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Solid State Polycondensation within Cyclodextrin Channels Leading to Watersoluble Polyamide Rotaxanes

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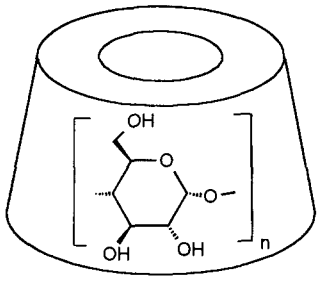
Abstract: α,ω-Aminocarboxylic acids form microcrystalline inclusion compounds with α-cyclodextrin. In these inclusion compounds cyclodextrins build up channel structures, in which the α,ω-aminocarboxylic acids can be polycondensed at 200-240°C. As the resulting polyamides are completely covered by cyclodextrin rings they are readily water-soluble. The dissociation of the polymeric inclusion compounds can be prevented by the introduction of bulky substituents within the polymer chain. © 1997 Elsevier Science Ltd.

Polyamides have reached a high practical importance because of their form stability and their high melting points[1, 2]. Due to strong intermolecular hydrogen bonds, these polymers are insoluble in most solvents except e.g. concentrated formic or sulfuric acid or solutions of LiCl in DMF or of $CaCl_2$ in methanol.[3-7] Polyamides are technically produced by ring opening polymerization of the corresponding lactams[8] or by the bulk polycondensation of the salt of the amine and the acid component at high temperature. In the following, we describe a new method to obtain watersoluble polyamides by the polycondensation of alkyl ammonium carboxylates within the cavities of cyclodextrins.[9]

Cyclodextrins are cyclic oligomers of amylose consisting of six, seven or eight glucose units (α-, β-, γ-cyclodextrin, **1a**, **1b**, **1c**).[10-12] The cyclodextrin molecules resemble a hollow truncated cone, at the narrow side are the primary, at the wide side the secondary hydroxyl groups. No hydroxyl groups are inside the cavity, therefore this region of the molecule is hydrophobic and able to include hydrophobic guest molecules. It was as early as 1938 that Freudenberg discovered that cyclodextrins form inclusion complexes with organic guest molecules.[13] Later Cramer studied the formation of such inclusion compounds and derived rules for their preparation.[14-16]

For the formation of stable inclusion compounds it is important that the guest molecule fits within the cavity of the host and fills it as complete as possible.[12] Thus, **1a** forms inclusion complexes with linear aliphatic guest molecules like α,ω-alkane diols or α,ω-alkane diamines. With aromatic guests, **1a** forms only addition

compounds, where the cyclodextrin ring is deformed to an ellipsoid and the guest molecules only partially enters the interior of the host. The next bigger homolog, β-cyclodextrin **1b**, includes many aromatic guests as those fit closely into its cavity.[17] γ-Cyclodextrin **1c** can accommodate big molecules, like steroids or C_{60} , as well as two guests together, in its cavity.



1a,b,c n = 1, 2, 3

The inclusion of polymers by cyclodextrins is of growing interest as it renders the possibility to change the physical and chemical properties of the polymers without the necessity of polymer analogous reaction. In principle, there are two methods to obtain inclusion compounds of polymers:

(I) threading cyclodextrin rings onto polymer chains, or

(II) polymerization of the cyclodextrin inclusion compound of a monomer.

The 'threading method' (I) has the advantage to start with a well-defined known polymer. Threading can be performed in a solvent (e. g. water) which can be different from the solvent necessary for the synthesis of the polymer. Harada et al. discovered that **1a** can be threaded onto polyethylene glycol[18, 19] and poly(oxytrimethylene)[20], **1b** onto polypropylene glycol[21, 22] and **1c** onto poly(methyl vinyl ether)[23]. They could prove by wide angle X-ray powder diffractometry that the cyclodextrin rings are ordered in a channel structure and that the polymers are inside these channels. The resulting polymeric inclusion compounds are insoluble in water and only soluble in highly polar solvents (e.g. DMF) with dissociation of the supramolecular structure. We obtained the first soluble cyclodextrin inclusion compounds of polymers by threading cyclodextrins onto watersoluble poly(imino-oligomethylene)s or ionenes.[24-28] The kinetics of the inclusion of the polymer chain were investigated by ^{1}H-NMR-spectroscopy. In addition the kinetics of the dissociation of cyclodextrin rings from the polymer chains were studied by quantitative dialysis experiments. Bulky groups were fixed at the polymer chain to hinder the rings from sliding off the polymer. Stable polyrotaxanes were produced this way.[24]

The 'inclusion polymerization method' (II) might have the advantage that the monomers are more soluble than the resulting polymers. Therefore polymers might be included which are otherwise insoluble in water. Ogata already studied in the year 1976 the phase boundary polycondensation of diamides and dicarboxylic acid dichlorides in the presence of **1b**.[29] He obtained polymeric inclusion complexes, e.g. of nylon-6,6, which are nearly insoluble in water. Maciejewski al. performed radical polymerizations of vinyl monomers (e.g. vinylidene chloride, styrene) in the presence of **1b** in DMF solution and also obtained

insoluble polymeric inclusion compounds.[30] Because of the low solubilities we conclude, that in these cases the polymer chains were covered by only a few cyclodextrin rings. Furthermore, our own experiments revealed a major drawback of this method: as the reactivity of the monomer is significantly lowered by inclusion, polymerization mainly takes place in the free state of the monomer.

