Macrocyclic Polymers. 1. Synthesis of a Poly(ester crown) Based on Bis(5-carboxy-1,3-phenylene)-32-crown-10 and 4,4'-Isopropylidenediphenol (Bisphenol A)

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ABSTRACT: A semirigid 32-membered ring diester crown ether, bis(5-carbomethoxy-1,3-phenylene)-32-crown-10 (3), has been synthesized in one step using methyl 3,5-dihydroxybenzoate (1) and tetra(ethylene glycol) dichloride (2) in the presence of sodium hydride in *N,N*-dimethylformamide (DMF). This diester crown has been converted to the diacid crown 5. A direct polycondensation reaction of bis(5-carboxy-1,3-phenylene)-32-crown-10 (5) and 4,4'-isopropylidenediphenol (Bisphenol A) (6) using tosyl chloride in pyridine in the presence of DMF formed a high molecular weight poly(ester crown) (7). The polymer is soluble in common organic solvents such as chloroform and THF. It has a glass transition temperature (T_g) of 65 °C; also it shows quite high thermal stability, 5% weight loss by TGA at 355 °C in air.

Introduction

Crown ethers as a relatively new class of compounds have received tremendous interest, especially in the area of complexation and host–guest chemistry.[1] Moreover, a good deal of work has been also done on polymeric crowns during the last 2 decades. Smid and co-workers[2,3] have been major contributors from the point of view of synthesis of polycrowns and study of their cation binding properties in comparison with their monomeric counterparts. They synthesized polycrowns based on the polymerization of vinylbenzo-15-crown-5 and vinylbenzo-18-crown-6. Later on, the acrylate[4,5] and acrylamide[6,7] derivatives were prepared. These monomers can be polymerized by radical initiators, and certain binding properties of these polymers have been reported. Blasius and co-workers,[8] who have been interested in the cation selectivity of these compounds, incorporated dibenzocrowns containing up to 30-membered rings into polymers as part of the backbone, by utilizing the reaction of dibenzocrown compounds with formaldehyde, or as pendent groups by alkylation of benzocrowns using chloromethylated polystyrene. Other early approaches included nitration of dibenzocrown ethers and reduction to the diaminobenzocrown compounds. The diamines may be reacted with diacid chlorides or anhydrides to yield polyamides, polyimides, etc.[9,10] Montanari and co-workers[11,12] have developed a number of polymer-anchored crowns for use as phase-transfer catalysts. Chloromethylated polystyrene can be used to alkylate a benzocrown compound or may be reacted with hydroxy- or azacrown compounds. A similar approach has been taken by Takekoshi and co-workers[13] in synthesizing crown ether polymers from the reaction of dibenzo-18-crown-6 with chloral, bromal, or glyoxylic acid using Lewis acid catalysts.

In the second decade the same approaches have continued to be used by many research groups to incorporate crowns into polymeric materials as backbone and pendent moieties. Just a few examples of these approaches are polymer-bound crown ethers by polycondensation reaction of dibenzocrown ethers with different reagents[14] and liquid crystalline polymers containing crown ethers as backbone[15] or pendent groups.[16,17] Some newer methods of incorporation include cyclopolymerization of divinyl ethers or other difunctional monomers under proper conditions into polymeric crowns.[18-23]

In these polymeric crowns the macrocycles are mostly in the range of 15–18-membered rings. To our knowledge, there are no examples of polymers which contain macrocycles larger than 30-membered rings; only one mention of a 30-membered ring polymer was found.[8] As was mentioned earlier, these polymers have been synthesized through free radical, step growth, and other polymerization techniques. Those that have been made by polycondensation reactions are mostly a mixture of different isomers as the result of functionalization of dibenzocrown ether monomers (preformed crowns) after their syntheses.

Crown ethers in the range of 30-membered rings and higher have the ability to bind two metal ions per cavity[24] and also to complex with large organic cations.[25] Moreover, macrocycles in this size range can be threaded by aliphatic and/or aromatic linear species, providing rotaxane structures, which offer unique possibilities for controlling physical properties in polymeric systems.[26,27] In this paper we report the synthesis of a novel and well-defined poly(ester crown) which contains a semirigid large (32-membered) macrocycle in the main chain.

