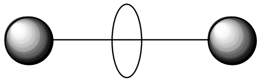
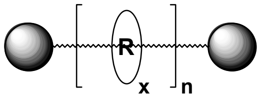
Polyrotaxanes

Polymer Architectures



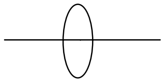
1

Rotaxane



3

Polyrotaxane



2

Pseudorotaxane

Methods of preparing mainchain (pseudo)polyrotaxanes

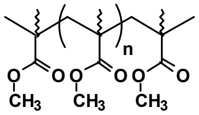
- Cyclisation in the presence of linear macromolecules
- Polymerisation of rotaxanes
- Chemical conversion of rotaxane precursor after polymerisation

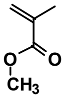
Polyrotaxanes: Why?

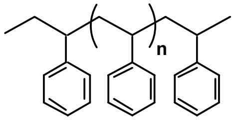
- Solubilities are altered
- Particular chance of improving solubility and processibility of rigid rod polymers
- Glass transitions follow the Fox equation sometimes
- Glass transition sometimes remain distinct for each species
- Thermal stability can be enhanced
- Control of polymer backbone through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

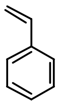
Consideration

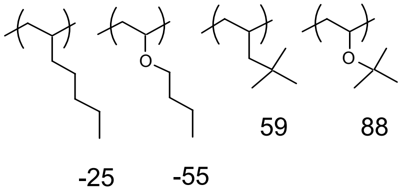
- Blocking groups may be unnecessary due to entrapment of cyclic units in chain folds
- Using rotaxane precursors is unlikely to be of synthetic value







