Synthesis and Characterization of New Aromatic Polyamides Bearing Crown Ethers or Their Dipodal Counterparts in the Pendant Structure. I. Benzo-12-crown-4 and ortho-Bis(2-ethoxyethoxy)benzene

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ABSTRACT: Two novel isophthalic diacid-based monomers have been synthesized by inclusion in ring position 5 of a functionalized benzoyleamine moiety. The functionalization includes a 12-crown-4 ether group fused with the benzene subunit and a dipodand substructure, formally a disubstitution of the benzene ring, with two sequences of ethyl-terminated ethylene oxide units, which represent the open-chain counterpart of the alicyclic crown moiety. The polycondensation of the two diacids with five aromatic diamines yielded 10 new polyamides with crown or podand pendant substructures. The polyamides had previously been chemically characterized by NMR, IR, and elemental analysis. The polymers showed high glass transition temperatures of up to 349 °C, good thermal stability ($T_d$ onset, N2 ≈ 400 °C), and improved solubility in organic solvents. The presence of acyclic or alicyclic oxyethylene sequences as crown ether or podand substructures and an additional amide side group per repeat unit made the polymers essentially amorphous and improved their water absorption ability in comparison with nonsubstituted polyamides. Water uptake values as high as 12% were observed at 65% relative humidity. All the polyamides showed a good film-forming ability, and the mechanical properties of these films are considered to be satisfactory for experimental aromatic polyamides.

INTRODUCTION

Crown ethers or coronands are alicyclic polyethers made up of ethylene glycol units that are capable of selective interaction with cations through ion-dipole interactions. Their structures and the binding capability of their alkali metal ions were first described by Pedersen in 1967.1,2 This initial research planted the seeds of supramolecular or host-guest chemistry and was further advanced by the work of Professors Cram and Lehn who, together with Pedersen, were awarded the 1987 Nobel Prize in Chemistry for pioneering research in this area.

In 1979, Vogtle and Weber coined the term podands for acyclic host molecular structures with binding sites for guest molecules as anions, cations, or neutral molecules.3 The simplest
Podands are merely acyclic analogues of crown ethers, such as oligo or poly(ethylene glycol). Podands usually exhibit less cation affinity than crown compounds because of unfavorable enthalpic and entropic effects, although their higher conformational flexibility allows them to engage in multiple bridging and helical binding modes that the crowns can not adopt. When two or three oligo(ethylene glycol) subunits are close in space in the same molecule, the podand concept is extended to two or three dimensions. This structure is called as dipodal or tripodal molecule and is able to encapsulate its guests more fully. Furthermore, if the podand or multipodand is terminated by rigid functionality (e.g., aryl), binding is enhanced because of the extra degree of organization given to the podand host by the rigidifying influence of the endgroup.

Much of the research into crown ether structures now focuses on the inclusion of these supra-molecules in a polymer matrix or in a polymer structure because of the wide-ranging applications of such systems in high technology applications, such as, sensors, actuators, permselective membranes, and catalysts, among others. This is because crown ethers can selectively recognize alkali, alkaline earth metal ions, and other cations, including lanthanides, actinides, and transition metal ions.

Nowadays, most studies of metal ion transport processes through membranes manufactured with crown ethers and polymers are usually carried out using PVC, and involve dispersion of the host molecule within the polymer matrix. The lack of thermal, mechanical, and chemical stability in these kinds of polymers and the migration of the host molecules to the solutions in which the membrane is immersed prevents such systems from being used in a large number of technological applications, in which resistance to high temperatures, organic solvents resistance, or mechanical stability are prerequisites.

Polymers that include crown ether or podands moieties in their chemical structure are of considerable interest and importance because they are expected to demonstrate selective capabilities that differ from their monomers in complex formation with metal cations and because a stable mechanical support is required for most technological applications. Materials that possess a polymer backbone with pendant crown ethers or podand subunits can easily be transformed by casting in fixed site carrier membranes. These may then be employed in selective metal ion transport studies for analytical devices, such as ion selective electrodes or ion sensing; or for environmental applications, such as recovery of metal ion pollutants or nuclear waste; or for heterogeneous catalysts in synthetic organic applications.

Bearing this in mind, we were able to chemically anchor crown ether and dipodand substructures in aromatic polyamides. These polymers are characterized by their excellent balance of thermal and mechanical properties, outstanding chemical resistance and poor solubility in common organic solvents, which makes them useful material for engineering applications.

Polymides containing crown ether in the main chain are not new and were first reported by Feigenbaum and Michel. Different authors have synthesized diverse chemical structures containing these kind of macrocycles, and studies on the cation binding properties and other applications of these polymers have also been performed. Currently, the anomalous behavior of the polymerization of crown ether diacid monomers with diamines under Yamazaki conditions is focusing the attention of different researchers.

