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Rotaxane Building Blocks bearing Blocked Isocyanate Stoppers: Polyrotaxanes through Post-Assembly Chain Extension**

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Given the high cost of introducing new chemical building blocks, an important challenge for the development of new functional polymers is to try to assemble existing cheap monomeric building blocks in new ways, by using novel types of molecular-level architectures to improve characteristics and provide "added value". For instance, it is thought that by incorporating rotaxanes into macromolecules,[1] some of the properties seen for rotaxanes in solution (that is, the ability to switch, shuttle, or alter shape[2]) could be transferred across to the solid state where easier handling and processibility might provide the basis for new types of "smart" materials and/or molecular-based devices.[3] However, relatively few strategies for polyrotaxane synthesis are suitable for making mechanically interlocked derivatives of commercial polymers on a practical scale.[1] Herein we report the convenient synthesis and polymerization (to give main-chain, side-chain, and cross-linked network polyrotaxane architectures) of cheap and readily obtainable rotaxane monomers (**3**–**5**) stoppered by bulky, blocked (i.e., masked) isocyanate groups. Blocked isocyanates are widely used in commercial heat-curable systems (e.g., powder coatings and heat-setting adhesives)

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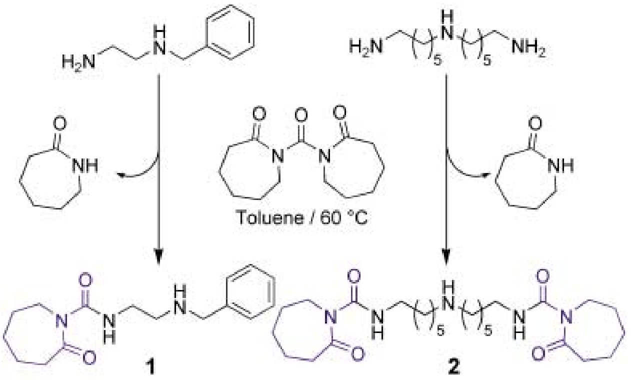
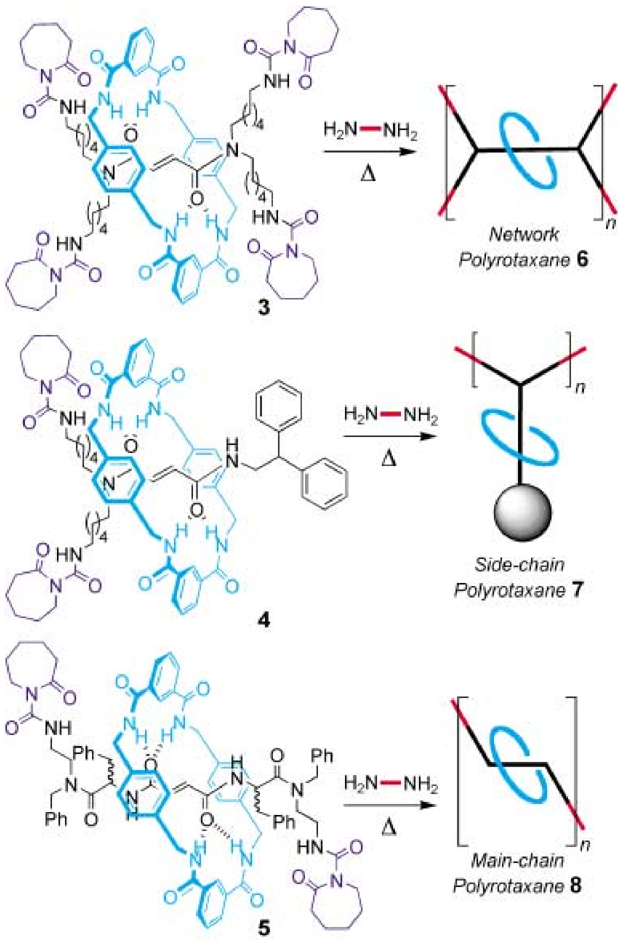
because of their relative stability at ambient temperatures compared to conventional isocyanates.[4] At elevated temperatures (> 150 °C), however, they react rapidly with amino or hydroxy difunctional comonomers to produce polyureas and polyurethanes. Blocked isocyanate rotaxane derivatives can thus act as cheap and readily accessible building blocks for polyrotaxane topological analogues of a wide range of commercial polymer systems.[5] We illustrate this versatility by synthesizing three different polyrotaxane topologies (**6**–**8**) using monomeric rotaxane building blocks **3**–**5** and a single, standard α,ω-amino-terminated polyether. In addition to providing a simple and practical route to a variety of mechanically interlocked architectures, the macrocycle is not able to dissociate from the growing polymer chain during the synthesis, and therefore the degree of macrocycle threading in the final product can be controlled with great precision.[6]