The major advantage of our new method, described in the following, is to avoid the dissociation of the inclusion compound of the monomer by performing the polymerization in the solid state. A high coverage of the polymer chain can be reached by the polycondensation of included monomers in the channel of the crystalline host (fig. 1). Although polymerizations in host crystals (clathrates) are well known for a long time,[31] non ring shaped matrices like urea,[32] deoxycholic acid,[33] or perhydrotriphenylene[34] were mostly used to polymerize monomers like substituted butadienes. On the other hand, ring-shaped matrices have the advantage that the supramolecular order partially remains after the dissolution of the polymeric product. The radiation induced solid state polymerization of vinyl monomers included in cyclodextrin **1b** was already described by Maciejewski et al..[35] We found a solid state polycondensation within cyclodextrin **1a** leading to polyamide inclusion compounds.[9]

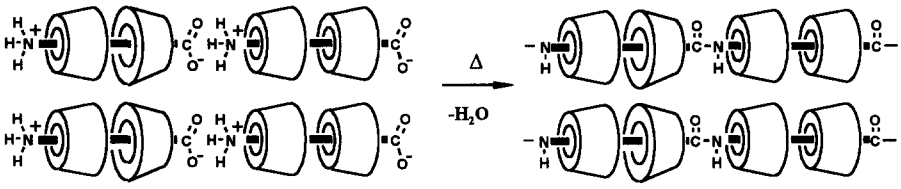


Fig.1:Schematic representation of the polycondensation of α,ω-alkylammonium carboxylates within the channel of cyclodextrin molecules

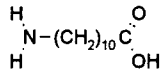
Results

1. Formation of the inclusion compounds of reactive monomers

To produce cyclodextrin inclusion compounds of monomeric guest molecules, we dissolved α,ω-aminocarboxylic acids (Fig. 2) and **1a** in warm water. The inclusion compounds precipitated after cooling down rapidly. The stoichiometry of the inclusion compounds was determined by integration of the ^{1}H NMR signals of H-1 of the host **1a** and of the aliphatic protons of the guest, e.g. 11-aminoundecanoic acid **2**. Depending on the molar ratio of guest and cyclodextrin, one molecule of **2** was included in 1 or 2 cyclodextrin rings. Well-defined inclusion compounds, **2**·**1a** or **2**·**1a**$_2$, are obtainable. The microcalorimetric titration of **2** by **1a** at pH = 4.7 and 25°C also revealed a stepwise inclusion process with binding constants of K_1 = 9580 ± 790 M^{-1} and K_2 = 2340 ± 290 $M^{-1}$and inclusion enthalpies of $\Delta H°_1$ = -22.6 ± 0.3 kJ mol^{-1} and $\Delta H°_2$ = -4.0 ± 0.6 kJ mol^{-1}. The shorter α,ω-aminocarboxylic acids, e.g. 8-aminooctanoic acid only form inclusion compounds with

a 1:1 stoichiometry of host and guest.

Also ternary crystalline inclusion compounds with a well defined stoichiometry of 1:1:4 for α,ω-diamine, α,ω-dicarboxylic acid and **1a** were obtained. Consequently, both guest molecules are included together and both guests by two cyclodextrins each. The 1:1 stoichiometry of diamine and diacid was attributed to a strong interaction between ammonium and carboxylic end groups. These ternary inclusion compounds were only built in the case of similar lengths of the aliphatic chains of the diamino component and the dicarboxylic acid. While the yield of the inclusion compound was 38% for 1,10-diamino decane **6** and 1,8-octane dicarboxylic acid **7**, only a 8 % yield was obtained for **6** and 1,10-decane dicarboxylic acid. For **6** and 1,6-hexane dicarboxylic acid, and **1a** no crystalline precipitate was found at all. Neither diamines nor dicarboxylic acids alone form precipitates of crystalline inclusion compounds with **1a**.



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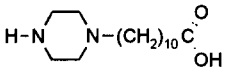

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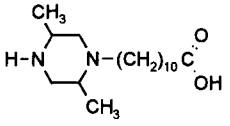

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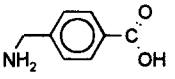

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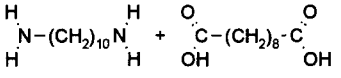

6 + **7**

Fig. 2: Monomeric guest molecules suitable for inclusion in cyclodextrins

2. Investigation of the Structure of the Inclusion Compounds

One major requirement for the polycondensation of guest molecules included by cyclodextrins is a crystal structure in which amino and acid groups are direct neighbors. This requirement is fulfilled, if all cyclodextrins are packed unidirectionally in a channel. The wide angle X-ray powder diffractogram in fact supports such a channel structure (see fig. 3). Especially the reflection at $2\Theta = 19.63°$ (d = 4.53 Å) is similar to those of known channel inclusion compounds.[19, 36] Only the inclusion compound **5**·**1b** was found to be an exception. It showed a great number of reflections which are typical for a herring-bone structure.[19,36,37]

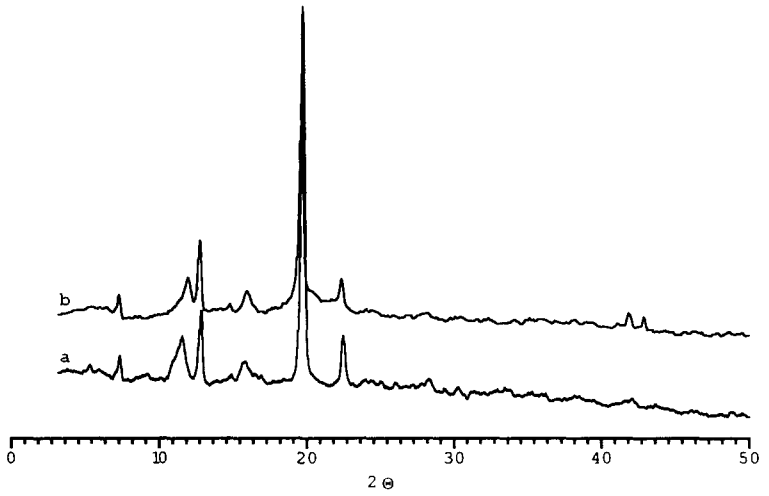

Fig. 3: Wide angle X-ray diffraction diagram of inclusion compound **2**·**1a**$_2$
a) before, b) after annealing, for 5 h at 240°C