Recently, for example, a set of polyamides with crown ether macrocycles as pendant substructures of the main polyamide chain was reported. The overall mobility and the accessibility to any kind of guest molecule of a target host pendant chemical substructure covalently bonded to a polymer backbone, such as a “comb” structure, are much higher those that obtained when this substructure is part of the main chain, where the rigidity and interchain physical bonds (i.e., hydrogen bonds, London dispersive forces and van der Waals interactions) restrict the accessibility at the core of the target substructure. From this perspective, pendant crown ether polyamides are promising alternatives to main chain crown ether polyamides in applications that involve different interactions between the target host crown ethers and the guest, mainly positively charged molecules.

The scientific interest and the wide range of possible technological applications of polymers with pendant crown ether moieties can be expanded to polyamides bearing single or multipodand arms, such as lateral moieties of the polymeric structural units. The higher conformational mobility of multipodands compared with the homologous alicyclic crowns endow such polymers with different thermal properties and solubility, due not only to difference in cohesive...
energy but also to different complexation patterns. Every single podand can conformationally adapt to diverse cation shapes, and, considering the overall polymer structure, podands of different structural units could group toward a specific ion in a way that discrete podands or crowns can not.

This study describes the synthesis and characterization of two diacid monomers containing a benzo-12-crown-4 moiety or a benzo-dipodand substructure, which corresponds to the open-chain counterpart of the alicyclic crown ether, formed with two podand arms ortho bonded to a benzene ring. The reactions of these diacids with five commercial aromatic diamines have rendered 10 novel polyamides that bear crown ether or dipodand substructures as pendant groups. We consider it worthwhile to synthesize and compare the properties of polyamides with crown ether moieties and their open-chain counterparts, the so-called podands, as such polymers might well exhibit a different behavior toward applications involving ions. This could eventually expand the field in which these kinds of functionalized polymers are applied. The polyamides have been completely characterized by common organic and macromolecular analytical methods.

To the best of our knowledge, this is the first time that polyamides containing pendant crown ethers substructures and comparable alicyclic oxyethylene sequences (dipodand) in their structural units have been analyzed to compare polymer synthesis, solubility, water uptake, and mechanical and thermal properties. Moreover, other interesting comparisons, in terms of binding capabilities, will be discussed in future studies.

EXPERIMENTAL

Materials

All materials and solvents were commercially available and were used as received, unless otherwise indicated. Ethyl 3,4-dihydroxybenzoate was prepared by esterification of 3,4-dihydroxybenzoic acid with ethanol. 1,2-Bis(2-chloroethoxy)ethane was synthesized according to the procedure described by García et al. Ethoxyethyl tosylate was prepared from ethyleneglycol monoethylether and p-toluenesulfonyl chloride. N-Methyl-2-pyrrolidone (NMP) was vacuum distilled twice over phosphorous pentoxide, and then stored over 4 Å molecular sieves. Lithium chloride was dried at 400 °C for 12 h prior to use. Triphenylphosphite (TPP) was vacuum distilled twice over calcium hydride and then stored over 4 Å molecular sieves. Pyridine was dried with reflux over sodium hydroxide for 24 h and distilled over 4 Å molecular sieves. Commercially available m-phenylenediamine (MPD), p-phenylenediamine (PPD), 4,4′-diaminediphenyl sulfone (DDS), and 4,4′-diaminediphenyl ether (DDE) were all purified by vacuum sublimation, and finally, 2,2-bis(4-aminobenzo)-1,1,3,3,3-hexafluoropropane (6F) was crystallized from ethanol.

Intermediates and Monomers

4-Ethoxycarbonyl-benzo-12-crown-4

An 1-L flask fitted with a condenser and a mechanical stirrer was charged with 600 mL of dimethylformamide (DMF) and potassium carbonate (33.4 g, 240 mmol). After stirring and heating to 150 °C, a mixture of ethyl 3,4-dihydroxybenzoate (20.0 g, 110 mmol) and 1,8-dichloro-3,6-dioxaoctanate (25.4 g, 110 mmol) was slowly dropped into the reaction flask, following which the system was maintained at 150 °C for 24 h. The solvent was then removed by distillation, and the crude product obtained herein was extracted with dichloromethane. The organic phase was washed twice with basic water, vacuum concentrated to dryness, and finally extracted with boiling hexane. Upon cooling, a mixture of white crystals of 4-ethoxycarbonyl-benzo-12-crown-4 and bis(4-ethoxycarbonyl-1,2-diphénylene)-24-crown-8 was obtained. The extraction procedure with hexane was repeated until the crystals obtained in the cooled hexane were negligible. The 4-ethoxycarbonyl-benzo-12-crown-4 product was isolated from the mixture of crown ethers by column chromatography using hexane/ethyl acetate (1:1) in the mobile phase and silica gel in the stationary phase. Yield: 24.4 g (50%); m.p.: 102 ± 1 °C.

