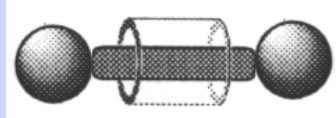


Synthese von Polyrotaxanen

10.06.2003

Thomas Albusat

Aufbau der Rotaxane



-Rotaxane bestehen aus einem Linearmolekül auf das Ringmoleküle aufgefädelt sind

-An den Enden der Kette befinden sich große Stoppermoleküle, die das „Herunterrutschen“ der Ringe verhindert

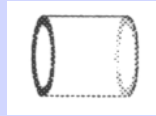
➔ Die Bausteine der Rotaxane werden nicht durch kovalente Bindungen, sondern durch eine „mechanische Bindung“ zusammengehalten

Keine Auftrennung in Ringe und Linearmolekül möglich

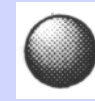
Nomenklatur



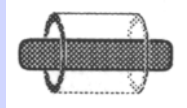
Faden



Ring



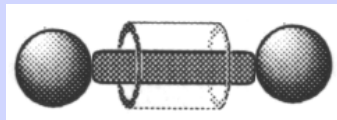
Stopper



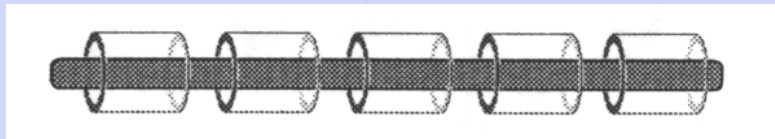
Pseudo-Rotaxan



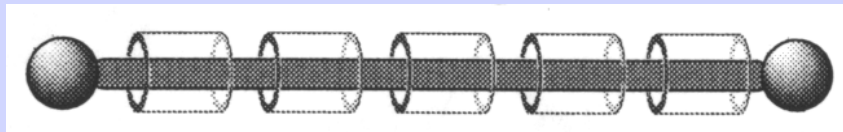
Hantel



Rotaxan



Pseudo-Polyrotaxan

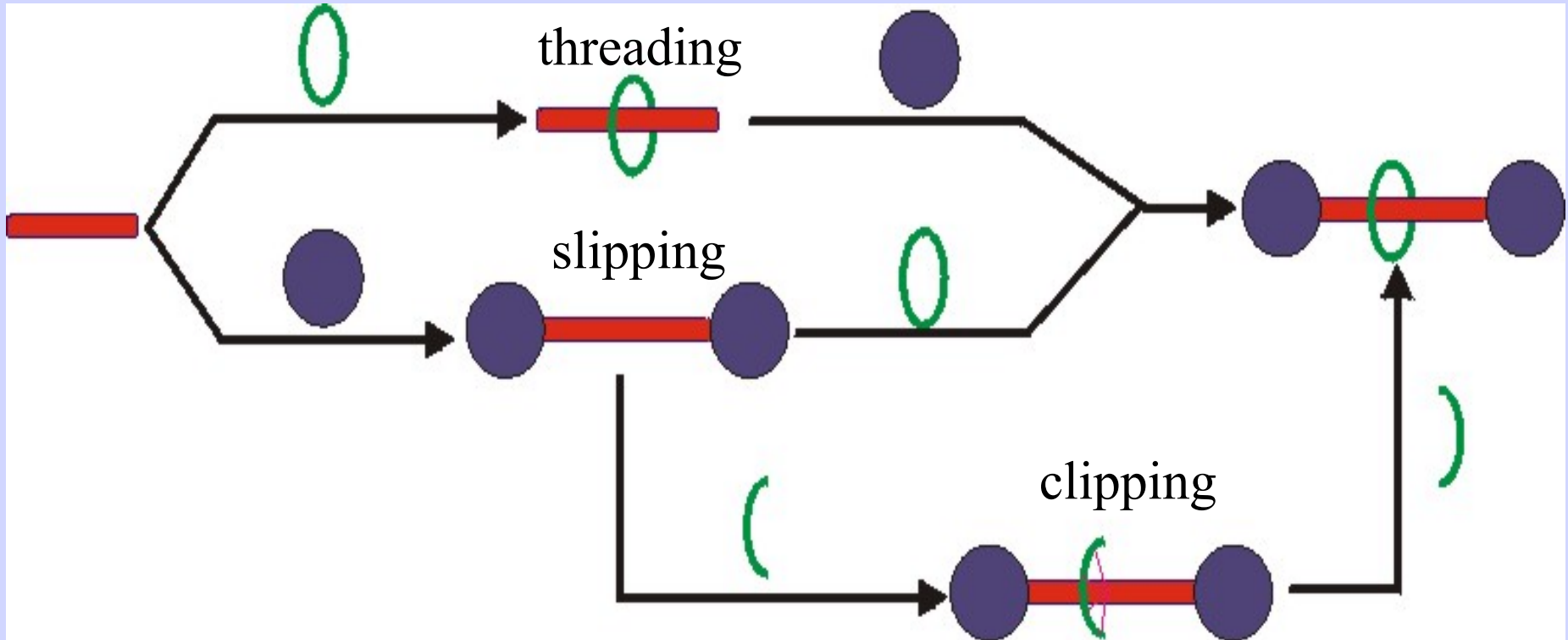


Polyrotaxan

[n]-Rotaxan: n ist die Anzahl der Hanteln + Anzahl der Ringe
= Anzahl der mechanisch verknüpften Moleküle

