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Mainchain pseudopolyrotaxanes *via* post-threading with cucurbituril

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Pseudopolyrotaxanes possessing a controllable number of cucurbituril molecules located along the backbone of poly(iminiohexamethylene chloride) have been prepared *via* an efficient post-threading route.

Although the synthesis of cucurbituril was described almost 100 years ago[1] the exploitation of the supramolecular chemistry of this rigid, nondecacyclic ligand only began recently. Mock and Pierpont reported a molecular switch[2] and both Kim *et al.*[3] and Buschmann *et al.*[4,5] synthesised various inclusion complexes based on cucurbituril. The latter two groups also prepared solid and solution state polyrotaxanes in which cucurbituril features as the macrocyclic component introduced as a pseudorotaxane monomer.[6,7] Steinke *et al.* used the ability of cucurbituril to catalyse 1,3-dipolar cycloadditions, a feature of cucurbituril discovered by Mock *et al.*[8,9] in the synthesis of catalytically self-threading polyrotaxanes.[10]

Formation of polyrotaxanes or pseudopolyrotaxanes *via* post-threading requires an attractive interaction between the macrocycle and the (preformed) polymer backbone. Investigations by Harada *et al.* provided the earliest example of post-threading exploiting the strong hydrophobic interactions between poly(ethylene glycol)s (PEG) and α-cyclodextrins (α-CD) in aqueous media.[11] Since then α-, β- and γ-cyclodextrins, crown ethers and cyclophanes have been post-threaded onto a number of different linear polymer backbones like poly(propylene glycol) (PPG),[12,13] poly(alkylimine)s,[14] PEO-PPO-PEO triblock copolymers,[15] poly(propylene),[16] poly(trimethylene oxide),[13] poly(isobutylene),[16] poly(ε-caprolactone),[16] poly(viologen)s,[16] aromatic poly(ether),[17] poly(ether ester)[17] and poly(urethane)s.[18,19] Recently calorimetric studies by Buschmann *et al.* suggested the formation of a pseudopolyrotaxane between PEG and cucurbituril.[20]

For our contribution to this area we decided to prepare cucurbituril-containing mainchain pseudopolyrotaxanes from poly(iminoalkylene)s. Poly(iminohexamethylene) was deemed to be the most promising linear polyamine because the protonated hexane-1,6-diamine moiety present in its backbone is known to form one of the most stable inclusion complexes with cucurbituril.[21] Poly(iminiohexamethylene chloride) was synthesised according to a procedure by Wenz *et al.*[14] in which Nylon 6,6 was reduced with $BH_3 \cdot Me_2S$ (Fig. 1). ^1H NMR of the polyamine confirmed that reduction was successful with less than 3% of residual amide groups remaining (M_n = 20000, M_w = 52000, against polystyrene). Cucurbituril was prepared according to the procedure by Behrend *et al.*[1] Samples for the subsequent time-dependent NMR studies were prepared by dissolving poly(iminohexamethylene) in 20% DCl to which the required amount of cucurbituril was added (Fig. 1).

Progress of the threading reaction was monitored at given time intervals by ^1H NMR (Fig. 2). Fig. 2 corresponds to a post-threading experiment carried out at 90 °C in DCl–D_2O (20% w/w) with a molar ratio of cucurbituril to the iminiohexamethylene repeat unit of 0.5 : 1.0. Upon threading the original three resonances of the α-, β- and γ-methylene groups of poly(iminiohexamethylene chloride) are split into an additional two sets of resonances (Fig. 2: **A**, **B**, **C** and **a**, **b**, **c**). The integrals of the new resonances are increasing with time to the same extent as the precursor polymer resonances are decreasing. The set of resonances coded **a**, **b** and **c** can be assigned to threaded hexamethylene segments based on complexation studies with the model compound 1,6-diaminohexane dihydrochloride salt carried out by us which is further supported by earlier work in formic acid carried out by Mock *et al.*[21] Resonances **A**, **B**, and **C** belong to unthreaded hexamethylene segments located next to threaded repeat units along the polymer backbone. This was confirmed by using a five-fold excess of cucurbituril. Under these conditions essentially all precursor resonances disappeared and only the two new sets of resonances remained (not shown). The degree of threading was calculated from the ratio of threaded to non-threaded methylene protons. In this particular example (after 384 h) 43% of all repeat units were threaded by cucurbituril. Threading is also reflected in a small downfield shift in the resonances of cucurbituril (Fig. 2: **QQ** = free macrocycle; **qq** = threaded) which is proportional to the degree of threading over time. Attempts to determine the molecular weight of these pseudopolyrotaxanes by GPC have been hampered by the fact that these polymers are only soluble in water and the necessary analytical equipment has not been available to us.