Experimental Section

Materials. Unless specified otherwise, reagent-grade reactants and solvents were used as received from chemical suppliers. Pyridine was distilled over CaH_2 and stored over molecular sieves. Tetra(ethylene glycol) dichloride (2) was synthesized according to a literature procedure.[28]

Measurements. Melting points were taken in capillary tubes with a Haake–Buchler melting point apparatus and have been corrected. ^{1}H NMR spectra were obtained at ambient temperature on a Varian Unity 400-MHz spectrometer using deuterated acetone, dimethyl sulfoxide, and chloroform solutions with CD_2HCOCD_2H ($\delta = 2.04$) or TMS ($\delta = 0$) as internal standards, respectively. Infrared spectra (KBr pellets) were recorded on a Nicolet MX-1 FTIR spectrometer. Mass spectra were measured with a VGA 7070E analytical mass spectrometer. Elemental analyses were performed by Atlantic Microlab of Norcross, GA. Intrinsic viscosity measurements were performed in DMF at 25 °C using a Cannon–Ubbelohde viscometer. Molecular weight and molecular weight distribution were analyzed by using a Waters 150-C17 gel permeation chromatograph equipped with an RI detector and Ultrastyragel column set (100, 500, 10^3, and 10^4 Å) in chloroform at 30 °C; molecular weight calculations were based on polystyrene standards. Weight-average molecular weight was determined using Chromatix KMX-6 low-angle laser light scattering (LALLS) in 1-methyl-2-pyrrolidinone (NMP). The glass transition temperature (T_g) was obtained by differential

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scanning calorimetry on a Du Pont DSC 912; scans were run at 10 °C/min, and the reported value was obtained from a second heating after quick cooling. Thermogravimetric analyses were performed on a Du Pont 951 TGA at a scan rate of 10 °C/min in air and N_2 atmospheres, respectively.

Methyl 3,5-Dihydroxybenzoate (1). This compound has been synthesized by reaction of 3,5-dihydroxybenzoic acid with diazomethane in the presence of acetic acid.[29,30] We modified this procedure by esterifying the 3,5-dihydroxybenzoic acid with methanol in the presence of concentrated sulfuric acid. A solution of 3,5-dihydroxybenzoic acid (100 g, 0.65 mol) and concentrated sulfuric acid (98%, 50 mL) in methanol (530 mL) was refluxed for 48 h. The solution was cooled, neutralized with $NaHCO_3$ to pH 7, and extracted with diethyl ether. The combined organic phase was dried over sodium sulfate, and the solvent was removed under vacuo to give solid material, which was recrystallized from water, 103.5 g, yield 95%, mp 167–169 °C (lit.[29] mp 167–169 °C). ^1H NMR (DMSO-d_6): δ 9.70 (2 H, s, OH), 6.84 (2 H, d, Ph-$H_{2,6}$, J = 2.3 Hz), 6.45 (H, t, Ph-H_4, J = 2.3 Hz), and 3.80 (3 H, s, OCH_3).

Bis(5-carbomethoxy-1,3-phenylene)-32-crown-10 (3). Tetra(ethylene glycol) dichloride (2) (13.15 g, 0.05 mol) in 250 mL of DMF was added to 225 mL of DMF containing 9.58 g (0.05 mol) of methyl 3,5-dihydroxybenzoate (1) and 2.76 g (0.115 mol) of sodium hydride. The solution was stirred vigorously at 85 °C for 48 h under a blanket of nitrogen, cooled, filtered, and evaporated to give a brown viscous oil. A short column of silica gel (7 g/1 g of crude products) with diethyl ether as eluent was then used. The smaller ring corand was the fast-moving fraction (R_f = 0.59), and the large macrocycle was the slow-moving fraction (R_f = 0.46, silica gel/ethyl acetate).