Allgemeine Synthesemöglichkeiten

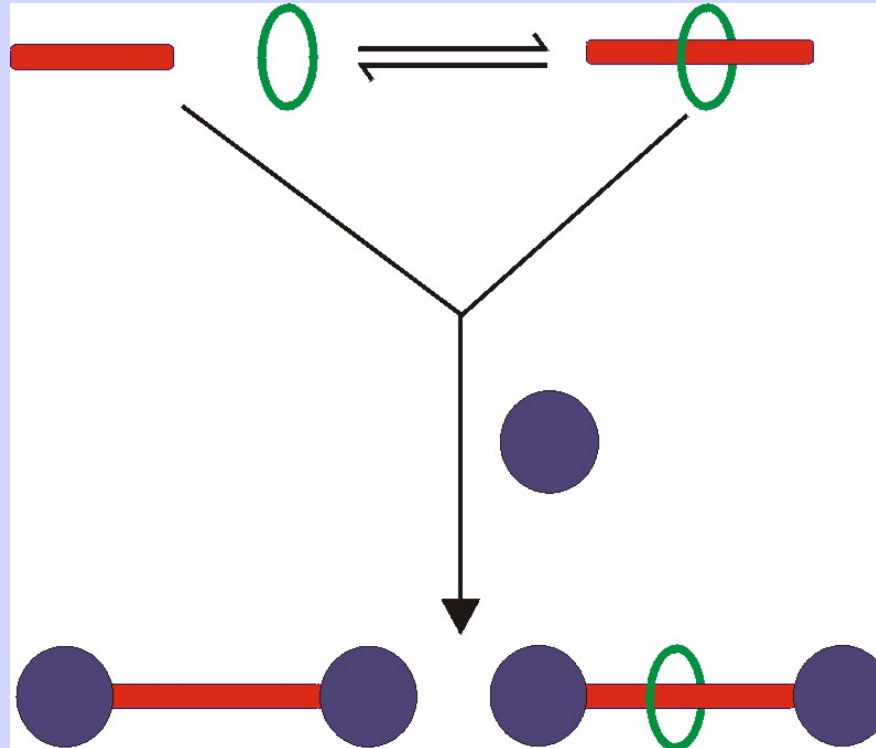
- es gibt 3 Möglichkeiten Rotaxane darzustellen



-welche Methode geeignet ist, hängt vom System ab

Probleme der Rotaxansynthese

Gleichgewicht



Steuerungsmöglichkeiten:

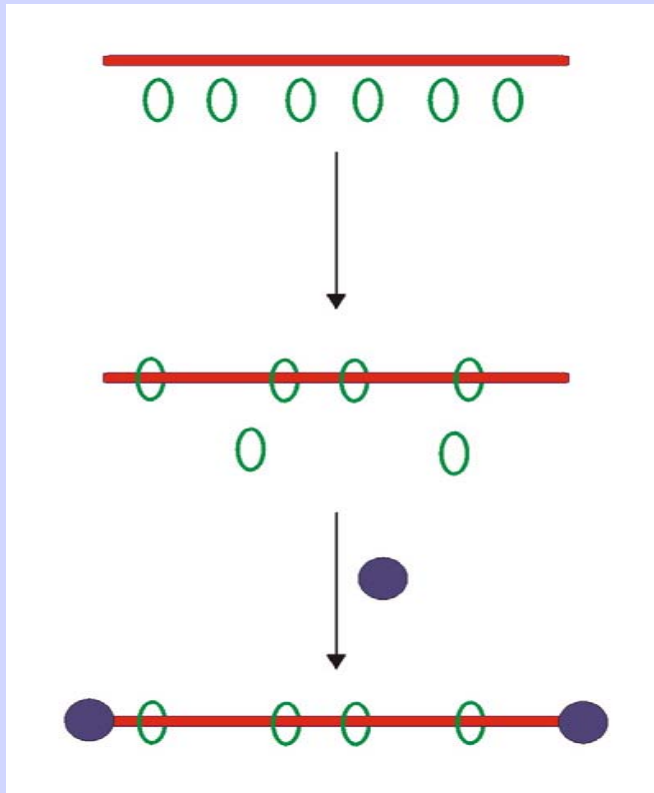
-Prinzip von Le Chatelier

-Schlüssel-Schloss Prinzip

Allgemeine Synthesemöglichkeiten der Polyrotaxane

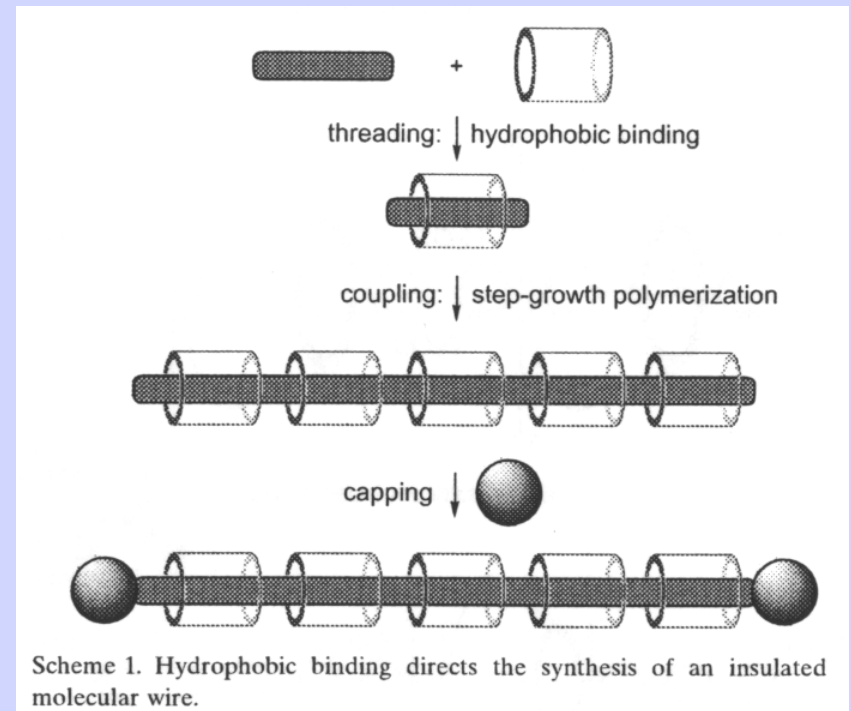
-Polyrotaxane werden klassisch durch threading dargestellt

threading



(Wenz, Harada)

