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Synthesis of a mechanically linked oligo[2]rotaxane

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Abstract—A bifunctional [2]rotaxane, bearing two free functional groups each in the ring and axial parts, was synthesized, followed by its polycondensation with methylene diphenyl diisocyanate leading to a mechanically linked oligo[2]rotaxane. © 2003 Elsevier Science Ltd. All rights reserved.

Synthesis of polymers, in which monomers are connected through mechanical bonds,¹ is attracting growing interest, not only for its basic physical properties, i.e. thermal, rheological² and stimuli response,³ but also for its possible applications as potential low-temperature elastomers. Although polymers containing catenane structures in the main chain have been synthesized,⁴ mechanically linked polyrotaxanes⁵ **b** (Scheme 1) have not been successfully attempted, except for the synthesis of functional rotaxanes and their dimerization^{6,7} or polypseudorotaxanes.⁸ The functional rotaxane synthesized by Tsivgoulis and collaborators has a potential to be converted to poly[2]rotaxane by deprotection–condensation cycles.⁶

Our strategy towards the polymer, in which monomers are linked by rotaxane interaction, is to synthesize a [2]rotaxane, bearing two free functional groups in the ring and the axial parts, respectively, followed by its polycondensation or polyaddition to obtain a poly[2]rotaxane (Scheme 1). In the case of using two similar functional groups, a poly[2]rotaxane could be formed with three mechanically linked head-to-head, tail-to-tail and head-to-tail monomers (Scheme 2).

In order to design the suitable structure for the bi-functional rotaxane, we have synthesized several mono- or bi-functional rotaxanes, with a lower synthetic yield compared to non-functional rotaxanes. This is explained by steric and/or electronic effects^{6,9} of the functional groups incorporated in the rotaxane ring, during the self-assembly¹⁰ reaction.

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For the polyrotaxane synthesis, reports in the literature^{6,11} have shown carboxylic acid or hydroxymethyl groups directly attached to the tetracationic



Scheme 1. Schematic view of the polymerization reaction from a [2]rotaxane a bearing two functional groups A and B leading to a mechanically linked poly[2]rotaxane b.



Scheme 2. Schematic view of head-to-head I, tail-to-tail II and head-to-tail III apparent monomers.

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component, are inactive towards esterification reactions. Furthermore, the functional groups reactivity in the rotaxane can be significantly decreased, owing to the steric and/or electronic effects of the rotaxane structure.

In our molecular design of a bifunctionalized [2]rotaxane, we chose not to introduce a protecting group in the rotaxane structure, as a result of the limited stability of the bis(4,4'-bipyridinium)cyclophane derivative under basic conditions. Under acidic conditions, other groups such as specific silyloxy groups can display instability. In addition, the rotaxane structures are known to be unstable to heat in solution.

The key step for synthesis of the axial component, $\mathbf{8}$, corresponds to the introduction of functionality to the thread by incorporating two hydroxymethyl groups in the main chain of the polyether derivative, followed by monosilylation of 7 to introduce the second stopping group (Scheme 3).

3,5-Bis(bromomethyl)(hydroxymethyl)benzene^{11,13} 11 (Scheme 4) was obtained by bis-bromination reaction of 1,3,5-tris(hydroxymethyl)benzene¹⁴ 10.

The donor-acceptor template-directed synthesis of the [2]rotaxane $13 \cdot 4PF_6$ was attempted by reacting 8, 11 and $12 \cdot 2PF_6$, in DMF, at ambient temperature and subjected to ultra high-pressure 10 kbar for 110 h (Scheme 5). The bifunctionalized [2]rotaxane $13 \cdot 4PF_6$ was obtained in relatively low yield 5.5%. The ¹H NMR



Scheme 3. Synthesis of the axial part 8. Reagents and conditions: (i)¹⁰ t-BuOK, t-BuOH, reflux (92 h), 100%; (ii) (i-Pr)₃SiCl, imidazole, DMF, 46%; (iii) Et₃N (1.5 equiv.), CH₂Cl₂, TsCl (1.5 equiv.), rt (overnight), 98%; (iv) NaH 60% in oil (1.17 equiv.)/DMF, bis(hydroxymethyl)-p-cresol (1.17 equiv.), room temperature 17 h then 8 h at 60°C, 83%; (v) imidazole (2.10 equiv.)/DMF, (i-Pr)₃SiCl (1.05 equiv.), 42%.



