Polyamide Pseudorotaxanes, Rotaxanes, and Catenanes Based on Bis(5-carboxy-1,3-phenylene)-(3*x*+2)-crown-*x* Ethers

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ABSTRACT: We previously reported that the polyamide **3a** derived from bis(5-carboxy-1,3-phenylene)-32-crown-10 (BCP32C10, **1a**) and 4,4′-oxydianiline (ODA, **2**) was completely insoluble and attributed this to the formation of mechanical cross-links via self-threading of the crown ether moieties by the amide backbone through hydrogen bonding. Moreover, polycondensation of **1a** with bis[4-(*m*-aminophenoxy)-phenyl]phenylphosphine oxide (*m*-BAPPO, **4**) produced polyaramide **5a** that, like its analogue **3a**, was insoluble in all solvents examined, including H_2SO_4. In the present work bis(5-carboxy-1,3-phenylene)−(3*x*+2)-crown-*x* ethers [BCP(3*x*+2)C*x*] with 26-membered (BCP32C10, **1b**), 20-membered (BCP20C6, **1c**) and 14-membered (BCP14C4, **1d**) rings were utilized to investigate further the proposed topological branching via in situ threading during polymerization. Condensation of BCP26C8 (**1b**) with ODA (**2**) and *m*-BAPPO (**4**) gave two new poly(amide crown ether)s, **3b** and **5b**, which were soluble in dipolar aprotic solvents. However, the GPC traces of aramides **3b** and **5b** exhibited bimodal behavior indicative of two distinct molecular weight fractions, one very high, $DP_n > 800$! Similarly the aramide **3c** formed by condensation of BCP20C6 (**1c**) and ODA (**2**) displayed a bimodal GPC curve. As a reference system BCP14C4 (**1d**) was prepared and polymerized with ODA; the resultant aramide **3d** displayed a monomodal GPC trace and relatively narrow molecular weight distribution. Mass spectrometric studies show that cyclic aramides (lactams) form in the larger crown ether-based systems **3b** and **5b**. Model aramide **6** from isophthalic acid and ODA also contains cyclic polymers, as expected from Kricheldorf's recent results, but has a "normal" molecular weight distribution. Mass spectrometric examination of aramides **3c** and **3d** does not indicate any cyclic polymer formation. Inasmuch as lactam formation by itself does not necessarily produce branching or cross-linking, e.g., **6**, we conclude that threading of the crown ether moieties is the key step, leading to polypseudorotaxane, polyrotaxane and polycatenane structures to an extent dependent upon the their cavity size *and* the propensity for cyclization of the polymer backbone.

Introduction

Crown ethers are an important class of compounds that undergo complexation with metal ions[1] and other species, in some cases leading to the formation of threaded structures known as pseudorotaxanes and rotaxanes.[2] Polymers containing small crown ethers, most commonly 18-membered rings, were known as early as 1970, mainly for study of cation binding.[3−5] Polyaramides derived from dibenzo-18-crown-6 have been made via interfacial polymerization of diaminodibenzo-18-crown-6 with aromatic and aliphatic diacid chlorides.[5−7] A variety of other approaches has produced polymers containing crown ethers.[8−14]

In our laboratory, we have utilized crown ethers to synthesize a variety of polypseudorotaxanes and polyrotaxanes (Scheme 1).[2,15−26] By carrying out step-growth polymerizations in the presence of crown ethers, main chain polypseudorotaxanes of type A (Scheme 1) were prepared based on polyester[15,16] and polyurethane backbones.[17−20] Similarly polyrotaxanes of type B resulted from use of bulky monomers in step-grown polymerizations in the presence of crown ethers, as exemplified by the preparation of poly(ester rotaxane)s[20,21] and poly(urethane rotaxane)s.[22] Chain-growth polymerizations analogously yielded poly(styrene rotaxane)s[23] and poly(acrylonitrile rotaxane)s[24] of types A and B. Main chain poly(acrylate rotaxane)s and poly(methyl methacrylate rotaxane)s of type A were also prepared using free radical polymerization.[25] Polymerization of suitable methacrylate monomers in the presence of crown ethers also yielded side chain polyrotaxanes of type D.[25] Side chain pseudorotaxane polymers of type C have also been investigated in our laboratories,[26] as well as main chain pseudorotaxane polymers of type E.[27] Other investigators have also prepared such topologically interesting systems.[2,28]

Inasmuch as the more efficient polyrotaxane syntheses are based on hydrogen bonding interactions between the crown ethers and the monomer and/or polymer, we studied systems in which the crown ether was functionalized and could self-associate via hydrogen bonding.[29−31] As a result of such self-association, we anticipated that self-threading of these monomers would occur, yielding mechanically branched or cross-linked polyrotaxanes similar in structure to those of type F. Indeed, reaction of poly(methacryloyl chloride) with 5-hydroxymethyl-1,3-phenylene-1,3-phenylene-32-crown-10, a reaction

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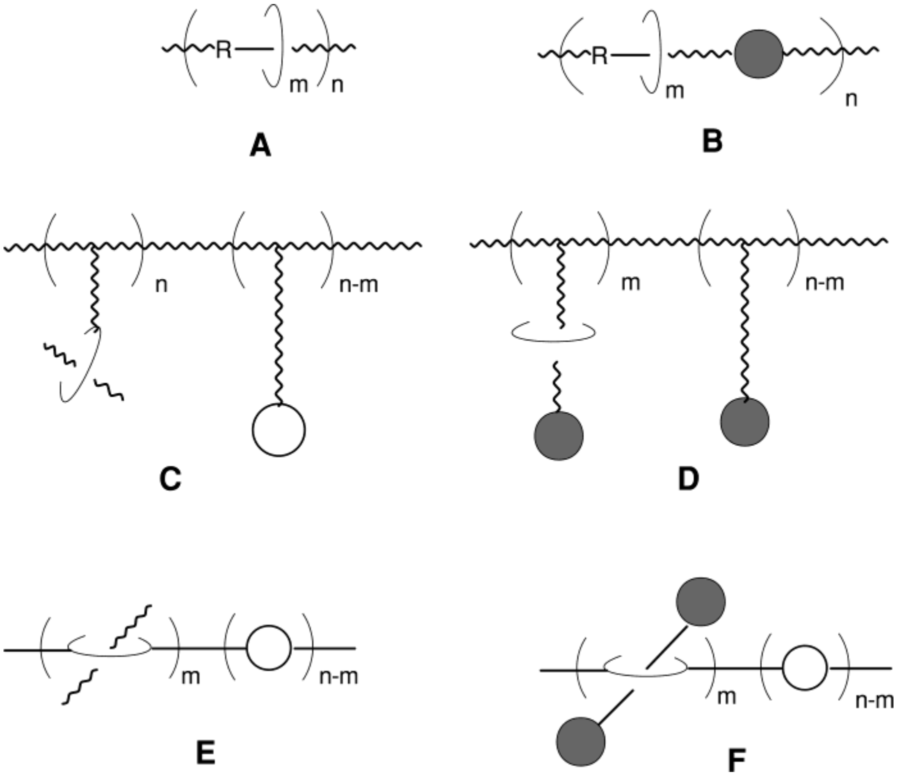
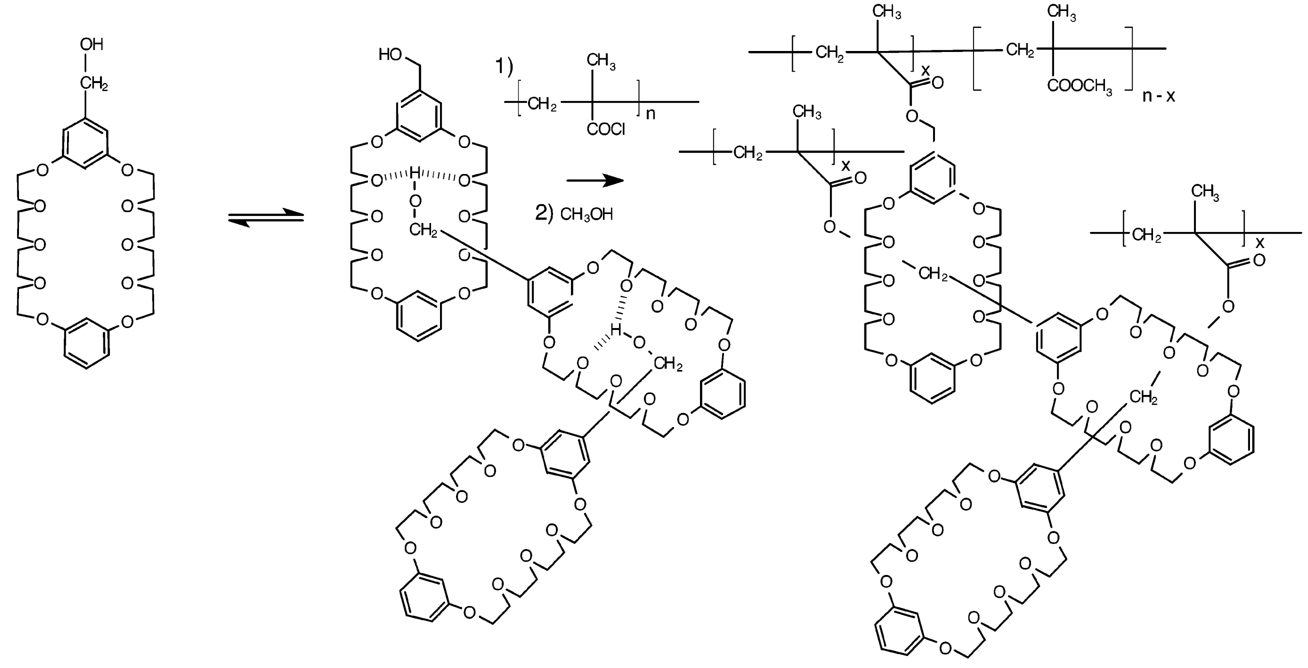
Scheme 1. Cartoon Representations of Various Types of Polypseudorotaxanes (A, C, E) and Polyrotaxanes (B, D, F)[a]



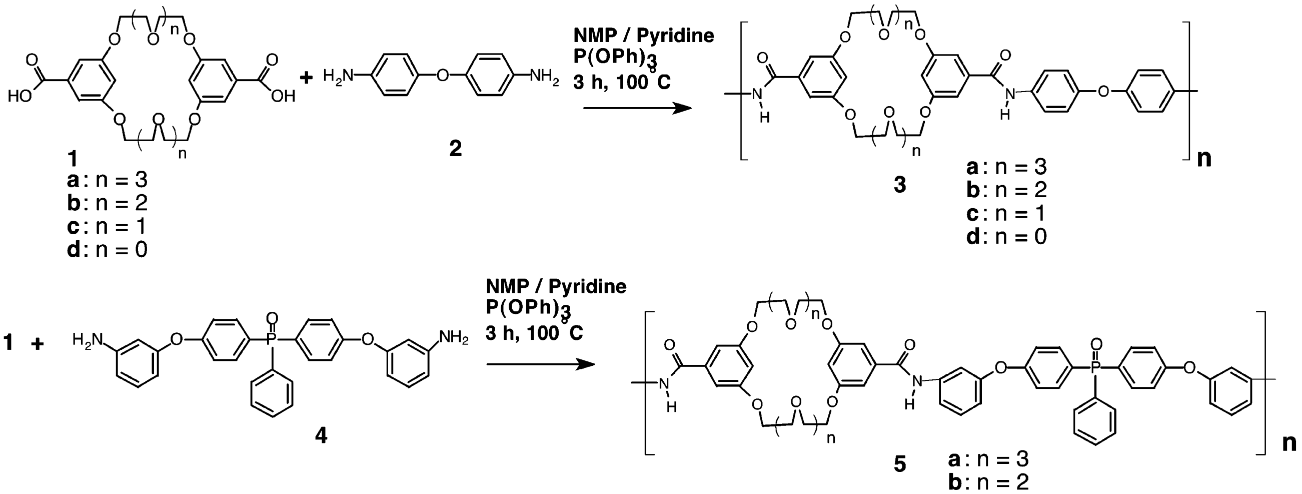
[a] A, B, E, and F are main chain systems and C and D are side chain systems. Circles and ellipses represent cyclic species; straight or wiggly lines represent linear components. Filled circles represent bulky "stoppers" that prevent dethreading of the cyclic component from the linear.

