ChemComm

Catalytically self-threading polyrotaxanes

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Received (in Cambridge, UK) 14th April 1999, Accepted 24th June 1999

A mainchain polyrotaxane is formed in which polymerisation and rotaxane formation occur simultaneously, due to the presence of the catalytically-active self-threading macrocycle cucurbituril.

Exerting increasing architectural control in the synthesis of polymers is key to the development of new materials.[1] This has been exemplified in the case of dendrimers where for the first time truly single entity synthetic polymers have been prepared.[2] The convergent approach in particular highlights how a well-established synthetic concept from one area of chemistry (protection/deprotection chemistry) can have a tremendous impact on another one (polymer synthesis). In a similar vein we describe in this communication a unique route for the synthesis of structurally perfect mainchain polyrotaxanes (Fig. 1).

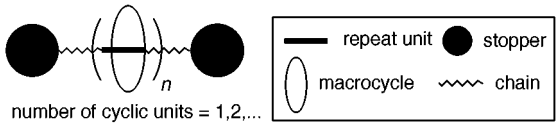

Fig. 1 A perfect polyrotaxane.

Polyrotaxanes represent a relatively recent addition to the repertoire of polymer architectures. Seminal work by Gibson,[3] Stoddart,[4] Harada[5] and Wenz,[6] and more recently Kim,[7] has produced a wealth of polyrotaxane structures and identified key synthetic parameters.[8] Earlier work was limited to the statistical synthesis of mainchain polyrotaxanes, but the current state-of-the-art uses directed (templated) strategies applied to the synthesis of mainchain, sidechain and hyperbranched polyrotaxanes and polypseudorotaxanes.[9,10] Perfect linear mainchain and networked polyrotaxanes have also been prepared, albeit in the solid-state only.[11]

Here we would like to add to the repertoire of polyrotaxane syntheses. In our approach polymerisation and rotaxane formation occur simultaneously to yield a perfectly threaded polyrotaxane due to the presence of cucurbituril, a macrocycle that catalyses 1,3-dipolar cycloadditions. Cucurbituril has also been used recently by Meschke *et al.* as the statistically threaded macrocyclic component in an interfacial condensation polymerisation.[12]

There are principally three ways in which to ensure that each polymer repeat unit is threaded by an integer number of cyclic units: (i) to polymerise a preformed rotaxane monomer, (ii) to select a polymer backbone that can bind strongly and selectively to a suitably chosen macrocycle, or (iii) to ensure that during the polymerisation step each added monomer contains an integer number of cyclic units. We opted for the third alternative by employing cucurbituril as macrocyclic component (Fig. 2). It was established by Mock *et al.*[13] in the 1980s that cucurbituril is capable of catalysing 1,3-dipolar cycloadditions in an enzyme-like fashion (Fig. 2).

The bond forming process requires the complexation of an ammonium azido and an ammonium alkyne compound to each of the carbonyl-fringed portals of cucurbituril. Complexation is accompanied by the displacement of solvent molecules from the hydrophilic interior of the macrocycle. The resulting complex is slightly strained. The release of this strain is responsible for the catalytic effect of cucurbituril on the cycloaddition reaction leading to an acceleration by a factor of 10^5.[14]

We decided to utilise this intriguing reaction for the synthesis of polyrotaxanes since each cycloaddition reaction catalysed by cucurbituril not only leads to a chemical bond but also to the self-threading of the macrocyclic catalyst. From a polymer synthesis point of view this means that each additional repeat unit added to a polymer chain is inevitably accompanied by the threading of exactly one cyclic unit.

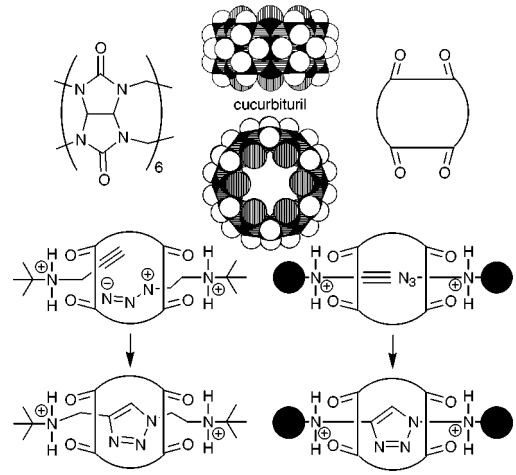

Fig. 2 1,3-Dipolar cycloaddition catalysed by cucurbituril.

Cucurbituril was synthesised according to a literature procedure.[15] The required diazide and dialkyne monomers have been synthesised efficiently as shown in Fig. 3. Monomer A was synthesised by treating **1** with propargylamine (propargyl = prop-2-ynyl), followed by formation of the dihydrochloride salt in 86% overall yield. The synthesis of monomer B also started from **1**, reacting first with 2-aminoethanol. Subsequent treatment with $SOCl_2$, followed by substitution with sodium azide and formation of the dihydrochloride salt gave monomer B in 4 steps and 39% overall yield.