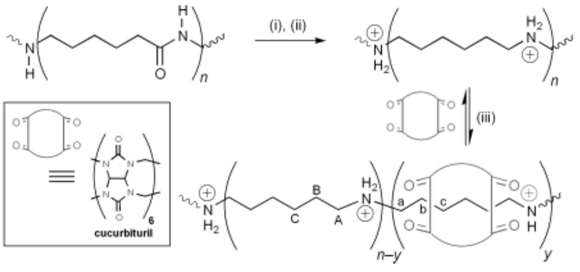

Fig. 1 Synthesis of cucurbituril-threaded mainchain poly(iminiohexamethylene chloride); (i) $BH_3 \cdot Me_2S$, THF, 20 h, rt, 66%; (ii) DCl–D_2O (20% w/w), rt, 100%; (iii) cucurbituril, 0 to 384 h, 90 °C.

Data of this very slow threading process are shown in Fig. 3 which suggest that equilibrium has been reached after *ca.* 400 h

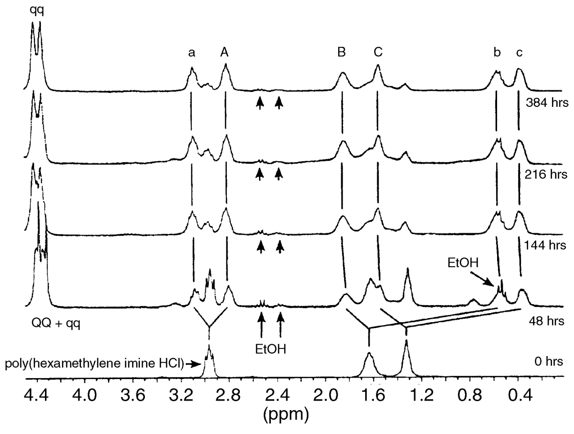

Fig. 2 Progression of post-threading followed by ^1H-NMR at 90 °C in DCl–D_2O (20% w/w) with a molar ratio of cucurbituril to iminiohexamethylene repeat unit of 0.5 : 1.0.[27] (Arrows indicate traces of the ethanol inclusion complex with cucurbituril (ethanol was used as co-solvent during recrystallisation). The signal intensity is decreasing with time being replaced by polymer chain repeat units.)

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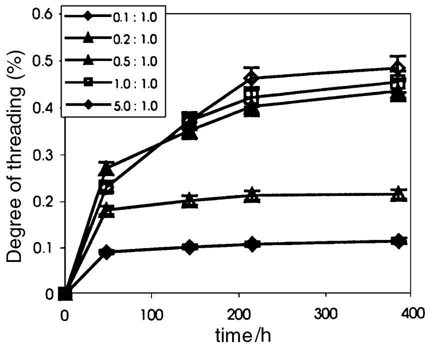

Fig. 3 Time-dependence of the threading of cucurbituril onto poly(iminiohexamethylene chloride) at 90 °C in DCl–D_2O (20% w/w). Molar ratios of cucurbituril to repeat unit: 0.1 : 1.0; 0.2 : 1.0; 0.5 : 1.0; 1.0 : 1.0; 5.0 : 1.0.