1H NMR (CDCl₃, ppm): δ 7.71 (dd, 1H), 7.68 (d, 1H), 6.95 (d, 1H), 4.34 (q, 2H), 4.23 (m, 4H), 3.89 (m, 2H), 3.83 (m, 2H), 3.78 (s, 4H), 1.37 (t, 3H).

13C NMR (CDCl₃, ppm): δ 166.18, 154.97, 149.85, 125.31, 120.16, 115.90, 72.70, 71.43, 70.96, 70.75, 69.82, 69.71, 60.90, 14.44.

EI-LRMS m/z 320, (17) 319, (100) 307, (25) 297, (47) 296, (33) 289, (13) 155, (20) 154 (77).

Ethyl 3,4-bis-(2-ethoxyethox)benzoate

This compound was prepared in a manner similar to that of 4-ethoxycarbonyl-benzo-12-crown-4, from ethyl 3,4-dihydroxybenzoate (20.0 g, 110

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mmol), ethoxyethyl tosylate (53.6 g, 220 mmol), potassium carbonate (33.4 g, 240 mmol) and DMF (250 mL). The crude product, however, was not extracted with hexane, and was used in the following synthetic step without further purification. Yield: 31.5 g (88%).

$^1$H NMR (CDCl$_3$, ppm) δ 7.57 (dd, 1H), 7.50 (d, 1H), 6.81 (d, 1H), 4.23 (q, 2H), 4.10 (m, 4H), 3.72 (m, 4H), 3.51 (m, 4H), 1.27 (t, 3H), 1.13 (t, 6H).

$^{13}$C NMR (CDCl$_3$, ppm) δ 166.12, 162.34, 152.82, 148.15, 123.78, 114.96, 112.50, 68.78, 68.72, 68.57, 66.73, 66.66, 60.58, 15.04, 14.24.

EI-LRMS m/z 327 (M$^+$; 8), 326, (42) 208, (7) 137, (9) 73 (100).

4-Carboxybenzo-12-crown-4

A 1-L round-bottomed flask fitted with a condenser was charged with 4-ethoxycarbonyl-benzo-12-crown-4 (25.0 g, 84 mmol), ethanol (150 mL), and a solution of sodium hydroxide in water (150 mL, 25%). The mixture was then refluxed for 6 h, following which the solvent was removed under vacuum. The crude product obtained herein was dissolved in 100 mL of water, acidified to pH 3 with HCl, and then extracted with dichloromethane. The organic phase was dried with anhydrous sulfate, filtered off, and then concentrated in a rotary evaporator to obtain a white solid. The product was collected and dried overnight. Yield: 18.7 g (83%); m.p.: 155.618°C.

$^1$H NMR (DMSO-d$_6$, ppm) δ 7.59 (dd, 1H), 7.55 (d, 1H), 7.09 (d, 1H), 4.14 (m, 4H), 3.72 (m, 4H), 3.66 (m, 4H), 3.59 (s, 4H).

$^{13}$C NMR (DMSO-d$_6$, ppm) δ 166.92, 154.59, 149.54, 124.80, 124.29, 119.61, 116.21, 72.28, 70.44, 70.33, 69.80, 68.66.

EI-LRMS m/z 268 (M$^+$; 42), 181, (10) 180, (100) 165, (50) 124, (14) 96 (12).

3,4-Bis-(2-ethoxyethoxy)benzoic Acid

This compound was prepared in a similar manner to 4-carboxybenzo-12-crown-4, from ethyl 3,4-bis(2-ethoxyethoxy)benzoate (40.0 g, 122 mmol), ethanol (150 mL), and a solution of sodium hydroxide in water (150 mL, 25%). Yield: 34.9 g (96%); m.p.: 101.618°C.

$^1$H NMR (DMSO-d$_6$, ppm) δ 7.67 (dd, 1H), 7.58 (d, 1H), 6.87 (d, 1H), 4.17 (m, 4H), 3.79 (m, 4H), 3.58 (dq, 4H), 1.18 (hex, 6H).

$^{13}$C NMR (DMSO-d$_6$, ppm) δ 170.85, 152.95, 147.63, 124.18, 121.45, 114.59, 111.84, 68.16, 68.00, 67.92, 66.24, 14.52.

3,4-Bis-(2-ethoxyethoxy)benzoic Acid

This compound was prepared in a similar manner to 4-carboxybenzo-12-crown-4, from ethyl 3,4-bis(2-ethoxyethoxy)benzoate (40.0 g, 122 mmol), ethanol (150 mL), and a solution of sodium hydroxide in water (150 mL, 25%). Yield: 34.9 g (96%); m.p.: 101 ± 1°C.

$^1$H NMR (DMSO-d$_6$, ppm) δ 7.67 (dd, 1H), 7.58 (d, 1H), 6.87 (d, 1H), 4.17 (m, 4H), 3.79 (m, 4H), 3.58 (dq, 4H), 1.18 (hex, 6H).

$^{13}$C NMR (DMSO-d$_6$, ppm) δ 170.85, 152.95, 147.63, 124.18, 121.45, 114.59, 111.84, 68.16, 68.00, 67.92, 66.24, 14.52.

