



Main chain polyamide rotaxanes from aliphatic crown ethers



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ABSTRACT

Main chain polyaramides were prepared by the Higashi protocol from oxydianiline (ODA) and isophthalic acid (ISOPA) in the presence of 30-crown-10 and "60-crown-20". Relatively small amounts of the smaller macrocycle were incorporated (<2 mass %), but the larger one resulted in ~17 mass % incorporation. These polymers display a previously observed irreversible high temperature exothermic transition that is attributed to a solid-state reorganization to intermolecularly hydrogen bonded amide pairs. An analogous set of polymers was prepared from bis(*p*-aminophenyl)fluorene (FLUODA) and ISOPA, with similar results, except that the exothermic transition was not observed. A main chain polypseudorotaxane was also prepared from Nylon-6,6 by condensation of adipoyl chloride and hexamethylene diamine in the presence of 30-crown-10; again only a small amount (~5 mass %) of the macrocycle was threaded onto the backbone.

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1. Introduction

Pseudorotaxanes in recent years have attained a special status in supramolecular chemistry because they are intermediates in the formation of rotaxanes and catenanes [1] (Scheme 1) and their polymeric analogs.[2] In prior efforts we have prepared both main chain and side chain polypseudorotaxanes and rotaxanes from a variety of macromolecules; of particular interest in the present context, we have examined polyester rotaxanes [3] and polyurethanes [4] synthesized in the presence of aliphatic crown ethers and also from bis(*m*-phenylene)-based crown ether diols [3g,3h,3i,4e] and polyamides using bis(*m*-phenylene)-based crown ether diacids.[5] We have also prepared and studied polystyrene-[6] and poly(meth)acrylate-based polyrotaxanes [7] prepared by polymerizations in crown ether solvents.

Aliphatic and aromatic polyamides are important classes of polymers because of their useful properties, e. g., high thermal stability, hydrolytic stability, solvent resistance and good mechanical properties.[8] Polyamides can be obtained by interfacial, solution or melt polycondensation and by ring opening polymerization. In the synthesis of polyaramides, the preferred method is usually

low temperature polycondensation using diacid chlorides and diamines. Alternatively, Higashi et al.[9] have reported the syntheses of a great variety of aramides by direct polycondensation of aromatic diacids and diamines in solution using phosphites in the presence of metals salts. Depending on the monomers and other reaction parameters, high molecular weight aromatic polyamides can be obtained. Semi-aromatic polyamides can also be synthesized in this way. [9j]

However, these polymers are usually difficult to process because of their low solubilities, high melting temperatures and viscosities. Thus, the synthesis of polyamide pseudorotaxanes or rotaxanes seemed to be an attractive way to improve the solubility and processability by incorporating polar, highly soluble crown ethers on the main chain (threading), while retaining other useful properties. Hydrogen bonding of crown ethers with diamines and dicarboxylic acids was perceived as a driving force to form the requisite pseudorotaxane intermediates (Scheme 1).

2. Results and discussion

2.1. Isophthalic acid-oxydianiline-based polymers

2.1.1. Model system and 30-crown-10-based polyrotaxanes

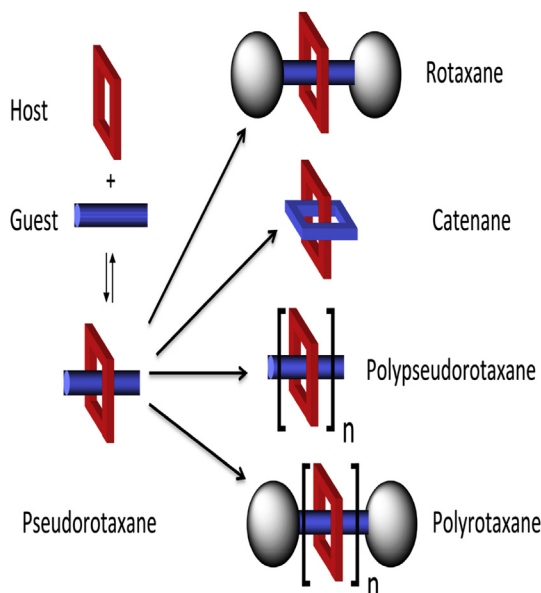
To explore these possibilities we initially chose to use the common monomers isophthalic acid (ISOPA) and 4,4'-oxydianiline (ODA). We first prepared the polyamide from ODA and ISOPA using the Higashi protocol (Scheme 2). Then, the same reaction was done