Scheme 2. Branching/Cross-Linking in Poly(methacryloyl chloride) Modification as a Result of Self-Threading of 5-Hydroxymethyl-1,3-phenylene-1,3-phenylene-32-crown-10 via Association Driven by Hydrogen Bonding of the OH Groups to the Ether Oxygen Atoms[29]

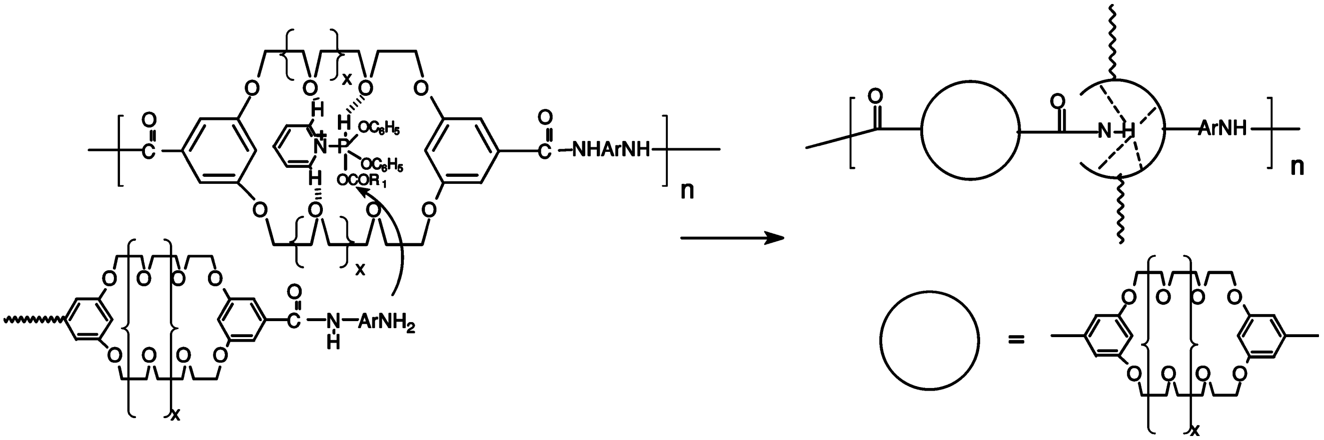


involving side chain modification by a reagent with only a single chemical functionality (Scheme 2), resulted in highly branched or cross-linked product polymer, depending on the concentrations; threading was demonstrated by nuclear Overhauser effect spectroscopic (NOESY) NMR experiments.[29] The use of bis(5-carboxy-1,3-phenylene)-32-crown-10 (**1a**) to prepare polyesters resulted in higher molecular weight products than did use of the homologous 26- and 20-membered crown ethers **1b** and **1c** (Scheme 3); this was attributed to self-threading via self-association of the crown ether diacids, with the most threading taking place with the largest macrocycle.[30] Reaction of the diol analogue of **1a**, bis-(5-hydroxymethyl-1,3-phenylene)-32-crown-10, with se-

Scheme 3. Synthesis of Polyamides from Bis(5-carboxy-1,3-phenylene)-(3*x*+2)-crown-*x* Compounds



Scheme 4. Schematic Representation of in Situ Threading as a Result of Host–Guest Complexation of Pyridinium Ion with the Macrocycle[a]



[a] Dashed lines represent hydrogen bonds. The curved arrow represents the nucleophilic attack of the amine on the activated phosphite ester carbonyl group, leading to a threaded (rotaxane) structure since the macrocycles cannot pass through each other under normal conditions. The rotaxane is stabilized by hydrogen bonding of the amide moieties with the ether oxygens of the crown ethers. The circles and ellipses represent the cyclic component, and the straight or wiggly lines represent linear segments.

bacoyl dichloride under neat conditions resulted in complete gelation, again presumably via self-threading to produce a mechanically interlocked network structure.[30] NOESY experiments in this case were not informative. Finally, use of the same diol, the analogue of diacid **1a**, in preparation of polyurethanes afforded precise control of branching up to and including complete gel formation by variation of its feed ratio and use of solvents that either allowed or prevented self-association of the cyclic monomer; NOESY experiments again confirmed that the mechanism of branching/cross-linking was indeed self-threading of the crown ether component.[31]

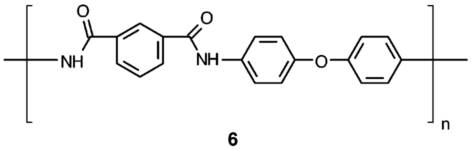
These results are entirely in keeping with the fact that bis(*m*-phenylene)-32-crown-10 macrocycles form [2]-pseudorotaxane (i.e., threaded) complexes with *N,N′*-dialkyl-4,4′-bipyridinium salts[2,32] and thence catenanes (interlocked rings),[2,33] and with dibenzylammonium salts [3]pseudorotaxane complexes are formed in which *two* of the guest species occupy the cavity of the crown ether,[2,34] as clearly evidenced by X-ray crystal structures. All of these complexation processes are driven thermodynamically by hydrogen bonding interactions of the guest with the host, as well as π-stacking interactions between the aromatic moieties, again as demonstrated in the X-ray structures.[2,32−34]

Earlier we synthesized a new class of aramides containing the 32-membered macrocycle **1a** via step growth polymerizations.[35] The resultant poly(amide crown)s **3a** and **5a** formed via reaction with diamines **2** and **4**, respectively, (Scheme 3) were completely insoluble (even with added salts) in all dipolar aprotic solvents, as well as H_2SO_4, which is normally a very effective polyamide solvent even for Kevlar, but swelled in dipolar aprotic solvents. The insolubility was particularly noteworthy with **5a** because the triarylphosphine oxide linkage promotes solubility even for high molecular weight aromatic polyamides.[36] These results were indicative of a “loose” network, as would be the case for self-threading of the polymer backbone through its crown ether component. In fact, it was possible to obtain an ^{1}H NMR spectrum of swollen polymer **3a** and confirm the integrity of the crown ether and other moieties present. On the basis of these results and the results for other systems mentioned above, we hypothesized that the cross-linking was due to in situ threading of the polymer chain through the macrocyclic moiety of the monomer **1a** via an H-bonded complex as shown in Scheme 4 or hydrogen bonding of the amine, protonated amine and/or the amide moieties with the ether oxygen atoms of the crown ether macrocycles that are part of the backbone. These hypotheses were consistent with a number of facts: the well-known complexation of crown ethers with neutral amines via hydrogen bonding,[37,38] the established binding of ammonium ions by crown ethers,[2,32−34,38−40] including dibenzo-24-crown-8[40] and bis(*m*-phenylene)-26-crown-8,[34] the facility with which poly(urethane rotaxane)s of types A and B form during polymerization in the presence of a crown ether,[17] the demonstrated self-threading that takes place during polyurethane formation from the diol analogue of **1a**,[31] the threading of preformed polyurethanes by crown ethers,[41] and the clearly demonstrated (by infrared and NMR spectroscopies) hydrogen bonding interaction of the urethane N−H moieties and the crown ether.[18]

To establish self-threading of the crown ether monomer more firmly as the mechanism of this cross-linking/branching phenomenon, in the present work we studied the formation of analogous polyamides derived from smaller crown ether diacid analogues, 26-, 20- and 14-membered macrocycles bis(5-carboxy-1,3-phenylene)-26-crown-8 (BCP26C8, **1b**),[42,43] bis(5-carboxy-1,3-phenylene)-20-crown-6 (BCP20C6, **1c**),[30] and bis(5-carboxy-1,3-phenylene)-14-crown-4 (BCP14C4, **1d**),[44] respectively. Our expectation was that there would be less threading and hence less polydispersity for the smaller crown ethers, and eventually, the cavity would be too small to allow threading and a normal unimodal molecular weight distribution with polydispersity ca. 2.0 would then be observed.

Results

A. Polymerizations 1. Model Polymerizations, Aramides 6 and 7. To establish proper conditions for polymerization we first carried out polyamide syntheses using “standard” monomers for polycondensation, isophthalic acid with 4,4′-oxydianiline (ODA, **2**) to form aramide **6** and isophthalic acid with bis[4-(*m*-aminophenoxy)phenyl]phenylphosphine oxide (*m*-BAPPO, **4**) to produce **7**, using the Yamazaki procedure (lithium chloride, triphenyl phosphite, and pyridine in NMP).[45]



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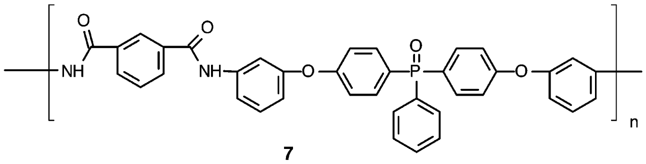

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2. Polymerization of the 26-Membered Crown Ether Monomer 1b. X-ray studies of the dimethyl ester of 32-membered **1a** revealed a conformation whose cavity size is relatively large: 4.9 × 7.8 Å, taking into account van der Waals radii (Figure 1a).[46] In contrast, X-ray studies of the dimethyl ester of 26-membered **1b** reveal a puckered structure in which the two aromatic rings are essentially antiparallel to each other with a much smaller cavity size, on the order of 2.6 × 7.0 Å, taking into account van der Waals radii (Figure 1b).[46]

Two new poly(amide crown ether)s, **3b** and **5b**, were synthesized by application of the Yamazaki polycondensation conditions using BCP26C8 (**1b**) with ODA (**2**) and *m*-BAPPO (**4**), respectively (Scheme 3). Both polymers **3b** and **5b** were soluble in dipolar aprotic solvents such as DMSO, NMP, and DMF. Recall that homologous polymers **3a** and **5a** derived from bis(5-carboxy-1,3-phenylene)-32-crown-10 (**1a**) were insoluble in all dipolar aprotic solvents (as well as H_2SO_4), but there was considerable swelling in normal solvents for aramides (DMF, NMP, etc.).

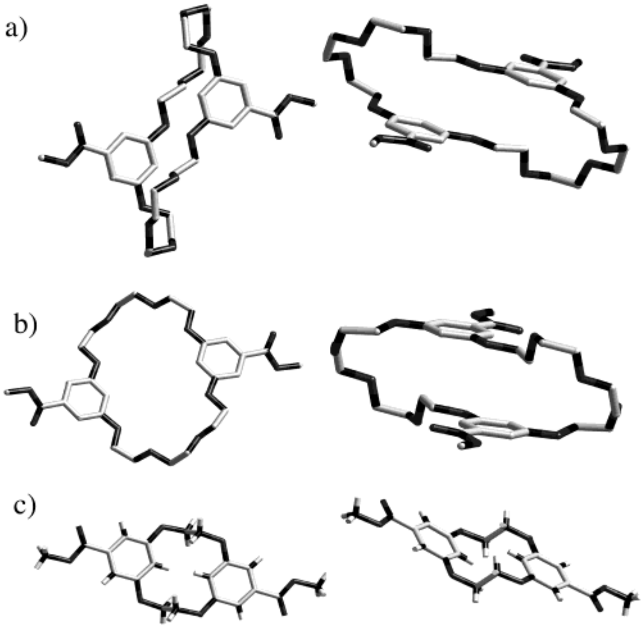


Figure 1. Single-crystal X-ray structures of (a) bis(5-carbomethoxy-1,3-phenylene)-32-crown-10 (**1a**), (b) bis(5-carbomethoxy-1,3-phenylene)-26-crown-8 (**1b**), and (c) bis(5-carbomethoxy-1,3-phenylene)-14-crown-4 (**1d**).[40] Hydrogen atoms are not shown in parts a and b.