3. Investigation of the Inclusion Compounds by Solid-State ^{13}C NMR Spectroscopy

For a further characterization of the inclusion compounds of 11-amino-undecanoic acid **2** and **1a**, we used solid state ^{13}C CP MAS NMR spectroscopy. This method allows to observe the changes of the conformations and of the mobility of both the cyclodextrin rings and the included guest due the formation of the crystalline inclusion compounds.[38-42]

The ^{13}C CP MAS NMR spectra of the both inclusion compounds **2**·**1a** and **2**·**1a**$_2$ show sole signals for each of the carbon atoms C-1 till C-6 (s. figs. 4b, 4c). This finding is indicative for a C_6 symmetry of the conformation of **1a**. In contrast, for the crystalline empty **1a** splitting of most signals especially of the signal of C-1 into 6 signals is known (s. fig. 4a). This signal splitting of empty **1a** is due to a pronounced deviation of the conformation from C_6 symmetry which leads to different situations for the six anhydroglucose units. This finding was supported by X-ray structure analysis which shows that one of the six anhydroglucose units is twisted towards the C_6-axis and fill the empty space inside **1a**.[43, 44] The guest **2** apparently fills the cavity of **1a** completely so that the C_6 symmetry of the macrocycle is recovered. Consequently, the guest **2** has to be inside the cavity of **1a**. Also no empty **1a** could be detected in the inclusion compounds **2**·**1a** and **2**·**1a**$_2$.

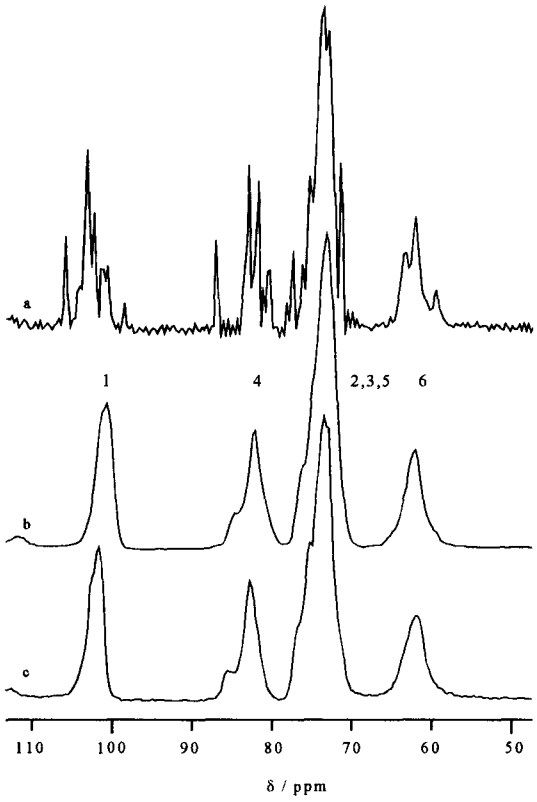

Fig. 4: Partial ^{13}C-CP-MAS solid-state NMR spectra, range of cyclodextrin of a) **1a**, b) **2**·**1a**, c) **2**·**1a**$_2$

The signals of the methylene carbons of the guest **2** were found in the range between 25 and 45 ppm of the ^{13}C-CP-MAS NMR spectrum (fig. 5). Inclusion compound **2**·**1a**$_2$ (fig.5c) shows one significant signal at 35 ppm similar to the crystal of the free guest **2** (fig. 5a). This signal was attributed to the *trans* conformation of the paraffin chain as the signals of the *gauche* conformation are usually located at higher field (30 - 32 ppm). Indeed, for **2**·**1a** a high amount of signal intensity was at 30 ppm (fig. 5b). This shows that the paraffin chain is in a rather coiled conformation. As the guest (contour length 13*1.25 Å = 17 Å) is much too long for the host (height about 8 Å) a strong coiling of **2** is necessary for a good fit of **2** within the cavity of one **1a**. In addition, the distance between two adjacent cyclodextrins in the crystal lattice might be increased along the C_6 axis to accommodate this long guest. On the other hand, the length of guest **2** perfectly fits into two cyclodextrins **1a**. Therefore, the inclusion compound **2**·**1a**$_2$ appears to be more highly ordered than **2**·**1a** as evidenced by the line widths of the ^{13}C-CP-MAS-NMR spectra and the X-ray diffraction diffractograms. For a more exact determination of the crystal structures of **2**·**1a** and **2**·**1a**$_2$ it would be necessary to perform X-ray structure analysis. However it was impossible up to now to grow suitable crystals.

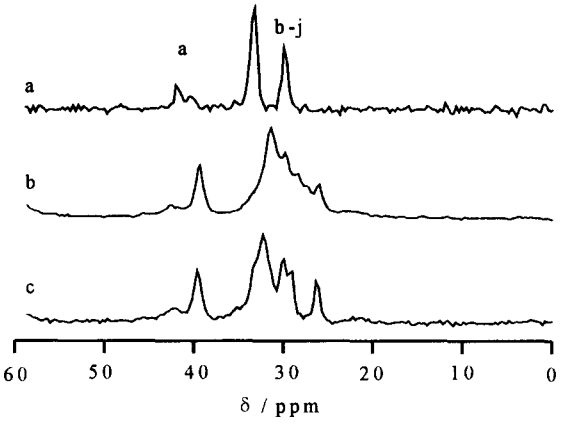

Fig. 5: Partial ^{13}C-CP-MAS solid-state NMR spectra, range of the guest molecule **2** of a) **2**, b) **2**·**1a**, c) **2**·**1a**$_2$,

4. Solid-State Polycondensation of Inclusion Compound **2**·**1a**$_2$

For the polycondensation of alkylammonium carboxylates to polyamides normally temperatures above 200°C are necessary.[2] Cyclodextrins withstand these harsh conditions as long as there are no acid, base or oxygen present. Therefore the inclusion compounds **2**·**1a**$_2$ and **2**·**1a** were heated under vacuum for several hours at temperatures between 190°C and 240°C. Afterwards their colors had turned to yellow or brown depending on reaction time and temperature. Both the X-ray diffractograms and the solid state NMR spectra of the products show that the channel packing and the chemical structure of the cyclodextrin molecules remain intact. Complete decomposition was observed for temperatures above 250°C. Black amorphous products were obtained in this case.

