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Received 14 February 2006; accepted 18 April 2006
DOI: 10.1002/pola.21510
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This article describes the synthesis and characterization of two diacid monomers, each containing a benzo-15-crown-5 subunit or its dipodal counterpart. Both novel monomers were reacted with technical aromatic diamines with Yamazaki’s direct polyamidation method to render modified polyisophthalamides with high molecular weights containing side moieties of cyclic and acyclic ethylene oxide sequences. All the polymers were soluble in aprotic polar solvents and showed high glass-transition temperatures in the range of 190–345 °C. The polymers with side crown ethers showed much higher glass-transition temperatures than those with acyclic linear side ethylene oxide arms. The chemical composition, particularly with respect to the diamine and the open or closed character of the pendent ethylene oxide sequence, also affected other general properties such as the mechanical resistance, mechanical modulus, or water absorption. © 2006 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 44: 4063–4075, 2006

Keywords: crown ethers; gelation; monomers; podands; polyamides

INTRODUCTION

Crown ethers or coronands are cyclic polyethers made up of ethylene oxide units that display a series of intriguing properties. For instance, their ability to selectively interact with metal cations through ion–dipole interactions means they are useful chemical substructures in the preparation of phase-transfer catalysts, ion-selective electrodes, liquid, supported, or fixed-site carrier membranes, and so forth.1 Their structure and alkali-metal-ion binding capabilities were first described by Pedersen in 1967.2,3 On the other hand, podands or podal structures are acyclic host molecular structures with binding sites for guest molecules such as anions, cations, and neutral molecules.4 For example, podands such as oligoethylene oxides and poly(ethylene oxide) are the acyclic analogues of crown ethers.
In a previous article, we reported the synthesis and characterization of aromatic polyamides bearing benzo-12-crown-4 and their dipodal counterparts as pendant substructures. In this article, the scope of our study is extended to polyamides containing pendant moieties of benzo-15-crown-5 and their dipodal counterparts. Our initial assumption was that the wider diameter of the 15-crown-5 cavity compared with the 12-crown-4 moiety and the longer podal arms of the corresponding open-chain counterpart would greatly influence the properties of the novel polymers.

Moreover, monomer synthesis with crown subunits is facilitated to some extent by the crown cavity diameter: one of the synthetic steps in the synthesis of the diacid monomer with a benzo-12-crown-4 substructure was accomplished with low yields because of the formation of dimer byproducts that had to be separated by column chromatography, whereas the complete set of synthetic steps that led to the diacid monomer bearing the benzo-15-crown-5 resulted in high yields without significant byproducts.

It should be noted that when the crown cavity diameter is increased or when longer dipodal arms are employed, the standard Yamazaki polymerization conditions have to be modified to prevent the formation of a polymer gel.

The two novel monomers described in this work were designed to obtain polymers with cation-binding capability provided by the benzo-crown ether subunit or its open-chain counterpart. Hence, the aim of this work is to compare the behavior and properties of the polyamides derived from these monomers, which present novel chemical structures. It also offers the possibility of comparing the property differences of a cycle structure and its corresponding open-chain structure, while maintaining the chemical characteristics of the ethylene oxide sequences. The high performance of the aromatic polyamide backbone, along with the complex capabilities of the dipodal or crown pendant moieties, means that these polymers are suitable in a number of applications, such as the recovery of cations in wastewater by means of reversible and reusable solid–liquid extraction technology, cation membrane transport applications, and cation sensing.

**EXPERIMENTAL**

**Materials**

All materials and solvents were commercially available and were used as received, unless otherwise indicated. N-Methyl-2-pyrrolidinone (NMP) was distilled twice over phosphorous pentoxide under reduced pressure and stored over molecular sieves (4 Å). Lithium chloride was dried at 400 °C for 12 h before use. Triphenylphosphite (TPP) was distilled twice over calcium hydride under reduced pressure and stored over molecular sieves (4 Å). Pyridine was dried via refluxing over sodium hydroxide for 24 h and distilled over 4 Å molecular sieves. Commercially available samples of m-phenylenediamine (MPD), p-phenylenediamine (PPD), 4,4′-diaminediphenylsulfone (DDS), and 4,4′-diaminediphenyl ether (DDE) were purified twice by vacuum sublimation. 2,2-Bis(4-aminophenyl)-1,1,3,3,3-hexafluoropropane (6F) was recrystallized from ethanol. The synthesis of 1,11-dichloro-3,6,9-trioxaundecane, 1-chloro-3,6-dioxaoctane, and ethyl 3,4-dihydroxibenzoate was accomplished with previously reported procedures.