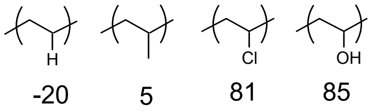


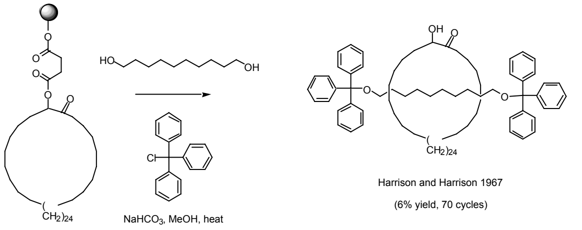


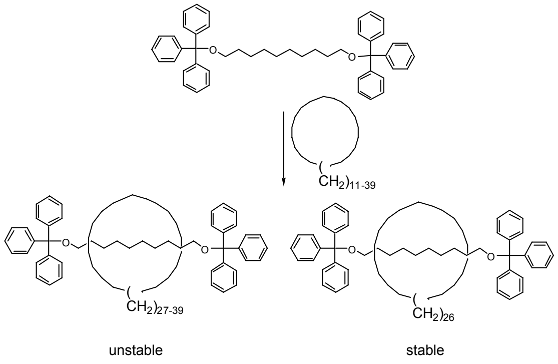
Rotaxanes

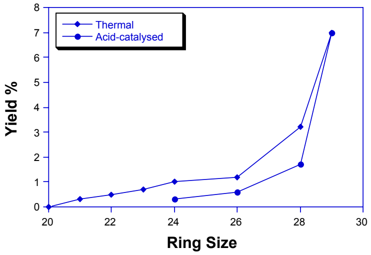
In 1910 envoked

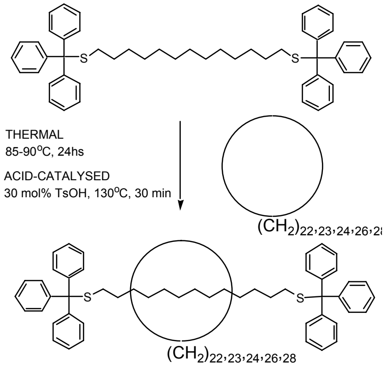
In 1967 proposed and proven

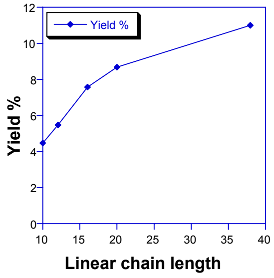


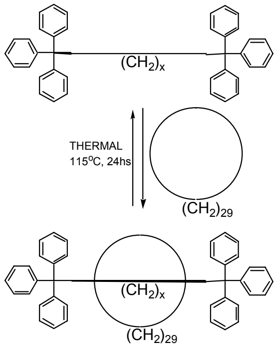


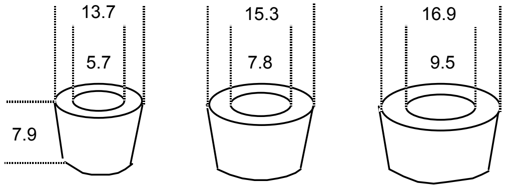


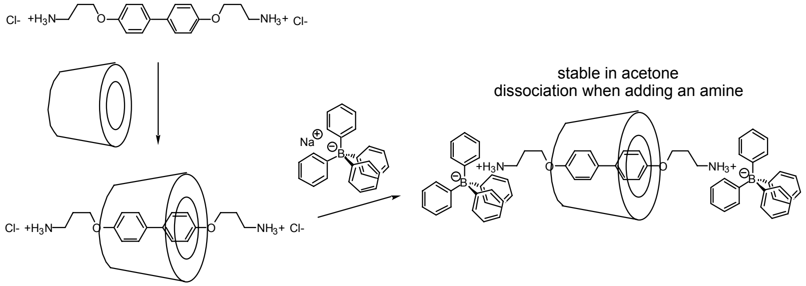












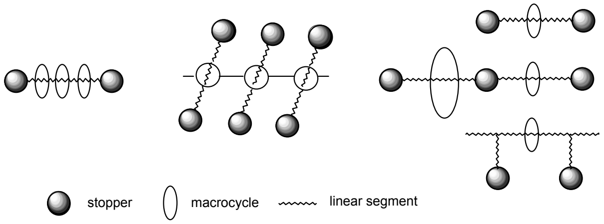
Homorotaxanes and Heterorotaxanes

Homorotaxanes are composed of cyclic and linear species that are chemically equivalent, e.g., a polyrotaxane constructed from poly(ethyleneoxide) and a crown ether[1,10-11].

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[25], affording alternatives to classical copolymer architectures.

Mainchain and Sidechain Polyrotaxanes

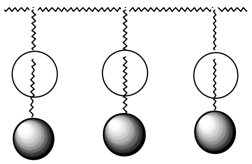
Mainchain Polyrotaxanes

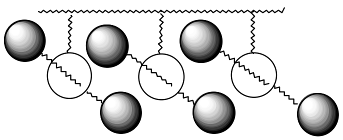


Approaches to mainchain polyrotaxanes

- 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





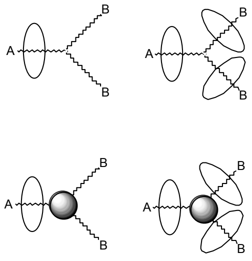
Approaches to sidechain polyrotaxanes - cyclic orthogonal to backbone

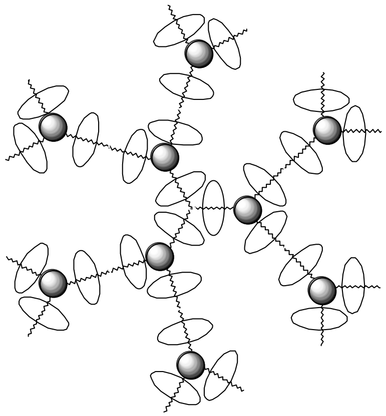
- Threading of preformed graft copolymer plus end-capping
- Grafting in presence of cyclic unit and linear link
- Grafting of preformed rotaxane monomer
- Polymerisation of macromonomer in the presence of cylic unit
- Polymerisation of preformed macromonomeric rotaxane

Approaches to sidechain plyrotaxanes - cyclic parallel to backbone

- Threading of preformed pendant cyclic graft copolymer
- Grafting of cylic 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



