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Macrocyclic Polymers. 2.† Synthesis of Poly(amide crown ether)s Based on Bis(5-carboxy-1,3-phenylene)-32-crown-10. Network Formation through Threading

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ABSTRACT: Novel poly(amide crown ether)s **4a** and **4b** have been synthesized by direct polycondensation reactions of bis(5-carboxy-1,3-phenylene)-32-crown-10 (BCP32C10, **2**) with 4,4′-oxydianiline (ODA, **3a**) and bis[4-(*m*-aminophenoxy)phenyl]phenylphosphine oxide (*m*-BAPPO, **3b**). These polymers with semirigid 32-membered crown ethers in the main chain are insoluble in any solvents. The insolubility is attributed to in situ threading of linear segments of one polymer chain through the macrocyclic cavity of another during polymerization, i.e., physical cross-linking.

Introduction

Crown ethers and cryptands have been incorporated as part of the backbone or as pendant groups into polymeric structures such as polyesters and polyamides through the polycondensation approach. In terms of historical background Feigenbaum and Michel did some pioneering research work on polymeric crown ethers. They prepared a series of polyamides with dibenzo-18-crown-6 moieties in the backbone.[1] The poly(amide crown ether)s were insoluble in normally good polyamide solvents such as *N,N*-dimethylacetamide (DMAc) and *N*-methylpyrrolidinone (NMP), but they were soluble in hexamethylphosphotriamide (HMPT) and hexafluoroisopropyl alcohol (HFIP).[1]

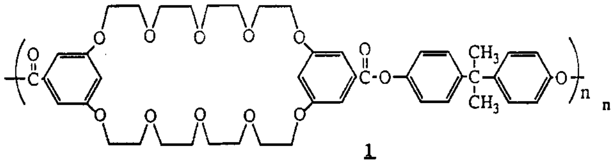
On the basis of this research, other researchers prepared high molecular weight poly(amide crown ether)s based on the interfacial polycondensation reaction of diaminodibenzo-18-crown-6 and different aromatic and aliphatic diacid chlorides.[2,3] These polymers were soluble in HMPT and HFIP, and films were cast from these solvents.

In all these polymeric crowns the macrocycles are in the range of 15–18-membered rings. The nitration of the preformed dibenzo-18-crown-6 followed by reduction to prepare the diaminodibenzo-18-crown-6 gives a mixture of isomers which is hard to separate and therefore is used as such in poly(amide crown ether) formation.[3]

Crown ethers in the range of 30 and higher membered rings have the ability to bind two metal ions per cavity[4] and also to complex with large organic cations.[5] Moreover, macrocycles in this 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.[6,7] Recently we have reported the synthesis and characterization of a novel poly(ester crown ether) (**1**) based on bis(5-carboxy-1,3-phenylene)-32-crown-10 (BCP32C10) and 4,4′-isopropylidenediphenol (Bisphenol A).[8]

In this paper we report the syntheses of novel and well-defined poly(amide crown ether)s which contain the same semirigid large (32-membered) macrocycle in the main chain.

Experimental Section



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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. Syntheses of BCP32C10,[8] bis[4-(*m*-aminophenoxy)phenyl]phenylphosphine oxide (*m*-BAPPO),[9] and bis(*m*-phenylene)-32-crown-10 (BMP32C10)[10] have been published elsewhere.

Measurements. Infrared spectra (KBr pellets) were recorded on a Nicolet MX-1 FTIR spectrometer. The ^{1}H NMR spectra were obtained at ambient temperature on a Varian Unity 400-MHz spectrometer in deuterated dimethyl sulfoxide in the gel state with TMS ($\delta = 0.0$ ppm) as internal standard. The glass transition temperatures (T_g) were obtained by differential scanning calorimetry on a Du Pont DSC 912. Scans were run at 10 °C/min, and the reported values were obtained from a second heating after quick cooling. Dynamic thermogravimetric analyses were performed on a Du Pont 951 TGA at a scan rate of 10 °C/min in air and N_2 atmospheres.