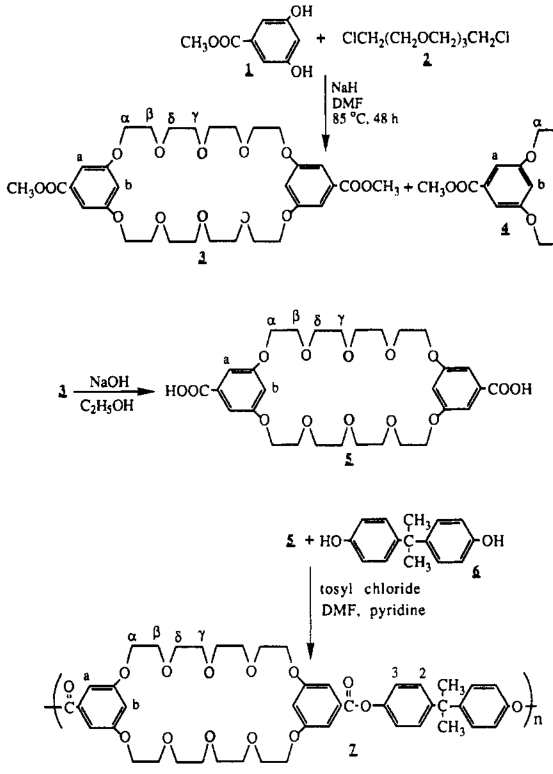
This produced bis(5-carbomethoxy-1,3-phenylene)-32-crown-10 (3) as a crystalline solid, 1.65 g, 9% yield, mp 106.5–107.5 °C. IR: 1717 (C=O), 1600 (C=C), 1067–1137 (C–O–C) cm^{-1}. ^1H NMR (CD_3COCD_3): δ 7.08 (4 H, d, H_a, J = 2.5 Hz), 6.71 (2 H, t, H_b, J = 2.5 Hz), 4.11 (8 H, t, α-OCH_2, J = 4.7 Hz), 3.83 (6 H, s, OCH_3), 3.80 (8 H, t, β-OCH_2, J = 4.7 Hz), 3.62 (16 H, m, γ/δ-OCH_2). MS (EI$^+$): m/z 652 (M^+), 621 (M^+ - OCH_3), 590 (M^+ - 2 OCH_3). Anal. Calcd for $C_{32}H_{44}O_{14}$ (MW 652): C, 58.88; H, 6.80. Found: C, 58.67; H, 6.86.

5-Carbomethoxy-1,3-phenylene-16-crown-5 (4) was isolated from the above reaction products, 2.85 g, 15% yield, as a needle-like crystalline solid, mp 71.5–72.5 °C. IR: 1717 (C=O), 1600 (C=C), 1129 (C–O–C) cm^{-1}. ^1H NMR (CD_3COCD_3): δ 7.34 (1 H, t, H_b, J = 2.3 Hz), 7.08 (2 H, d, H_a, J = 2.3 Hz), 4.32 (4 H, t, α-OCH_2, J = 4.7 Hz), 3.83 (3 H, s, OCH_3), 3.75 (4 H, t, β-OCH_2, J = 4.7 Hz), 3.58 (4 H, m, γ-OCH_2), and 3.50 (4 H, m, δ-OCH_2). MS (EI$^+$): m/z 326 (M^+), 295 (M^+ - OCH_3), 267 (M^+ - $COOCH_3$), 239 (M^+ - $COOCH_3$ and CH_2CH_2). Anal. Calcd for $C_{16}H_{22}O_7$ (MW 326): C, 58.89; H, 6.80. Found: C, 58.96; H, 6.83.

Bis(5-carboxy-1,3-phenylene)-32-crown-10 (5). A mixture of diester crown 3 (4.8 g, 7.4 mmol), ethanol (430 mL), and sodium hydroxide (4 M, 100 mL) was refluxed for 24 h. The reaction mixture was allowed to cool to room temperature, and it was acidified with 4 M hydrochloric acid solution. The diacid crown 5 precipitated after cooling to 0–5 °C, the solution was filtered, and the white precipitate was washed with cold water. Recrystallization from ethanol afforded 4.5 g (100%) of pure diacid crown, mp 169.5–170.5 °C. IR: 3501 (O–H), 1696 (C=O), 1600 (C=C), 1129 (C–O–C) cm^{-1}. ^1H NMR (CD_3COCD_3): δ 7.34 (2 H, s, COOH, exchangeable), 7.14 (4 H, dd, H_a, J = 1.1 Hz), 6.74 (2 H, dt, H_b, J = 1.1 Hz), 4.13 (8 H, t, α-OCH_2, J = 3.8 Hz), 3.81 (8 H, t, β-OCH_2, J = 3.8 Hz), 3.62 (16 H, m, γ/δ-OCH_2). MS (EI$^+$): m/z 624 (M^+). Anal. Calcd for $C_{30}H_{40}O_{14}$ (MW 624): C, 57.67; H, 6.46. Found: C, 57.40; H, 6.48.