**Intermediates and Monomers**

**4-Ethoxycarbonyl-benzo-15-crown-5**

A 1-L flask fitted with a condenser and a mechanical stirrer was charged with 500 mL of dimethylformamide (DMF) and potassium carbonate (33.4 g, 240 mmol). The reaction was heated to 150 °C, after which a mixture of ethyl 3,4-dihydroxybenzoate (20.0 g, 110 mmol) and 1,11-dichloro-3,6,9-trioxaundecane (25.4 g, 110 mmol) was slowly dropped into the reaction flask while subjected to vigorous stirring. The reaction was maintained at 150 °C for 24 h, and then the solvent was removed under reduced pressure. The crude product obtained herein was dissolved with dichloromethane and washed in a separation funnel with basic water. The organic layer was dried with anhydrous sodium sulfate, filtered off, vacuum-concentrated to dryness, and finally extracted with hot hexane. Upon cooling, white crystals of 4-ethoxycarbonyl-benzo-15-crown-5 were obtained. The extraction procedure with hexane was repeated until the amount of crystals obtained in the cooled hexane was negligible.

Yield: 24.4 g (65%). mp: 65 ± 1 °C. 1H NMR [deuterated chloroform (CDCl₃), ppm, δ]: 7.61 (dd, 1H), 7.49 (d, 1H), 6.80 (d, 1H), 4.29 (q, 2H), 4.13 (m, 4H), 3.87 (m, 4H), 3.71 (s, 4H), 1.33 (t, 3H). 13C NMR (CDCl₃, ppm, δ): 166.37, 153.05, 148.40, 132.86, 123.14, 114.46, 111.96, 71.09, 70.39, 70.28, 69.39, 69.25, 68.96, 68.54, 14.41. Low-resolution electron-impact mass spectrometry (EI-
Ethyl 3,4-Bis[2-(2-ethoxyethoxy)ethoxy]benzoate

This reagent was prepared in a similar manner to 4-ethoxycarbonyl-benzo-15-crown-5 from ethyl 3,4-dihydroxybenzoate (20.0 g, 110 mmol), 1-chloro-3,6-dioxaoctane (33.6 g, 220 mmol), potassium carbonate (37.7 g, 272 mmol), and DMF (250 mL) and, in the next step, employed as a crude product without any further purification.

Yield: 43.3 g (95%). 1H NMR (CDCl 3, ppm, δ): 7.63 (dd, 1H), 7.55 (d, 1H), 6.88 (d, 1H), 4.31 (q, 2H), 4.20 (m, 4H), 3.87 (m, 4H), 3.72 (m, 4H), 3.58 (m, 4H), 3.51 (oct, 2H), 1.35 (t, 3H), 1.19 (t, 6H). 13C NMR (CDCl 3, ppm, δ): 166.37, 152.86, 148.25, 123.97, 123.37, 114.95, 112.63, 71.08, 71.02, 69.97, 69.69, 69.58, 68.87, 66.63, 66.74, 60.85, 15.24, 14.47. EI-LRMS m/z: 341 (M⁺; 12), 340 (66), 295 (11), 208 (64), 193 (20), 186 (33), 165 (14), 164 (16), 163 (100).

4-Carboxybenzo-15-crown-5

A 1-L round flask fitted with a condenser was charged with 4-ethoxycarbonyl-benzo-15-crown-5 (25.5 g, 75 mmol), ethanol (150 mL), and a solution of sodium hydroxide in water (150 mL, 25%). The mixture was then refluxed for 6 h, after which the solvent was removed in vacuo. The crude product obtained herein was dissolved in 100 mL of water, acidified to pH 3 with HCl, and extracted with dichloromethane. The organic phase was dried with anhydrous sodium sulfate, and filtered off, and after concentration under reduced pressure, a white solid appeared. The product was collected and dried overnight.

Yield: 20.4 g (87%). mp: 171 ± 1 °C. 1H NMR (CDCl 3, ppm, δ): 7.56 (dd, 1H), 7.52 (d, 1H), 6.88 (d, 1H), 4.19 (m, 4H), 3.92 (m, 4H), 3.76 (s, 4H), 3.60 (s, 8H). 13C NMR (CDCl 3, ppm, δ): 167.23, 152.53, 148.01, 123.57, 123.17, 113.83, 112.26, 70.65, 69.78, 69.67, 68.83, 68.66, 68.54, 68.31. EI-LRMS m/z: 312 (M⁺; 45), 180 (35), 165 (23), 117 (91), 73 (100), 59 (26).