Polyamide 4a: The polymer was synthesized according to the method described by Yamazaki and co-workers.[11] A mixture of 4,4′-ODA (**3a**) (0.500 g, 2.50 mmol), diacid crown **2** (1.560 g, 2.50 mmol), lithium chloride (0.25 g, 5.90 mmol), pyridine (1.25 mL), triphenyl phosphite (1.56 g, 5.05 mmol), and NMP (5 mL) was heated at 100 °C under nitrogen. A homogeneous solution was formed. The reaction mixture changed from clear to cloudy and viscous in 30 min and finally to a gel in about 45 min. After 3 h at 100 °C the polymer was isolated by precipitation with methanol. The precipitate was filtered and then washed with hot methanol and dried in vacuo. The polymer was swelled in DMAc and reprecipitated from methanol one more time, filtered, and dried in vacuo at 50 °C to afford hard solid polymer **4a**, 2.0 g (100%). IR: ν 3300–3350 (NH), 1660 (C=O), 1122 (COCO) cm^{-1}. ^{1}H NMR: δ 10.2 (2 H, s, NH), 8.0–6.6 (14 H, m, H_{arom}), 4.1 (8 H, s, α-OCH_2), 3.7 (8 H, s, β-OCH_2), 3.3 (16 H, m, γ/δ-OCH_2), 3.2 (H_2O from deuterated solvent).

Polyamide 4b: The same procedure as above was followed; diacid crown **2** (1.560 g, 2.50 mmol), *m*-BAPPO (**3b**) (1.230 g, 2.50 mmol), lithium chloride (0.25 g), triphenyl phosphite (1.32 mL), pyridine (1.25 mL), and NMP (5 mL) were used. The polymer **4b**, 2.7 g (100%), was obtained as a white fibrous solid. IR: ν 3300–3350 (NH), 1670 (C=O), 1170 (P=O), 1115 (COCO) cm^{-1}. ^{1}H NMR: δ 10.1 (2 H, s, NH), 7.8–6.6 (27 H, m, H_{arom}), 4.1 (8 H, s, α-OCH_2), 3.7 (8 H, s, β-OCH_2), 3.3 (16 H, m, γ/δ-OCH_2), 3.2 (H_2O).

Polyamide 5 in the presence of BMP32C10 (6): The same procedure as above was followed; terephthalic acid (TA; 0.415 g, 2.50 mmol), *m*-BAPPO (**3b**; 1.230 g, 2.50 mmol), BMP32C10 (**6**;

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† Part 1: Reference 10.

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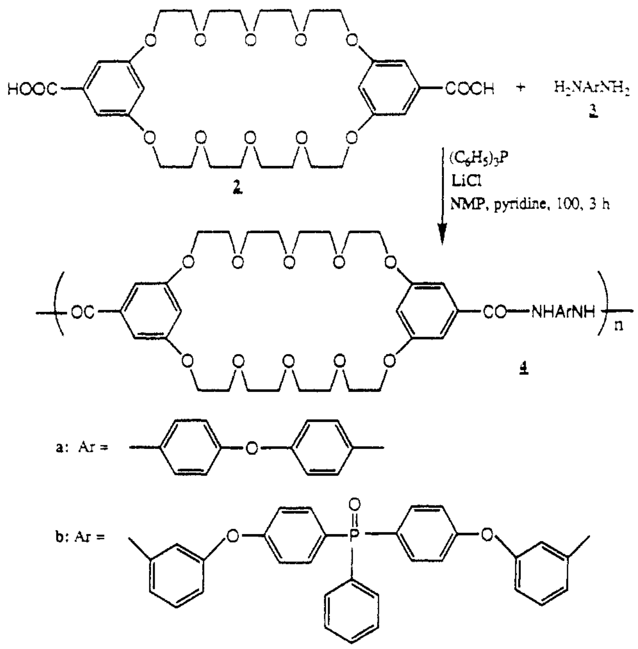
Scheme I
Synthesis of Poly(amide crown ether)s 4a and 4b

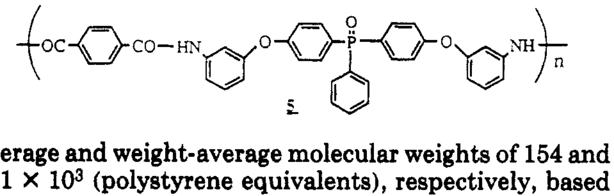


1.341 g, 2.50 mmol), lithium chloride (0.25 g), triphenyl phosphite (1.32 mL), pyridine (1.25 mL), and NMP (5 mL) were used. The polymer **5**, 1.5 g (100%), was obtained as a white fibrous solid. IR: ν 3300–3350 (NH), 1669 (C═O), 1607, 1587, and 1539 (C═C), 1436 (ArP), 1260 (ArOAr), 1170 (P═O) cm^{-1}. ^{1}H NMR: δ 10.48 (2 H, s, NH), 8.0–6.8 (25 H, m, H$_{arom}$).