Scheme 4. Synthesis of 3,5-bis(bromomethyl)(hydroxymethyl)benzene 11. *Reagents and conditions*: (i) LAH/THF (100%); (ii) CBr₄/PPh₃/THF (35%).

spectrum recorded in acetonitril- d_3 (Fig. 1), is in accordance with the assigned structure. The protons of the 1,4-dioxybenzene ring show an upfield shift from 6.84 ppm for the axial component **8** to 3.4–4.0 ppm (overlapped by the resonances from the OCH₂ protons) for [2]rotaxane **13·4PF₆**, as observed for the related rotaxanes.^{12,15} The electrospray mass spectrometry shows a peak at 1822.8 assigned to (Mr–PF₆)⁺ ion.[†]

The copolymerization of rotaxane $13\cdot4PF_6$ with methylene diphenyl diisocyanate bridging unit was carried out in acetonitrile and at room temperature. The reaction was followed by ¹H NMR, Mass Spectrometry and Gel Permeation Chromatography (GPC) analysis at 500 nm, using DMF/10 mM LiBr, as eluent. In the reaction mixture, only compounds based on rotaxane structure absorb at 500 nm wavelength, due to the charge transfer interaction between the complementary π -electron rich and deficient aromatic units. ¹H NMR of the product is shown with the monomer of the rotaxane in Figure 1. The resonances around δ 4.4, associated with methylene protons of the two hydroxymethyl groups of the starting difunctional [2]rotaxane 13·4PF₆, are no longer present in the ¹H NMR spectrum of the product.



Scheme 5. From the monomeric [2]rotaxane $13.4PF_6$ to poly[2]rotaxane $14.n(4PF_6)$.

 $^{^{\}dagger}$ Mr = Molecular ion of the rotaxane monomer, Mi = Molecular ion of the methylenediphenyldiisocyanate.



Figure 1. ¹H NMR spectra of the rotaxane monomer $13 \cdot 4PF_6$ (top) and the reaction product of $13 \cdot 4PF_6$ and methylene diphenyl diisocyanate (bottom) recorded in CD₃CN at 25°C (270 MHz).

On the contrary, resonances around δ 5.1 are observed in the case of the product for the methylene groups showing that, indeed, condensation has occurred.¹¹ In addition new resonances for aromatic protons for the diphenylmethyl group in the linker are present around δ 7.3. The electrospray mass spectrometry of the crude product shows peaks at 1822, 1947 and 2072 assigned to $(Mr-PF_6)^+$, $(2Mr+Mi-2PF_6)^{2+}$, $(Mr+Mi-PF_6)^+$ ions,[†] respectively. The peaks corresponding to the higher molecular weight could not be observed due to the electrospray mass spectrometer limits. The monomer GPC analysis, using DMF/10 mM LiBr as eluent, displayed at high concentration abnormal peak shape, achieving higher apparent molecular weight, probably due to the aggregation. In the present case, the degree of aggregation decreased considerably, by reducing the monomer concentration during the injection process in the spectrometer. The GPC analysis of the polyrotaxane, using polystyrene standards, in DMF/10 mM LiBr gave 4514 apparent molecular weight, as opposed to 1967.83 for the rotaxane monomer $13.4PF_6$. The significantly low values can be considered as a result of increased compact structure of $14 \cdot n(4PF_6)$ due to the charge transfer interaction between monomer units compared to the polystyrene coil of similar molecular weight. The lower limit of the degree of the polymerization was estimated as 2 based on the apparent Mw in GPC and the electrospray mass spectrometry, but further investigations are needed to obtain the information on the real molecular size of the obtained polymer.

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