The conversion y of the polycondensation reaction was measured by two independent methods, namely IR spectroscopy and gravimetry.

The formation of the polyamide p-**2** could be followed by detection of the amide band at λ = 1733 cm^{-1} (fig. 6). In comparison to normal amide bands (λ = 1650 - 1690 cm^{-1}) the peak maximum is somewhat shifted to a higher wave number which might be due to some stress exerted by the cyclodextrin channel onto the polymer chain. The yield y was determined from the integral of the absorbance of the amide band from ν = 1640 to 1850 cm^{-1}, $\int$abs(amide), relative to the integral of the absorbance of the alkyl band from ν = 2820 to 2990 cm^{-1}, $\int$abs(alkyl), which was taken as an internal reference. Thus the yield was calculated according to formula (1). The constants k and a were determined from a totally converted and an unreacted sample, respectively.

$$y = k\int abs(amide) / \int abs(alkyl) - a \qquad (1)$$

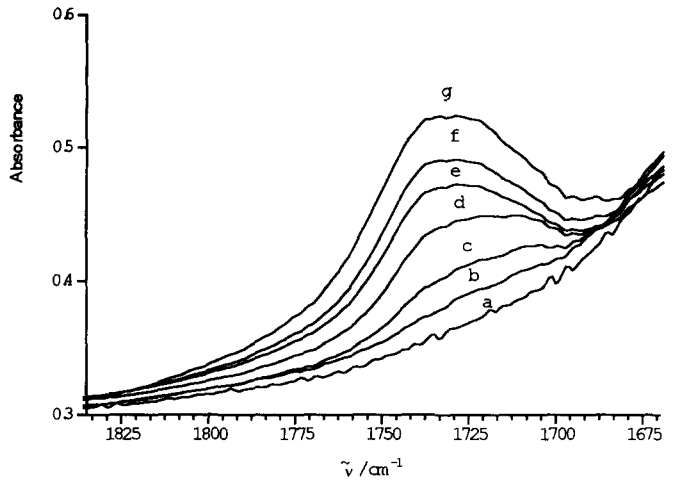

Fig. 6: Control by IR-spectroscopy of the polycondensation of **2·1a$_2$** after a) 0 h, b) 0.5 h, c) 1 h, d) 1.5 h, e) 3 h, f) 4 h g) 6 h at 220°C

In addition, the yield was determined by gravimetry of the produced polyamide p-**2**. For this purpose cyclodextrin was cleaved completely by heating the samples in 1% HCl at 80°C for 24 h. The free polyamide p-**2** precipitates and was isolated by filtration. The yields determined by both methods were in good agreement. For low conversions the IR method was better suited than the gravimetric one as oligomeric products are partially watersoluble.

5. Kinetics of the Polycondensation of **2·1a$_2$**

The kinetics of the polycondensation of **2·1a$_2$** was investigated in some detail (fig. 7). At a temperature of 190°C the reaction was still rather slow. For example it took 22 h to reach a conversion of k = 12 %. At temperatures higher than 190 °C the reaction became much faster and conversions close to 100 % could be reached.

The kinetics were simple first order and data points could be fitted by equation (2).

$$k = 1\text{-}\exp(-k_1 t) \qquad (2)$$

These observed first order kinetics are in good accordance with the following model for the polycondensation process. The reaction takes place in N_0 independent reaction sites with the same probability. Each site consists of a alkylammonium carboxylate moiety. The rate of polycondensation -dN/dt is proportional to the number of unreacted sites N accordingt to $-dN/dt = k_1 N$. Integration and the substitution $1\text{-}N/N_0 = k$ leads to the first order law eq. (2).

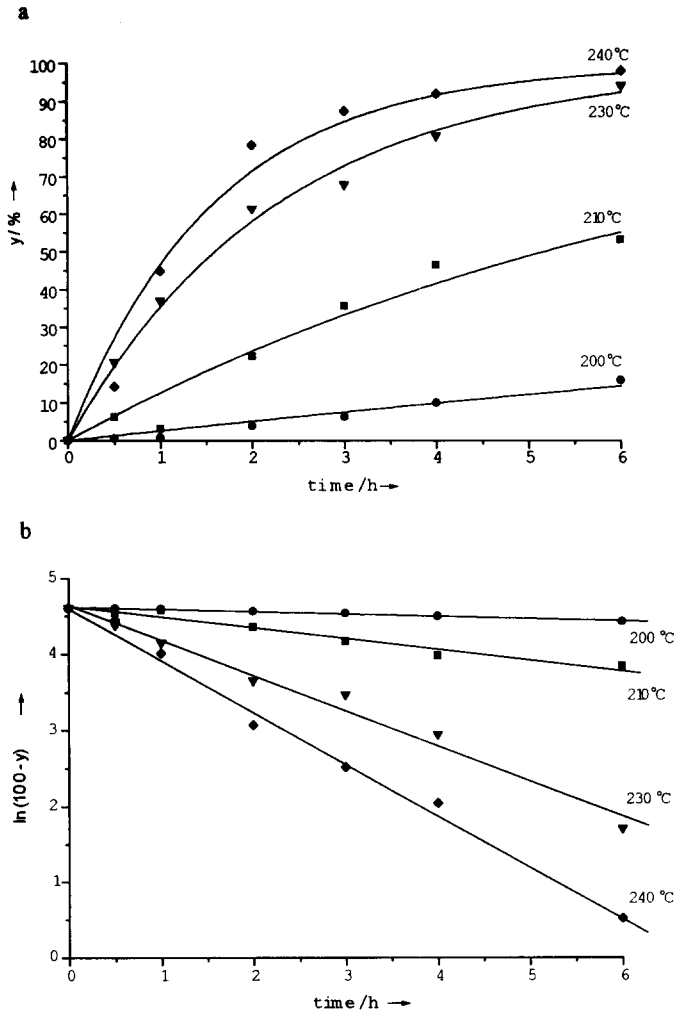

Fig. 7: Kinetics of the polycondensation of **2·1a**$_2$; a) yield y versus time, curves calculated according to eq. (2); b) first order plot