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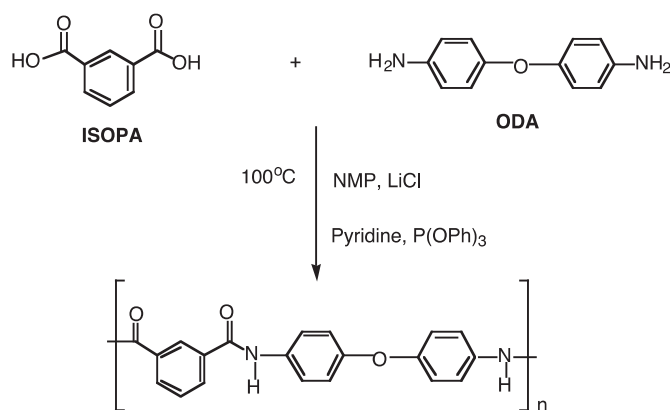
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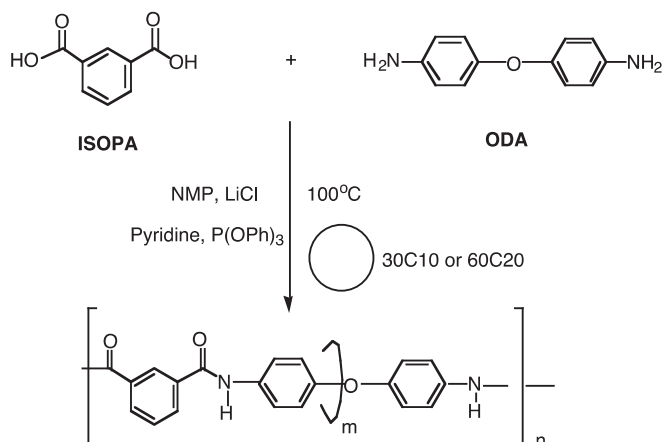


Scheme 1. Pseudorotaxanes as intermediates to rotaxanes, catenanes, polypseudorotaxanes and polyrotaxanes.



Scheme 2. Synthesis of polyamide from ISOPA and ODA.

in the presence of 30-crown-10 (30C10) (Scheme 3). As can be seen, these polymers had about the same molecular weights (Table 1,



Scheme 3. Synthesis of polyamide-rotaxa-crown ethers from ISOPA and ODA.

HL31, HL33). Precise stoichiometry between the two monomers is an important factor in polycondensation reactions. However, because the supply of crown ether was limited, all reactions were done in small scale and thus imprecise stoichiometry likely explains the relatively low molecular weights. In addition, the molecular weights of the polyrotaxanes are lower than their model counterparts. This could be explained by the excess of crown ether employed, which resulted in lower monomer concentrations. Moreover, Higashi et al. [9b] showed that poly(ethylene oxide) (PEO) can greatly influence the molecular weight of the final polyamide. When 0.5 wt of PEO (M_n 20–500 kDa) was added to the reaction mixture, higher molecular weights were obtained. However, when the amount of PEO was increased or the M_n was decreased (e. g., to 400 Da), lower molecular weights were found than in the absence of PEO [9b]. Since crown ethers derive from the same repeat unit, it is reasonable to think that they may have the same influence as the low molecular weight PEO.

An important factor with the synthesis of polyrotaxanes is the purification step. The polymers were dissolved in NMP and precipitated into methanol several times in order to remove any free (unthreaded) macrocycle. The polyamide rotaxanes were studied by GPC in order to detect the presence of free macrocycle (Fig. 1). As can be seen, 30C10 elutes with the solvent, and from these results we conclude that there is no free 30C10 in the polyrotaxane after the second precipitations. For later discussion it should be noted that the larger macrocycle (“60C20”) behaved similarly in GPC elution. These results are consistent with earlier findings; aliphatic crown ethers elute near the solvent, well removed from their polyrotaxanes [3a,3d,3f,4a,4b,6a,6b,7c].

To corroborate this conclusion the polymers were studied by ^1H NMR spectroscopy. The ^1H NMR spectrum of the model polymer from reaction between ODA and ISOPA (**HL33**) contains the two expected doublets for H_e and H_f at 7.79 and 7.03 ppm, respectively. The three protons H_a , H_b and H_c from the isophthalic moiety give three resonances at 8.51, 8.13 and 7.67 ppm, respectively, and a peak at 10.44 ppm corresponds to the CO–NH protons. The polyrotaxane counterpart **HL31** gave the same spectrum with nearly the same chemical shifts with the addition of resonances from the 30C10 (Fig. 2). After the first precipitation, a strong signal from the free macrocycle can be seen at 3.49 ppm; however, a shoulder located slightly upfield at 3.48 ppm is assigned to the threaded macrocycle, as we previously observed with this rather small crown ether when it is threaded onto polymers containing aromatic backbone units. [3c,3e,3f,4d] The shift for the threaded macrocycle is due to the shielding effect of the intimately enshrouded aromatic rings. After two or three precipitations, all free macrocycle was removed, as shown for **HL-51** in Fig. 3.

The polymer compositions were determined after the second or third precipitation, affording the m/n values, the molar ratios of macrocycle to repeat units of the polymer backbone (Table 1), using the integrals of the threaded crown ether signal and H_a of the ISOPA unit at ca. 8.55 ppm.

2.1.2. “60-crown-20”-based polyrotaxanes

The use of one “equivalent” of “60C20” [10,11] led to much higher threading yields in the ISOPA–ODA polymerization (**HL139**, Fig. 4). This is simply a result of the larger ring sizes of “60C20” vs. 30C10. The ring sizes are designated in terms of the total number of atoms in the ring, i. e., circumference, which is $2\pi r$ (r = radius), whereas the area of the fully opened ring in a cyclic conformation is πr^2 . In the crystal of 30C10 tetrahydrate the cavity area is $7.5 \text{ \AA} \times 11.4 \text{ \AA} = 85.5 \text{ \AA}^2$ [12]. Thus, the ratio of fully open cavity sizes of the 30- vs. the 60-membered crown ethers would be 1:4; that is, the cavity size of 60C20 would be $4(85.5 \text{ \AA}^2) = 342 \text{ \AA}^2$. However, “60C20” is in fact a mixture of much larger macrocycles

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