3,4-Bis[2-(2-ethoxyethoxy)ethoxy]benzoic Acid

This reagent was prepared in a similar manner to 4-carboxybenzo-15-crown-5 from ethyl 3,4-bis[2-(2-ethoxyethoxy)ethoxy]benzoate (41.4 g, 100 mmol), ethanol (150 mL), and a solution of sodium hydroxide in water (150 mL, 25%).

Yield: 37.8 g (98%). 1H NMR (CDCl 3, ppm, δ): 7.54 (dd, 1H), 7.47 (d, 1H), 7.06 (d, 1H), 4.14 (dt, 4H), 3.76 (q, 4H), 3.60 (m, 4H), 3.48 (m, 4H), 3.42 (dq, 4H), 3.32 (s, 1H), 1.09 (t, 6H). 13C NMR (CDCl 3, ppm, δ): 165.94, 154.67, 147.83, 126.57, 124.43, 114.99, 111.65, 70.31, 70.26, 69.23, 69.21, 68.87, 68.62, 68.43, 68.18, 65.80, 14.53.

4-Chlorocarbonylbenzo-15-crown-5

4-Carboxybenzo-15-crown-5 (20.0 g, 64 mmol) was refluxed with 19 mL (256 mmol) of thionyl chloride and three drops of DMF. After 4 h, the remaining thionyl chloride was vacuum-distilled, and the crude product was immediately used in the next step without further purification.

Yield: 20.7 g (98%). 1H NMR (CDCl 3, ppm, δ): 7.80 (dd, 1H), 7.52 (d, 1H), 6.88 (d, 1H), 4.19 (m, 4H), 3.92 (m, 4H), 3.76 (s, 4H). 13C NMR (CDCl 3, ppm, δ): 165.94, 154.67, 147.83, 126.57, 124.43, 114.99, 111.65, 70.31, 70.26, 69.23, 69.21, 68.87, 68.62, 68.43, 68.18, 65.80, 14.53.

3,4-Bis[2-(2-ethoxyethoxy)ethoxy]benzoyl Chloride

The preparation of the reagent was similar to the preparation of 4-chlorocarbonylbenzo-15-crown-5 from 3,4-bis[2-(2-ethoxyethoxy)ethoxy]benzoic acid (30.0 g, 78 mmol), thionyl chloride, (23 mL, 310 mmol), and three drops of DMF.

Yield: quantitative. 1H NMR (CDCl 3, ppm, δ): 7.43 (d, 1H), 7.24 (s, 1H), 6.66 (d, 1H), 3.92 (d, 4H), 3.59 (s, 4H), 3.43 (s, 4H), 3.24 (s, 4H), 3.21 (m, 4H), 0.91 (m, 6H). 13C NMR (CDCl 3, ppm, δ): 165.94, 154.67, 147.83, 126.57, 124.43, 114.99, 111.65, 70.31, 70.26, 69.23, 69.21, 68.87, 68.62, 68.43, 68.18, 65.80, 14.53.

4-(3,5-Dicarboxyphenylaminocarbonyl)benzo-15-crown-5 (C5)

4-Chlorocarbonyl-benzo-15-crown-5 (20.0 g, 61 mmol) was added to a solution of 11.0 g (61 mmol) of 5-aminoisophtalic acid and 70 mL of dimethylacetamide (DMA) under nitrogen. The mixture was stirred for 30 min at room temperature and then at 60 °C for 3 h. Upon cooling to room temperature, the mixture was slowly poured into 500 mL of distilled water. The pale yellow precipitate that formed was filtered off, dried at 50 °C, and finally purified four times by solution precipitation in DMA/water.

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Yield: 23.2 g (80%). mp: 181–184 °C. 1H NMR [deuterated dimethyl sulfoxide (DMSO-d$_6$), ppm, δ]: 10.39 (s, 1H), 8.66 (d, 2H), 8.20 (t, 1H), 7.66 (dd, 1H), 7.59 (d, 1H), 7.07 (d, 1H), 4.13 (m, 4H), 3.79 (m, 4H), 3.61 (s, 4H). 13C NMR (DMSO-d$_6$, ppm, δ): 166.71, 165.22, 154.83, 152.01, 148.03, 140.10, 131.71, 126.60, 124.87, 121.79, 113.30, 112.79, 70.21, 69.41, 69.08, 68.86, 68.78, 68.66, 68.4. EI-LRMS m/z: 307 (24), 289 (11), 163 (9), 154 (100), 155 (27).