The Arrhenius plot (fig. 8) of the obtained first order rate constants k_1 did not show linearity which would be expected if only one activation process would control the reaction rate. At low temperatures the slope of the data points is high corresponding to an activation energy of E_a = 260 kJ/mol. At higher temperatures the slope becomes smaller equivalent to a smaller activation energy of E_a = 100 kJ/mol. At the low temperatures the reaction might be lattice controlled. At the high temperatures some partial melting or softening of the crystal might occur which facilitates the motion of the functional groups towards each other necessary for the polycondensation. The activation energy E_a = 100 kJ/mol is in a good agreement with those activation energies observed for normal melt polycondensations of ammonium carboxylates without cyclodextrins.[45]

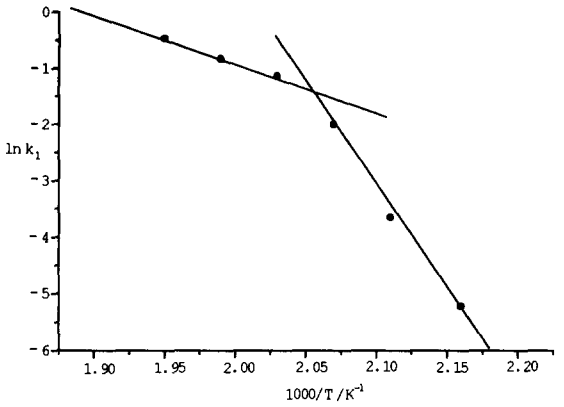

Fig. 8: Arrhenius plot of the first order rate constants k_1 of the polycondensation of **2**·**1a**$_2$

6. Determination of the Molecular Weight of the Nylon-11 Inclusion Compound p-(**2**·**1a**$_2$)

For the determination of the molecular weight of p-(**2**·**1a**$_2$) the free polyamide p-**2** was isolated after acidic hydrolysis of the threaded cyclodextrin **1a**. After conversion of the polyamide into the more soluble N-trifluoracetyl derivative p-(**2**-$COCF_3$) the peak molecular weight M was determined by SEC.[46,47] From the obtained value of M_w of p-(**2**-$COCF_3$) the corresponding values of M for polyamide p-**2** and the inclusion compound p-(**2**·**1a**$_2$) were calculated (s. tab. 1). The degree of polymerization DP of the polymer p-**2** was 19. Higher degrees of polymerization could not be reached up to now as an increase of both the duration and temperature of the polycondensation caused an intolerable decomposition of the cyclodextrin. Therefore no material suitable for drawing fibbers could be prepared.

7. Solution Properties of p-(**2**·**1a**$_2$)

To our surprise the polycondensate p-(**2**·**1a**$_2$) was completely soluble in water at room temperature. For comparison, the free polymer p-**2** is absolutely insoluble in water. The ^{1}H-NMR spectrum of this solution comprises the signals of both the threaded α-cyclodextrin rings and the polymer backbone (fig. 9). The signals were broadened in comparison to the monomer **2** as typical for polymers. There was no indication for any aggregation of p-(**2**·**1a**$_2$). In the mixed solvent, [D_6]-DMSO / CD_3COOD, p-(**2**·**1a**$_2$) was also soluble. The ^{1}H-NMR spectrum was better resolved than in D_2O. Especially for the proton H-1 of **1a** a sharp signal was found. Therefore any covalent bond between the polymer and the cyclodextrin ring could be excluded as this would break the C_6 symmetry of the ring. The composition of two rings per repeat unit of the polymer was confirmed by integration of the ^{1}H-NMR signals. This high coverage of the polymer chain by **1a** appears to be the reason for the high solubility of the polymer.