A procedure was recently discovered[7] in which blocked isocyanates can be formed in near-quantitative yields from amines and carbonyl biscaprolactam (CBC). During this reaction, one of the two caprolactam rings in CBC is selectively replaced by an amine forming a blocked isocyanate. The reaction exhibits exquisite selectivity for primary over secondary amines; in molecules containing both functional-group types the primary amine reacts exclusively at temperatures less than 100 °C, leaving the secondary amine available for further elaboration. The synthesis of stoppers containing one (**1**) or two (**2**) caprolactam-blocked isocyanate groups was thus achieved by reacting CBC with either *N*-benzylethylenediamine or bis(hexamethylene)triamine, respectively (Scheme 1). The free secondary amine moiety was then used to attach the polymerizable stopper to a suitable template for rotaxane formation. We chose the fumaramide group, which directs the five component assembly of benzylic amide macrocycle-containing rotaxanes from isophthaloyl dichloride and *p*-xylylenediamine in high efficiency.[8] This modular approach allowed us to attach different combinations of stoppers **1** and **2** onto the monomeric thread to produce rotaxane monomers (**3**–**5**) which, upon reaction with the suitable bisamine comonomer Jeffamine, produced polyrotaxanes of different topologies (Scheme 2).[9] The blocked isocyanate rotaxane building blocks proved stable for several months (at least) at room temperature.



Scheme 1. The synthesis of bulky stopper groups **1** and **2** containing caprolactam-blocked isocyanates from the selective reaction of a di- or triamine with carbonyl biscaprolactam.



Scheme 2. The polymerization of monomer rotaxanes containing caprolactam-blocked isocyanate stopper groups (**3**–**5**) leading to cross-linked (**6**), linear side-chain (**7**), and linear main-chain (**8**) polyrotaxane topologies.

The rotaxane comonomers were synthesized through treatment of the blocked isocyanate threads with *p*-xylylenediamine and isophthaloyl dichloride (CHCl$_3$, Et$_3$N, 2 h, high dilution) to give rotaxanes **3**–**5** in 70, 70, and 45 % yield, respectively. In each case, crystals suitable for investigation by X-ray crystallography were obtained through slow diffusion of diethyl ether into a solution of the rotaxane in chloroform. The crystal structures (Figure 1) confirm the interlocked architectures and the unhindered environment of the blocked isocyanates for further chain extension.[10]

Rotaxane building block **5**, comprised of two mono-blocked isocyanate stopper groups **1** (one each side of the fumaramide template), incorporated an additional phenylalanine residue to prevent dethreading of the macrocycle during polymerization.[11] In all cases, the rotaxane building blocks were obtained as colorless powders with melting points in the range 155–170 °C, facilitating handling and storage, consistent with other blocked isocyanate systems used in commercial heat-curable systems.