5-{3,4-Bis[2-(2-ethoxyethoxy)ethoxy]benzoylamino}isophthalic acid (P6)

The preparation and purification of this monomer followed the same method used for the synthesis of C5 from 3,4-bis[2-(2-ethoxyethoxy)ethoxy]benzoyl chloride (20.0 g, 49 mmol) and a solution of 8.9 g (49 mmol) of 5-aminoisophtalic acid in 65 mL of DMA.

Yield: 19.7 g (73%). 1H NMR [dimethyl sulfoxide (DMSO), ppm, δ]: 13.29 (s, 1H), 10.40 (s, 1H), 8.68 (s, 2H), 8.23 (s, 1H), 7.64 (t, 2H), 7.12 (d, 1H), 4.19 (m, 4H), 3.77 (m, 4H), 3.60 (m, 4H), 3.47 (m, 4H), 3.40 (q, 4H), 1.07 (h, 6H). 13C NMR (DMSO, ppm, δ): 166.72, 165.16, 151.62, 147.78, 140.14, 131.71, 126.60, 124.87, 121.79, 113.30, 112.79, 70.21, 69.41, 69.08, 68.57, 68.35, 65.70, 15.22. EI-LRMS m/z: 573 (16), 572 (51), 550 (M$^+$; 28), 549 (13), 369 (19), 307 (18), 155 (26), 154 (100).

Polymer Synthesis

A typical polymerization reaction is described. In a 50-mL, three-necked flask fitted with mechanical stirring, 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 the proper quantity of NMP.

Measurements

1H and 13C NMR spectra were recorded at 399.92 and 100.57 MHz, respectively, on a Varian Inova 400 spectrometer with CDCl$_3$ or DMSO-d$_6$ as the solvent. Low-resolution electron-impact mass spectra were obtained at 70 eV on an Agilent 6890N mass spectrometer. High-resolution mass spectrometry was carried out on a Micromass AutoSpect Waters mass spectrometer. Fourier
Transform infrared spectra (FT-IR) were recorded with a Nicolet Impact spectrometer. Elemental analyses were performed on a Leco CHNS-932 microanalyzer. The inherent viscosity (η\text{inh}) values were measured with an Ubbelohde viscometer at 25 ± 0.1 °C with NMP as a solvent at a 0.5 dL/g concentration. Differential scanning calorimetry (DSC) data were recorded on a PerkinElmer Pyris I analyzer from 10 mg of a sample under a nitrogen atmosphere at a scanning rate of 20 °C/min. Data obtained from thermogravimetric analysis (TGA) of a 5-mg sample were recorded on a Mettler-Toledo TGA\SBTA851 analyzer at a scanning rate of 10 °C/min under a nitrogen atmosphere. The polymer solubility was determined through the mixing of 10 mg of the polymer with 1 mL of the solvent, followed by stirring for 24 h at room temperature. Polymer films were prepared by the evaporation of cast solutions in DMA. In most cases, a concentration of 10% by polymer weight was used, and the solvent was eliminated via heating at 100 °C for 4 h in an air-circulating oven and then at 120 °C for 4 h in vacuo (1 mmHg). For the measurement of the mechanical properties, strips 5 mm wide, 30 mm long, and 40–60 μm thick were cut from polymer films and tested on an MTS Synergie 200 universal testing dynamometer at room temperature. The mechanical clamps were used, and an extension rate of 5 mm/min was applied with 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 on powdered polymer samples of about 300 mg, which were previously dried at 120 °C for 24 h over phosphorus pentoxide. They were placed in a closed desiccator containing a saturated aqueous solution of NaNO\textsubscript{2} maintained at 20 °C and at a relative humidity of 65%. The samples were periodically weighed over 24 h and

Scheme 1. Experimental sequences for the synthesis of C5.
were then allowed to humidify for 2 more days, at which point they had equilibrated with their surroundings and no further weight changes occurred.

