-20-9; $H_2N(CH_2)_{12}NH_2$, 2783-17-7; $F_3CC(O)OC(O)CF_3$, 407-25-0.