The solubility of **3b** and **5b** allowed the obtention of their NMR spectra (Figures 2 and 3, respectively). The most important result from these spectra is that there is no evidence of any chemical defect structures; the spectra do not show any indication of opening of the crown ether ring or other side reaction that would lead to covalently branched or cross-linked structures. Relative to the starting dicarboxy crown ether **1b**, the protons associated with the macrocyclic portions of **3b** and **5b** underwent only small changes (<0.06 ppm) in chemical shifts. 2D COSY experiments confirmed that the assigned H_a and H_b signals of **3b** and **5b**, respectively, were indeed coupled to each other.

3. Polymerization of the 20-Membered Crown Ether Monomer 1c. It has generally been accepted,[2] based on data derived early in the study of rotaxanes using small molecules,[47,48] that the minimum ring size for threading by a polymethylene chain is 22−24 atoms chosen from C, N, and O.Therefore, we utilized the 20-membered crown ether monomer **1c**[30] in reaction with ODA (**2**) to form a polyamide, in the belief that this would provide a reference system that did not involve threading.

^{1}H NMR spectroscopy provided no indication that the macrocyclic component of resultant aramide **3c** had undergone ring opening; no new peaks appeared as might have been expected if ring opening had taken place. This was confirmed by the ^{13}C NMR spectrum (Figure 4); with the exception of solvent peaks (not shown), the correct number of signals with the expected chemical shifts is observed. Again, as in the cases of self-

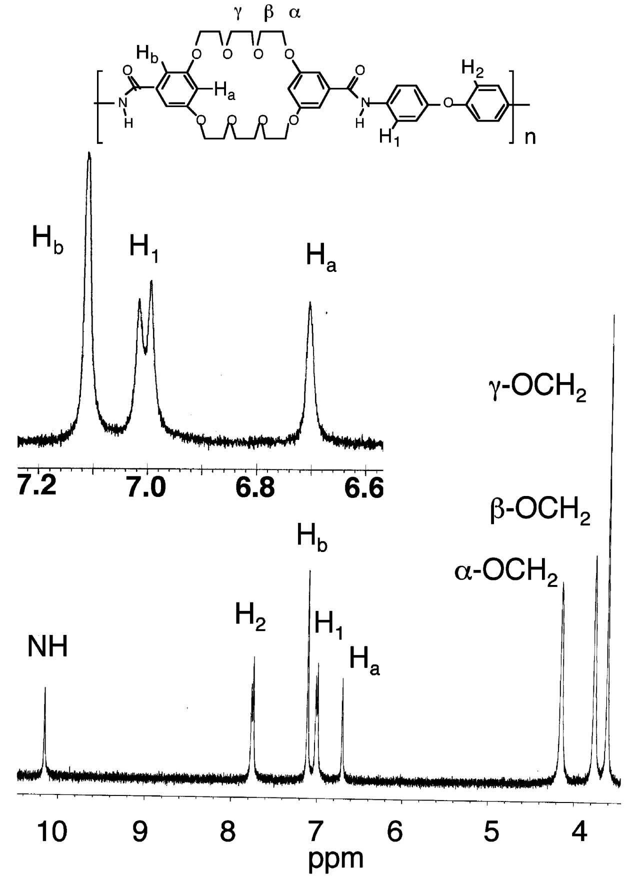


Figure 2. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of polymer **3b**. The *y*-axis scale is arbitrary; the *x*-axis scale is parts per million chemical shift relative to tetramethylsilane.

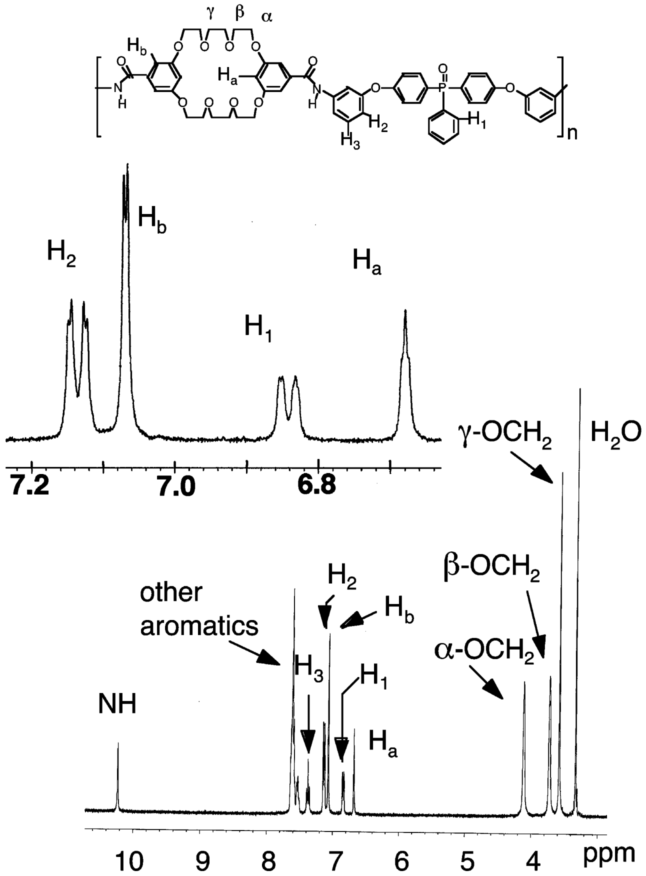


Figure 3. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of polymer **5b**. The *y*-axis scale is arbitrary; the *x*-axis scale is parts per million chemical shift relative to tetramethylsilane.

threaded polymethacrylates,[29] the threaded species also could not be detected by chemical shift differences, and NOESY techniques successfully employed with the polyurethane[30] and poymethacrylate[29] systems failed. Use of competitive complexation of the vacant crown ethers with low molecular weight guests to differentiate them from threaded cyclics by chemical shift changes, as used with polyurethanes,[31] was not possible because of the insolubility of aramide **3c** and the guest in a common appropriate (i.e., nonpolar) solvent.

To test whether a phenol potentially resulting from ring opening of the crown ether monomer (e.g., by attack of a nucleophile such as COOH on the ArOCH$_2$ linkage) might react, isophthalic acid and bisphenol A were exposed to the Yamazaki polyamidification conditions. No polymer formed, nor was there evidence of any condensation process.

4. Polymerization of the 14-Membered Crown Ether Monomer 1d. To differentiate more clearly between the two possibilities of self-threading and ring opening as explanations for the results obtained earlier, we synthesized the 14-membered crown ether diacid **1d**, which is clearly not amenable to threading on the basis of the crystal structureof its dimethyl ester (Figure 1c: cavity opening 2.1 × 3.5 Å^2)[44] and which presumably possesses more ring strain than its larger homologues **1a**, **1b**, and **1c**. On this basis, we reasoned that the aramide **3d** resulting from condensation of **1d** with ODA (**2**) would possess a normal, unimodal molecular weight distribution if it did not undergo ring opening. This would provide evidence corroborating the self-threading of aramides **3a**−**3c** based on the larger crown ether diacids **1a**, **1b**, and **1c**.

As with the aramides **3a**, **5a**, **3b**, and **3c** from the larger crown ether monomers, the ^{1}H NMR spectrum of aramide **3d** (Figure 5) shows no evidence of ring opening. The signals for the aromatic protons of the macrocycle are broadened into singlets just as in the other systems, but no new signals appear, as would be expected if ring opening occurred; this is particularly true of the ethyleneoxy signal, because ring opening would cause the CH$_2$ units to no longer be equivalent, and thus at least two signals would have been observed in this region.

B. Molecular Weight Determinations by GPC. The model aramides **6** and **7** were of reasonably high molecular weights and number-average degrees of polymerization (DP$_n$ ~ 150) (Table 1).

As a reference point we found that condensation of isophthalic acid and ODA (**2**) under our reaction conditions produced aramide **6** with a molecular weight distribution of 2.0 or slightly less [Table 1, samples **6** (DSN), **6** (HW), and **6** (SB1)], as theoretically expected for a step-growth process. Likewise the *m*-BAPPO-based (**4**) polymer **7** was of reasonably high molecular weight with PDI close to 2.

Molecular weight distributions (obtained by gel permeation chromatography, GPC) for polymers **3b** (Figure 6) and **5b** (Figure 7) are broad and bimodal, extending to the exclusion limit of the column set. The results are summarized in Table 1. In **3b** the low molecular weight fraction had DP$_n$ = 98.0 and the high molecular weight fraction had DP$_n$ = 853 (at the maxima); in **5b**, the corresponding values were DP$_n$ = 118 and DP$_n$ = 806. The DP$_n$s of the high molecular weight fractions are

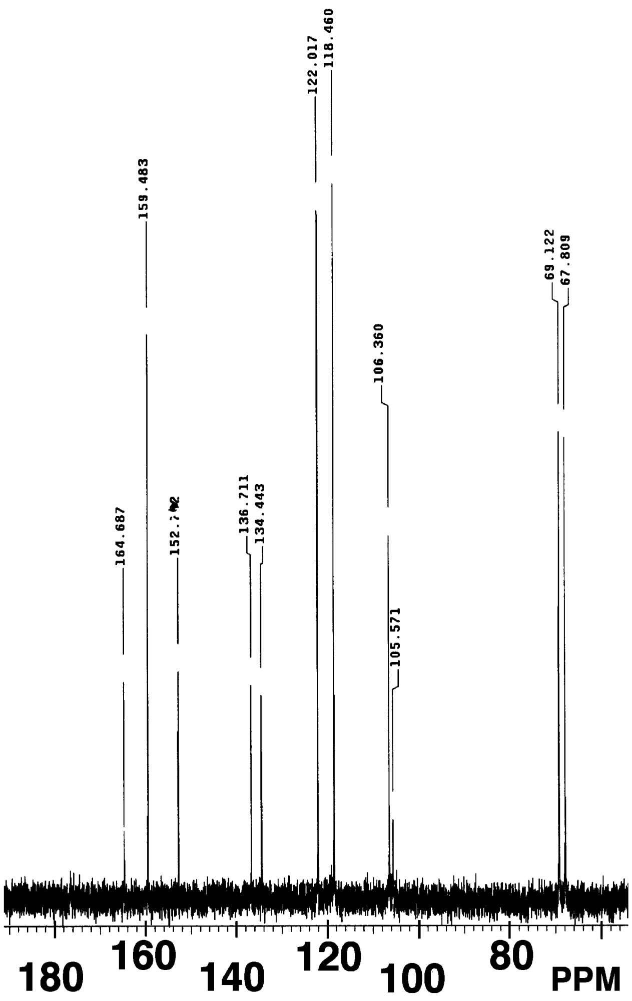


Figure 4. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of polymer **3c**. The *y*-axis scale is arbitrary; the *x*-axis scale is parts per million chemical shift relative to tetramethylsilane. There are 11 signals from the polymer, as required. Assignments: *C*ONH (164.69 ppm), C_{Ar}–O–CH_2 (159.48 ppm), C_{Ar}–O–C_{Ar} (152.76 ppm), C_{Ar}–CO (136.71), C_{Ar}–N (134.44), and CH_2O (67.81 and 69.12 ppm); signals at 122.02, 118.46, 106.36, and 105.57 ppm are due to the remaining aromatic carbons.

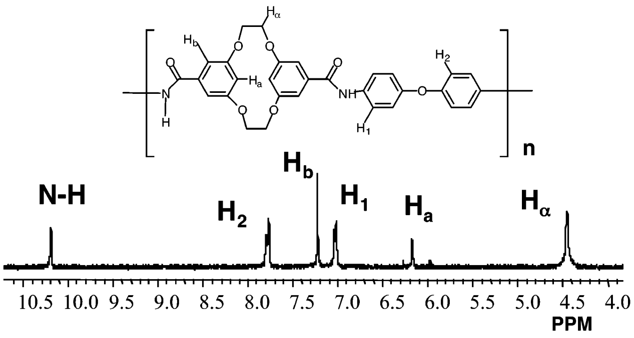


Figure 5. ^1H NMR (400 MHz) spectrum of polymer **3d** in DMSO-d_6. The *y*-axis scale is arbitrary; the *x*-axis scale is parts per million chemical shift relative to tetramethylsilane.

clearly too large to be linear polyamides formed by this step growth process.