Results and Discussion

Direct polycondensations of BCP32C10 (**2**) with 4,4′-ODA (**3a**) and *m*-BAPPO (**3b**) using triphenyl phosphite and pyridine in NMP solution containing LiCl according to the procedure reported by Yamazaki and co-workers[11] formed the poly(amide crown ether)s **4a** and **4b** in quantitative yields (scheme I).

It is known that aromatic polyamides are usually insoluble in organic solvents and only soluble in concentrated sulfuric acid. However, we expected that in the case of poly(amide crown ether)s the presence of the ethyleneoxy linkages would promote solubility. The poly(amide crown ether) based on diaminodibenzo-18-crown-6 and isophthaloyl chloride was soluble in HFIP and HMPT.[1,2] The one based on terephthaloyl chloride was not soluble in pure dimethyl sulfoxide (DMSO), but it was soluble in the presence of K$^+$ (KSCN).[3] More interesting is the fact that incorporation of flexible bridging units such as phosphine oxide into the rigid polyamide backbone generally makes the polymer more soluble; thus, a very high molecular weight polyamide (**5**), with number-average and weight-average molecular weights of 154 and 441 × 10^3 (polystyrene equivalents), respectively, based on *m*-BAPPO and terephthalic acid (TA) was soluble completely in aprotic dipolar solvents such as DMSO, *N,N*-dimethylformamide (DMF), DMAc, and so on.[12]



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But to our surprise both of the poly(amide crown ether)s bearing a semirigid 32-membered crown ether were insoluble in any solvents, such as aprotic dipolar solvents like NMP even in the presence of salt. For example, a sample of 0.10 g of polymer **4a** was stirred in 60 mL of NMP/LiBr (5% by weight) solution for more than 3 months, but it did not show any sign of solubility. The application of heat did not change the solubility behavior of these poly(amide crown ether)s. HMPT and HFIP, which are good solvents for smaller ring poly(amide crown ether)s, did not dissolve these polymers. Different solvents such as NMP and DMF have been tried to extract any solution portion of the polymers; this was not successful. They degrade as they dissolve in concentrated sulfuric acid; the ether groups attached to the rings are extremely susceptible to electrophilic attack. They are also amorphous by nature. Lack of crystallinity argues against insolubility because of the pseudo para linkages. Both polymers swell very well (up to 2 times their original volume) and form gels in aprotic polar solvents such as DMF, DMAc, DMSO, and NMP. As a result of this swelling we were able to obtain ^{1}H NMR spectra of these polymers in DMSO in the gel state with good resolution (Figure 1).