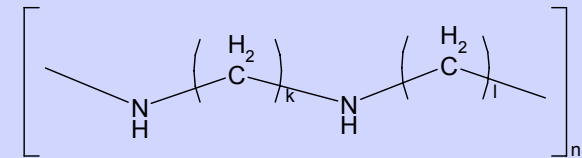
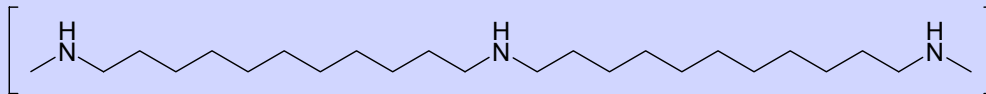
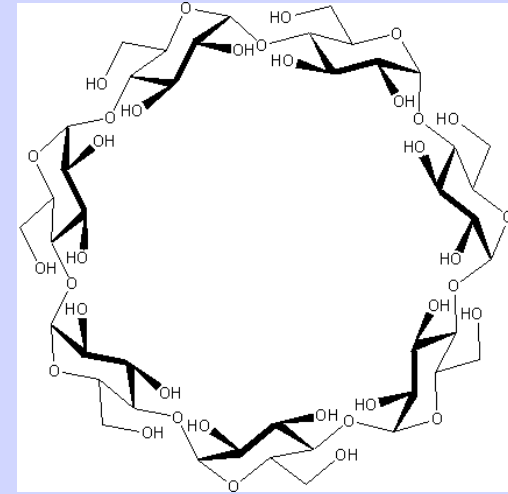
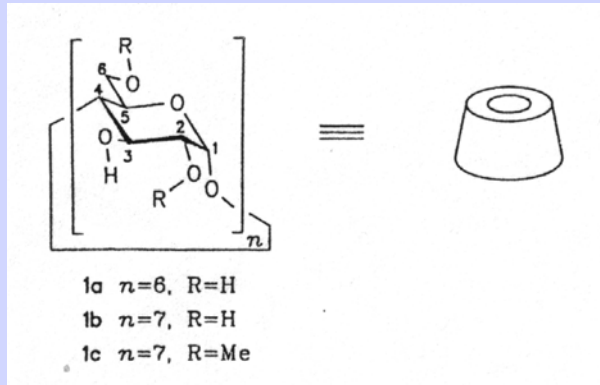
Rotaxanpolymerisation



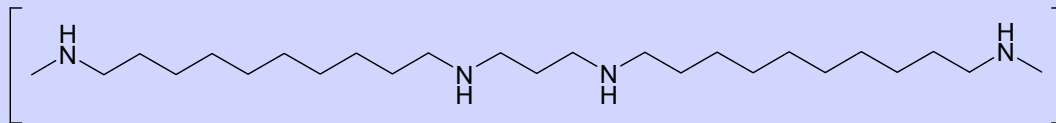
(Anderson)

Cyclodextrinringe auf Polymerketten

(Gerhard Wenz und Bruno Keller)

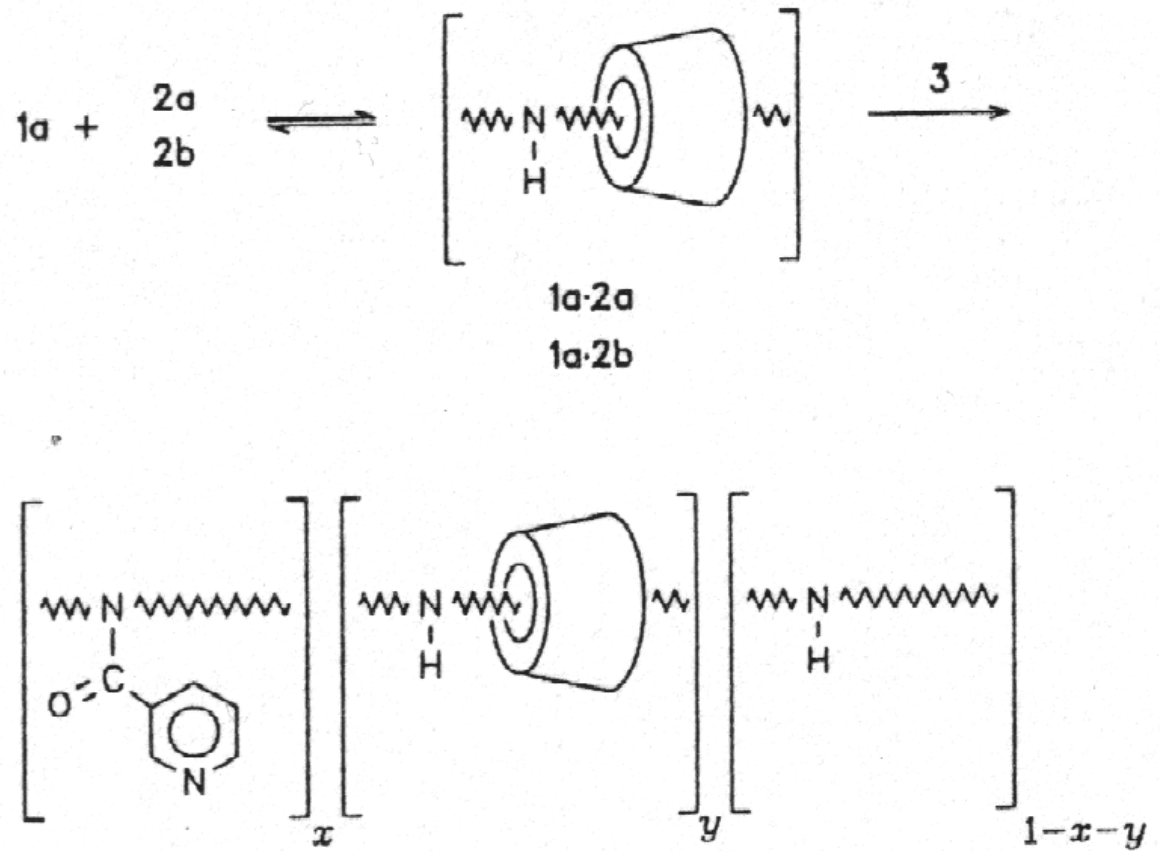


- 1.) $k=l=11$
- 2.) $k=10, l=3$



Cyclodextrinringe auf Polymerketten

(Gerhard Wenz und Bruno Keller)



4a $k=l=11, x=0.025, y=0.10$

4b $k=10, l=3, x=0.25, y=0.67$

Scheme 1.