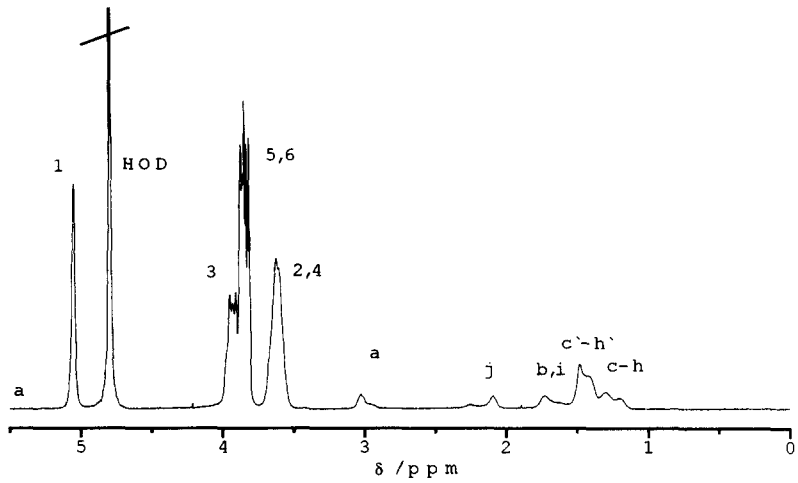

Fig. 9: ^{1}H-NMR spectrum of p-(**2**·**1a**$_2$) in a) D_2O at 25 °C

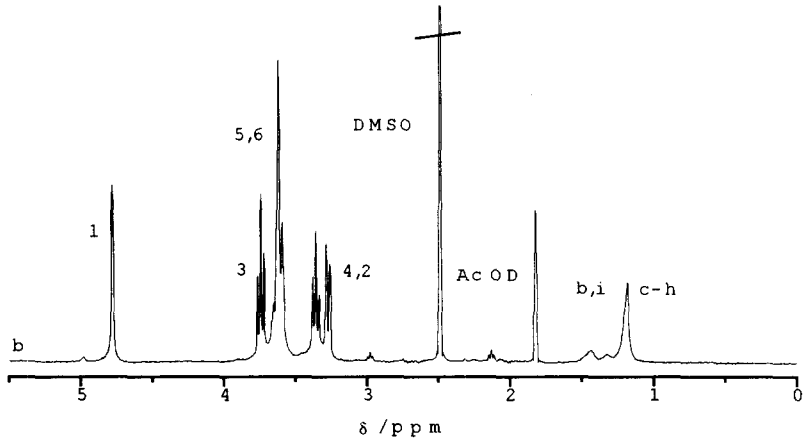

Fig. 9: ^{1}H-NMR spectrum of p-(**2**·**1a**$_2$) in b) DMSO at 25 °C

After some hours, the aqueous solution of p-(**2**·**1a**$_2$) turns turbid and some polymer precipitates. This precipitate had a 30 % lower content of α-cyclodextrin corresponding to a composition p-(**2**·**1a**$_{1.4}$). Because of this precipitation, ^{1}H-NMR spectra of p-(**2**·**1a**$_2$) had to be measured directly after dissolution of the polymer. Apparently the polymeric inclusion compound p-(**2**·**1a**$_2$) starts to dissociate in solution. The free parts of the polymer chain start to aggregate and precipitate later, due to the strong intermolecular hydrogen bonds between the NH-and the CO-groups of the polyamide. Not all threaded rings can leave the polymer before it has precipitated.

8. Scope of the Solid-State Polycondensation in the Cyclodextrin Channels

Beside **2**·**1a**$_2$ a series of other cyclodextrin inclusion compounds of alkylammonium carboxylates was investigated. Upon heating of these inclusion compounds to 200 - 240 °C also polycondensation takes place as evidenced by IR spectroscopy and gravimetric determination of the formed polymer (Tab. 1).

Table 1: Peak Molecular Weights **M** and Degrees of Polymerization **DP** of the Inclusion Polyamides

Inclusion Polyamide	M / g mol^{-1}	DP
p-(**2**·**1a**)	11000	10
p-(**2**·**1a**$_2$)	40000	19
p-(**3**·**1a**$_2$):	19000	9
p-(**4**·**1a**):	4300	2-4
p-(**6**·**7**·**1a**$_4$)	13000	6

Compared to p-(**2**·**1a**$_2$) the degree of polymerization obtained for shorter aminocarboxylic acids decreased with decreasing length of the monomeric guest. 6-Aminohexanoic acid did not show any polycondensation in the α-cyclodextrin channel. Maybe this monomer is too short to allow a close contact between the reactive groups in the crystal.

Also the ternary inclusion compound consisting of 1,10-decanedioic acid **7** and 1,10-diaminodecane **6**, both included in two α-cyclodextrin rings each, could be polycondensed. A degree of polymerization was DP = 6 This finding shows that the two different guests are included in an alternating sequence in the cyclodextrin channel. This alternating sequence was attributed to the formation of strong hydrogen bonds and Coulomb interactions between the ammonium and carboxylate groups.

11-(N-piperazinyl)-undecanoic acid **3** can also be polycondensated within the α-cyclodextrin channel. The piperazinyl moieties might be located in the space between two adjacent cyclodextrin rings. A moderate degree of polymerization was achieved. Especially in the case of the dimethylated 11-piperazinyl-undecanoic acid **4**, some decomposition became obvious as the sample turned brown upon annealing at 230 °C. Therefore only a low degree of polymerization DP = 2 - 4 of the resulting polyamide p-**4** was reached. The NMR-spectra showed that **1a** remained mostly intact. The polymeric inclusion compound p-(**4**·**1a**$_2$) was permanently soluble in water. Therefore low molecular weight byproducts could be removed by aqueous ultrafiltration. A polymer fraction p-·**1a**$_2$ was isolated in 58 % yield. The ^{1}H-NMR spectrum of it shows the signals of the threaded cyclodextrin rings. The signals of protons H-1 (and H-3) were shifted to lower (higher) field in comparison to free **1a**, which proves the supramolecular structure of p-(**4**·**1a**$_2$).[24] Consequently, p-(**4**·**1a**$_2$) is a polyrotaxane. The methyl substituents at the piperazin apparently hinder the dissociation of the cyclodextrin rings from the polymer chain.

Only for the inclusion compound of aromatic guest **5** no polycondensation was observed. The herring

bone arrangement of the host and guest molecules seems to prevent a close contact between carboxylic and ammonium groups which is necessary for a polycondensation.

In conclusion, a great variety of alkylammonium carboxylates could be polycondensed in their α-cyclodextrin inclusion compounds. As the reactivity of the included monomers depends on the lengths of the monomers, some topochemical control[48-50] of the solid-state reactivity appears reasonable. Due to the restricted mobility within the crystalline array the reactive groups have to be in appropriate positions to allow any reaction. α-Cyclodextrin was found to be surprisingly stable at high temperatures (up to 240°C), but not stable enough to obtain high molecular weight polyamides. For the synthesis of high molecular weight polymers within the cyclodextrin channels polycondensations have to be found with lower reaction temperatures. A synthetic challenge would be the synthesis of high tensile strength polyaramides within the channels of β-cyclodextrin. This task will be the topic of future investigations.