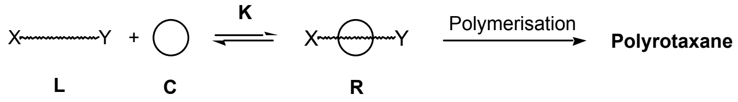


Synthesis of Polyrotaxanes

Statistical Approach

Le Chatelier

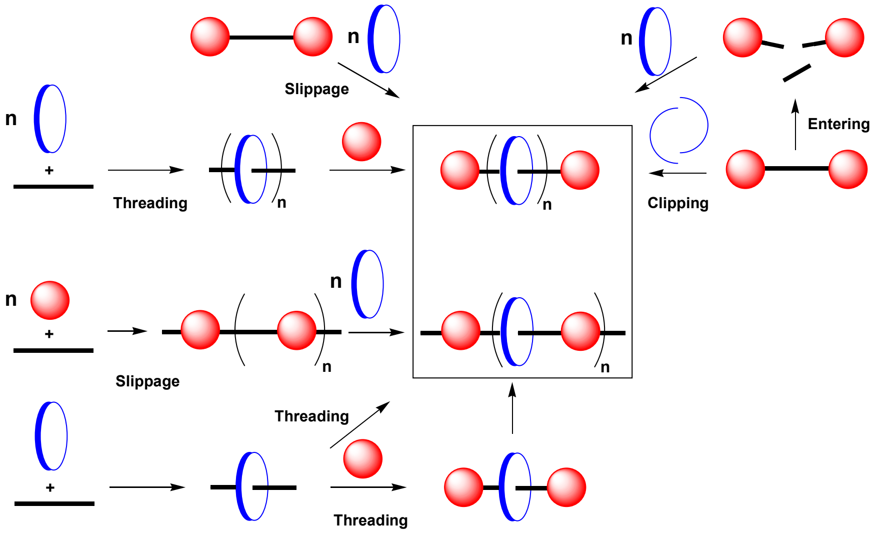
Equilibrium constant (0.05 to 5 l/mol

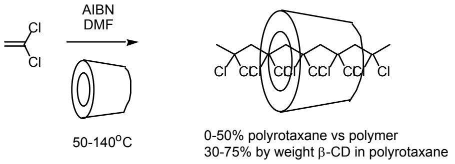


$$K = e^{-(\Delta G/RT)} = [R]/[L][C]$$

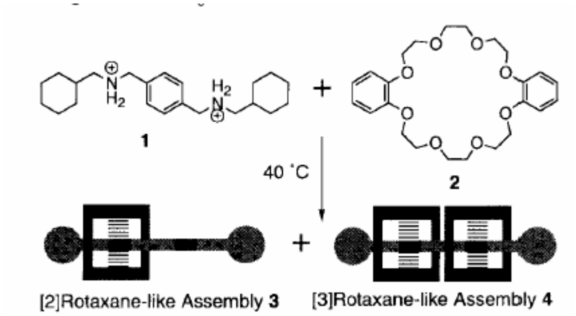
$$\ln K = -(\Delta G/RT) = -(\Delta H - T\Delta S)RT = -\Delta H/RT + \Delta S/R$$

entropically driven = (ΔH small)





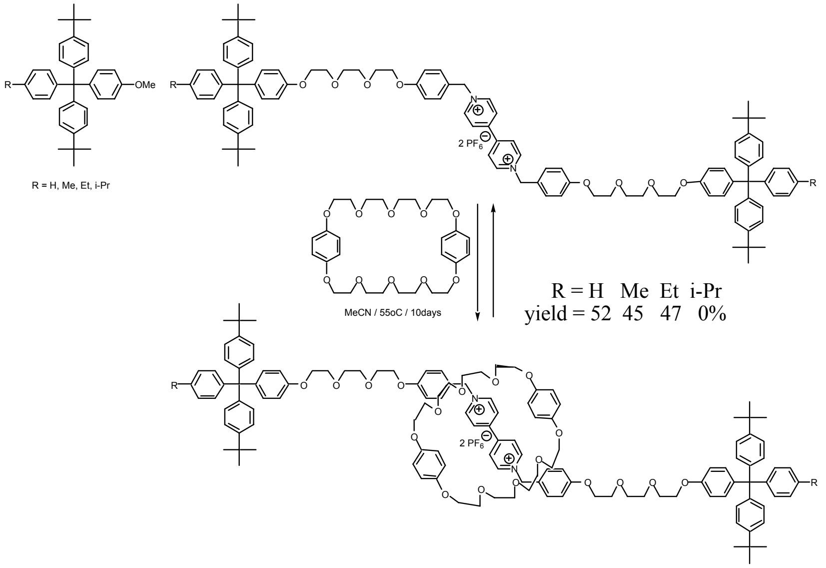
0-50% polyrotaxane vs polymer
30-75% by weight β-CD in polyrotaxane