Charakterisierung der Cyclodextrinringe auf Polymerketten

(Gerhard Wenz und Bruno Keller)

$^1\text{H-NMR}$

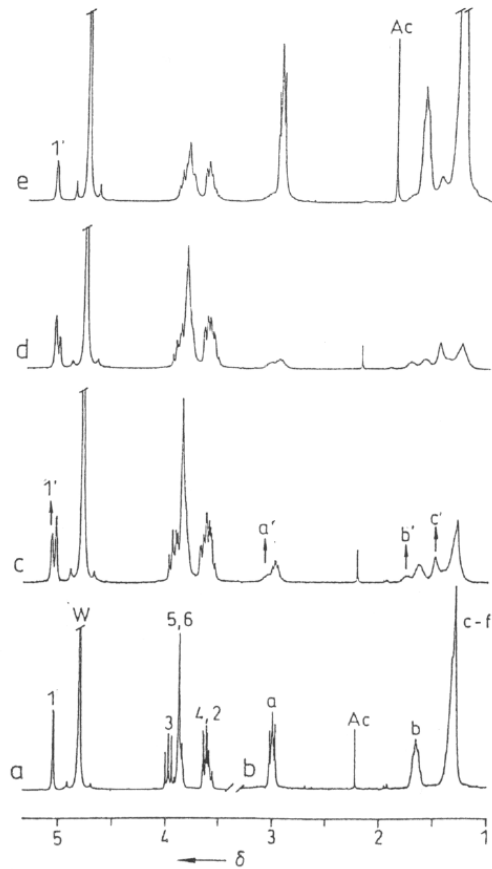


Fig 1. Part of the $^1\text{H-NMR}$ spectra at 20° for a) 1a, b) 2a, c) 45 mM 1a + 45 mM 2a after 5 min, d) 45 mM 1a + 45 mM 2a after 3.5 h, e) 4a[7]; W = water, Ac = acetate.

Viskositätsmessung

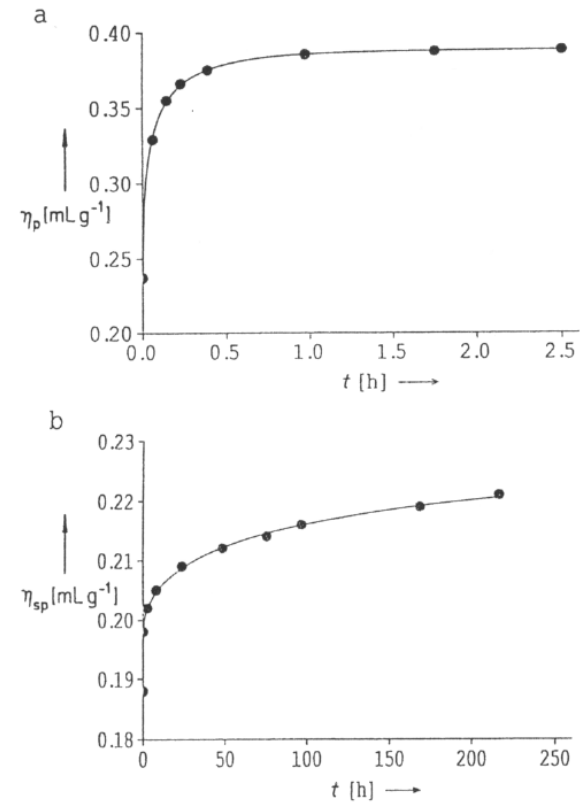
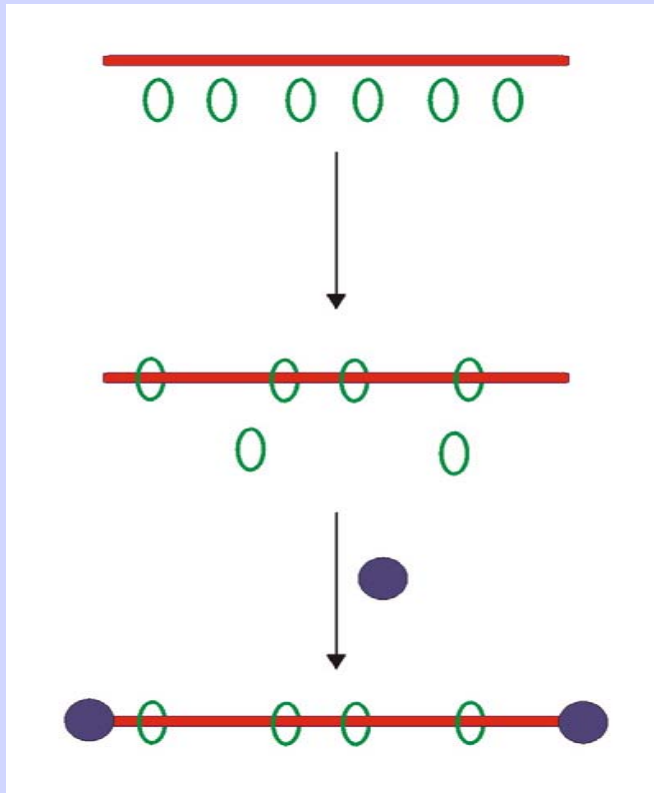


Fig. 2. Specific viscosity η_{sp} at 25° for a) 11.8 mM 1a + 11.8 mM 2a and b) 9.5 mM 1a + 9.5 mM 2b as a function of time t .