Polyester 7: Polycondensation of Bis(5-carboxy-1,3-phenylene)-32-crown-10 (5) with Bisphenol A (6). The polymer was synthesized according to the method described by Higashi and co-workers.[31] A solution of tosyl chloride (1.24 g, 6.5 mmol) in pyridine (5 mL) and DMF (15 drops) was maintained at room temperature for 30 min and added to the diacid crown 5 (1.56 g, 2.5 mmol) in pyridine (5 mL). The mixture was maintained at room temperature for 10 min and then at 120 °C for 10 min. To this solution was added dropwise over 20 min at 120 °C Bisphenol A (6) (0.570 g, 2.5 mmol) in pyridine (5 mL). The reaction was maintained at 120 °C for 3 h. The polymer was isolated by precipitation with methanol. The precipitate was filtered and then washed with water and methanol. The polymer was dried under vacuum at 45 °C for 24 h, 2.0 g, 100% yield. IR: 1737 (C=O), 1600 and 1505 (C=C aromatics), 1129 (C–O–C) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.33 (4 H, d, H_a, J = 2.1 Hz), 7.28 (4 H, d, H_3, J = 8.7 Hz), 7.1 (4 H, d, H_2, J = 8.7 Hz), 6.76 (2 H, t, H_b, J = 2.1 Hz), 4.15 (8 H, t, α-OCH_2, J = 4.7 Hz), 3.87 (8 H, t, β-OCH_2, J = 4.7 Hz), 3.72 (16 H, m, γ/δ-OCH_2), 1.70 (6 H, s, CH_3). Glass transition temperature (T_g): 65 °C. TGA: 5% weight loss at 353 °C in air and 352 °C in N_2. Gel permeation chromatography of the poly(ester crown) with comparison to polystyrene standards in chloroform at 30 °C gave $\bar{M}_n = 55.7 \times 10^3$ and $\bar{M}_w = 133 \times 10^3$ with a polydispersity $\bar{M}_w/\bar{M}_n$ = 2.32. Low-angle laser light scattering (LALLS) of the polymer gave a molecular weight ($\bar{M}_w$) of 91.7×10^3 in NMP.

Scheme I



Results and Discussion

In order to synthesize polymers with large macrocycles in the backbone or as pendent groups, we are interested in producing functionalized macrocycles in significant quantities by simple, fast, and inexpensive ways. There are two approaches for synthesizing functionalized large crown compounds. The conventional method is the synthesis of the macrocycle followed by functionalization through aromatic electrophilic substitution; this usually consists of few steps but produces mixtures of regioisomers in the case of dibenzocrown compounds. The approach we have devised is to use a functionalized resorcinol and choose a proper synthesis procedure to preserve the functionality during the macrocycle formation.

We have developed a method to synthesize bis(5-carbomethoxy-1,3-phenylene)-32-crown-10 (3) (Scheme I). Thus, methyl 3,5-dihydroxybenzoate (1) was treated with tetra(ethylene glycol) dichloride (2) in DMF in the presence of NaH at 85 °C for 48 h to produce (9%) the desired macrocycle as well as a second new compound, 5-carbomethoxy-1,3-phenylene-16-crown-5 (4) (15%). Use of different bases such as potassium hydride or cesium carbonate did not show significant changes in the yields of macrocycles.