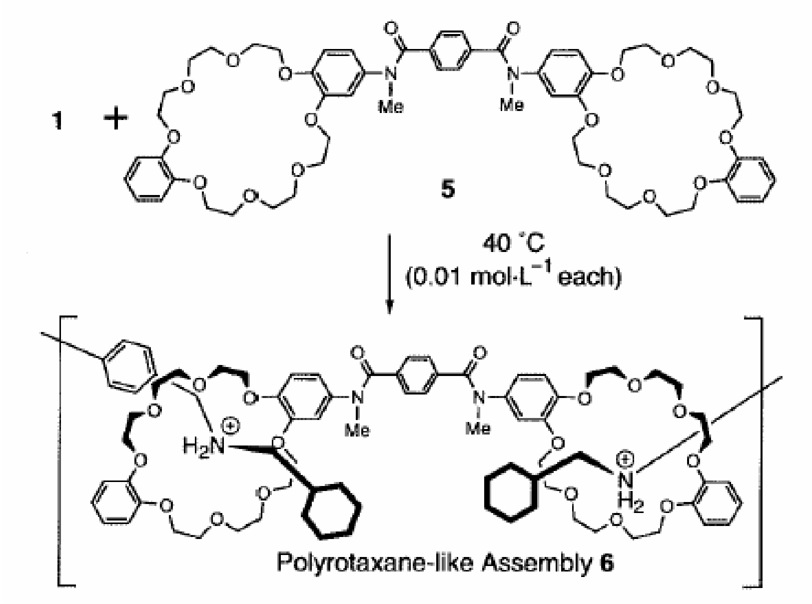
Directed Synthesis

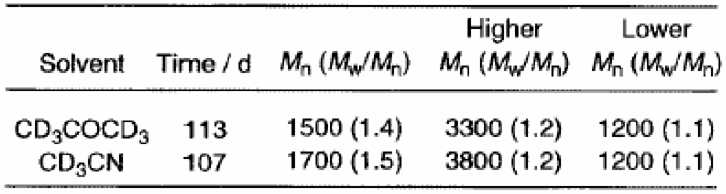
Preformed Monomer

Slippage



R = H Me Et i-Pr
yield = 52 45 47 0%

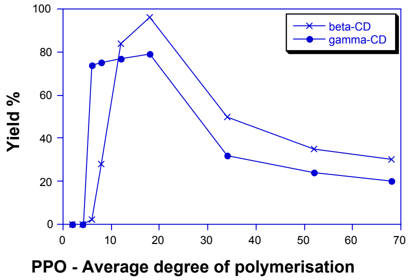


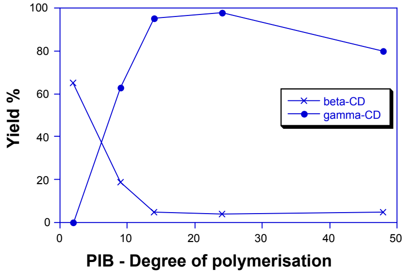


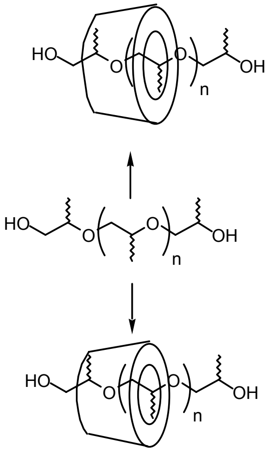
Solvent	Time / d	M_n (M_w/M_n)	Higher M_n (M_w/M_n)	Lower M_n (M_w/M_n)
CD_3COCD_3	113	1500 (1.4)	3300 (1.2)	1200 (1.1)
CD_3CN	107	1700 (1.5)	3800 (1.2)	1200 (1.1)

	α-cyclodextrin	β-cyclodextrin	γ-cyclodextrins
PPO (MW 1000)	0%	96%	80%
		2:1 complex	
PEO	~ 100%	low	~100%
	2:1 complex		2:1 complex (double)

Similarly polyethylene glycols form crystalline complexes with α-CD but not β-CD[21].