Allgemeine Synthesemöglichkeiten der Polyrotaxane

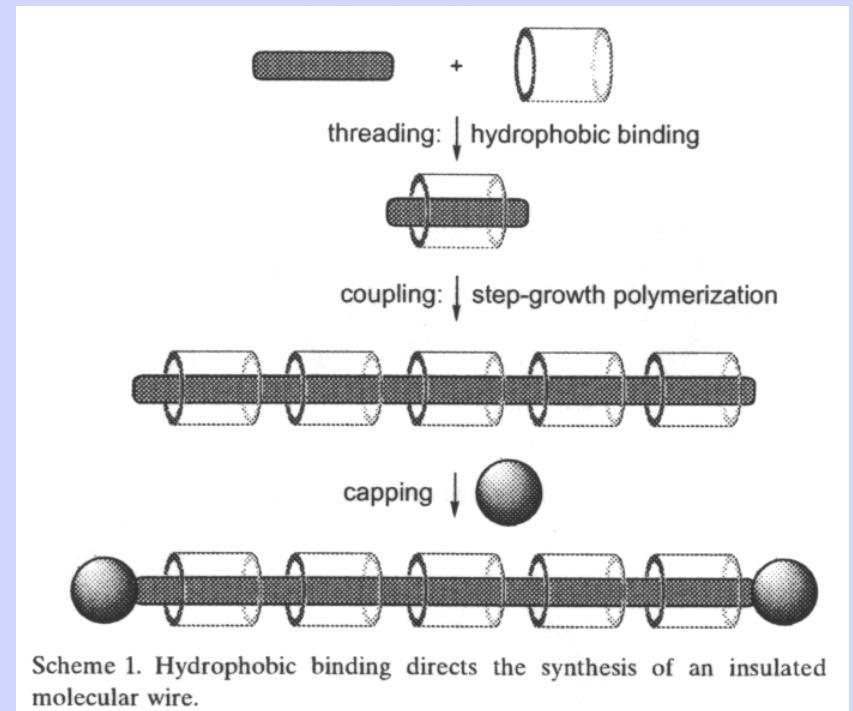
-Polyrotaxane werden klassisch durch threading dargestellt

threading



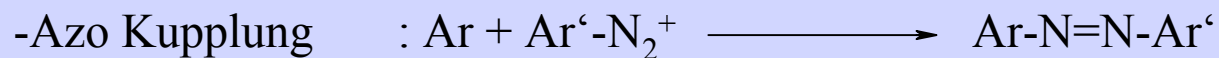
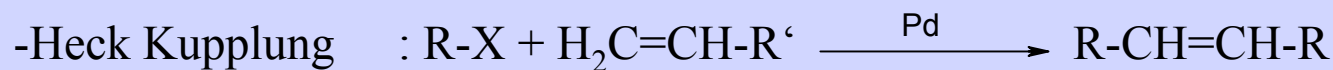
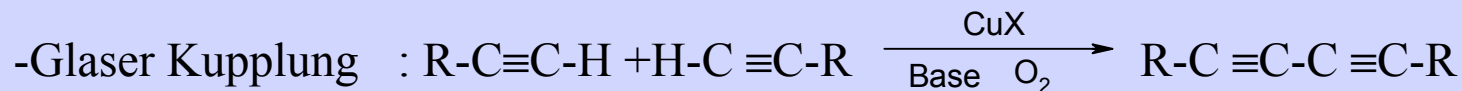
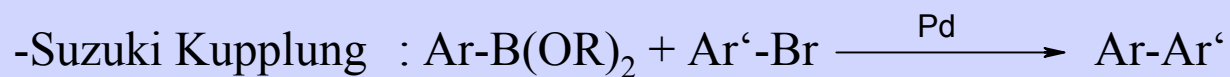
(Wenz, Harada)

Rotaxanpolymerisation

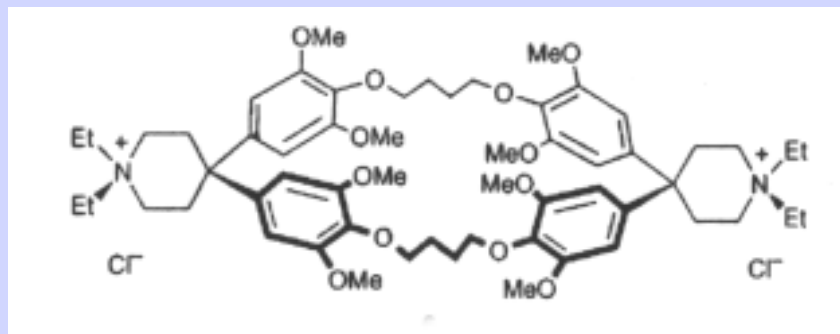
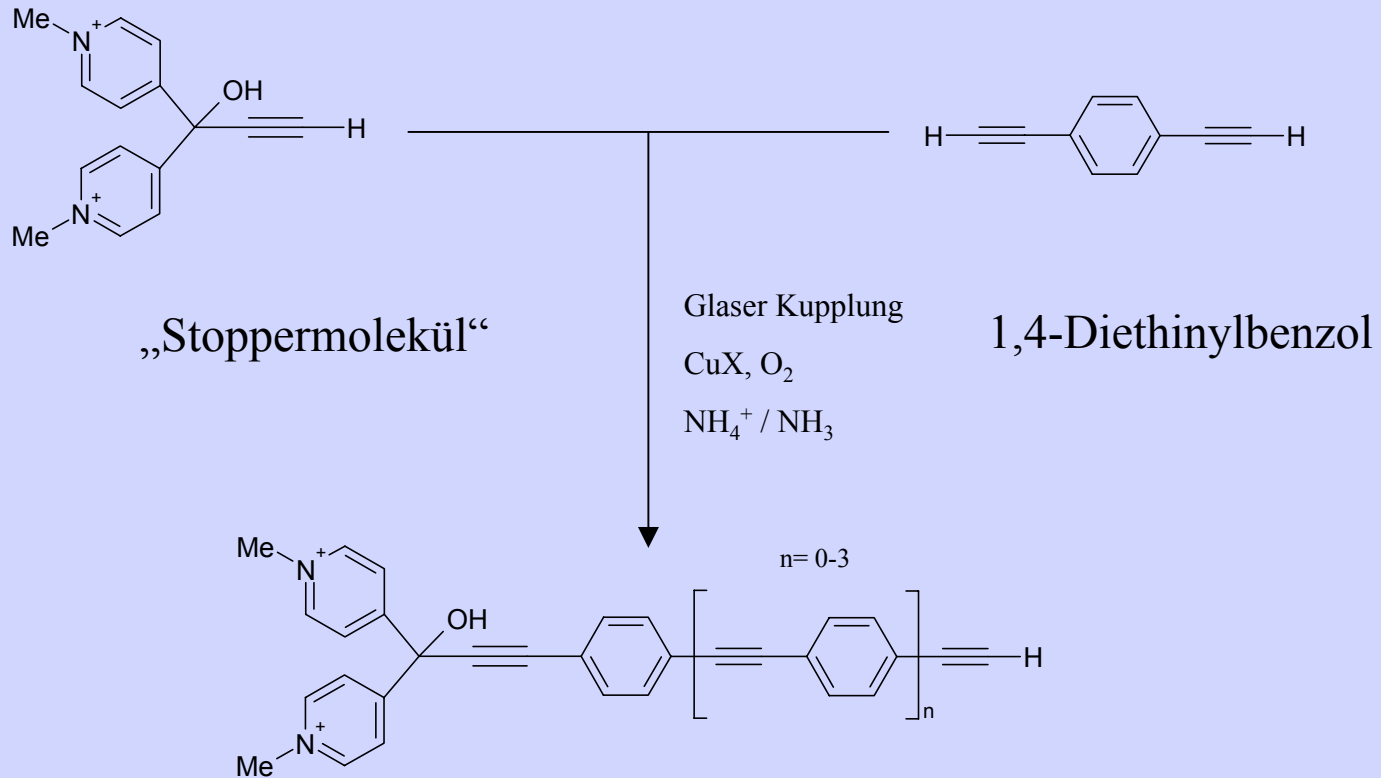