4-Chlorocarbonylbenzo-12-crown-4

About 20.0 g of 4-carboxybenzo-12-crown-4 (75 mmol) was refluxed with 30 mL of thionyl chloride and 3 drops of DMF. After 4 h, any remaining thionyl chloride was vacuum distilled. The crude product was immediately used without further purification. Yield: quantitative.

$^1$H NMR (CDCl$_3$, ppm) δ 7.85 (q, 1H), 7.73 (d, 1H), 6.98 (d, 1H), 4.24 (m, 4H), 3.92 (m, 2H), 3.82 (m, 2H), 3.77 (m, 4H).

$^{13}$C NMR (CDCl$_3$, ppm) δ 157.64, 150.08, 128.63, 122.34, 114.59, 111.84, 73.53, 71.61, 72.28, 70.44, 70.33, 69.80, 68.66.

EI-LRMS m/z 286 (M$^+$; 17), 251, (25) 180, (12) 168, (14) 163 (100).

3,4-Bis-(2-ethoxyethoxy)benzoyl Chloride

This compound was prepared in a manner similar to that of 4-chlorocarbonylbenzo-12-crown-4, from 3,4-bis(2-ethoxyethoxy)benzoic acid (30.0 g, 100 mmol), thionyl chloride (35 mL), and 3 drops of DMF. Yield: quantitative.

$^1$H NMR (CDCl$_3$, ppm): δ 7.75 (d, 1H), 7.57 (d, 1H), 6.92 (d, 1H), 4.19 (m, 4H), 3.80 (m, 4H), 3.58 (q, 4H), 1.19 (m, 6H).

$^{13}$C NMR (CDCl$_3$, ppm) δ 167.17, 155.39, 148.62, 127.38, 125.49, 116.01, 112.36, 69.15, 68.82, 68.56, 67.02, 66.93, 15.21.

4-(3,5-Dicarboxyphenylaminocarbonyl)benzo-12-crown-4

About 20.0 g (70 mmol) of 4-chlorocarbonylbenzo-12-crown-4 was poured over a solution of 12.6 g (70 mmol) of 5-aminoisophthalic acid in 75 mL of dimethyl acetamide (DMA) under a nitrogen blanket. The mixture was stirred for 30 min at room temperature and then heated at 60 °C for 3 h. After cooling to room temperature, it was slowly poured into 500 mL of distilled water, and a pale yellow precipitate was formed. The product was filtered off, dried at 50 °C, and purified by four cycles of solution in DMA and reprecipitation in water. Yield: 27.1 g (90%); m.p.: >300 °C.

$^1$H NMR (DMSO-d$_6$, ppm) δ 10.41 (s, 1H), 8.67 (s, 2H), 8.22 (s, 1H), 7.70 (t, 2H), 7.15 (d, 1H), 4.18 (m, 4H), 3.71 (m, 4H), 3.59 (m, 4H).

$^{13}$C NMR (DMSO-d$_6$, ppm) δ 166.71, 165.06, 153.82, 149.56, 140.09, 131.72, 127.70, 124.81.
123.12, 118.38, 116.40, 72.23, 70.56, 70.43, 70.03, 69.00, 68.72.

EI-LRMS m/z 431 (M⁺; 20), 252, (13) 251, (100) 163, (61) 79, (21) 78, (14) 63 (21).

5-[3',4'-Bis-(2-ethoxyethoxy)benzoylamino]isophthalic Acid

This compound was prepared and purified in a manner similar to that of 4-(3',5'-dicarboxyphenylaminocarbonyl)benzo-12-crown-4, from 3,4-bis(2-ethoxyethoxy)benzoyl chloride (30.0 g, 95 mmol) and a solution of 17.1 g (95 mmol) of 5-aminoisophthalic acid in 75 mL of DMA. Yield: 36.0 g (73%); m.p.: 237 ± 1 °C.

1H NMR (DMSO, ppm) δ 10.40 (s, 1H), 8.67 (s, 2H), 8.22 (s, 1H), 7.65 (t, 2H), 7.11 (d, 1H), 4.17 (m, 4H), 3.71 (m, 4H), 3.51 (m, 4H), 1.11 (hex, 6H).

13C NMR (DMSO, ppm) δ 166.72, 165.18, 151.64, 147.78, 140.12, 131.71, 126.55, 124.86, 121.84, 113.24, 112.73, 68.56, 68.45, 68.33, 65.92, 15.21.

EI-LRMS m/z 462 (M⁺; 27), 307, (24) 289, (12) 281, (13) 155, (26) 154 (100).

Measurements

1H and 13C NMR spectra were recorded with a Varian Inova 400 spectrometer operating at 399.92 and 100.57 MHz, respectively, using either deuterated chloroform (CDCl₃) or deuterated dimethylsulfoxide (DMSO-d₆) as solvents. Low resolution electron impact mass spectra (EI-LRMS) were obtained at 70 eV on an Agilent 6890N mass spectrometer.