Condensation of 20-membered crown ether diacid **1c** and ODA (**2**) led to aramide **3c** that displayed a bimodal molecular weight profile (Figure 8) and thus a broad molecular weight distribution (Table 1).

The aramide **3d** resulting from condensation of BCP14C4 (**1d**) and ODA (**2**) had a number-average molecular weight that was similar to that of homolgous **3c**, but whose distribution was clearly monomodal [see Supporting Information (SI)] with a polydispersity of 2.8

Table 1. Properties of Aramides

aramide	M_n[a] (kg/mol)	M_w[a] (kg/mol)	PDI[a] (°C)	T_g[b] (°C)	$T_{5\%}$[c] (°C)
3a[34]	insoluble	insoluble	insoluble	114	366[d]/325[e]
5a[34]	insoluble	insoluble	insoluble	127	385[d]/334[e]
3b (DSN)[f]	36.0[g] 166[h]	189[g] 649[h]	5.24[g] 3.92[h]	156	415[d]/376[e]
5b (DSN)	25.6[g]	235[g]	9.18[g]	174	450[d]/383[e]
3c (SB)[i]	12.9[g] 49.0[h]	55.2[g] 212[h]	4.28[g] 4.33[h]	207	390[d]/390[e]
3d (HW)[j]	53.8[h]	151[h]	2.81[h]	261	437[d]/406[e]
6 (DSN)	50.2[g]	88.7[g]	1.77[g]	264	477[d]481[e]
6 (HW)[k]	82.2[h]	139[h]	1.69[h]	267	434[d]/437[e]
6 (SB1)[i]	50.2[g]	101[g]	2.01[g]		
6 (SB2)[i,l]	71.8[g]	157[g]	2.19[g]		
6 (SB3)[i,m]	11.4[g]	20.1[g]	1.76[g]		
6 (SB4)[i,n]	13.7[g]	23.1[g]	1.69[g]		
6 (SB5)[i,o]	20.7[g]	34.3[g]	1.66[g]		
7 (DSN)	65.1[g]	104[g]	1.60[g]	247	463[d]/462[e]

[a] M_n = number-average molecular weight; M_w = weight-average molecular weight, determined by GPC. PDI = M_w/M_n. [b] T_g = glass transition temperature, determined by DSC at a scan rate of 10 °C/min. [c] $T_{5\%}$ = temperature at which 5% weight loss occurs, determined by TGA at a scan rate of 10 °C/min. [d] In nitrogen.[e] In air. [f] Initials of experimentalist are indicated in parentheses. [g] With 20 mM P_2O_5 in NMP at 60 °C and 1 mL/min using Styragel columns, viscosity detection and the universal calibration. [h] With 50 mM LiBr in DMF at 0.5 mL/min using Phenogel columns, refractive index detection and poly(methyl methacrylate) calibration. [i] Note that this polymer was prepared under more dilute concentration conditions than the others. [j] Intrinsic viscosity = $[\eta]$ = 0.854 dL/g (NMP, 30 °C). [k] Intrinsic viscosity = $[\eta]$ = 0.553 dL/g (NMP, 30 °C). [l] In the presence of 0.500 equiv of crown ether **8**. [m] In the presence of 0.500 equiv of crown ether **8**, but without added LiCl. [n] In absence of both crown ether **8** and LiCl. [o] In the presence of crown ether **20**.

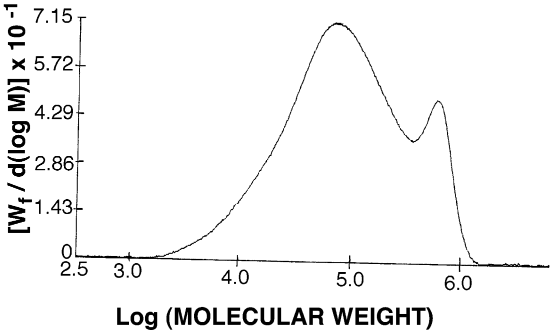


Figure 6. Molecular weight distribution of polymer **3b** determined by GPC (20 mM P_2O_5 in NMP, 60 °C) using a viscosity detector and the universal calibration. W_f = weight fraction; M = molecular weight.

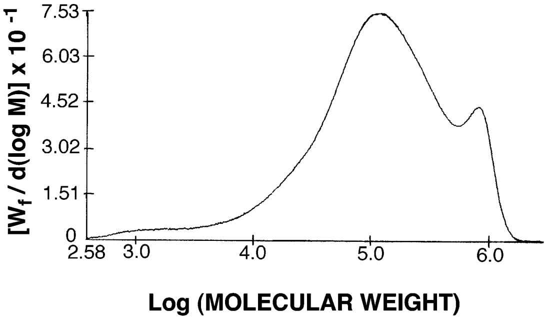


Figure 7. Molecular weight distribution of polymer **5b** determined by GPC (20 mM P_2O_5 in NMP, 60 °C) using a viscosity detector and the universal calibration. W_f = weight fraction; M = molecular weight.

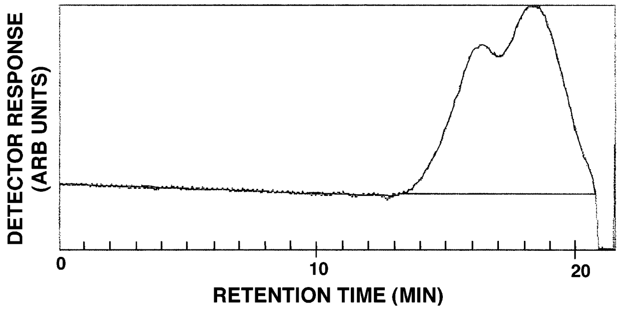
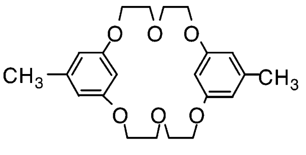


Figure 8. GPC trace of polymer **3c** (50 mM LiBr in DMF, flow rate 0.50 mL/min, 25 °C, refractive index detector).

(Table 1). The molecular weight of this aramide is indeed comparable to model system **6**.

To address the fact that the PDI of aramides **3c** and **3d** were greater than the theoretically expected value of 2.0, a further test was carried out by preparing model polyamide **6** (SB2) in the presence of nonfunctionalized bis(5-methyl-1,3-phenylene)-20-crown-6 (**8**). **6** (SB2) had a PDI somewhat greater than 2 and its molecular weight was somewhat higher than that of **6** (SB1) prepared in the absence of the crown ether (Table 1), even though no branching is possible either by double threading or ring opening of **8**. ^{1}H NMR spectroscopy (DMSO-d_6) revealed the presence of **8** in the polymer even after extensive Soxhlet extraction with ethanol; however, in DMSO-d_6 solution the chemical shifts of the small amount (2.3 mol %) of recalcitrant crown ether were exactly the same as those in pure **8**.



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C. Mass Spectrometric Results. Matrix assisted laser desorption-time-of-flight (MALDI−TOF) mass spectrometry (MS) was applied to the polyamide samples using a dithranol matrix. The clusters of peaks for each species correspond to various isotopically substituted molecules.[49] For the present aramides these include two isotopes each for H, C, and N and three isotopes for O. In polymeric systems, the range of peaks due to isotopic abundances can be quite broad as we see here and as is documented in the literature.[49] Also recall that when the compound contains more than 90 carbon atoms, the $(M + 1)^+$ isotopic signal is larger than the M^+ signal; for these polymers this is the case for any species containing more than three crown ether repeat units or more than five units of model polymer **6**.

For the bis(*m*-phenylene)-26-crown-8/ODA-based aramide **3b** signals were detected up to $m/z = 9100$ Da with spacings of 700.27 Da (Figure 9a), which corresponds to the repeat unit molecular weight ($^{12}C_{38}{}^{1}H_{40}{}^{14}N_2{}^{16}O_{11}$). In the expanded presentations in Figure 9, parts b and c, only minor amounts of linear structures are detected, consisting of linear amino acids (AA) ($m/z = 700n + 18$), diacids (DAc) ($m/z = 700n + 536$), and diamines (DAm) ($m/z = 700n + 200$). The weak cluster at $m/z \sim 2858$ Da (Figure 9b) corresponds to the K adduct of the tetrameric amino acid (AA$_4$), 4(700.27) + 18 + 39 = 2856. The cluster at $m/z \sim 2866$ Da (Figure 9b) corresponds to the silver adduct of the macrocyclic tetramer (M$_4$) that has lost CO$_2$: 4(700.27) − 44 + 106.95 = 2864 and 4(700.27) − 44 + 108.95 = 2866 for ^{107}Ag (51.3%) and ^{109}Ag (48.7%), respectively. The remaining signals for the predominant cyclic species are observed as $(M + H)^+$, $(M + Na)^+$ and $(M + K)^+$ adducts, as illustrated for the tetramers M$_4$ (exact mass 2801.06 for $^{12}C_{152}{}^{1}H_{160}{}^{14}N_8{}^{16}O_{44}$) in the series of signals at $m/z = 2800{-}2840$ (Figure 9c); the corresponding silver adducts $(M_4 + Ag)^+$ (theory: 2908 and 2910) are observed in Figure 9b in the cluster at $m/z \sim 2911$ Da.

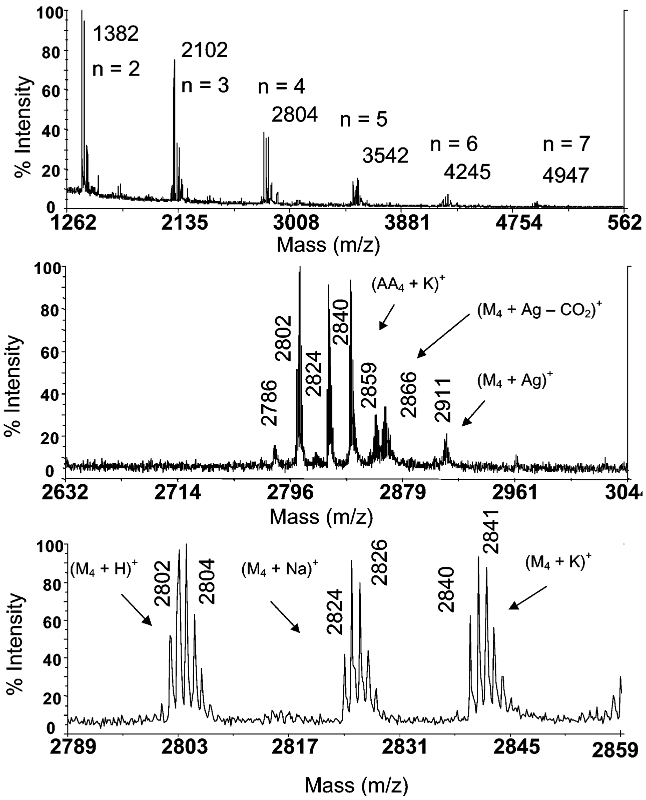


Figure 9. MALDI−TOF MS of aramide **3b** in dithranol with silver trifluoroacetate: (a, top) full scan, (b, middle) tetramer region, (c, bottom) expanded view of tetramer region. The cluster at $m/z = 2805$ corresponds to (cyclic tetramer + H)$^+$, that at $m/z = 2825$ to (cyclic tetramer + Na)$^+$, and that at $m/z = 2841$ to (cyclic tetramer + K)$^+$. The cluster at $m/z = 2858$ corresponds to the to (linear tetrameric amino acid + K)$^+$, and the cluster at $m/z = 2866$ is (tetrameric macrocycle + Ag − CO$_2$)$^+$, while that at $m/z = 2911$ corresponds to (cyclic tetramer + Ag)$^+$.