(Anderson)

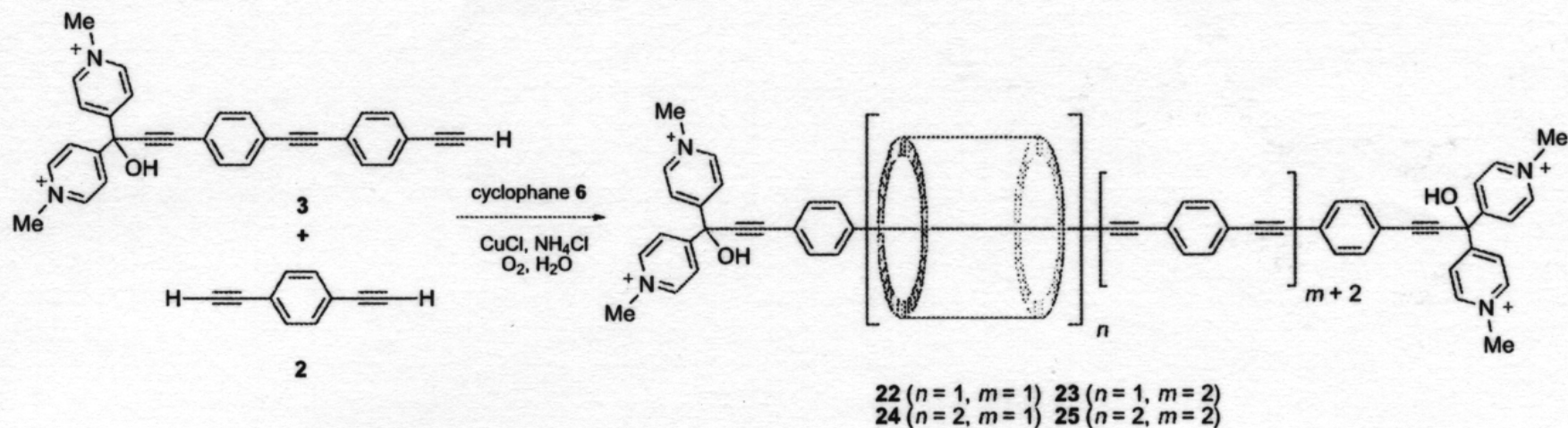
Kupplungsmethoden in Wasser



Makrocyclen auf Polymerketten (Anderson)