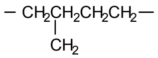
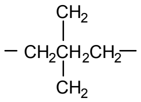




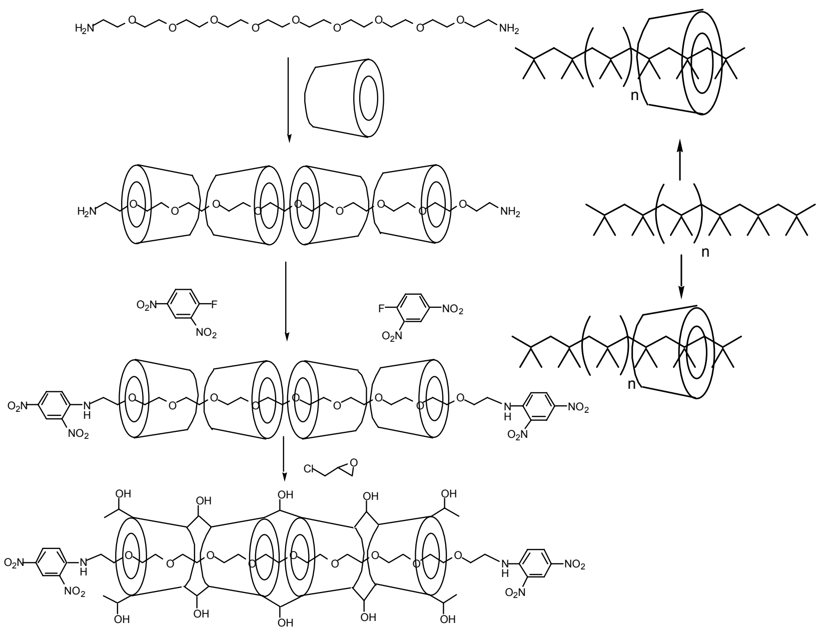


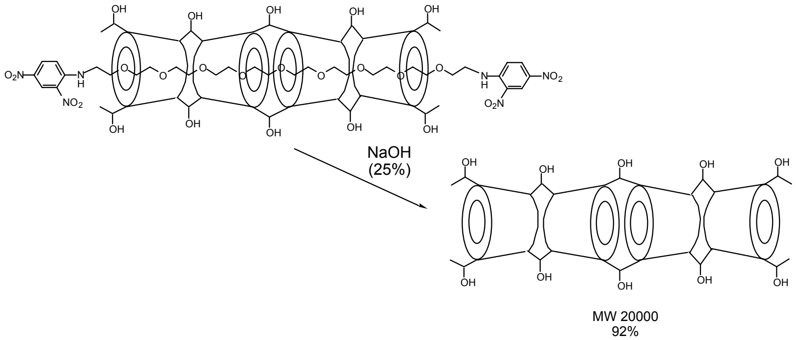
Cyclodextrins and Hydrophobic Polymers

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

Polymer/Oligomer	Structure	MW	α-CD	β-CD	γ-CD
			4.5 Å	7.0 Å	8.5 Å
OE	-CH_2CH_2-	563	63	0	0
Squalane	 $-CH_2\underset{\displaystyle CH_2}{\underset{\vert}{C}}H_2CH_2CH_2-$	423	0	62	24
PIB	 $-CH_2\overset{\displaystyle CH_2}{\overset{\vert}{\underset{\displaystyle CH_2}{\underset{\vert}{C}}}}H_2CH_2-$	~800	0	8	90

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.

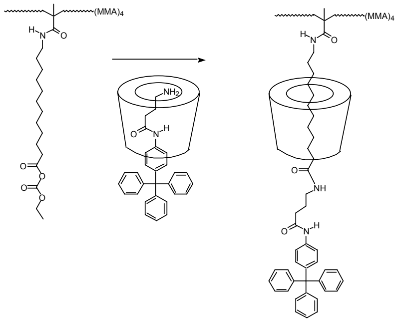




PEG 1450 (approx. 33 repeat units)

about 16 aCDs times MW 1200 = MW 20000

not soluble in water anymore!