RESULTS AND DISCUSSION

This work describes the synthesis of 10 novel polyamides bearing crown ethers and their dipodal oligoethylene oxide counterparts. The polymers were obtained through the combination of five commercial diamines with two new diacid monomers bearing either a crown ether moiety or dipodal oxyethylene sequences.

The synthetic routes for the monomers are depicted in Schemes 1 and 2. The overall yields of the four-step synthesis of C5 and P6 were 44 and 68%, respectively. The lower yield of one single synthetic step corresponded to the synthesis of the crown ether from 3,4-dihydroxybenzoate and the dichloro derivative (65%), contrasting with the formation of the dipodal structure from 3,4-dihydroxybenzoate and the monochloro derivative that proceeded with a yield of 95%. This fact can be probably attributed to the intramolecular cyclization, less favored than the dipolar structure formation.

The polymers were synthesized according to the method described by Yamazaki et al. Among its other chemicals, the initial monomer concentration (IMC) contained 0.5 mol of diamine and diacid per liter of NMP. Under standard Yamazaki conditions, an IMC of 0.5 M for most mono-

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Scheme 2. Experimental sequences for the synthesis of P6.
mers will supposedly yield soluble aromatic polyamides with higher average molecular weights.

The polycondensation of the diacid monomer containing the benzo-dipodal substituents with commercial diamines, under standard Yamazaki conditions, rendered high-molecular-weight polyamides, except in the case of the 6F diamine, which resulted in an insoluble gel. The same behavior was observed when the benzo-crown diacid monomer was condensed with any of the commercial diamines with a 0.5 M IMC. A homogeneous solution formed in the first minutes of the reaction, turned into a cloudy and viscous mixture in 30 min, and finally turned into a gel after approximately 45 min. The gels were insoluble in all solvents, even in the presence of salts.

Although the Yamazaki method is not a clean process, we think that the unknown side reactions are not responsible for the crosslinking phenomenon. The polymerization of isophthalic diacid with lateral benzo-12-crown-4 or their dipodal counterpart followed a standard polymerization under Yamazaki conditions, yielding high-molecular-weight soluble polyamides. The same pendant oxyethylene sequences should undergo the same unclean reactions under the same conditions. It is not expected that the increase from three to four oxyethylene sequences in the diacid lateral subunits, from benzo-12-crown-4 to benzo-15-crown-5 pendant moieties, or from two to three oxyethylene sequence in each podal side arm could lead to new chemical crosslinking side reactions.

An analogous gelation process was observed by Delavid and Gibson in the synthesis of polyamides with crown ethers in the main chain, 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 by a segment of another polymer chain during polycondensation, which resulted in the formation of an insoluble network.

However, the gelation process can also be attributed to various physical factors:

1. Physical crosslinking through the formation of interchain sandwich structures (crown/cation/crown).
2. The threading of one polymer chain segment through the macrocyclic cavity of another polymer chain during the polymerization reaction to yield polyrotaxanes.
3. The threading of a polymer chain segment through a cyclic oligoamide chain during the polymerization reaction to yield polyrotaxanes.

However, there was no evidence, in our case, to confirm that any of the outlined explanations accounted for the gelation. In further experiments, working on the assumption that salts might be responsible for the gel formation, we also performed the polycondensation reactions in the absence of LiCl and in the absence of pyridine to avoid the formation of pyridinium salt. The results proved negative, and gelation was evident in both cases.

To explore possible threading of one polymer chain segment through the macrocyclic cavity of another polymer chain during polymerization to yield polyrotaxanes, studies were carried out on model compounds (see Scheme 3). The reaction of

![Scheme 3. Synthesis of the polyamide model compounds under Yamazaki conditions in the presence of benzo-15-crown-5.](image-url)
terephthalic acid with \( p \)-toluidine or 2,6-dibromo-4-methylaniline in the presence of a large amount of benzo-15-crown-5 under Yamazaki conditions was monitored with \(^1\)H NMR and fast atom bombardment mass spectrometry. However, the presence of rotaxane species was not observed in any instance, and this indicated that the gel formation was in all probability not due to crown ring threading. Moreover, no byproducts were observed in the model reactions, and this supported the idea that the crosslinking phenomenon, which yielded gels in the polymerization, could not be attributed to unclean chemical reactions during polymerization.