at 90 °C for all ratios of cucurbituril to polymer repeat unit. Excess of cucurbituril has very little impact on the maximum degree of threading being close to 50% (experimental error ±2%). From the limiting degree of threading (50%) and the clear splitting of the original ^1H NMR signals of the iminiohexamethylene repeat unit into two new sets of peaks of equal intensity, we conclude that a pseudopolyrotaxane has been formed where encapsulated and uncomplexed repeat units alternate. Further evidence comes from encapsulation studies between cucurbituril and bis(6-aminohexyl)amine (a model 'dimer' of the polymer backbone).[22] A two-fold excess of cucurbituril led to 45% threading, a value which is very close to that found for the polymeric case. The inactivity of cucurbituril in the catalytic self-threading of pseudopolyrotaxanes involving hexane-1,6-diamine repeat units[10] can also best be rationalised by assuming that it is energetically unfavourable for two molecules of cucurbituril to complex to the same secondary ammonium ion. We have considered the possibility of other substructures analogous to recent ^1H NMR investigations by Hodge *et al.*[17] However, an alternating sequence of complexed and uncomplexed repeat units is the most consistent interpretation of our experimental data.

The slow kinetics of the threading process can be explained through a combination of factors. By far the most important contribution arises from the strong binding constant of cucurbituril to the protonated hexamethylene-spaced repeat unit.[21] A high activation energy is needed for cucurbituril to 'hop' efficiently along the polymer chain during the threading process. This interpretation is supported by recent results from Harada's groups related to slow threading kinetics also affected by strong ionic interactions between macrocycle and polymer chain.[23] Wenz *et al.* have modelled a hopping mechanism for the post-threading of α-CD onto ionene-6,10† which enabled them to explain their observed threading kinetics.[14] Their pseudopolyrotaxane system also required elevated temperatures and long reaction times (120 h at 80 °C in water) to reach a degree of threading of 0.5. Furthermore we invoke that threading kinetics in our system are retarded further by cucurbituril moieties having to queue. The existence of queuing has been demonstrated by Parsons *et al.*[24,25] during the threading of pseudopolyrotaxanes. The effect of queuing becomes more significant for higher levels of threading as indicated by the corresponding slower threading kinetics (Fig. 3).

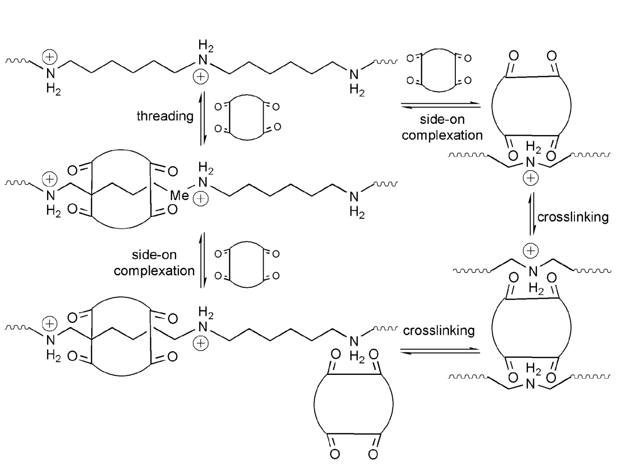

Fig. 4 Modes of complexation of cucurbituril with the corresponding equilibria expected to take part in the threading of cucurbituril onto protonated, linear poly(iminooligoalkylene)s.

The retarded threading kinetics at higher ratios of cucurbituril could also be explained by invoking 'side-on' complexation of cucurbituril to the ammonium groups along the polymer backbone (Fig. 4). Cucurbituril binds to all types of ammonium ions other than quaternary ones.[21,26] Fig. 4 is therefore a more accurate representation of the various competing modes of complexation that have to be considered for our system. However only through further experiments will it be possible to distinguish between queuing and 'side-on' complexation.

Post-threading of cucurbituril onto protonated linear poly(iminohexamethylene) results in a new, synthetically accessible class of pseudopolyrotaxanes, which contain a controllable number of macrocyclic units.

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Notes and references

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27 We have so far been unable to explain the presence of the resonance at 0.8 ppm in the spectrum recorded after 48 h.