Experimental

General. α-Cyclodextrin was donated from Consortium für elektrochemische Industrie GmbH (Wacker Chemie), München, Germany. All other reagents were purchased from Aldrich and used without further purification. α-Cyclodextrin was dried in vacuum for 24 hours at 90°C before use. The ^{1}H NMR spectra were measured with a Bruker AM 400 spectrometer, operating at 400.14 MHz for ^{1}H and 100.62 MHz for ^{13}C, using D_2O or a mixture of [D_6]-DMSO / CD_3COOD as the solvent and the HOD signal at δ = 4.80 ppm or the DMSO signal at δ = 2.49 ppm as internal reference. All chemical shifts are quoted in ppm on the δ scale, J values are expressed in Hz. The carbon atoms in the α-cyclodextrin are numbered from 1 to 6, the carbon atoms in aliphatic chains were numbered from a to k starting at the amino group. The solid-state ^{13}C-CP-MAS NMR spectra were recorded by a Bruker MSL-300 spectrometer, at the Max-Planck Institut für Polymerforschung, Mainz, Germany, using dipolar decoupling, cross polarization time 1.5 ms, 1000 scans rotational frequency 3000 Hz. The IR spectra were recorded by a Bruker FT-IR spectrometer IFS 28 using KBr pellets. Wide angle X-ray powder diffractograms (WAS) were measured with a Siemens S-5000 diffractometer with Cu K_α radiation at 22°C. Size exclusion chromatography (SEC) was performed with Waters Styragel Columns, calibrated with narrow molecular weight polystyrene standards using THF as the eluent. The microcalorimetric titration was performed in sodium acetate buffer with an OMEGA instrument from Microcal Inc., Northampton, USA. Data were processed by the program ORIGIN.

Monomeric Inclusion compounds

2·**1a**: 1.16 g (5.74 mmol) of 11-aminoundecanoic acid **2** and 5.6 g (5.74 mmol) of **1a** were dissolved in 80 ml of water and heated to 80°C upon stirring. The solution was then quickly cooled to 5°C. After 24 hours the resulting precipitate was filtered, washed with water (400 ml) and dried under vacuum at 90°C. Yield: 3.66 g (55 %). ^{1}H-NMR (D_2O): δ = 5.07 (d, 6 H, ^{3}J (H,H) = 3.44 Hz, H-1), 4.80 (HOD), 3.92 (t, 6 H, ^{3}J

(H,H) = 7.38 Hz, H-3), 3.85 - 3.75 (m, 18 H, H-5, 6), 3.70 - 3.55 (m, 12 H, H-2,4), 3.03 (m, 2 H, H-a), 2.09 (m, 2 H, H-j), 1.73 (m, 4 H, H-b, i), 1.48 - 1.20 (m, 12 H, H-c-h) ppm. IR (KBr): ν = 3367 s, 2927 s, 1630 m, 1560 m, 1408 m, 1361 m, 1329 m, 1152 s, 1078 s, 1030 s, 949 m, 938 m, 703 m, 572 m cm^{-1}. ^{13}C-CP-MAS: δ = 182 (C-k), 103 (C-1), 83 (C-4), 73 (C-2,3,5), 64 (C-6), 39 (C-a), 33.0, 29.5, 28.2, 25.3 (C-b-j) ppm. WAXS: 2 Θ = 5.47, 7.30, 11.16, 11.91, 12.84, 15.86, 22.39, 19.56°. EA: calc.: C: 48.07, H: 7.12, N: 1.19, found: C: 47.90, H: 7.21, N: 1.54 %.

2·1a$_2$: 5 g (24.9 mmol) of 11-aminoundecanoic acid **2** and 125 g (129 mmol) of **1a** were dissolved in 250 ml of water and heated to 80°C upon stirring. The solution was then quickly cooled to 5°C. After 24 hours the resulting precipitate was filtered, washed with water (400 ml) and dried under vacuum at 90°C. Yield: 3.957 g (65.0 %). ^{1}H-NMR (D_2O): δ = 5.05 (s, 12 H, H-1), 4.80 (HOD), 3.93 (t, 12.5 H, ^{3}J (H,H) = 8.9 Hz, H-3), 3.85 - 3.75 (m, 38.5 H, H-5, 6), 3.70 - 3.55 (m, 24.4 H, H-2, 4), 3.02 (m, 0.7 H, H-a), 2.09 (m, 0.6 H, H-j), 1.73 (m, 1.75 H, H-b, i), 1.48-1.20 (m, 11.6 H, H-c-h) ppm. ^{1}H-NMR ([D_6]-DMSO / CD_3COOD 10:1): δ = 4.78 (d, 12 H, ^{3}J (H,H) = 1.73 Hz, H-1), 3.74 (t, 12 H, ^{3}J (H,H) = 8.9 Hz, H-3), 3.63 (m, 36 H, H-5,6), 3.37 (t, 12 H, ^{3}J (H,H) = 8.86 Hz, H-4), 3.26 (dd, 12 H, ^{3}J (H,H) = 1.73 Hz, ^{3}J (H,H) = 8.86 Hz, H-2), 2.73 (t, 1.7 H, ^{3}J (H,H) = 7.38 Hz, H-a), 2.15 (t, 1.7 H, ^{3}J (H,H) = 7.39 Hz, H-j), 1.47 (m, 3.7 H, H-b,i), 1.23 (s, 12 H, H-c-h) ppm. IR (KBr): ν = 3408 s, 2925 s, 1635 m, 1410 w, 1362 w, 1291 w, 1246 w, 1202 w, 1162 s, 1095 s, 938 m cm^{-1}. ^{13}C-CP-MAS: δ = 182 (C-k), 103 (C-1), 83 (C-4), 71 (C-2,3,5), 64 (C-6), 39 (C-a), 33.5, 30.5, 28.5, 26 (C-b-j) ppm. WAXS: 2 Θ = 5.43, 7.42, 11.64, 12.80, 15.03, 19.57, 22.49°. EA: calc.: C: 46.43, H: 6.71, N: 0.65, found: C: 45.52, H: 7.03, N: 1.14 %.