Moreover, a gel was also obtained when the monomer bearing a benzo-dipodal open-chain structure was condensed with the 6F diamine, suggesting a different crosslinking phenomenon. Previous results for the polymerization of acrylic monomers bearing 12-crown-4, 12,13 15-crown-5, 18-crown-6, benzo-12-crown-4, benzo-15-crown-5, and benzo-18-crown-6\(^{14}\) would seem to support this statement. Furthermore, it has been reported that the polymerization of a diamine monomer containing a benzo-15-crown-5 moiety with different diacid dichlorides and dianhydrides under low-temperature polymerization conditions renders soluble aromatic polyamides and polyimides.\(^{15}\)

The 15-crown-5 substructure, which has a 15-membered ring, has a small cavity in which threading difficulty might occur. However, the threading phenomenon does occur in higher membered crown ethers, as demonstrated by Gong and Gibson\(^{16}\) in the poly(methacryloyl chloride) reaction with 5-hydroxymethyl-1,3-phenylene-1,3-phenylene-32-crown-10. The driving force for the threading is supposed to be the association of the OH groups and the ether oxygen atoms by hydrogen bonding.

We were finally able to prevent gel formation by lowering the concentration of the monomers in the polymerization mixture. Although the standard IMC is 0.5 M under Yamazaki conditions, an IMC of 0.5–0.05 mol/L was used to synthesize the polymers described in this article. Through this approach, 10 novel soluble polyamides with high \( \eta_{inh} \) values were synthesized. Scheme 4 depicts the chemical structures and acronyms of the polyamides. Table 1 shows the \( \eta_{inh} \) values, the IMC values employed for the polymer synthesis, and the elemental analyses of the soluble polyamides. As an example, the IR and NMR spectra of polyamide C5/6F are reproduced in Figure 1.

The influence of the monomer concentration on the molecular weights, in terms of \( \eta_{inh} \), was also studied. Figure 2 depicts \( \eta_{inh} \) versus IMC and the limiting initial monomer concentration (LIMC) that gave rise to gelation. In all the polymerizations, an exponential growth of \( \eta_{inh} \) was observable as IMC approached LIMC. LIMC was different for each diamine, and the slope of the viscosity growth in the vicinity of LIMC also varied between diamines. For example, in the polycon-
densation of MPD and C5, an increase in IMC of only 0.01 M brought about an increment in \( \eta_{inh} \) of 1.10 dL/g, and an additional increase of 0.01 M resulted in an insoluble gel.

A low concentration of monomers should favor cyclization to yield polyamide or oligoamide lactams, as stated by the theory of kinetically controlled polycondensation proposed by Kricheldorf and coworkers.\(^{17-27}\) Gibson et al.\(^{28}\) described the possible formation of polyrotaxanes, catenanes, and polycatenanes due to lactam formation associated with cyclization in the polymerization reaction in the following way: “a continuous production of lactams of larger ring size throughout the polymerization gives rise to the possibility of forming branched and ultimately crosslinked catenate species.” However, at the same time, the low concentration of monomers should also bring about a lowering of the molecular weights that, in theory, should diminish the cyclization tendency.\(^{23}\) Moreover, once the cycles are formed, the lower concentration strongly diminishes the probability of random threading of various lactams to give rise to polycatenanes.

Table 1 summarizes the polymerization conditions (IMC) and details of those soluble polymers that registered the highest \( \eta_{inh} \) values. \( \eta_{inh} \) was high in every case, and this indicated that polymers with sufficiently high molecular weights were obtained. Moreover, all the polyamides showed good film-forming ability, and this made them suitable to be tested as fixed-site carrier...
membranes for cation separation, ion-selective membranes, solid–liquid extraction of cations, or other technological applications.

Thermal Properties

The thermal behavior of these polymers was evaluated with DSC and TGA. Glass-transition temperatures ($T_g$'s) ranged between 190 and 346 °C (Table 2), whereas $T_g$ of what is technically a wholly aromatic polyamide such as poly($m$-phenylene isophthalamide) is 272 °C, a value almost midway between those obtained for the polyamides synthesized in this work. On the other hand, $T_g$ of poly($m$-phenylene 5-benzoylaminoisophthalamide), a related polyamide with a pendant unsubstituted benzoylimine group, is 298 °C, 42 °C higher than $T_g$ of C5MPD. This indicates that the bulkier substituents and the interaction of the ether linkages of the crown ether moieties with amide groups diminish the strong interchain amide–amide interactions, thereby lowering $T_g$. Moreover, these effects are stronger still when the ethylene oxide sequences are present as acyclic podand arms because these moieties do not have the conformational restrictions imposed by the cyclic structure. In fact, $T_g$ of P6MPD was 200 °C, 56 °C lower than that of its crown ether counterpart and 98 °C lower than that of poly($m$-phenylene 5-benzoylaminoisophthalamide). As a general rule, it may therefore be stated that polymers with dipodal substituents have significantly lower $T_g$'s than their counterparts with crown ether moieties.