For the bis(*m*-phenylene)-26-crown-8/phosphine oxide-based aramide **5b** molecular weights approaching 10 000 Da were observed with spacings corresponding to the repeat unit mass, 992.34 Da ($^{12}C_{56}{}^{1}H_{53}{}^{14}N_2{}^{16}O_{13}{}^{31}P$) (Figure 10). Here linear structures that would exhibit signals at $m/z = 992n + 18$ (AA), $992n + 536$ (DAc), and $992n + 200$ (DAm) are completely absent. Figure 10b is an expanded view of the series of signals from 2970 to 3030, corresponding to the cyclic trimers (exact mass 2977.01, $^{12}C_{168}{}^{1}H_{159}{}^{14}N_6{}^{16}O_{39}{}^{31}P_3$) containing $(M_3 + H)^+$, $(M_3 + Na)^+$ and $(M_3 + K)^+$ clusters.

Turning now to the bis(*m*-phenylene)-20-crown-6/ODA-based aramide **3c**, in Figure 11 it can be seen that the situation is more complex. Five distinct repeating clusters of peaks with spacings of 612.22 Da ($^{12}C_{34}{}^{1}H_{32}{}^{14}N_2{}^{16}O_9$) were observed up to $m/z \sim 4000$; these are labeled **A**−**E**. **A** clusters correspond to the lithium adducts of linear AA species ($m/z = 612n + 18 + 7$). The **B** series are sodium adducts of the linear DAm ($m/z = 612n + 200 + 23$), and the **C** series correspond

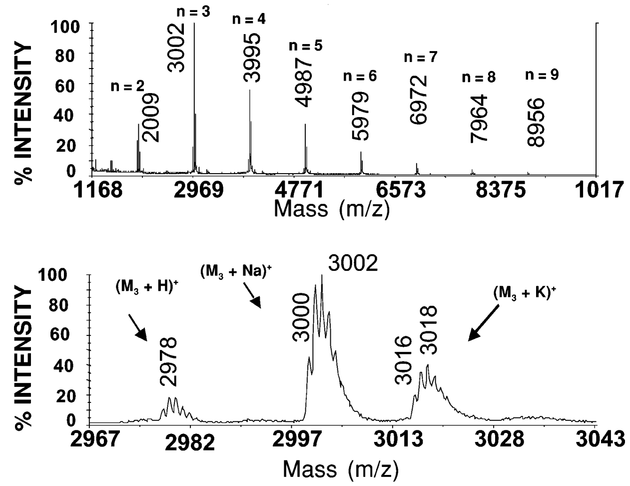


Figure 10. MALDI−TOF MS of aramide **5b** in dithranol with silver trifluoroacetate: (a, top) full scan and (b, bottom) trimer region. In part b, the cluster at $m/z = 2978$ corresponds to (cyclic trimer + H)$^+$, $m/z = 3002$ to (cyclic trimer + Na)$^+$ and $m/z = 3018$ to (cyclic trimer + K)$^+$.

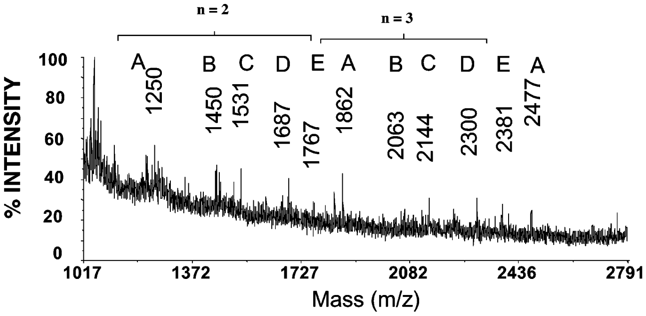


Figure 11. MALDI−TOF MS of aramide **3c** in dithranol with silver trifluoroacetate: (A) clusters = (amino acids + Li)$^+$, (B) clusters = (diamines + Na)$^+$, (C) clusters = (diamines + Ag)$^+$, (D) clusters = (amino methyl esters)$^+$, and (E) clusters = (amino acids − $C_6H_4NH_2$ + Li)$^+$.

to silver adducts of the linear DAm ($m/z = 612n + 200 + 107$ or 109). The **D** clusters appear to be DAc with one end esterified with methanol (from quenching of the reaction) ($m/z = 612n + 448 + 14$). And finally the **E** series can be assigned to the Li adducts of linear AA after loss of the *p*-aminophenyl fragment ($^{12}C_6{}^1H_6{}^{14}N$, 92.05 Da). Thus, no cyclic species are observed in **3c**.

The model isophthalic acid-ODA-based aramide **6** (SB-1) afforded a series of peaks with a spacing of 330.10 Da, corresponding to the repeat unit mass ($^{12}C_{20}{}^1H_{14}{}^{14}N_2{}^{16}O_3$), up to $m/z \sim 10\,000$ (Figure 12). In this case the major signals correspond to cyclic structures. Although Li adducts of linear amino acids ($m/z = 330n + 18 + 7$) differ from Na adducts of cyclics ($m/z = 330n + 23$) by only two mass units, the formation of cyclics was confirmed by careful study in the presence of NaI and LiCl (see SI).

No meaningful results were obtained under these conditions with the polyamide **3d** prepared from BCP14C4 (**1d**).

D. Thermal Properties of the Aramides. Polymers **3b** and **5b** from BCP26C8 (**1b**) exhibited T_g values higher than those of polymers **3a** and **5a** derived from BCP32C10 (**1a**) (Table 1). And **3c** from BCP20C6 (**1c**) has a higher T_g than both **3a** and **3b**. Likewise T_g for **3d** from BCP14C4 (**1d**) is higher than that of **3c**, and remarkably it is very similar to that of the model isophthalic acid-based polymer **6**.

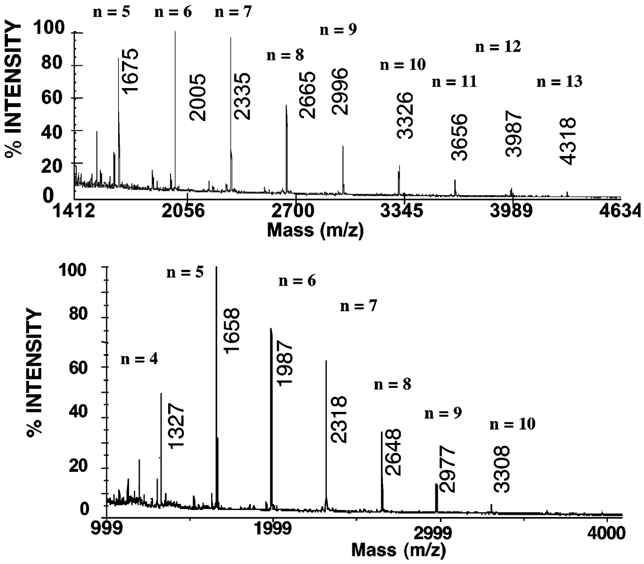


Figure 12. MALDI−TOF MS partial scans of aramide **6** (SB1) in dithranol with (a, top) NaI and (b, bottom) LiCl. All prominent signals correspond to cyclic species as either Na or Li adducts.

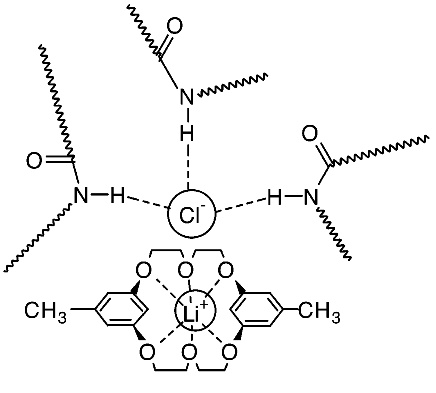
The thermal stabilities of the aramides follow a similar trend (Table 1). Polymer **3d** from the smallest crown **1d** is more stable than aramide **3b** from the 26-membered monomer **1b**, which is more stable than aramide **3a** from the largest crown ether monomer **1a**. The stability of aramide **3c** is lower than that of **3b** in air, but not in nitrogen, perhaps a reflection of the lower M_n of **3c**. In fact, the smallest crown-based aramide **3d** is nearly as stable as model polymer **6**. Of course the phosphine oxide-containing aramides **5a**, **5b**, and **7** are more stable than their ODA analogues **3a**, **3b**, and **6**, as expected.[36]

Discussion

We originally believed that aramides **3b** and **5b** were highly branched as a result of in situ threading of the polymer chains through the crown ether moieties of other macromolecules, i.e., formation of polyrotaxanes of type F (Scheme 1) during polymerization.

However, threading was not detected in terms of ^1H NMR chemical shift changes. In the cases of self-threaded polymethacrylates,[29] the threaded species also could not be detected by chemical shift differences. Unfortunately, attempts to detect the threading of polyamide **3b** unequivocally through use of NOESY techniques successfully employed previously with the polyurethane[31] and polymethacrylate[29] systems failed. Furthermore, due to the insolubility of the aramides and low molecular weight guests in low polarity solvents, use of competitive complexation of the unthreaded crown ether moieties to bring about chemical shift changes that expose the threaded cyclics, as used with polyurethanes,[31] was not possible.

A. Model Polyamide 6. We believe that the presence of macrocycle **8** in purified model polymer **6** (SB2) is due to the formation of a complex with the LiCl component of the polymerization reaction. Small crown ethers are well-known to complex alkalai metal ions;[1] more specifically, complexations of lithium ion by 11-crown-3,[50] 12-crown-4,[51,52] 13-crown-4,[53,54] 14-crown-4,[54,55] 15-crown-5,[52,56] 16-crown-5,[54] 18-crown-6[52,57] and 21-crown-7[58] derivatives have been well studied. Amides complex chloride ion;[59] in fact, the reason that LiCl is included in aramide syntheses is to improve solubility, via this means as well as complexation of the metal ion by the carbonyl group.[60] Thus, binding of Li^+ by **8** would be expected in the reaction solution. However, the complex would probably not be totally soluble in the precipitation solvent, methanol, nor the extraction solvent, ethanol; the chloride counterion would hydrogen bond to the polyamide, making it difficult to dissociate the resultant complex. Moreover, binding of chloride ion by two or more aramide chains would serve as a noncovalent cross-link, **9**, and possibly broaden the molecular weight distribution as detected by GPC. In support of this hypothesis, by preparative thin-layer chromatography from polymer **6** (SB2) we isolated a small amount of a polar component, whose FAB mass spectrum contained a peak at *m*/*z* 429, which corresponds to $(\mathbf{8} + \mathrm{LiCl} - \mathrm{H})^+$. Indeed, when the polymerization was carried out in the absence of LiCl but again in the presence of **8**, the resultant polymer, **6** (SB3), after the initial precipitation, contained no detectable **8** by ^{1}H NMR spectroscopy and the molecular weight distribution was less than 2 (Table 1). The large reduction in molecular weight of **6** (SB3) relative to **6** (SB2) was due to the lack of LiCl as shown by the results for **6** (SB4) formed in the absence of both **8** and LiCl (Table 1).



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B. Polyamide 3c from 20-Membered Crown Ether Monomer 1c. We initially reasoned that, since the 20-membered crown ether **1c** yielded aramide **3c** that was bimodal, it also had undergone threading analogous to that observed with larger homologues **1a** and **1b**, because ring opening does not occur and alcohols and phenols do not polymerize under the Yamazaki reaction conditions, as shown above. Note that the molecular weight of aramide **3c** is substantially less than that of its 26-membered crown-containing homologue **3b** (Table 1). This fact is consistent with self-threading as the source of the observed branching, since the smaller macrocycle in **3c** should undergo less threading due to its smaller cavity size.