High-resolution mass spectrometry (HRMS) was carried out using a Micromass AutoSpect Waters mass spectrometer, infrared spectra (FTIR) with a Nicolet Impact spectrometer, and elemental analyses using a LECO CHNS-932 microanalyzer.

Inherent viscosities were measured with an Ubbelohde viscometer at 25 ± 0.1 °C with NMP as a solvent at a concentration of 0.5 g/dL.

Differential scanning calorimetry (DSC) data were recorded on a PerkinElmer Pyris I analyzer from a 10 mg sample under a nitrogen atmosphere at a scan rate of 20 °C/min. Thermogravimetric analysis (TGA) data were recorded on Mettler-Toledo TGA/SDTA851 analyzer from a 5 mg sample under a nitrogen or oxygen atmosphere at a scan rate of 10 °C/min.

The polymer solubility was determined by stirring 10 mg with 1 mL of solvent for 24 h at room temperature.

Polymer films were prepared by evaporation of cast solutions in DMA. In most cases, a concentration of 10% by polymer weight was used, and the solvent was eliminated by heating at 100 °C for 4 h in an air-circulating oven and then at 120 °C for 4 h under vacuum (1 mmHg). To determine the tensile properties of the polymers, strips (5 mm in width and 30 mm in length) were cut from polymer films of 30–100 μm thickness and tested on a MTS Synergy 200 Universal Testing dynamometer equipment at 20 °C. Mechanical clamps were used, and an extension rate of 5 mm/min was applied using a gauge length of 10 mm. At least six samples were tested for each polymer, and the data were then averaged out.

Water sorption measurements were determined gravimetrically at 20 °C. Powdered polymeric samples of about 300 mg, previously dried at 120 °C for 24 over phosphorus pentoxide, were placed in a closed box containing a saturated aqueous solution of NaNO₂ at 20 °C, which provided a relative humidity of 65%. The samples were periodically weighed over a period of 24 h and were then allowed to humidify for a further 8 days, until they had equilibrated with their surroundings and presented no further changes in weight.

Polymer Synthesis

The following process describes a typical polymerization reaction. In a 50-mL three-necked flask fitted with a mechanical stirring device, 10 mmol of diamine, 10 mmol of diacid, and 1.4 g of lithium chloride were dissolved in a mixture of 6 mL of pyridine, 22 mmol of TPP, and 20 mL of NMP. The solution was stirred and heated at 110 °C under a dry nitrogen blanket for 4 h. The system was then cooled at room temperature, and the solution precipitated in 300 mL of methanol, rendering a swollen fibrous precipitate. The polymer obtained herein was filtered off and washed with distilled water and acetone, and then extracted with acetone for 24 h in a Soxhlet apparatus, and dried in a vacuum oven at 80 °C overnight. Yields were quantitative for all the polymers.

RESULTS AND DISCUSSION

Two novel diacid monomers have been synthesized in good yields following the inexpensive synthetic routes depicted in Schemes 1 and 2. The intermediates and the monomers were characterized by 1H and 13C NMR spectroscopy and
by mass spectrometry, confirming the chemical structure of the two compounds.

The reaction of ethyl 3,4-dihydroxybenzoate with 1,8-dichloro-3,6-dioxaoctane yielded two compounds that were easily separated by column chromatography: a monoester as the main product, 4-ethoxycarbonyl-benzo-12-crown-4, and a diester byproduct, bis(4-ethoxycarbonyl-1,2-diphenylene)-24-crown-8 (Scheme 1). To increase the mono to diester ratio, the template approach was followed,25,26 and LiCl and LiBr were added to the reaction medium, but no increase in general yield or improved mono to diester ratios were obtained. An increase in the overall monoester yield was only obtained using a higher dilution medium and by a much slower addition of the dichloro derivative to the reaction vessel. This was ~30% higher than the one previously described for other benzo-12-crown-4 derivatives.27,28

The formation of the diester might be attributed to the fact that the reaction of the phenoxide with one end of the dichloro derivative leading to a product with restricted conformational mobility of the short oxyethylene chain, thereby impairing the ability of the chlorinated end of the aliphatic sequence of the molecule to undergo the intramolecular nucleophilic substitution that eventually yields the benzo-12-crown-4. Moreover, this leads to the reaction of the latter molecule with a second dichloro derivative, instead of undergoing intramolecular cyclization, which will finally yield the undesired diester. Thus, the dibenzo-24-crown-8 is favored thermodynamically, and only template effects or high-dilution reaction media can displace the reaction product ratio towards the benzo-12-crown-4.

The polymers were synthesized according to the method described by Yamazaki et al.29 The general polyamide structures and acronyms are depicted in Scheme 3. Yields were essentially quantitative in every case. Elemental analysis and inherent viscosity of the polymers are given in Table 1. All the polymers were characterized by $^{13}$C NMR, $^1$H NMR, and FTIR spectroscopy. As an illustrative example, Figure 1 shows the spectra of polyamide P4DDE along with the proposed signal assignment.