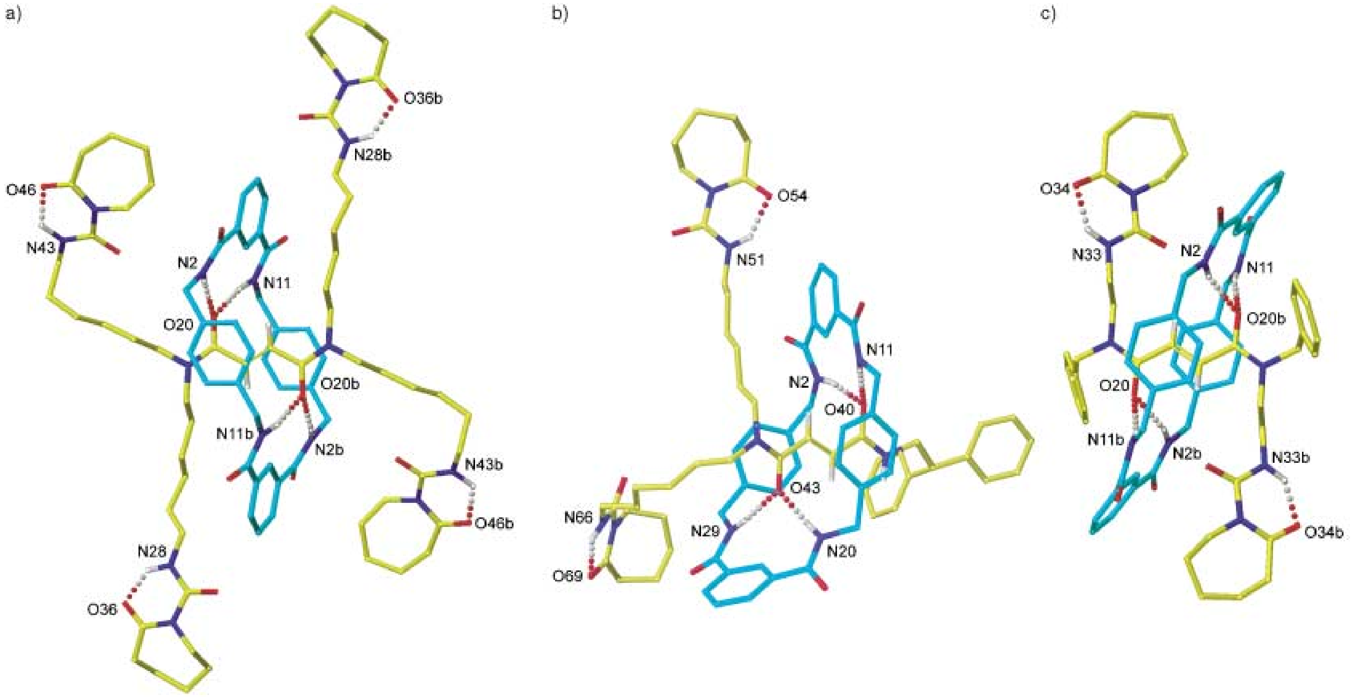


Figure 1. The solid-state structures of a) **3**, b) **4**, and c) a derivative of **5**, as determined by X-ray crystallography. Carbon (macrocyclic rings), light blue; carbon (threads), yellow; oxygen, red; nitrogen, dark blue. Non-amide or alkene hydrogen atoms have been removed for clarity. Hydrogen-bond distances [Å]: a) O20-HN2/O20b-HN2b 2.35, O20-HN11/O20b-HN11b 2.13, O36-HN28/O36b-HN28b 1.77, O46-HN43/O46b-HN43b 1.67; b) O40-HN2 2.12, O40-HN11 2.30, O43-HN20 2.14, O43-HN29 2.25, O54-HN51 1.83, O69-HN66 2.00; c) O20-HN2b/O20b-HN2 2.18, O20-HN11b/O20b-HN11 2.48, O34-HN33/O34b-HN33b 1.86. Hydrogen bond angles [°]: a) O20-HN2/O20b-HN2b 162.0, O20-HN11/O20b-HN11b 171.1, O36-HN28/O36b-HN28b 151.1, O46-HN43/O46b-HN43b 136.5; b) O40-HN2 165.4, O40-HN11 177.1, O43-HN20 169.5, O43-HN29 173.9, O54-HN51 141.7, O69-HN66 138.4; c) O20-HN2b/O20b-HN2 171.5, O20-HN11b/O20b-HN11 164.8, O34-HN33/O34b-HN33b 137.7.[10]

The bulk polymerizations of rotaxanes **3**–**5** were performed by heating a stoichiometric mixture of rotaxane and comonomer at 175 °C for 1 hr under a nitrogen atmosphere. The comonomer (Jeffamine D400) is an amino-terminated polyether with an average molecular weight of 400 $\mathrm{g\,mol^{-1}}$ that is used in a variety of commercial polyurethanes and polyureas. The flexible polyether chains generally afford materials with low glass-transition temperatures (T_g) and should thus allow for mobility of the rotaxane units at ambient temperatures and conditions. In addition, linear polyethers are generally soluble in solvents suitable for ^{1}H NMR spectroscopy and size exclusion chromatography (SEC), which make the resulting polyrotaxanes easy to characterize.

Reaction of the tetrablocked isocyanate rotaxane **3** with two equivalents of difunctional comonomer at 175 °C produced a cross-linked material which proved insoluble in common organic solvents. ^{1}H NMR spectra of a swollen sample of polyrotaxane **6** in $CDCl_3$, however, confirmed that the rotaxane building blocks remained intact during the polymerization process (Figure 2). Repeated extraction of the polymer with solvents that dissolve both monomers did not result in the leaching out of any unreacted material, which verified that the rotaxane units form an integral part of the network polymer. Dynamic mechanical testing (DMTA) measurements on a thin film of polyrotaxane gave a plateau modulus of 10^6 Pa, which confirmed that the material is a stable cross-linked rubberlike polymer. Stress–strain experiments on the polyrotaxane film gave an elongation-at-break value of $>100\,\%$, further confirming the rubbery nature of the material.