Threading of the 20-membered crown ether is contrary to the widely held belief that this ring size is too small to be threaded.[2] However, it should be pointed out that Schill et al. did report that 21-membered rings could be threaded.[48] Moreover, as noted above, the somewhat larger 24-membered dibenzo-24-crown-8 is readily threaded to form pseudorotaxane structures;[40] in fact, this system has been the basis for several of our recent studies of pseudorotaxanes.[61] On this basis, the small degree of threading of the 20-membered monomer **1d** required to yield the observed result would not be surprising. By way of comparison, there was only 3.7% threading in the case of the self-threaded polyurethane that also was bimodal in molecular weight distribution, having an overall PDI of 23.6. [31]

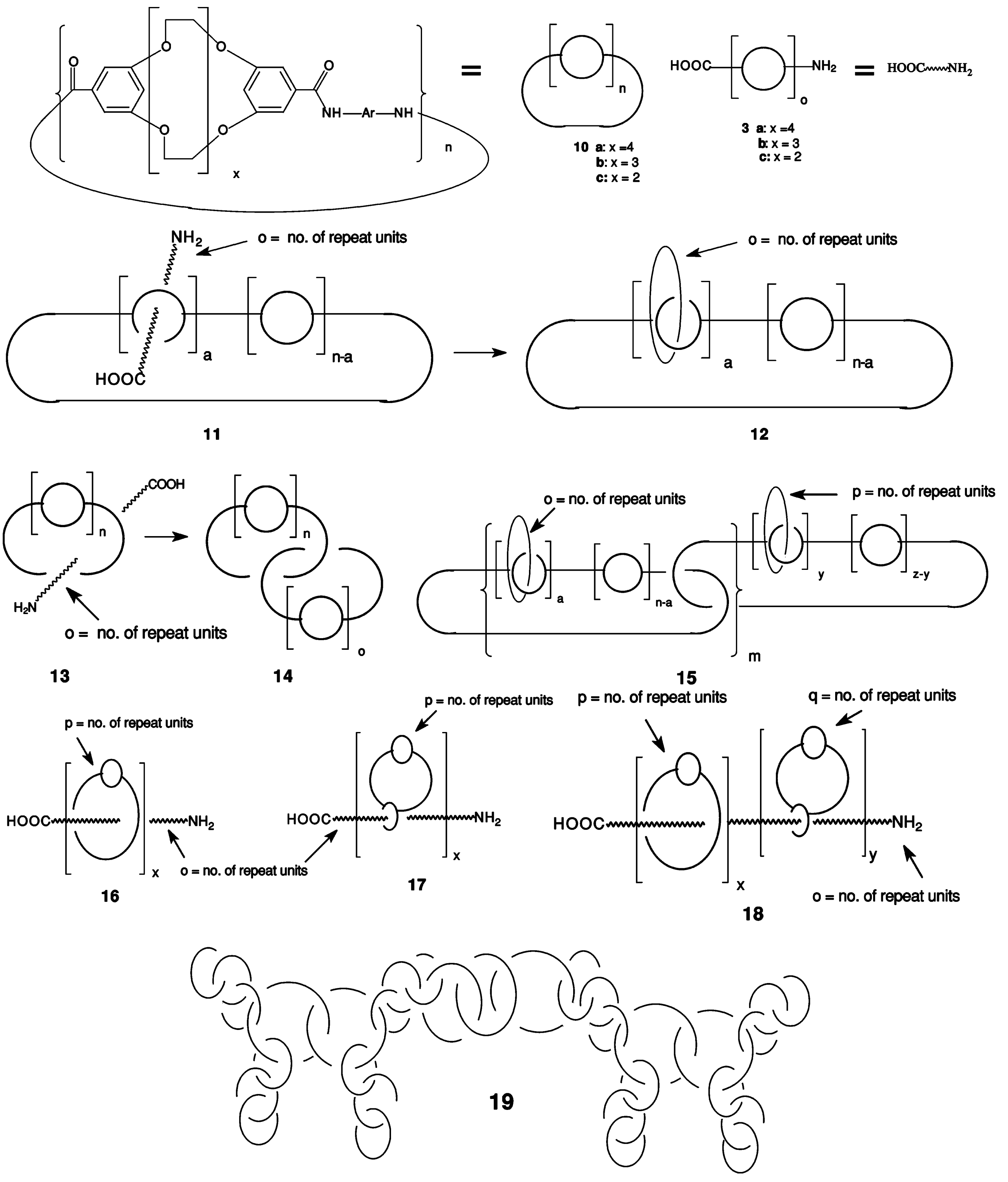
C. Polyamide 3d from 14-Membered Crown Ether Monomer 1d. On the basis of the results described above for model aramide **6**, we attribute, at least in part, the larger PDI of aramide **3d** observed by GPC in LiBr/DMF to noncovalent branching due to such complexation by the crown ether component, which is present in every repeat unit and whose smaller cavity size makes it a better host for Li^+ than the larger crown ether moieties.[1,50−58] The effect on the PDI, therefore, is weaker with the larger crown-containing polymers and contributes in only a minor way to the observed broadening for the larger crown ether polyamides. The 50% higher intrinsic viscosity observed for **3d** relative to that of **6** (HW) (Table 1) is consistent with the conclusion that the crown ether units of **3d** are complexed with LiCl during the polymerization, resulting in branching analogous to that suggested in **9**.

D. The Source of Branching/Cross-Linking in Aramides 3 and 5. An astute referee of the original version of this paper suggested that we consider the recent articles by Kricheldorf et al.,[62] which refute, both theoretically and experimentally, the long-held view that cyclization in step-growth polymerizations can generally be ignored. To quote: “it is a fundamental tendency of all step-growth polymerizations to yield cycles as stable end products” and “a characteristic consequence of a high extent of cyclization is the tendency toward bimodal mass distribution...”. In this regard, it is particularly noteworthy that the bimodal molecular weight distributions observed in Figures 6, 7, and 8 are very similar to ones reported by Kricheldorf et al. Therefore, we examined the aramides by mass spectrometry as described above and these key results indicate an alternate contribution to the observed branching/cross-linking and its dependence on the nature of the crown ether monomer.

First it must be noted that the MALDI−TOF MS do not, of course, provide a complete picture of the distributions of molecular weights and structures that exist in these aramides; only the low molecular weight ends of the distributions are observed by this technique. Nonetheless, this technique provides valuable information about these polyamides. Since these reactions are essentially irreversible, once formed, cyclic (lactams) will persist; hence, the presence of lactams in various systems indicates the tendency to cyclize. More specifically, it indicates the relative tendency of the individual growing oligomers for cyclization to lactams **10** (Scheme 5) vs chain extension. This judgment has to be tempered by the realization that higher conversions will lower percentages of low molecular weight linear species, so comparison of different polymers, indeed even different samples of the same polymer, will reflect this aspect as well.

In 26-membered crown ether/ODA-derived **3b**, it can be seen from Figure 9 that only 15−20% of each oligomer consists of “linear species” and the rest are “cyclics”. For the corresponding phosphine oxide diamine-based **5b** no “linear species” are detected at all (Figure 10). Considering the 20-membered crown ether/ODA aramide **3c** the converse situation exists: no

Scheme 5. Schematic Representations of Cyclic Lactam Polymers (10), Polyrotaxanes (11, 13, 16–18), Catenanes (12, 14, 15), and Polycatenanes (19) Formed via Threading of both Crown Ether Rings and Lactams by Linear Aramides



"cyclic species" were observed (Figure 11). The aramide **3d** derived from the 14-membered crown ether diacid **1d** revealed no low molecular weight components. The model isophthalic acid/ODA polymers **6** (DSN), **6** (HW), and **6** (SB-1) yielded spectra consisting only of "cyclics" (Figure 12). Thus, we can rank the apparent tendency to cyclize to lactams: **5b** $\sim$ **6** $>$ **3b** $\gg$ **3c** $\sim$ **3d**.

Interestingly the "cyclic species" detected are not necessarily simple. Each cluster may in fact correspond to several isomeric species, both constitutional and topological. This arises because of the strong amide-amide hydrogen bonding that occurs in these systems. It is well-known from the work of Vögtle,[63] Hunter,[64] Leigh,[65,66] and others [67] that these atttractive forces are very effective in producing pseudorotaxanes and thence catenanes; indeed, amides are known to be effective gelators due to their strong H-bonding abilities.[68] This type of interaction of large cyclics augmented by the threading of the crown ether moieties as indicated in Scheme 4 can lead to a diversity of catenated species.

Therefore, for example, the tetramers observed in Figure 10 include as constitutional isomers the cyclic tetramer **10b**, $n = 4$ itself (Scheme 5), [2]catenanes derived from the cyclic monomer and the cyclic trimer, [2]catenanes derived from two cyclic dimers, and [3]-catenanes derived from two cyclic monomers and the cyclic dimer. Furthermore, within each of these catenane species, topological isomers also exist, because the catenanes can be threaded via either the lactam ring or the crown ether ring or both. For example, the following [2]catenane topological isomers of the tetramers of **10b** may form: **12**, $n = 2$, $a = 1$, $o = 2$; **12**, $n = 3$, $a = 1$, $o = 1$; **14**, $n = o = 2$ and **14**, $n = 1$, $o = 3$. And the following [3]catenane topological isomers are possible: **12**, $n = a = 2$, $o = 1$; **15**, $\mathrm{m} = n = \mathrm{a} = o = 1$, $y = 0$, $z = 2$; **15**, $m = 2$, $n = 1$, $\mathrm{a} = y = 0$, $z = 2$.

The number of isomeric possibilities expands exponentially as the number of repeat units in the species increases, leading to a variety of combinations of ring sizes and threading motifs.

Of course in order for a catenane to form, a pseudorotaxane or rotaxane must first be self-assembled; hydrogen bonding interactions of the type indicated in Scheme 4 can lead to threading of the crown ether moieties, forming (pseudo)rotaxane **11**, and amide–amide hydrogen bonding can lead to threading of the oligomeric lactams, forming pseudorotaxane **13** (Scheme 5). Since the crown ether rings probably cannot pass through each other, in cases in which the threaded unit is flanked by two crown ether moieties on the linear component, these are considered to be polyrotaxanes. Of course other isomers involving threading of both the crown ether and larger lactam rings are also possible. As a result, the “linear species” observed by MALDI–TOF MS are not necessarily simple linear macromolecules either: they also include polypseudorotaxanes and polyrotaxanes. For example, the “linear” tetramer signal for **3b** at ~2858 Da (Figure 9c) could consist of a range of constitutionally isomeric [2]pseudorotaxanes involving threading of the large lactam rings: i.e., a linear trimer with a cyclic monomer threaded upon it, **11**, $n = a = 1$, $o = 3$, or **13**, $n = 1$, $o = 3$; or a linear dimer with a cyclic dimer threaded upon it, **11**, $n = 2$, $a = 1$, $o = 2$, or **13**, $n = 2$, $o = 2$; or a monomer with a threaded trimer, **11**, $n = 3$, $a = 1$, $o = 1$ or **13**, $n = 3$, $o = 1$. And it may include a range of constitutionally isomeric [3]pseudorotaxanes, i.e., a linear dimer with two cyclic monomers, **16**, $p = 1$, $x = 2$, $o = 2$, or **17**, $p = 1$, $x = 2$, $o = 2$ or **18**, $x = \mathrm{y} = \mathrm{p} = q = 1$, $o = 2$; or a linear monomer with a cyclic dimer and a cyclic monomer, **18**, $x = y = 1$, $p = 2$, $q = 1$, $o = 1$, or **18**, $x = y = 1$, $p = 1$, $q = 2$, $o = 1$. The total number of isomers grows exponentially with increasing molar mass. In fact, it is particularly noteworthy that if threading were highly efficient no “cyclic species” would be detected; they would appear as pseudorotaxanes or rotaxanes, i.e., “linears”. Under this scenario the absence of signals for low molar mass lactams in the mass spectrum would be indicative of efficient threading.

