Polyrotaxanes

Polymer Architectures

1

Rotaxane

3

Polyrotaxane

Methods of preparing mainchain (pseudo)polyrotaxanes
- Cyclisation in the presence of linear macromolecules
- Polymerisation of rotaxanes
- Chemical conversion of rotaxane precursor after polymerisation

Polyrotaxanes: Why?
- Solubilities are altered
- Particular chance of improving solubility and processibility of rigid rod polymers
- Glass transitions follow the Fox equation sometimes
- Glass transition sometimes remain distinct for each species
- Thermal stability can be enhanced
- Control of polymer backbone through cylics that crystallise
- New types of polymer chain compatibilisation
- “Insulated wire approach”

Consideration
- Blocking groups may be unnecessary due to entrapment of cyclic units in chain folds
- Using rotaxane precursors is unlikely to be of synthetic value

Rotaxanes

In 1910 evoked
In 1967 proposed and proven
Homorotaxanes and Heterorotaxanes

Homorotaxanes are composed of cyclic and linear species that are chemically equivalent, e.g., a polyrotaxane constructed from poly(ethyleneoxide) and a crown ether.

Heterorotaxanes on the other hand, involve cyclic and linear species having different chemical structures, e.g., a polyrotaxane derived from poly(ethylene) and α-cyclodextrin, affording alternatives to classical copolymer architectures.

Mainchain and Sidechain Polyrotaxanes

Mainchain Polyrotaxanes

Approaches to mainchain polyrotaxanes

- Polymerisation of preformed rotaxane
- Threading of linear molecule through preformed macrocycle
- Polymerisation of macrocycle in presence of linear species followed by end-capping
**Sidechain Polyrotaxanes**

**Approaches to sidechain polyrotaxanes - cyclic orthogonal to backbone**
- Threading of preformed graft copolymer plus end-capping
- Grafting in presence of cyclic unit and linear link
- Polymerisation of macromonomer in the presence of cyclic unit
- Polymerisation of preformed macromonomeric rotaxane

**Approaches to sidechain polyrotaxanes - cyclic parallel to backbone**
- Threading of preformed pendant cyclic graft copolymer
- Grafting of cyclic unit in presence of linear species followed by end-capping
- Grafting of preformed rotaxane to linear backbone
- Polymerisation of a preformed species followed by postpolymerisation end-capping
- Polymerisation of preformed rotaxane

**Dendritic and Hyperbranched Polyrotaxanes**

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**Synthesis of Polyrotaxanes**

**Statistical Approach**

Le Chatelier

Equilibrium constant (0.05 to 5 l/mol)

\[
K = e^{-\Delta G/RT} = [R]/[L][C]
\]

\[
\ln K = -\frac{\Delta G}{RT} = -\frac{\Delta H-T\Delta S}{RT} = -\frac{\Delta H}{RT}+\frac{\Delta S}{R}
\]

entropically driven = ($\Delta H$ small)

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**Threading**

**Slippage**

**Clipping**

**Entering**
Directed Synthesis
Preformed Monomer
Slippage

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Time / d</th>
<th>$M_n$ (M_H/M_L)</th>
<th>Higher</th>
<th>Lower</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD$_3$COCD$_3$</td>
<td>113</td>
<td>1500 (1.4)</td>
<td>3300 (1.2)</td>
<td>1200 (1.1)</td>
</tr>
<tr>
<td>CD$_3$CN</td>
<td>107</td>
<td>1700 (1.5)</td>
<td>3800 (1.2)</td>
<td>1200 (1.1)</td>
</tr>
</tbody>
</table>

Similarly polyethylene glycols form crystalline complexes with α-CD but not β-CD.21
Cyclodextrins and Hydrophobic Polymers

PIB was added to saturated aqueous solutions of both β- and γ-CDs under sonication, the solution became turbid and the complexes were formed as crystalline precipitates.

<table>
<thead>
<tr>
<th>Polymer/Oligomer</th>
<th>Structure</th>
<th>MW</th>
<th>α-CD</th>
<th>β-CD</th>
<th>γ-CD</th>
</tr>
</thead>
<tbody>
<tr>
<td>OE</td>
<td>-CH2CH2-</td>
<td>563</td>
<td>63</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Squalane</td>
<td>CH3CH2CH2CH3</td>
<td>423</td>
<td>0</td>
<td>62</td>
<td>24</td>
</tr>
<tr>
<td>PIB</td>
<td>CH3</td>
<td>~800</td>
<td>0</td>
<td>8</td>
<td>90</td>
</tr>
</tbody>
</table>

the relative sizes of the cavities of cyclodextrins and the cross-sectional areas of the polymers are essential in complex formation in the absence of non-hydrophobic effects.
PEG 1450 (approx. 33 repeat units) about 16 α-CDs times MW 1200 = MW 20000 not soluble in water anymore!

The threading of α-CD was followed by 1H-NMR spectroscopy, in which significant downfield shifts of CD protons are observed as the polyrotaxane forms. The larger β-CD derivative is threaded several orders of magnitude more rapidly than the smaller α-CD.

The structure and the molecular weight of the polyamines dramatically affect both threading and dethreading rate (11 more than two orders of magnitude faster than 12). Reaction of the amino groups with nicotinyl chloride gave stable polyrotaxanes with up to 0.67 α-CD units per amino group in the case of 11; this corresponds to 37 α-CDs per macromolecule or one α-CD per 9 backbone atoms.
Plasticisation
TI: ROTAXANES, CATENANES, POLYROTAXANES, POLYCATENANES AND RELATED MATERIALS
AU: GIBSON_HW, BHEDA_MC, ENGGEN_PT
JN: PROGRESS IN POLYMER SCIENCE, 1994, Vol.19, No.5, pp.843-945

TI: alpha Cyclodextrin/polyethylene glycolpolyrotaxane: A study of the threading process
AU: Ceccato_M, LoNostro_P, Baglioni_P

TI: Self-threading-base approach for branched and/or cross-linked poly(methacrylate rotaxane)s
AU: Gong_CG, Gibson_HW

TI: Design and construction of supramolecular architectures consisting of cyclodextrins and polymers
AU: Harada_A

TI: Photochemical synthesis of polyrotaxanes from stilbene polymers and cyclodextrins
AU: Herrmann_W, Schneider_M, Wenz_G

Interlocked macromolecules

Encapsulated conducting polymers