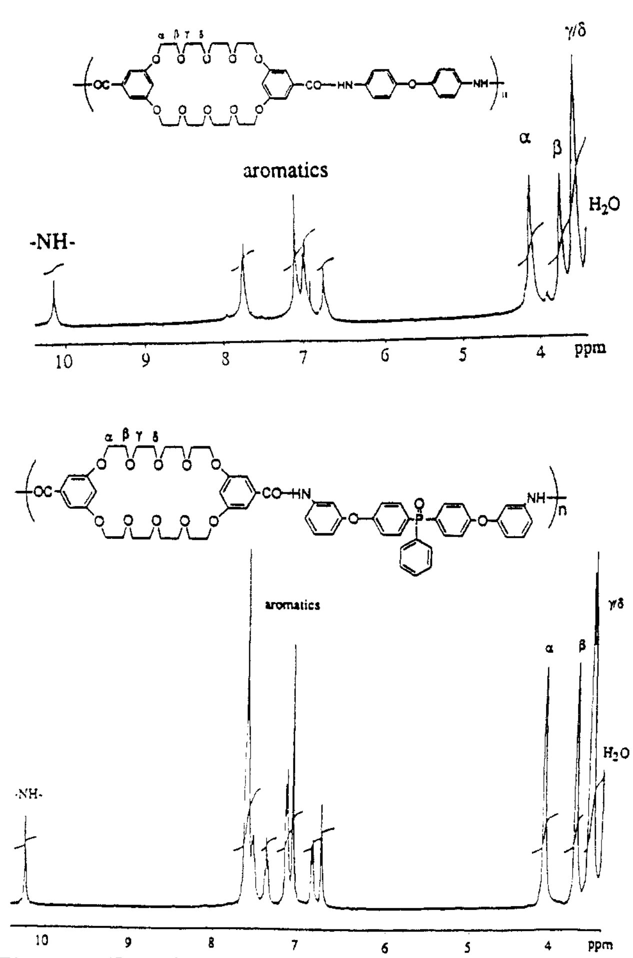
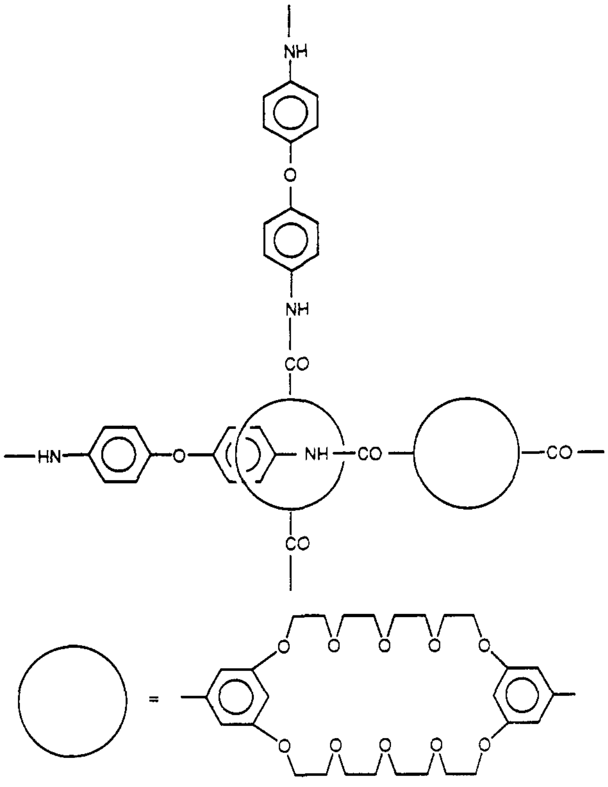


Figure 1. ^{1}H NMR spectra of poly(amide crown ether)s **4a** and **4b**.

It is helpful to know that the crown ether based on BMP32C10 is like a molecular box, and its cavity is capable of formation of 1:1 complexes as a host with large organic cations such as [diquat][PF$_6$]$_2$ and [paraquat][PF$_6$]$_2$ in solution and solid state.[5] These 1:1 complexes have been confirmed by ^{1}H NMR and X-ray crystallography.[5] We were also able to form 1:1 complexes of bis(5-methyl-1,3-phenylene)-32-crown-10 and [paraquat][PF$_6$]$_2$ and determine the X-ray crystal structure of this system.[13]

There are two possible explanations for the insolubility of **4a** and **4b**. First, polyaramides are known to form hydrogen bonds through amide linkages; one typical example is Kevlar which is soluble only in concentrated sulfuric acid. The poly(amide crown ether)s can have

Chart I
Proposed Threaded Structure of Polyamide 4a

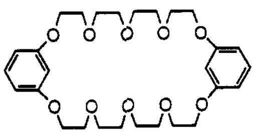


hydrogen bonds between crown ether and amide linkages too. But the formation of hydrogen bondings between oxygen linkages of the crown ether and the amide linkages will compensate (replace) the stronger hydrogen bonding of the amide–amide linkages, and as a result of this the poly(amide crown ether)s should be more soluble in comparison to the polyamides. Anyway, summation of all these strong intermolecular interactions could be one reason for insolubility.

The second possibility could be in situ threading of the macrocyclic cavity of one polymer chain by a segment of another polymer chain during polymerization (Chart I). A small fraction of threading of high molecular weight poly(amide crown ether) molecules will result in formation of a network that makes the whole system insoluble.