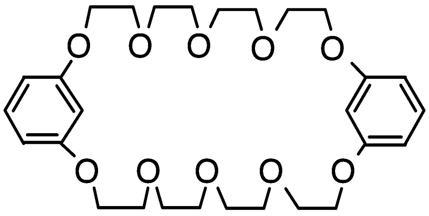
Continuous production of lactams of larger ring size throughout the polymerization gives rise to the possibility of forming branched and ultimately cross-linked catenated species as illustrated in cartoon **19**.

As Kricheldorf et al. pointed out, [62] the tendency to form cyclic species in such polymerizations is related to the geometry and flexibility of the monomer units involved. In the cases of the present aramides although ODA (**2**) is para-substituted, it possesses a kinked structure due to the diphenyl ether moiety, and this, coupled with the rigidity of the phenylene units, is conducive to cyclization. The phosphine oxide diamine **4** is likewise kinked via the phosporous atom and also because of the meta-substituted phenylene units, so this otherwise rigid monomer can quite easily accommodate cyclization through crankshaft rotations.

Recalling that the aramides **3a** and **5a** from the 32-membered crown ether **1a** were completely insoluble, but swellable, while polyamides **3b** and **5b** were soluble, but bimodal, as was polyamide **3c**, we attribute the trend primarily to the decreasing flexibilty of the crown ether as the ring size decreases. That is, the tendency to cyclize is limited by the rigidity of the pseudo-para-linked crown ether components (**1**) of the polymers. Kricheldorf et al. pointed out that para-substitution diminishes cyclization. [62] However, the 32-membered crown ether and its derivatives fold very readily because of the flexibility in the eight ethyleneoxy units, as demonstrated by the tendency of these hosts to form “taco” or “hot dog” complexes.[69] The 26-membered crown component **1b** also tends to fold, but with less facility, and hence produces a lower percentage of cyclic polymeric products. This trend continues for the 20- and 14-membered crowns, **1c** and **1d**. The diacid crown **1d** is quite rigid, making it a truer para-substituted structure conformationally; this is consistent with the fact that MALDI–TOF MS was unable to detect low molecular weight cyclic species in aramide **3d** from it. Since the amidification reaction is essentially irreversible, low molecular weight cyclic species once formed remain in the product as isolated species or become threaded and appear as (pseudo)rotaxanes or catenanes; if cyclization does not occur, the linear species will continue to grow into high molecular weight linear macromolecules and neither low molar mass linears nor cyclics will remain at the end of the process, as observed for **3d**.

The cyclic species present in model aramides **6** (Figure 12) arise because not only is ODA (**2**) amenable to cyclization, but the diacid component, isophthalic acid, is meta-substituted, further promoting this process relative to the situation in “pseudo-para” aramide **3d**. A key question is as follows: “If model polymer **6** has a high tendency for cyclization to the lactam structures, why then are the molecular weight and molecular weight distribution low in comparison to the crown ether-based polyamides **5a**, **5b**, **3a,** and **3b**?” If lactamization were the key step leading to branching/cross-linking, we would expect model aramide **6** to also be branched. The fact that **6** does not exhibit significant branching, despite its significant lactam content, indicates that the crown ether components provide the driving force for the threading processes in the polymers containing larger crown ether moieties. In other words, it appears that threading of the crown ether rings as shown in **11** and **17** is more important than threading of the larger lactam rings to form **13** and **16** (Scheme 5), leading preferentially to catenanes **12** rather than the isomeric **14**.

To demonstrate such threading under the polymerization reaction conditions aramide **6** (SB5) was prepared in the presence of 0.50 equiv of bis(*m*-phenylene)-32-crown-10 (**20**),[32] the unsubstituted analogue of diacid **1a**. After purification by Soxhlet extraction with ethanol 0.71 (0.15) mol % of crown ether was found per repeat unit of **6** (SB5) by ^{1}H NMR spectrocsopy. This level of



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threading is believed to be sufficient to produce observable branching/cross-linking in related aramide **3a** and **5a**, especially when coupled with the likely facile production of cyclic polymers in these cases. Indeed, in closely related work we have shown that 30-crown-10 is threaded onto aramide **6** and related aramides during synthesis to an extent dependent on the overall concentrations; large aliphatic crown ethers are threaded to a considerable extent (up to 20 mol %).[70] Since model aramide **6** possesses no bulky groups, it is likely that some initially threaded **20** was dethreaded during polymerization, as we have observed with polyesters.[20] Dethreading of once-threaded crown ether rings in aramides derived from the crown ether diacids is very unlikely since passage of one crown unit through another is unlikely; therefore, the percentage of threading retained in **6** (SB5) is more than likely much less than in aramides **3a** or **5a**.

Consistent with the hypothesis that it is the crown ether moieties that are threaded predominantly is the observation of a broad molecular weight distribution in aramide **3c** derived from the 20-membered crown coupled with the observation of no lactams in its mass spectrum (Figure 12). Ignoring the possibility that all of the low molar mass lactams became threaded, this may be a case in which self-threading of the crown ether is solely responsible for the observed branching. This would be consistent with our previous unambiguous demonstrations of self-threading of crown ethers[29,31] and the fact that little threading is actually required to produce PDI broadening (recall that only 3.7% self-threading produced PDI 23.6 [31]). An alternative explanation is that Li^+ complexation by the 20-membered crown ether leads to molecular weight broadening via the intermediacy of species analogous to **9** discussed above.

So, in sum, the cross-linking/branching observed in these aramides can be attributed to mechanical linkages: polypseudorotaxanes, polyrotaxanes, and polycatenanes. For systems with relatively high preferences for cyclization, polycatenanes (via either the crown ether rings or the larger oligomeric lactam rings) can form, and these in the extreme represent network structures **19**, as we believe are observed for **3a** and **5a**. The formation of polypseudorotaxanes in the presence of the lactam oligomers and polymers to the extent that the lactam rings allow, and polyrotaxanes, depending on the cavity size (threadability) of the crown ether moieties, also contribute to the high molecular weight component. The broad molecular weight distributions observed in some systems by GPC must in part be due to the fact that the myriad of different isomeric species, cyclics, catenanes, pseudorotaxanes and rotaxanes present (Scheme 5) have different conformational properties and hence different hydrodynamic volumes and viscosity profiles. The molecular weight distributions of Table 1 are in accord with this general conclusion: the system most likely to form cyclics, **5b**, does indeed have the broadest distribution, followed by **3b** and **3c**.

E. Thermal Properties of the Aramides. The trends in glass transition temperatures and thermal stability are consistent with the more rigid character of the backbone as the ring size of the crown ether component decreases, resulting in less segmental flexibility.

Conclusions

Poly(amide crown ether)s based on 32-, 26-, and 20-membered crown ether diacids contain physical (mechanical) linkages formed by in situ threading; these linkages constitute topological branching or cross-linking sites. The 32-membered crown ether system **1a** produces fully cross-linked aramide gels **3a** and **5a** that are insoluble in all solvents.[35] The aramides **3b**, **5b**, and **3c** based on 26- and 20-membered crown ether diacids, **1b** and **1c**, respectively, are soluble but display bimodal molecular weight distributions. In contrast the aramide **3d** resulting from the 14-membered crown ether diacid **1d** was fully soluble, displayed a unimodal GPC trace and a molecular weight more consonant with a “normal” polycondensation reaction of this type. ^{1}H NMR spectra did not reveal evidence of ring opening even with the smallest crown ether monomer **1d**. Mass spectrometric studies show that cyclic amide (lactam) products are present in **3b** and **5b** from the 26-membered crown ether and also in model aramide **6**, but not in **3c** or **3d** from the smaller 20- and 14-membered crown ethers. Taken together these results indicate that the branching/cross-linking process predominantly involves threading of the crown ether moieties, the “self-threading” observed in previous studies, leading to polypseudorotaxanes, polyrotaxanes, and polycatenanes, i.e., mechanically linked structures, to an extent dependent upon the crown ether cavity size.

There has been great interest in polycatenanes over the last several years;[66,71] success in directed synthesis of such structures has been limited to polymers containing [2]catenane units, but not to the formation of truly polymeric mechanically linked cyclic repeat units, i.e., [*n*]catenanes. Intriguingly, it now appears that polycatenanes of types **12**, **14**, **15**, and **19** described in Scheme 5 have been with us for more than a decade,[35] but not in a recognizable form. The present findings suggest that by proper design better-defined polycatenane systems may be achievable.

Experimental Section

Materials. Bis(2-chloroethyl) ether (99%, Aldrich), chloroform (HPLC grade, Burdick and Jackson), chloroform-*d* (99.8% isotopic purity, with 0.05% v/v tetramethylsilane, Cambridge Isotope Laboratories), dimethyl sulfoxide (99+%, Aldrich), dimethyl sulfoxide-d_6 (99.9% isotopic purity, with 0.05% v/v tetramethylsilane, Cambridge Isotope Laboratories), ethanol (reagent grade, denatured, Aldrich), lithium chloride (reagent grade, Aldrich), methanol (ACS HPLC grade, Burdick and Jackson), *N*-methylpyrolidinone (NMP, 99.5%, anhydrous, Aldrich), nitrogen gas (∼100%, anhydrous, from in-house liquid nitrogen source), orcinol monohydrate (97%, Aldrich), *N*,*N*-dimethylacetamide (99+%, Aldrich), *N*,*N*-dimethylformamide (HPLC grade, Aldrich), potassium carbonate (reagent grade, anhydrous, J. T. Baker), silica gel (32−63 μm, 60 Å pore size, AdEdge), tetra(*n*-butyl)ammonium iodide (98%, Aldrich), tetrahydrofuran (reagent grade, 99+%, Aldrich) and water (deionized, purity not determined, in-house supply) were used as supplied. Bis[4-(*m*-aminophenoxy)phenyl]phenylphosphine oxide (**4**), prepared as reported,[72] was recrystallized from dimethylacetamide twice, and then precipitated from ethanol into water twice: mp 72−74 °C; reported[72] mp 72−74 °C. Bis-(5-carboxy-1,3-phenylene)-26-crown-8 (**1b**) was prepared as reported [43] and recrystallized from dimethyl sulfoxide three times: mp 259.6−261.3 °C; reported mp 259.1−260.8 °C.[43] Bis-(5-carboxy-1,3-phenylene)-20-crown-86 (**1c**) was prepared as reported [30] and recrystallized from pyridine three times: mp 320−323 °C; reported mp 310 °C dec.[30] Isophthalic acid (99%, Aldrich) was recrystallized from methanol three times. 4,4′-Oxydianiline (**2**, 97%, Aldrich) was recrystallized from tetrahydrofuran three times. All monomers were dried in vacuo at ca. 100 °C overnight or at room temperature over phosphorus pentoxide (98%, reagent grade, Aldrich) before polymerization. Pyridine (99.8%, anhydrous, Aldrich) was distilled from calcium hydride (95%, coarse granules, Aldrich) or phosphorus pentoxide (98%, reagent grade, Aldrich) just prior to its use during polymerization. Triphenyl phosphite (97%, Eastman Kodak) was vacuum distilled and stored over molecular sieves (5A, 4−8 mesh, Aldrich).