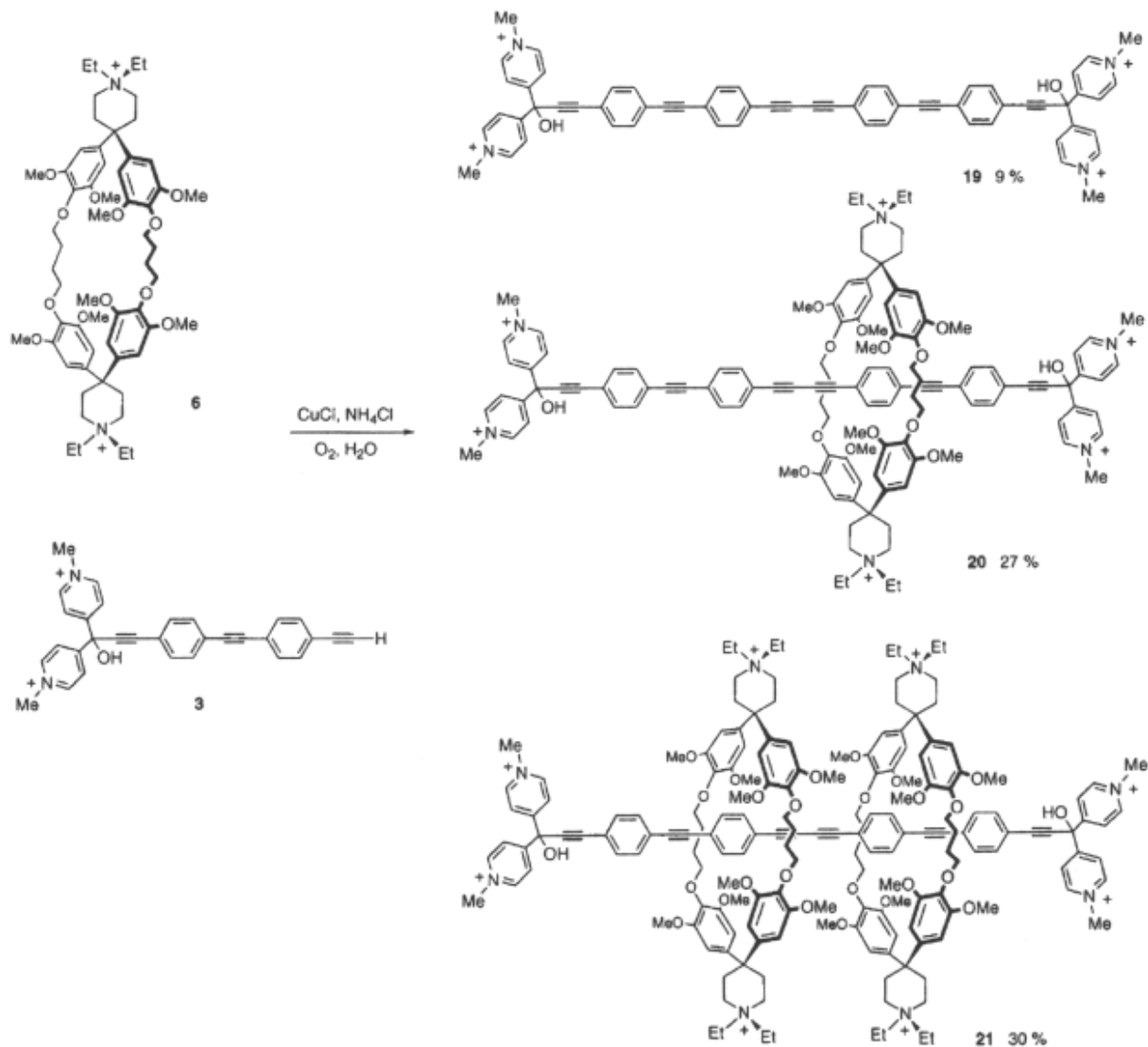


Makrocyclen auf Polymerketten (Anderson)



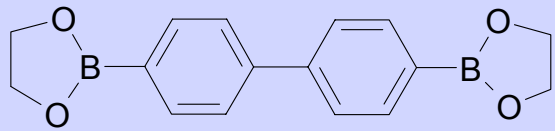
Scheme 5

Makrocyclen auf Polymerketten (Anderson)

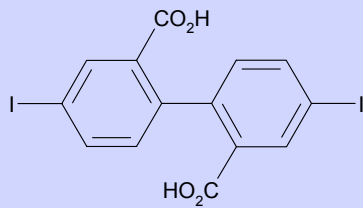


Cyclodextrine auf Polymerketten

Harry L. Anderson et.al. : Conjugated Polyrotaxanes by Suzuki-Coupling in Water



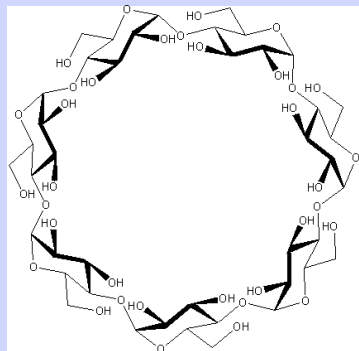
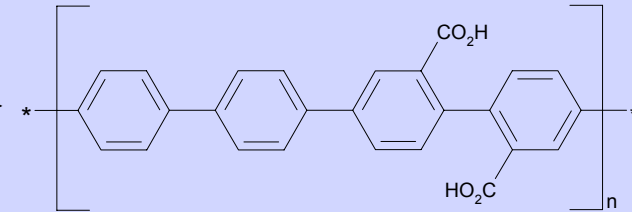
4,4'-Biphenylboronsäureester



2,2'-Dicarboxy- 4,4'-diiodobiphenyl

Suzuki-Kupplung

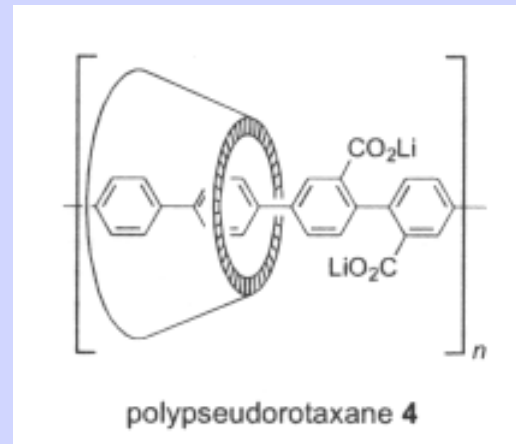
$\text{Pd}(\text{OAc})_2$



Suzuki-Kupplung

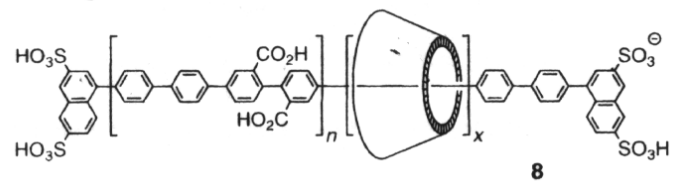
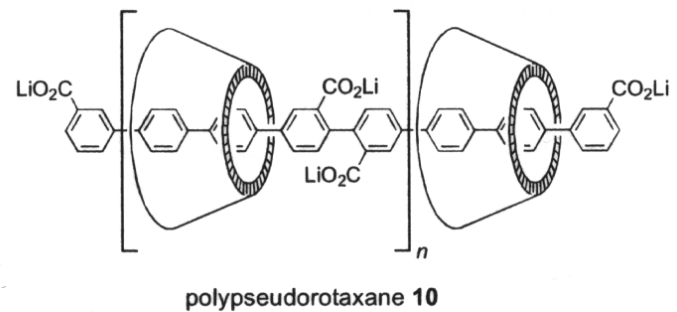
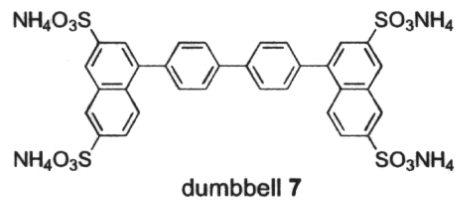
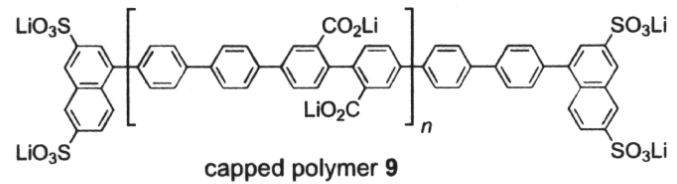
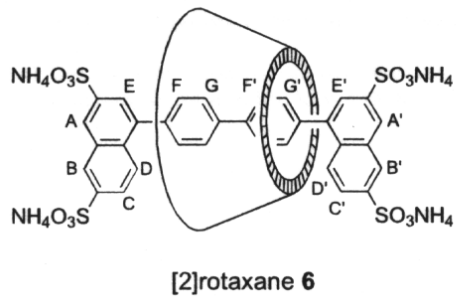
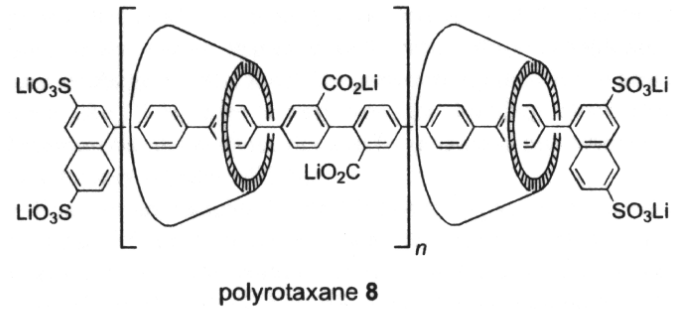
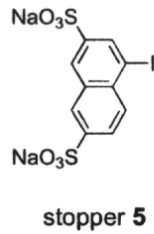
$\text{Pd}(\text{OAc})_2$