The polycondensation of the monomers under standard polymerization conditions rendered polyamides with high inherent viscosities, suggesting high molecular weight polymers (Table 1). No anomalous events were detected during the polymerization reactions, and clear highly-viscous solutions were obtained upon cooling the reaction vessel at the end of polymerization. After precipitation, the polymers were obtained as fibrous mat-

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Scheme 1. Experimental sequences for the synthesis of 4-(3',5'-Dicarboxyphenylamino)carbonyl)benzo-12-crown-4.
Scheme 2. Experimental sequences for the synthesis of 5-[3',4'-Bis-(2-ethoxyethoxy)-benzoylamino]isophthalic acid.

Scheme 3. Structure and acronyms of polyamides.
ter that could be completely redissolved and reprecipitated. In contrast, Gibson and coworkers observed that 21,22 obtained gels of amorphous polymers that were insoluble in any of the solvents (such as aprotic dipolar solvents, for example, NMP) they tested, despite the presence of salts in the synthesis of poly(amide crown ether)s based on bis(5-carboxy-1,3-phenylene)-32-crown-10. They proposed the in situ threading of the macrocyclic cavity of one polymer chain onto a segment of another polymer chain during polymerization, arguing that if only a small fraction of high molecular weight polyamide molecules were

<table>
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<th>Polymer</th>
<th>( \eta_{\text{inh}} ) (dL g(^{-1}))</th>
<th>Calculated (%)</th>
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<td></td>
<td></td>
<td>C</td>
<td>H</td>
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<tr>
<td></td>
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Figure 1. Characterization of polyamide P4DDE: (a) FTIR, (b) \(^1\)H NMR, and (c) \(^{13}\)C NMR.
threaded, it would result in the formation of a network that could adversely affect the solubility of the entire system. Moreover, it would lead to the formation of polyamide pseudorotaxanes, rotaxanes, and catenanes. In our system, the same kind of threading could be proposed, although the cavity of the crown is smaller than the one described by Gibson and coworkers, and the threading effects are not observed. As it is, our study detected this kind of phenomena in the polymerization of monomers with pendant benzo-15-crown-5, benzo-18-crown-6, and their benzo-dipodands counterparts. The results will be discussed elsewhere.

Thermal Properties

The thermal behavior of these polymers was evaluated by means of DSC and TGA.

Glass transition temperatures \( T_g \)s of all the polymers ranged between 207 and 349 °C (Table 2), whereas the \( T_g \) of a related polyamide, with a pendant unsubstituted benzoylamine group, poly \((m\)-phenylene 5-benzoylaminoisophthalamide) [PPBI], is 298 °C, which is virtually the same as the \( T_g \) of the C4MPD (299 °C). This implies that the effect on the \( T_g \) of an increase in the lateral volume of the pendant benzoylamine group due to the incorporation of a crown moiety, which could lead to a \( T_g \) increase due to an increment in chain rotation restrictions, is neutralized by the lower density of hydrogen bridges associated with higher interchain separations, its asymmetry, higher conformational mobility, and the plasticization that the cyclic ethylene oxide sequences of the crown moiety impart to the polymer structure.

On the other hand, the \( T_g \) of P4MPD is 218 °C, ~80 °C lower than the \( T_g \)s of C4MPD. Taking into account that the diamine residue is the same in P4MPD and C4MPD, the differences arise from the cyclic oxyethylene sequences of the crown substructure in C4MPD and from the acyclic oxyethylene sequences of the dipodand moieties in P4MPD. In accordance with this general fact, the polymers with podand substructures have \( T_g \)s that are between 50 and 100 °C lower than their counterparts with crown ether moieties. This could be attributed to the higher mobility of the linear oxyethylene sequences in comparison with the mobility restrictions imposed on the cyclic oxyethylene sequences fused with a rigid benzene subunit. Furthermore, the higher conformational mobility of the ether groups present in the podand moieties facilitates interaction with the amide groups due to hydrogen bonding, which diminishes the density of interchain hydrogen bonds, thereby lowering the \( T_g \).31

In each polyamide series, a trend was observed regarding the nature of the diamine. In each polymer series, for polyamides derived from diamines with two benzene rings separated with a spacer (DDS, 6F, and DDE), the \( T_g \) goes down in the order DDS > 6F > DDE. This is to be expected since DDS provides a higher polarity factor than DDE and 6F, and furthermore, the geometry of DDS leads to a more rigid molecular structure than DDE and 6F. A quantitative evaluation of steric factors was made using theoretical means developed by Alvarez et al.: the mobility restriction imposed by rotational barriers and the regular geometry structures, along with a higher polarity of the SO2 group, should give rise to highly