Instruments. A vacuum oven (Napco model 5831) was used in concert with a vacuum pump (Welch Duoseal model 1400) at ca. 1 Torr for drying samples. The syringe pump (Harvard Scientific model 355 or Sage Instruments model 355 or Kd Scientific model 200) was used with airtight syringes (SGE International Proprietary, Ltd.). NMR spectra were recorded at ambient temperature on Varian 400-MHz or Bruker 500-MHz spectrometers with tetramethylsilane (TMS, $\delta = 0$) as internal standard. TGA was performed on a Perkin-Elmer model TGA-7 under N_2 or air at a heating rate of 10 °C/min. The glass transition temperatures were obtained by differential scanning calorimetry on a Perkin-Elmer Unix DSC 7 model at heating rate of 10 °C/min, and the reported values (midpoints) were obtained from the second heating after cooling; the instrument was calibrated with indium and tin standards. Some GPC was conducted in-house on a Waters GPC/ALC 150-C chromatograph equipped with a differential refractometric detector (Waters, model R401) and an on-line viscometric detector (Viscotek, model 100) coupled in parallel. A series of five columns packed with Styragel HT was used with *N*-methylpyrolidinone containing 20 mM P_2O_5 as solvent at 60 °C. The system was calibrated with polystyrene standards with molecular weights between 1.25 and 1.13×10^3 kg/mol for both the refractive index and the viscosity detectors; the exclusion limit was ca. 1.25×10^3 kg/mol. A typical solution contained ca. 2 mg/mL, of which 200 μL was injected and eluted at 1.0 mL/min. Other GPC analyses were carried out at Scientific Polymer Products, Inc., Ontario, NY, using Phenogel linear columns, 50 mM LiBr in DMF, a refractive index detector (Optlab model 903), and poly(methyl methacrylate) standards. The solutions contained ca. 1 mg/mL, of which 20 μL was injected and eluted at 0.5 mL/min. Elemental analyses were provided by Atlantic Laboratories, Norcross, GA. MALDI−TOF MS spectra were obtained using a Voyager-DE STR (Applied Biosystems, Framingham, MA) operated in the positive ion reflector mode using an average of 200 shots with a 337 nm wavelength nitrogen laser (300 μJ, 3 ns pulses) operating at 20 Hz. The accelerating voltage was 25 kV and the grid voltage was 67% of the acceleration voltage; source pressure: 2×10^{-7} Torr. For MALDI MS a 0.1 M matrix solution of 1,8,9-anthracenetriol ("dithranol") in THF (Aldrich Chemical Co., Inc., Milwaukee, WI), salt solutions of 1 mg/mL of silver trifluoroacetate (AgTFA) in THF or NaI in methanol, and polymer stock solutions in DMSO (10 mg/mL) were prepared; sample solutions were produced by mixing the polymer, matrix, and salt solutions in a 2:5:2 volume ratio, respectively, and sample plates were spotted with 1 μL aliquots.

Polycondensation of BCP26C8 (1b) with ODA (2) To Form 3b. A solution containing **1b** (0.4025 g, 0.7502 mmol), **2** (0.1502 g, 0.7500 mmol), LiCl (75 mg), pyridine (0.4 mL), triphenyl phosphite (0.4 mL), and NMP (1.5 mL) was heated at 100 °C under N_2. The homogeneous solution became cloudy and viscous in 30 min and finally gelled in about 40 min. After 3 h at 100 °C, the polymer was isolated by precipitation into methanol, filtered, washed with water and methanol, and dried in a vacuum oven at 50 °C for 24 h, yielding 0.51 g (100%). ^{1}H NMR (DMSO-d_6, Figure 2), δ (ppm): 3.62 (γ-OCH$_2$, s, 8H), 3.76 (β-OCH$_2$, s, 8H), 4.15 (α-OCH$_2$, s, 8H), 6.70 (H$_a$, s, 2H), 7.00 (H$_1$, d, $J = 8.8$ Hz, 4H), 7.11 (H$_b$, s, 4H), 7.75 (H$_2$, d, $J = 8.8$ Hz, 4H), and 10.16 (s, 2H).

Polycondensation of BCP26C8 (1b) with *m*-BAPPO (4) To Form 5b. The same procedure was followed as for **3b**; **1b** (0.4025 g, 0.7501 mmol), **4** (0.3696 g, 0.7501 mmol), LiCl (75 mg), pyridine (0.4 mL), triphenyl phosphite (0.4 mL), and NMP (1.5 mL) were used. The polymer was isolated in 100% yield. ^{1}H NMR (DMSO-d_6, Figure 3), δ (ppm): 3.57 (γ-OCH$_2$, s, 8H), 3.73 (β-OCH$_2$, s, 8H), 4.11 (α-OCH$_2$, s, 8H), 6.68−7.64 (H$_{arom}$, m, 27H), and 10.23 (s, 2H).

Polycondensation of BCP20C6 (1c) with ODA (2) To Form 3c. The same procedure was followed as for **3b**: **1c** (0.3363 g, 0.7502 mmol), **2** (0.1502 g, 0.7500 mmol), LiCl (75 mg), pyridine (0.4 mL), triphenyl phosphite (0.4 mL), and NMP (5.0 mL). After 3 h at 100 °C, the mixture was diluted with NMP and the polymer was isolated by precipitation into methanol. The precipitation was done three times. The polymer was filtered, washed with water and methanol, and dried in a vacuum oven at 50 °C for 24 h, 0.4735 g (97%). ^{1}H NMR (DMSO-d_6), δ (ppm): 3.82 (β-OCH$_2$, s, 8H), 4.19 (α-OCH$_2$, s, 8H), 6.72 (bs, 2H), 6.99 (d, $J = 9$ Hz, 4H), 7.08 (d, $J = 2$ Hz, 4H), 7.74 (d, $J = 9$ Hz, 4H), and 10.13 (NH, s, 2H). ^{13}C NMR (DMSO-d_6, Figure 4), δ (ppm): 164.69, 159.48, 152.76, 136.71, 134.44, 122.02, 118.46, 106.36, 105.57, 69.12, 67.81.

Polycondensation of BCP14C4 (1d) with ODA (2) To Form 3d. The same procedure was followed as for **3b**: **1d** (0.27006 g, 0.7500 mmol), **2** (0.15003 g, 0.7492 mmol), LiCl (79 mg), pyridine (0.4 mL), triphenyl phosphite (0.4 mL), and NMP (1.5 mL). The polymer was precipitated three times and dried in a vacuum oven at 50 °C for 24 h, yielding 0.42 g (100%). ^{1}H NMR (DMSO-d_6), δ (ppm): 4.44 (OCH$_2$, s, 8H), 6.17 (H$_a$, s, 2H), 7.03 (H$_1$, d, $J = 8.8$ Hz, 4H), 7.22 (H$_b$, s, 4H), 7.78 (H$_2$, d, $J = 8.8$ Hz, 4H), and 10.19 (s, 2H). ^{13}C NMR (DMSO-d_6, Figure 5), δ (ppm): 165.05, 158.89, 153.43, 137.24, 134.96, 122.77, 120.99, 119.08, 109.55, 66.78.

Polycondensation of Isophthalic Acid with ODA (2) To Form Model Aramide 6. SB1. A solution containing isophthalic acid (0.2492 g, 1.500 mmol), **2** (0.3004 g, 1.500 mmol), LiCl (0.150 g), pyridine (0.8 mL), triphenyl phosphite (0.8 mL), and NMP (5.0 mL) was heated at 100 °C under N_2 for 3 h. The resulting solution was cooled, diluted with NMP and precipitated into methanol. The polymer was filtered, washed with methanol, water, and methanol, and dried in a vacuum at 50 °C for 24 h. The precipitation was done three times, yielding 0.48 g (87%). ^{1}H NMR (DMSO-d_6) δ (ppm): 7.04 (d, $J = 9$ Hz, 4H), 7.69 (t, $J = 8$ Hz, 1H), 7.81 (d, $J = 9$ Hz, 4H), 8.14 (d, $J = 8$ Hz, 2H), 8.53 (s, 1H), and 10.13 (NH, s, 2H).

SB2. The same procedure was employed as for **SB1** except that 0.2910 g (0.7502 mmol) of bis(5-methyl-1,3-phenylene)-20-crown-6 (**8**) was also included. After precipitation and Soxhlet extraction with ethanol for 3 days, the yield was 0.5283 g (96%).

SB3. The same procedure was used as for **SB2** except on $^1/_2$ scale and without LiCl, yielding 0.2527 g (92%).

SB4. The same procedure was used as for **SB1** except without LiCl, 0.5247 g (95%).

SB5. The same procedure was used as for **SB1** except that 0.4024 g (0.75 mmol) of crown ether **20** was included; the product after precipitation was Soxhlet extracted for 3 days with ethanol, yielding 04630 g (84%).

HW. The same procedure was used with isophthalic acid (0.1246 g, 0.7500 mmol), **2** (0.1503 g, 0.7505 mmol), LiCl (81.25 mg), pyridine (0.4 mL), triphenyl phosphite (0.4 mL), and NMP (1.5 mL); the precipitation was done three times, yielding 0.25 g (100%).

DSN. A solution containing isophthalic acid (0.3323 g, 2.000 mmol), **2** (0.4004 g, 2.000 mmol), LiCl (0.210 g), pyridine (1.0 mL), triphenyl phosphite (1.1 mL), and NMP (4.0 mL) was heated at 100 °C under N_2 for 3 h. After 30 min, the solution became cloudy and very viscous. The resulting solution was cooled, diluted with NMP, and precipitated into methanol. The polymer was filtered, washed with methanol, and dried in a vacuum, yielding 0.685 g (86%).

Polycondensation of Isophthalic Acid with *m*-BAPPO (4) To Form Model Aramide 7 (DSN). A solution containing isophthalic acid (0.3323 g, 2.000 mmol), **4** (0.9850 g, 2.000 mmol), LiCl (0.225 g), pyridine (1.0 mL), triphenyl phosphite (1.1 mL), and NMP (4.0 mL) was heated at 100 °C under N_2 for 3 h. After 30 min, the solution gelled and stirring stopped. The resulting mixture was cooled, diluted with NMP, and precipitated into methanol. The fibrous polymer was filtered and dried in a vacuum, 1.25 g (80%).

1,3-Bis(6-chloro-3-oxapentyloxy)-5-methylbenzene. To a suspension of 7.0 g (49 mmol) of orcinol and 27.64 g (200 mmol) of K_2CO_3 in 200 mL of DMF was added 107.3 g (750 mmol) of bis(2-chloroethyl) ether, and the mixture was heated at 80 °C for 5 days. The mixture was filtered, and the solvent was removed by rotoevaporation, leaving a dark brown viscous oil, which was purified by flash column chromatography using chloroform, affording 15.3 g (93%) of a colorless oil. ^{1}H NMR ($CDCl_3$), δ (ppm): 2.15 (s, 3H), 3.6 (m, 3H), 3.65–3.8 (m, 8H), 4.05 (m, 4H), 6.25–6.35 (m, 3H). ^{13}C NMR ($CDCl_3$), δ (ppm): 21.74, 42.77, 67.36, 68.82, 69.68, 98.81, 108.05, 140.14, 159.66 (nine peaks as required).

Bis(5-methyl-1,3-phenylene)-20-crown-6 (8). A solution of 10.0 g (30.0 mmol) of 1,3-bis(6-chloro-3-oxapentyloxy)-5-methylbenzene and 4.20 g (30.0 mmol) of orcinol in 50 mL of DMF was added by syringe pump at 0.50 mL/h to a suspension of 41.46 g (300 mmol) of K_2CO_3 and 20 mg of $(n\text{-Bu})_4NI$ in 1.5 L of DMF at 110 °C. After addition, the mixture was stirred vigorously at 110 °C for 5 days, cooled, and filtered through silica gel. After solvent removal via rotoevaporation, the product was recrystallized from methanol, affording 2.0 g (20%) of colorless crystals, mp 163.0–163.3 °C. ^{1}H NMR ($CDCl_3$), δ (ppm): 2.15 (s, 3H), 3.85 (t, J = 4.8 Hz, 8H), 4.10 (t, J = 4.8 Hz, 8H), 6.30 (d, J = 2.2 Hz, 4H), 6.45 (t, J = 2.2 Hz, 2H). ^{13}C NMR ($CDCl_3$). δ (ppm): 21.72, 67.75, 70.11, 99.87, 108.31, 139.96, 159.76 (7 peaks as required). Anal. Calcd. for $C_{22}H_{28}O_6$: C, 68.02; H, 7.27; O, 24.71. Found: C, 67.85; H, 7.23.

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Supporting Information Available: Figures showing the GPC trace of polymer **3d** and and MS spectra of **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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