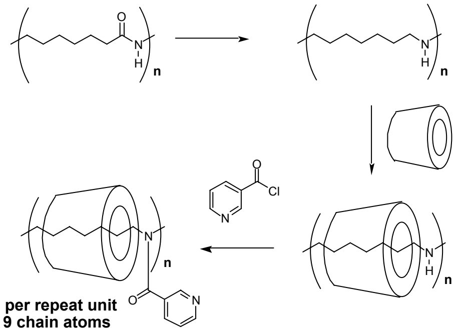
The threading of α-CD was followed by ^{1}H-NMR spectroscopy, in which significant downfield shifts of CD protons are observed as the polytrotaxane forms. The larger β-CD derivative is threaded several orders of magnitude more rapidly than the smaller α-CD.

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.

100-fold difference

Faster

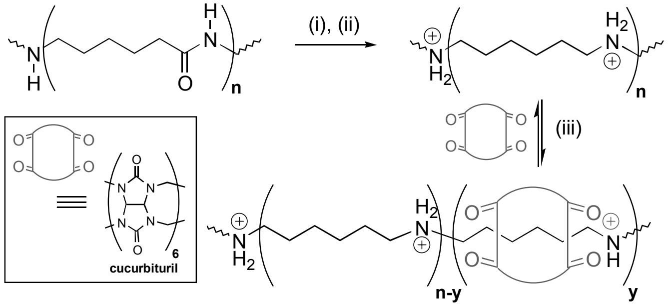
Slower

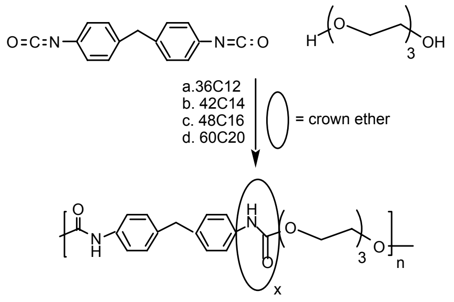


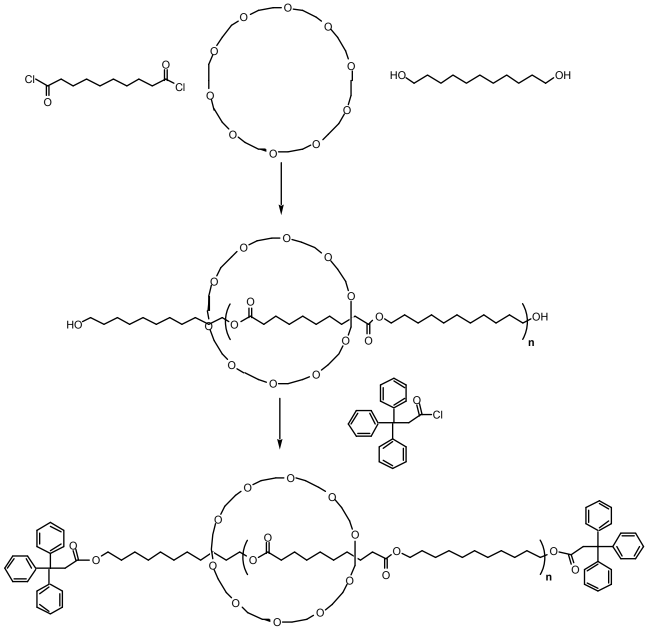
$-\left[NH(CH_2)_xNH(CH_2)_y\right]_z-$

x=y=11, z=43

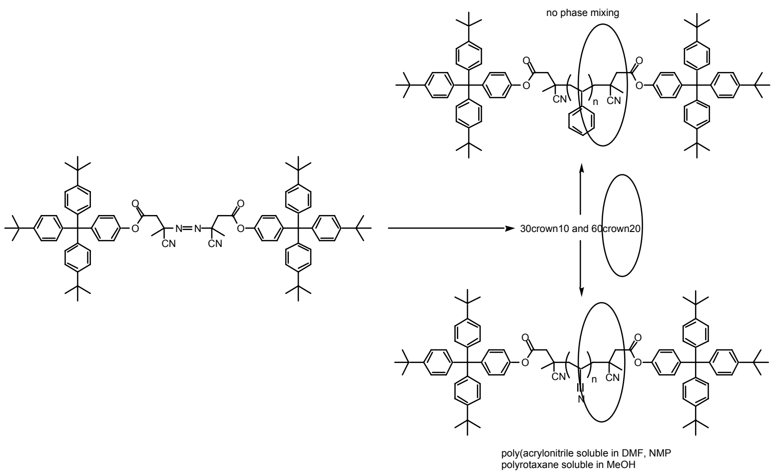
x=10, y=3, z=23

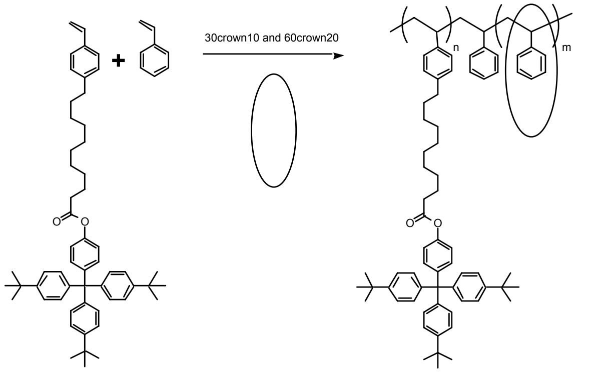


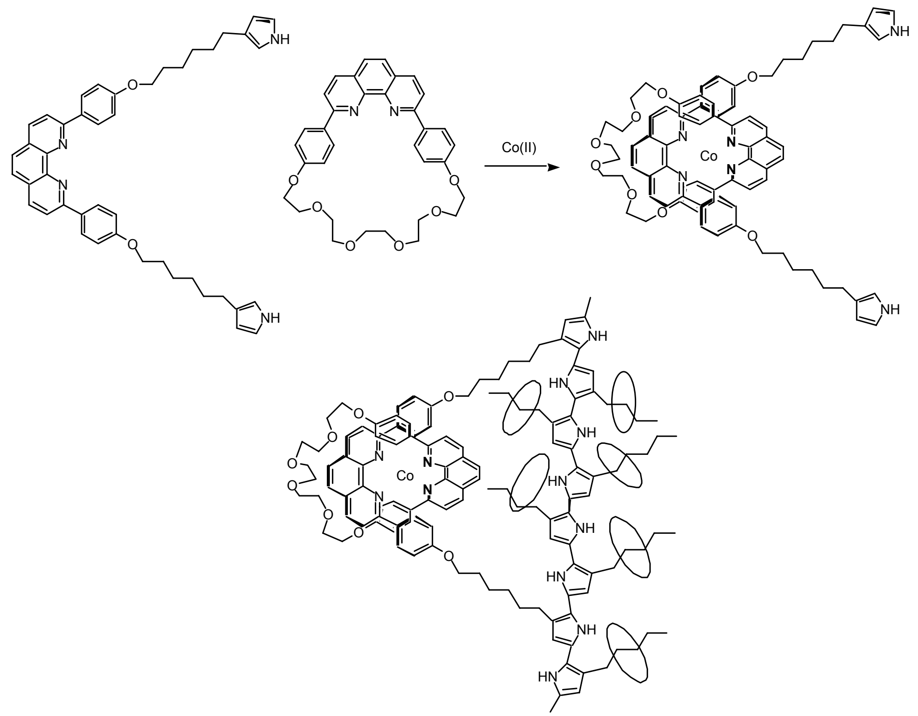




Plasticisation







TI: ROTAXANES, CATENANES, POLYROTAXANES, POLYCATENANES AND RELATED
MATERIALS
AU: GIBSON_HW, BHEDA_MC, ENGEN_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
JN: LANGMUIR, 1997, Vol.13, No.9, pp.2436-2439

TI: Self-threading-base approach for branched and/or cross-linked
poly(methacrylate rotaxane)s
AU: Gong_CG, Gibson_HW
JN: JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, 1997, Vol.119, No.25,
TI: Design and construction of supramolecular architectures
consisting of cyclodextrins and polymers
AU: Harada_A
JN: ADVANCES IN POLYMER SCIENCE, 1997, Vol.133, pp.141-191

TI: Photochemical synthesis of polyrotaxanes from stilbene polymers
and cyclodextrins
AU: Herrmann_W, Schneider_M, Wenz_G
JN: ANGEWANDTE CHEMIE-INTERNATIONAL EDITION IN ENGLISH, 1997,
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