Table 2. Thermal Properties and Solubility of the Polyamides

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( T_g ) (°C)</th>
<th>( T_d ) (°C)</th>
<th>DMF</th>
<th>DMA</th>
<th>NMP</th>
<th>DMSO</th>
<th>THF</th>
<th>p-Cresol</th>
</tr>
</thead>
<tbody>
<tr>
<td>C4MPD</td>
<td>299</td>
<td>390</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>–</td>
</tr>
<tr>
<td>C4PPD</td>
<td>349</td>
<td>415</td>
<td>+</td>
<td>++</td>
<td>++</td>
<td>±</td>
<td>–</td>
<td>+</td>
</tr>
<tr>
<td>C4DDS</td>
<td>297</td>
<td>420</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>±</td>
<td>–</td>
<td>++</td>
</tr>
<tr>
<td>C4DDE</td>
<td>257</td>
<td>420</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>–</td>
<td>+</td>
</tr>
<tr>
<td>C4/6F</td>
<td>278</td>
<td>425</td>
<td>+</td>
<td>+</td>
<td>++</td>
<td>±</td>
<td>–</td>
<td>+</td>
</tr>
<tr>
<td>P4MPD</td>
<td>218</td>
<td>410</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>–</td>
<td>++</td>
</tr>
<tr>
<td>P4PPD</td>
<td>251</td>
<td>400</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>–</td>
<td>+</td>
</tr>
<tr>
<td>P4DDS</td>
<td>235</td>
<td>410</td>
<td>+</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>–</td>
<td>++</td>
</tr>
<tr>
<td>P4DDE</td>
<td>207</td>
<td>420</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>P4/6F</td>
<td>223</td>
<td>420</td>
<td>+</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>–</td>
<td>+</td>
</tr>
</tbody>
</table>

++ , soluble at room temperature; +, soluble on heating; ± partially soluble; –, insoluble.
efficient chain packing, consistent with a higher $T_g$. The same considerations would explain the higher $T_g$s of 6F polymers with respect to DDE polymers. The presence of $p$-orientation of the phenylene rings in the polymer chain in polyamides derived from PPD increases the chain stiffness to an important extent and gives rise to the highest $T_g$s. Because of the lack of linearity of the 1,3-diphenyl substitution of the benzene ring of the MPD diamine, polyamides derived from MPD show considerably lower $T_g$ values than those derived from PPD (between 33 and 50 °C).

Figure 2 depicts the DSC thermograms of polyamides C4DDE and P4DDE. No endothermic peak attributable to melting temperature was observable with DSC in any of the cases. Thus, as a whole, the family of polysisophthalamides reported herein must be considered as amorphous materials with very high $T_g$s.

TGA data were used to evaluate the thermal stability in N$_2$. The thermal resistance, in terms of initial decomposition temperature ($T_d$ onset), was high and was practically the same for all the polyamides (Table 2), which is consistent with thermal decomposition that starts with the thermal break of the C—C or C—O bonds of the aliphatic oxyethylene sequences, leading to low molecular weight fragments that can easily escape from the polymer matrix. The $T_d$ of our polyamides is analogous with the $T_d$ observed in the reference polymer without a crown or podand subunit, poly($m$-phenylene 5-benzoylaminoisophthalamide) ($T_d = 415$ °C). The $T_d$ of all the polyamides in oxygen atmosphere (O$_2$) were about 50 °C lower than that obtained in an inert atmosphere (N$_2$), and were also similar for all the polymers. As an illustrative example, the TGA of polyamide C4/6F is depicted in Figure 3. The first step in the degradation curve corresponds in terms of weight loss to the weight percentage of the aliphatic crown or podand moieties in the polymeric structural units. The char yield at 800 °C was ~50% in N$_2$ and 0% in O$_2$.

Solubility

The solubility of all the polymers is shown in Table 2. All the polymers are soluble in aprotic polar solvents such as NMP, DMF, DMA, or DMSO and in protic cresol. It is interesting to note that there are no differences in solubility between the polymers with a benzo-crown ether substructure or with a benzo-podand moiety. Moreover, the difference in solubility between all the polymers is negligible, which supports the idea that this property is, practically speaking, controlled by the oxyethylene sequences present as crown or podand pendant structures.

Mechanical Properties

All the polyamides showed good film-forming ability, which makes them suitable for testing as fixed site carrier membranes for cation separation, ion selective membranes, or selective solid–liquid extraction of cations.
The mechanical properties of these films are listed in Table 3. They can be considered as acceptable for films made on a laboratory scale, with tensile strength of 56–88 MPa and Young modulus of 1.8–3.3 GPa. These values are in good agreement with values reported earlier for experimental aromatic polyamides. Thus, the incorporation of bulky side groups seems to have no substantial influence over the mechanical strength and modulus of these substituted poly(isophthalamides).34–36

Water Absorption

The ability to absorb water is an important characteristic that influences the thermal, mechanical, electrical, and dielectrical properties of polyamides. Moreover, the relatively hydrophilic oxyethylene sequences of the crown or dipodand substructure of the bulky side groups exercise greater influence over moisture absorption in the synthesized polyamides. This was measured by maintaining powdered polymer samples in a moisture-controlled atmosphere at room temperature. Table 3 shows the isothermal water sorption for the new polyamides.