The preparation of model compounds synthesised from monomer A and B with 2 equivalents of a corresponding *tert*-butylamine-derived mono-azido and mono-alkyne compound in the presence of cucurbituril yielded [3]rotaxanes in 88% and 67% yield respectively (for NMR see Fig. 5). The correspond-

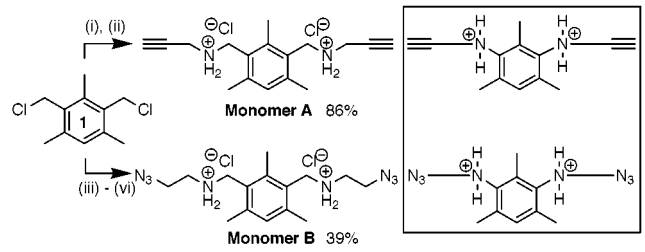

Fig. 3 Synthesis of monomers A and B. (i) $NH_2CH_2C{\equiv}CH$, neat, 0 °C → rt, 16 h, 100% (crude), (ii) 1 M HCl in Et_2O, rt, 86%, (iii) $NH_2CH_2CH_2OH$, neat, 5 h, 150–160 °C, 66%, (iv) $SOCl_2$, $CHCl_3$, 5 h, rt, 70%, (v) NaN_3, H_2O, 75 °C, 16 h, 87%, (vi) 1 M HCl in Et_2O, rt, 96%.

ing [2]rotaxane, first prepared by Mock *et al.*[14] was obtained in 76% yield. Polymerisation was carried out at room temperature by dissolving equimolar amounts of monomer A and monomer B in acidified water followed by the addition of 2 equivalents of cucurbituril (Fig. 4).

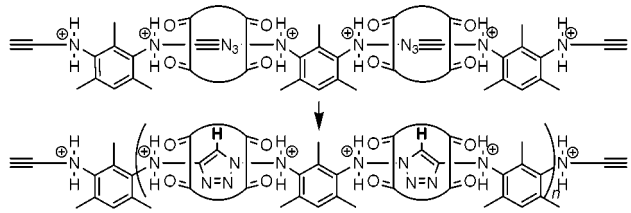

Fig. 4 Synthesis of a perfect mainchain polyrotaxane.

The reaction was followed by ^{1}H-NMR. Comparison of the relative intensities of the triazole proton to phenyl proton indicated the formation of possibly dimers (ratio 1 : 2) within the first 24 h of the reaction. After an additional 24 h the ratio had changed to a value close to 1 : 1. Longer reaction times had no bearing on the reaction outcome. Precipitation of the aqueous solution into acetone resulted in a white precipitate which was filtered, washed and dried *in vacuo* (yield: 68%). ^{1}H- and ^{13}C-NMR (^{13}C data of the corresponding carbon in brackets) are in agreement with the proposed structure. The crucial appearance of the triazole proton is documented in Fig. 5 and compared with a [3]rotaxane[16] and [2]rotaxane model compound (*vide infra*).

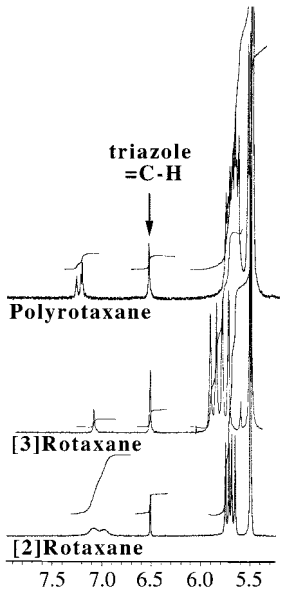

Fig. 5 ^{1}H-NMR overlay of the triazole region of the polyrotaxane and a [3][16] and [2]rotaxane model compound.

The triazole proton located inside the cavity of cucurbituril has a chemical shift of 6.54 ppm (122.7 ppm) which is further confirmed through the model [2]rotaxane and [3]rotaxane (Fig. 5). In an unprotonated triazole model compound the same proton appears at 7.52 ppm (120.8 ppm) and is shifted even further downfield in the same compound at 8.56 ppm (130.5 ppm) upon its diprotonation (formation of the dihydrochloride salt). Furthermore in the absence of cucurbituril polymerisation has not been observed. GPC data in DMF were obtained after anion exchange (Cl^- to PF_6^-) gave a M_n value of 5100 and a M_w value of 9000 based on polystyrene standards. MALDI-TOF showed very broad peak clusters and the reason for this is not known. Peak maxima are spaced by about *m/z* 1350 (molar masses of the repeat units are 1324.14 and 1386.17) with an average value close to 6000. ^{1}H-NMR allows an estimate of the molecular weight by comparing the integration of the triazole proton with the one located on the benzene ring. A ratio of 0.9 (triazole) to 1 translates into a molecular weight of about 13000. We have not been able to precisely establish the charge state of the polyrotaxane in our ES-MS measurements. Indications so far are of a molar mass of about 10000. Finally small angle light scattering measurements were attempted but have been unsuccessful because a reliable d*n*/d*c* value could not be obtained (maybe due to concentration dependent aggregation effects). Additional evidence for the formation of a polyrotaxane was also found in its solubility behaviour. Cucurbituril and the polyrotaxane are both soluble in acidic aqueous media, but *only* cucurbituril dissolves in a saturated solution of sodium chloride as shown by Kim.[17] Dissolution of cucurbituril in water through the presence of a sodium salt requires accessibility of the carbonyl portals to which sodium cations are complexed. This has become impossible (*vide infra*) once cucurbituril has been incorporated into a mainchain polyrotaxane architecture.

We have presented the first solution synthesis of a perfect mainchain polyrotaxane. Investigations are in progress to reveal mechanistic details of the polymerisation itself and to apply our approach to more complex polymer architectures.

We would like to thank the EPSRC for providing an IPSI project studentship for D. T. Thanks are also due to Dr Welham of the University of London ULIRS service for running MALDI-TOF spectra, Dr Ball for providing us with ES mass spectrometry data and the EPSRC RAPRA service for GPC characterisation data.

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Communication 9/02990G