The ^1H NMR spectra allowed us to distinguish between 3 and 4. The α-OCH_2 protons of crown 4 appeared at a

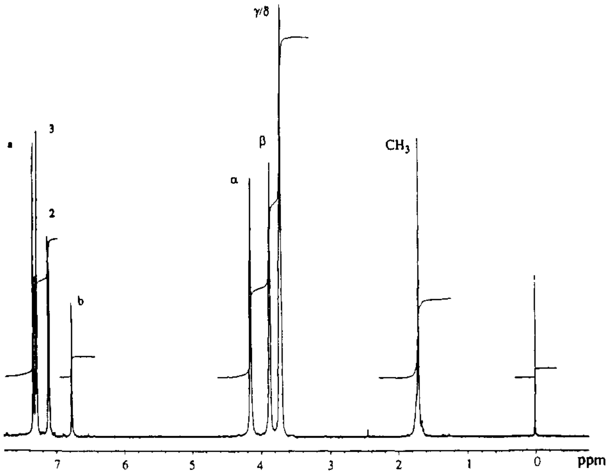


Figure 1. ^1H NMR spectrum of the poly(ester crown) 7.

lower field than those in the larger macrocycle **3** ($\Delta\delta$ = 0.21). The methylene protons of the tetra(ethylene glycol) chain of the large macrocycle were magnetically more equivalent (three absorption peaks with a 1:1:2 ratio) than in the smaller macrocycle (four distinct absorption peaks with a 1:1:1:1 ratio). The size of the ring also affects the chemical shift of the intraannular aromatic proton; i.e., in the 16-membered ring **4** the intraannular aromatic proton (H_b) shifts 0.63 ppm to lower field in comparison to the 32-membered ring macrocycle.

Traditional polymerization procedures such as high-temperature melt transesterification reaction of the diester crown **3** with ethylene glycol and different catalysts such as calcium acetate, antimony oxide, and titanium isopropoxide were tried without success. The reason for the failure of these methods is probably deactivation of the metal catalysts (poisoning) by very strong complexation with the macrocycle.

Therefore, we chose the direct polycondensation method as reported by Higashi et al.[31] The hydrolysis of the diester crown **3** to the diacid **5** was carried out in sodium hydroxide/ethanol with quantitative yield, and analytically pure monomeric diacid crown **5** was recrystallized from ethanol. The polycondensation reaction between the dicarboxylic crown **5** and Bisphenol A (**6**) takes place in the presence of tosyl chloride as the condensing agent and DMF as the catalyst in pyridine as the solvent. The reaction mixture stayed homogeneous during the polymerization time. A white fibrous polymer with 100% polymerization yield was obtained. It shows an intrinsic viscosity of 0.41 dL/g in DMF at 25 °C. $\bar{M}_w$ as determined by light scattering is 91.7×10^3. Comparison of the T_g of poly(ester crown) **7** (65 °C) with a classical aromatic polyester such as poly(Bisphenol A terephthalate) (T_g = 205 °C)[32] reveals the effect of the semiflexible macrocyclic backbone component on the solid-state properties of the polymer. The polymer is soluble in most common organic solvents such as tetrahydrofuran, chloroform, pyridine, DMF, DMSO, and *N,N*-dimethylacetamide. The ^1H NMR spectrum of the polymer in chloroform is shown in Figure 1. Transparent and flexible films can be cast from solution.

It was found that the poly(ester crown) has a narrower molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 2.3) than other aromatic polyesters prepared with the same conditions ($\bar{M}_w/\bar{M}_n > 3$).[31] The reason for this could be the better solubility of poly(ester crown) in the reaction medium during polymerization.

Conclusion

The first member of a new class of polymers containing large macrocycles in the backbone has been synthesized by the direct polycondensation of a dicarboxy macrocycle **5** and Bisphenol A (**6**). The reaction gives rise to high polymerization (100%) yield and high molecular weight polymer **7**.

The complexation abilities of polymer **7** and its monomeric precursors (**3** and **5**) with metal ions and organic cations, especially methyl viologen bis(hexafluorophosphate) are now under study. With respect to rotaxane formation,[26,27] we are interested in the threadability of the polymer with linear molecules. Results from these activities will be reported elsewhere.

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