β - Cyclodextrin



polypseudorotaxane 4

Cyclodextrine auf Polymerketten



Charakterisierung der erhaltenen Polyrotaxane

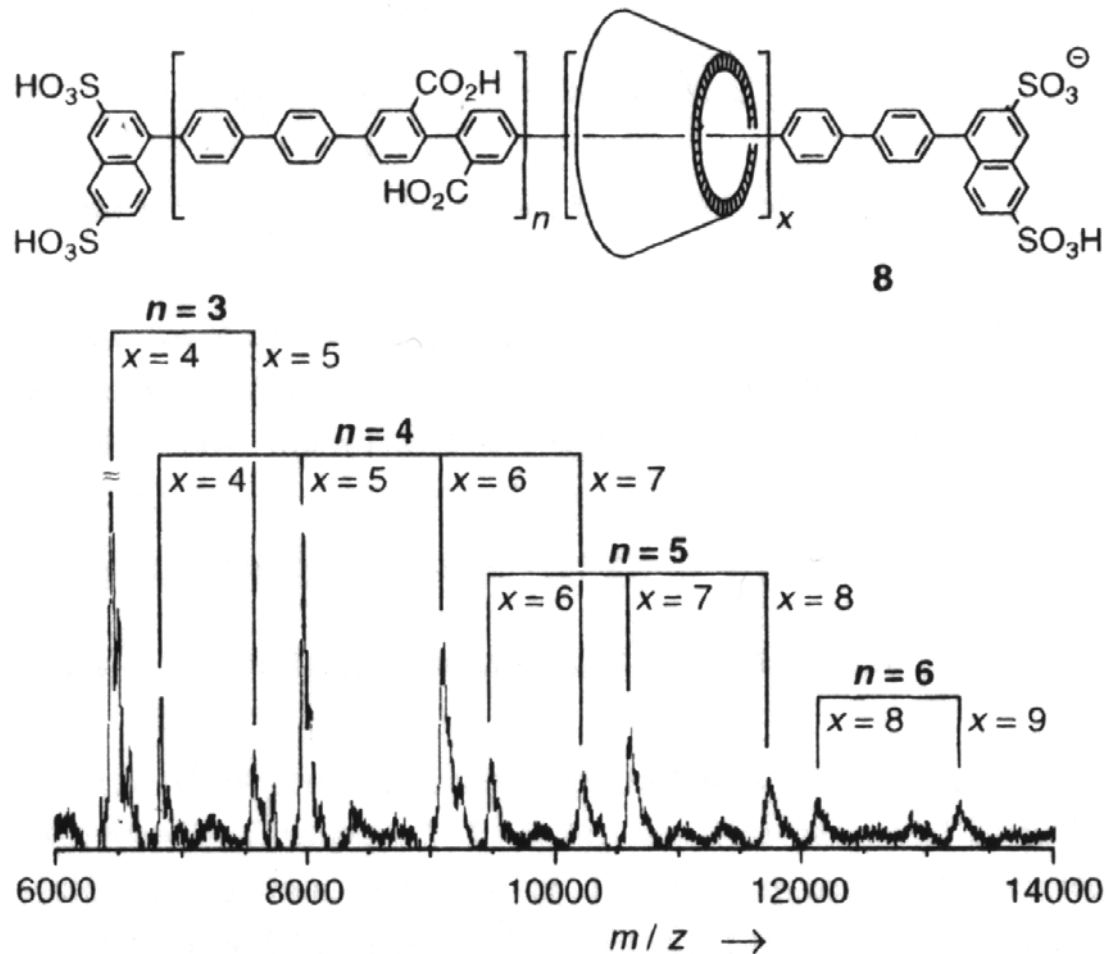


Figure 2. Negative-ion MALDI-TOF mass spectrum of the ammonium salt of polyrotaxane **8**, from a 2,5-dihydroxybenzoic acid matrix.

Zusammenfassung

1. Aufbau und Struktur von Polyrotaxanen
2. Charakterisierung / Nachweis von Polyrotaxanen
3. Synthese von Polyrotaxanen
 - a) Polyrotaxane über threading-Methode
 - b) Polyrotaxane über Pseudorotaxanpolymerisation
(Kupplungsmethoden in Wasser)

Quellen:

G. Wenz, B. Keller, *Angew. Chem.*, 1992, 31 (2), 197-199

Harry L. Anderson, *J. Chem. Soc., Perkin Trans. 1*, 1998, 2383-2397