The following facts have convinced us that the second possibility, threading of the macrocycles, is responsible for the insolubility of these macrocycle-containing polyamides. (1) The Yamazaki procedure generally results in formation of very high molecular weight aramides.[12] (2) The aramide derived from ODA and isophthalic acid is soluble in dipolar aprotic solvents up to relatively high molecular weight.[14,15] This system is far more rigid than polyamide **4a**, which contains the flexible ethyleneoxy linkages. Similarly, the aramide **5** derived from *m*-BAPPO and TA is soluble in dipolar aprotic solvents, demonstrating the solubilizing effect of the triarylphosphine oxide moiety.[12] (3) The polyamides based on dibenzo-18-crown-6 and either terephthalic or isophthalic acid are soluble.[1-3] The greater flexibility imbued by the large 32-membered crown ether ring in **4a** and **4b** should provide enhanced solubility. (4) Rings with less than about 23 C, O, or N skeletal atoms do not possess a cavity large enough to be threaded even by polymethylene chains (diameter ca. 4.5 Å),[16,17] let alone aromatic rings. The cavity of BCP32C10 is large enough to accommodate aromatic rings. Hence, the previously reported polycrowns could not undergo this threading process and were therefore soluble. (5) Polyamides **4a** and **4b** interact strongly with dipolar aprotic solvents, as evidenced by the high degree of swelling induced by these solvents; this behavior is analogous to classical, covalently cross-linked polymers.

To test the possibility of threading, polyaramide **5** was synthesized in the presence of bis(*m*-phenylene)-32-crown-10 (BMP32C10, **6**) with equimolar monomer feed ratios



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(1:1:1 of TA:*m*-BAPPO:BMP32C10) with the same experimental conditions as we used to synthesize poly(amide crown ether)s **4a** and **4b**. The polymer was dissolved in DMF and reprecipitated in methanol a few times. On the basis of ^{1}H NMR analysis, there was no detectable amount of macrocycle on the polymer chains. This could be explained partly because of the differences in the local concentration of the macrocycle between this system and polymerization leading to **4a** and **4b**. In the case of poly(amide crown ether)s **4a** and **4b** the macrocycle has the advantage of being part of the growing chain which probably enhanced the local concentration of the macrocycle and most likely the threading efficiency. Additionally in the macrocycle-containing polyamides intermolecular amide–amide hydrogen bonds may dispose the macrocycles in such a way as to facilitate threading.

It is noteworthy that the poly(ester crown ether) **1** based on BCP32C10 and Bisphenol A was very soluble in common organic solvents.[8] Less bulky bisphenols such as 4,4′-biphenol and hydroquinone also produce soluble polyesters with BCP32C10.[18] The question arises then as to why there is a large difference between the behavior of the poly(ester crown ether)s and poly(amide crown ether)s. The fact that in solution crown ethers hydrogen bond to the amide linkages could be a driving force for threading in the polyamides. Our syntheses of poly(urethane rotaxane)s[19] and poly(*p*-oxydiphenyleneisophthalamide rotaxane)s[20] show high degrees of threading in comparison to poly(butylene sebacate rotaxane),[6] indicating the positive effects of hydrogen bonding on threading efficiency. In view of the lack of network formation in polyester **1** by threading, we infer that under the relatively dilute conditions, i.e., monomer concentrations of ca. 0.3 M, hydrogen bonding of the crown ether moieties to either the amide groups of the monomer or the amide linkages as they form provides the enthalpic driving force for formation of a small number of threadings during the synthesis of polyamides **4a** and **4b**. Altenatively the intermediate pyridinium ion[11] may form a host–guest complex with BCP32C10 moieties, leading to threading. Examination of molecular models demonstrates that in order to dethread one macromolecule from another extreme deformations of the crown ether rings are required as they pass through one another, making such a process intrinsically extremely slow or impossible on a realistic time scale.

The glass transition temperature (T_g) of polymer **4a** was 114 °C, and it has quite high thermal stability, i.e., 5% weight loss by TGA at 366 and 325 °C in nitrogen and air, respectively. On the other hand, polymers containing phosphorus as an integral part of the backbone are known to be thermally stable and flame retardant. Polymer **4b** shows a T_g of 127 °C and 5% weight loss by TGA at 385 and 334 °C in nitrogen and air, respectively. As a result of incorporation of *m*-BAPPO in the backbone of polymer **4b**, it shows a high char yield, about 50%, in nitrogen atmosphere up to 700 °C.

Conclusion

Novel semiaromatic polyamides containing a 32-membered crown ether moiety in the main chain have been synthesized. The above-mentioned polymers are insoluble, which is most likely the result of permanent physical entanglements arising from threading of the macrocycles by the polyamide segments as they form, leading to an insoluble network.

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