An expected trend was observed with respect to the nature of the diamine. $T_g$ descended in the order of PPD > DDS > 6F > MPD > DDE for the two series, P6 and C5, and this agreed with previous work. DSC showed no observable endothermic peak, and an amorphous pattern was recorded with wide-angle X-ray scattering in all cases. Thus, the family of polyisophthalamides reported herein must be considered amorphous materials with very high $T_g$'s.

The thermal resistance, in terms of the initial decomposition temperature ($T_d$), was evaluated

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>Tetrahydrofuran</th>
<th>p-Cresol</th>
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<tr>
<td>C5MPD</td>
<td>256</td>
<td>410</td>
<td>++</td>
<td>++</td>
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<td>+</td>
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<td>++</td>
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<td>C5PPD</td>
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<td>+</td>
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<td>++</td>
<td>++</td>
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<td>-</td>
<td>++</td>
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<td>++</td>
<td>++</td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>C5/6F</td>
<td>269</td>
<td>415</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>++</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>P6MPD</td>
<td>200</td>
<td>410</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>P6PPD</td>
<td>231</td>
<td>410</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>+</td>
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<tr>
<td>P6DDS</td>
<td>214</td>
<td>405</td>
<td>+</td>
<td>+</td>
<td>++</td>
<td>+</td>
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<tr>
<td>P6DDE</td>
<td>190</td>
<td>405</td>
<td>++</td>
<td>+</td>
<td>++</td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>P6/6F</td>
<td>196</td>
<td>410</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
</tbody>
</table>

*a ++ = soluble at room temperature; + = soluble on heating; + = partially soluble; – = insoluble.*

Figure 2. $\eta_{inh}$ versus the initial diamine and diacid concentrations [moles of diamine or diacid/volume of NMP (L)] in polymerization reactions of polyamides giving rise to gels under standard Yamazaki polymerization conditions: (△) P6/6F, (■) C5MPD, (●) C5PPD, (▼) C5DDS, (○) C5DDE, and (▲) CF/6F.
by TGA. All the polymers showed relatively high $T_d$'s in N$_2$, ranging between 405 and 420°C (Table 2). The small differences observed in $T_d$ should be attributed to the fact that decomposition always started with the thermal break of the C—C or C—O bonds of the aliphatic oxyethylene sequences.32

### Solubility

All the polymers were soluble in aprotic polar solvents and also in m-cresol (Table 2). The solubility of these polyamides arose mainly from the oxyethylene sequences present as crown or podand pendant structures, and this implied that the main-chain aromatic backbone played a minor role. Consequently, there were hardly any observable differences in the solubility between the polymers in this series.

### Mechanical Properties

The tensile strength and Young modulus of the polyamides (Table 3), ranging from 48 to 103 MPa and from 1.7 to 3.3 GPa, respectively, can be considered satisfactory for unoriented films made via casting on a laboratory scale without any post-treatment. The mechanical properties are comparable to values reported earlier for experimental aromatic polyamides.5,33–35 However, the dispersed values for the tensile strength do not permit reliable conclusions to be reached regarding the relationship between the chemical composition and mechanical strength.

#### Water Absorption

Aromatic polyamides absorb water mainly through the interaction of water with the polar amide groups. This is a key attribute of polyamides in their application because the absorbed water diminishes $T_g$ and affects the mechanical, electrical, and dielectrical properties.

The incorporation of additional amide groups or the incorporation of other polar groups per structural unit generally increases the moisture absorption of polyamides in terms of water molecules per repeating unit. The water uptake is also affected by the accessibility to the absorption centers. Thus, the introduction of voluminous lateral groups generally decreases or inhibits crystallinity and also increases the free volume, favoring the accessibility of the water molecules to amide groups. In these polymers, the presence of lateral amide groups and the relatively hydrophilic ether groups present as bulky side cyclic or acyclic oxyethylene sequences, considerably increased the water uptake in comparison with unsubstituted aromatic polyamides.