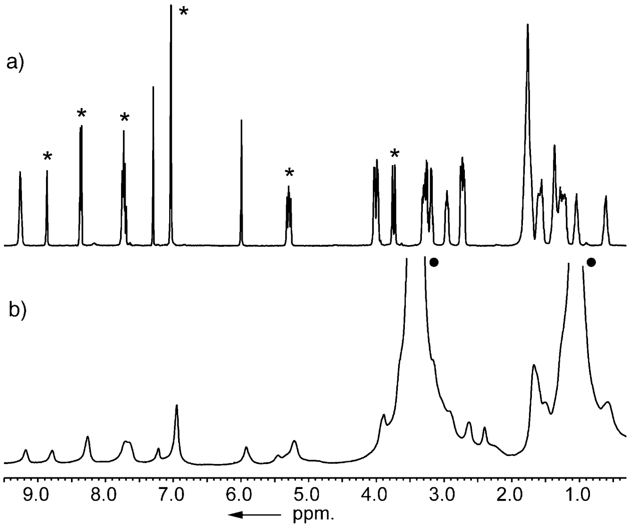


Figure 2. ^{1}H NMR spectra (300 MHz, $CDCl_3$, 298 K) of a) rotaxane monomer **3** and b) a swollen sample of the corresponding cross-linked network polyrotaxane **6** (* denotes macrocyclic protons; ● denotes Jeffamine protons in the polymer).

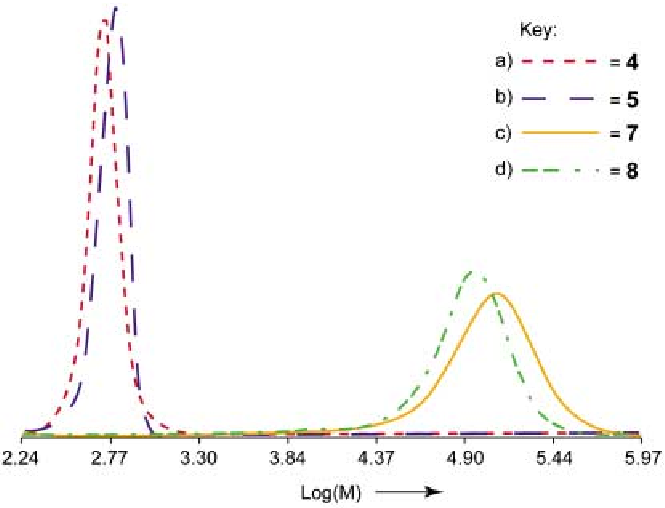


Figure 3. Size exclusion chromatogram of a) pure rotaxane monomer **4**, b) pure rotaxane monomer **5**, c) polyrotaxane **7** from the reaction between **4** and Jeffamine D400, and d) polyrotaxane **8** from the reaction between **5** and Jeffamine D400.

After treatment with one equivalent of Jeffamine D400 comonomer for one hour at 175 °C, rotaxanes **4** and **5** produced polymers with molecular weights (M_w) of 165 kg mol^{-1} ($M_w/M_n = 1.9$) and 86 kg mol^{-1} ($M_w/M_n = 1.6$), respectively (Figure 3), which corresponds to the linear side-chain polyrotaxane **7** (possessing, on average, 96 rotaxane units per polymer chain) and the linear main-chain polyrotaxane **8** (with an average of 46 rotaxane units per polymer chain), respectively.[12] ^{1}H NMR spectroscopy again confirmed the 1:1 ratio of macrocycle:Jeffamine repeat units. Initial studies have shown that there are clear differences in the properties (solubility, mechanical, photochemical, and so forth) of the various polyrotaxane architectures and the corresponding polythreads. Further studies are ongoing and will be reported elsewhere.

In conclusion, a simple, versatile route to polyrotaxanes with a variety of topologies is available through the synthesis and subsequent polymerization of readily accessible, stable, rotaxane monomers containing bulky, blocked isocyanate stopper groups. These monomeric [2]rotaxanes represent a new kind of functional-chain extender that is wholly compatible with methodologies currently used to make a range of commercial polymers and could thus lead to the facile incorporation of a number of rotaxane systems into materials where the effects of the mechanical bond could be tested and realistically exploited. In principle, this system can also be applied to the modular generation of rotaxane-based polymeric materials or "devices" in which individual components can be introduced in different combinations through "bottom-up" processing.

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[9] Full details of the experimental procedures can be found in the Supporting Information.

[10] Detailed crystallographic data for these compounds is reported in the Supporting Information.

[11] A rotaxane similar to **5** but without the extra phenylalanine residues (Figure 1 c) was synthesized through condensation of two equivalents of stopper **1** with fumaroyl chloride. Subsequent polymerization of this rotaxane monomer resulted in the dethreading of the macrocycle from the polymer as a result of the loss of the bulky caprolactam blocking group during chain extension.

[12] The calculated degree of polymerization was based on the SEC-determined average molecular weights of Jeffamine D400 and rotaxane monomers.