The two series of polyamides described in this study—polyamides with crown ethers and with dipodand substructures—show different water uptake. Polyamides with crown ether moieties absorb between 0.5 and 0.9 more molecules of water per structural unit than the polymers with dipodand moieties. A plausible explanation is that the oxyethylene sequences of the podand arms have higher conformational mobility than the cyclic oxyethylene sequences of the crowns and can establish intermolecular and intramolecular hydrogen bonds between the ether linkages and the amide groups, thus reducing the percentage of available polar amide groups able to interact with water, and thereby diminishing the overall water uptake.31

Table 3. Mechanical Properties and Moisture Absorption of the Polyamides

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Tensile Strength (MPa)</th>
<th>Young's Modulus (GPa)</th>
<th>Water Uptake (%)</th>
<th>Mol H₂O/rep. Unit</th>
<th>Mol H₂O/eq. Amide</th>
</tr>
</thead>
<tbody>
<tr>
<td>C4MPD</td>
<td>65</td>
<td>2.6</td>
<td>11.4</td>
<td>3.2</td>
<td>1.1</td>
</tr>
<tr>
<td>C4PPD</td>
<td>88</td>
<td>3.3</td>
<td>11.7</td>
<td>3.3</td>
<td>1.1</td>
</tr>
<tr>
<td>C4DDS</td>
<td>59</td>
<td>2.1</td>
<td>9.1</td>
<td>3.3</td>
<td>1.1</td>
</tr>
<tr>
<td>C4DDE</td>
<td>82</td>
<td>2.6</td>
<td>9.6</td>
<td>3.2</td>
<td>1.1</td>
</tr>
<tr>
<td>C4/6F</td>
<td>84</td>
<td>2.8</td>
<td>7.8</td>
<td>3.2</td>
<td>1.1</td>
</tr>
<tr>
<td>P4MPD</td>
<td>70</td>
<td>2.4</td>
<td>8.6</td>
<td>2.6</td>
<td>0.9</td>
</tr>
<tr>
<td>P4PPD</td>
<td>74</td>
<td>2.4</td>
<td>7.7</td>
<td>2.3</td>
<td>0.8</td>
</tr>
<tr>
<td>P4DDS</td>
<td>57</td>
<td>1.8</td>
<td>7.4</td>
<td>2.8</td>
<td>0.9</td>
</tr>
<tr>
<td>P4DDE</td>
<td>76</td>
<td>2.2</td>
<td>6.8</td>
<td>2.4</td>
<td>0.8</td>
</tr>
<tr>
<td>P4/6F</td>
<td>56</td>
<td>1.9</td>
<td>5.7</td>
<td>2.4</td>
<td>0.8</td>
</tr>
</tbody>
</table>

The uptake of water corresponding to the crown or dipodand substructure could then be estimated. Taking this into account, the crown substructure would be responsible for the uptake of one molecule of water per crown, and the dipodand substructure of 0.1–0.6 mol of water per subunit, depending on the polymeric structural unit.

This does not mean that the extra water content of the polyamides described herein is really bound into the oxyethylene sequences, which might be either lower or higher. Thus, the introduction of a more bulky side group affects the free volume of the structural unit, increasing the accessibility of water throughout the polymer chemical structure. Conversely, any possible interactions involving the oxygen atoms of the oxyethylene sequences with the amide groups through hydrogen bonding could diminish the real quantity of moles of water per amide group.31

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CONCLUSIONS

An inexpensive and relatively easy synthetic procedure has been followed to synthesize two novel isophthalic diacid-based monomers containing a benzo-12-crown-4 moiety as a pendant group or a benzo-dipodand pendant subunit, which represent the open-chain counterpart of the alicyclic crown moiety. The direct polycondensation of the two diacids with five commercial aromatic diamines under Yamazaki conditions proved to be a good method of obtaining soluble high molecular weight polyamides with crown or podand bulky pendant groups, and 10 new polyisophthalamides were obtained by following this procedure. These polyamides show high glass transition temperatures (up to 349 °C) and good thermal resistance, although lower than that exhibited by the fully aromatic polyamides because of the weight loss associated with the thermal break of the aliphatic C—C or C—O bonds of the oxyethylene sequences in crown or podand moieties. The presence of oxyethylene sequences as crown ether or dipodand pendant groups enhances the affinity for water of polyisophthalamides, although this affinity enhancement is significantly higher for benzo-crown substrutures. The polyamides show good film-forming ability due to the good processability associated with enhanced solubility of the polymers in polar aprotic solvents. The mechanical behavior of the films obtained by casting is considered satisfactory for experimental aromatic polyamides.

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REFERENCES AND NOTES

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