The isothermal sorption of water at 65% relative humidity was measured, and the values were related back to the polyamide structure. The absorption isotherms of polymers C5PPD and P6PPD are shown in Figure 3, and Table 3 presents the data obtained as the water absorption percentage, molecules of water per repeating unit, and molecules of water per amide group. The polyamide moisture absorption ranged from 5.6 to 12.0%, and the number of water molecules per repeating unit ranged from 2.3 to 4.0, the lowest value corresponding to P6MPD and the high-

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Tensile Strength (MPa)</th>
<th>Young Modulus (GPa)</th>
<th>Water Uptake (%)</th>
<th>$H_2O$ (mol)/Repeat Unit</th>
<th>$H_2O$ (mol)/Amide (equiv)</th>
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</thead>
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<tr>
<td>C5MPD</td>
<td>59</td>
<td>1.7</td>
<td>11.5</td>
<td>3.5</td>
<td>1.2</td>
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<tr>
<td>C5PPD</td>
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<td>2.9</td>
<td>12.0</td>
<td>3.6</td>
<td>1.2</td>
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<tr>
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<td>1.9</td>
<td>10.4</td>
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<td>1.3</td>
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<tr>
<td>C5DDE</td>
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<td>3.3</td>
<td>9.1</td>
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<td>1.1</td>
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<tr>
<td>C5/6F</td>
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<td>2.8</td>
<td>9.1</td>
<td>3.9</td>
<td>1.3</td>
</tr>
<tr>
<td>P6MPD</td>
<td>60</td>
<td>1.7</td>
<td>6.7</td>
<td>2.3</td>
<td>0.8</td>
</tr>
<tr>
<td>P6PPD</td>
<td>66</td>
<td>1.8</td>
<td>7.0</td>
<td>2.4</td>
<td>0.8</td>
</tr>
<tr>
<td>P6DDS</td>
<td>60</td>
<td>1.7</td>
<td>6.1</td>
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<td>0.9</td>
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<tr>
<td>P6DDE</td>
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<td>7.1</td>
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<tr>
<td>P6/6F</td>
<td>60</td>
<td>2.1</td>
<td>5.6</td>
<td>2.6</td>
<td>0.9</td>
</tr>
</tbody>
</table>
est one to C5DDS. Under the same conditions, the water absorption of the reference polyamides poly(m-phenylene 5-benzoylaminoisophthalamide) and m-phenyleneisophthalamide, in terms of moles of water per repeating unit, is 2.2 and 1.2, respectively.\textsuperscript{30,35} Thus, the polyamides described herein bearing the crown ether substructure absorbed approximately an average of 1.4 more water molecules per structural unit than poly(m-phenylene 5-benzoylaminoisophthalamide), and the polymers with dipodand moieties only absorbed an average of approximately 0.3 more water molecules than the reference polyamide.

The lower uptake of the polyamides bearing the dipodal substructures in comparison with the polymers with crown ether moieties could be attributed to the higher conformational mobility of the podal arms, which could lead to a higher interaction of ether linkages of the podal arms with the amide groups through hydrogen bonds, thereby reducing the percentage of polar amide groups available to interact with water.\textsuperscript{5,36}

CONCLUSIONS

Two new condensation monomers derived from isophthalic acid bearing linear and cyclic ethylene oxide sequences were prepared and successfully used in combination with aromatic diamines for the synthesis of novel aromatic polyamides. The presence of the substituents made the polyamides soluble in polar aprotic solvents and, on the other hand, decreased their thermal stability as all the polymers showed an initial $T_d$ in N\textsubscript{2} of about 400 °C. The polymer properties were greatly affected by the nature, cyclic or acyclic, of the side ethylene oxide sequence, and so $T_g$’s of polyamides with crown ethers were up to 100 °C higher than their counterparts with open ethylene oxide chains. The nature of the diamines also played an important role and greatly influenced the $T_g$’s, PPD and DDS providing much higher $T_g$’s than MPD, 6F, and DDE. The water uptake was higher for polymers of the C5 series because the crown ethers contributed to a more efficient chain-separation process and did not provide as many ether–amide secondary linkages as the linear ethylene oxide sequences.

The financial support provided by the Ministerio de Educación y Ciencia (MAT2005-01355) and the Junta de Castilla y León (BU003A05) is gratefully acknowledged, as is the grant received by E. M. Maya through the Ramón and Cajal Program of the Ministerio de Educación, Cultura y Deporte.

REFERENCES AND NOTES


Figure 3. Isothermal water absorption of C5PPD and P6PPD.