3·1a$_2$: in analogy to **2·1a$_2$**, yield: 3.388 g, (56 %). ^{1}H-NMR ([D_6]-DMSO / CD_3COOD 10:1): δ = 4.80 (d, 12 H, ^{3}J (H,H) = 1.73 Hz, H-1), 3.76 (t, 12.76 H, ^{3}J (H,H) = 8.9 Hz, H-3), 3,60 (m, 37.5 H, H-5,6), 3.39 (t, 12.6 H, ^{3}J (H,H) = 8.86 Hz, H-4), 3.28 (dd, 12.8 H, ^{3}J (H_1,H_2) = 1.73 Hz, ^{3}J (H,H) = 8.86 Hz, H-2), 3.06 (t, 3.93 H, ^{3}J (H,H) = 4.92 Hz, H-l), 2.56 (m, 3.54 H, H-k), 2.31 (t, 1.8 H, ^{3}J (H,H) = 7.39 Hz, H-j), 2.16 (t, 1.87 H, ^{3}J (H,H) = 7.39 Hz, H-a), 1.46 (m, 3.90 H, H-b,i), 1.21 (s, 12.4 H, H-c-h) ppm. IR (KBr): ν = 3364 s, 2927 s, 1568 s, 1366 w, 1331 w, 1162 s, 1090 s, 936 s, 759 w cm^{-1}. WAXS: 2 Θ = 3.46, 5.11, 6.03, 10.37, 12.58, 15.52, 16.34, 17.26, 17.82, 19.47, 22.05, 38.06°. EA: calc.: C: 46.81, H: 6.74, N: 1.10, found: C: 46.58, H: 6.93, N: 1.63 %.

4·1a$_2$: in analogy to **2·1a$_2$**, yield: 1.040 g, (17.2 %). ^{1}H-NMR (D_2O): δ = 5.06 (d, 12 H, ^{3}J (H,H) = 3.44 Hz, H-1), 4.80 (HOD), 3.93 (t, ^{3}J (H,H) = 7.38 Hz, 12 H, H-3), 3.85 - 3.75 (m, 36 H, H-5, 6), 3.70 - 3.55 (m, 24 H, H-2,4), 3.49 (m, 5.24 H, H-l,m,n,n′), 3.06 (t, ^{3}J (H,H) = 3.7 Hz, 1.87 H, H-a), 2.08 (m, 1.79 H, H-j), 1.65-1.45 (m, 3.78 H, H-b, i), 1.45 - 1.20 (m, 12 H, H-c-h), 1.26 (d, ^{3}J (H,H) = 3.2 Hz, 3 H, H-p), 1.22 (d, ^{3}J (H,H) = 3.2 Hz, 2.97 H, H-p′) ppm. IR (KBr): ν = 3359 s, 2926 s, 1568 s, 1366 w, 1332 w, 1162 s, 1090 s, 936 s, 759 w, 704 m, 583 m, 524 m cm^{-1}. WAXS: 2 Θ = 5.31, 10.84, 11.17, 19.55°. EA: calc.: C: 47.63, H: 6.91, N: 1.24, found: C: 47.60, H: 7.02, N: 1.64 %.

5·1a : 0.5 g (3,308 mmol) **5** and 4.3 g (3,789 mmol) **1b** were dissolved in 50 ml of water and heated to 80°C upon stirring. The solution was then quickly cooled to 5°C. After 24 hours the resulting precipitate was filtered, three times washed with water (30 ml) and dried under vacuum at 90°C. Yield: 2.86 g (67 %). ^{1}H-NMR ([D_6]-DMSO / CD_3COOD 10:1): δ = 7.97 (d, 2 H, ^{3}J (H,H) = 8.05 Hz, H-c), 7.54 (d, 2 H, ^{3}J (H,H) = 8.05 Hz, H-b), 4.81 (d, 7 H, ^{3}J (H,H) = 1.73 Hz, H-1), 4.09 (s, 2 H, H-a), 3.75-3.50 (m, 21 H, H-3, 5, 6), 3.40-3.25 (m, 14 H, H-2, 4), 1.86 (AcOD) ppm. IR (KBr): ν = 3357 s, 2917 s, 1598 m, 1555 m, 1372 m, 1297 s, 1155 s, 1080 s, 1029 s, 947 m, 848 m, 756 w, 707 w cm^{-1}. WAXS: 2Θ = 4.28, 5.69, 10.35, 12.28, 14.12, 15.22, 16.51, 18.00, 19.17, 20.65°.EA: calc.: C: 46.12, H: 6.11, N: 1.07, found: C: 46.32, H: 6.32, N: 1.54 %.

6·7·1a$_4$: in analogy to **2·1a$_2$**, yield: 4.72 g (38.3 %). ^{1}H-NMR ([D_6]-DMSO / CD_3COOD 10:1): δ = 4.78 (d, 24 H, ^{3}J (H,H) = 1.73 Hz, H-1), 3.74 (t, 24 H, ^{3}J (H,H) = 8.86 Hz, H-3), 3.61 (m, 48 H, H-5.6), 3.36 (t, 24 H, ^{3}J (H,H) = 8.86 Hz, H-4), 3.26 (dd, 24 H, ^{3}J (H_1,H_2) = 1.73 Hz,J_{2-3} = 8.86 Hz, H-2), 2.73 (t, 4 H, ^{3}J (H,H) = 7.38 Hz, H-a), 2.49 (AcOD), 2.15 (t, 4 H, ^{3}J (H,H) = 7.39 Hz, H-α), 1.45 (m, 8 H, H-b,β), 1.22 (s, 24 H, H-c-e,γ-ε) ppm. IR (KBr): ν = 3383 s, 2923 s, 1644 w, 1550 w, 1404 w, 1361 w, 1291 w, 1205 w, 1148 s, 1038 s, 938 m, 756 w, 610 w, 570 w cm^{-1}. WAXS: 2 Θ = 5.36, 7.21, 9.06, 10.90, 11.71, 12.72, 15.77, 17.06, 19.72, 20.56, 22.57, 33.24°. EA: calc.: C: 46.11, H: 6.80, N: 0.66, found: C: 45.92, H: 7.03, N: 1.03 %.

Polymeric inclusion compounds and Polymers

p-(**2·1a$_2$**) : 203 mg of **2·1a$_2$** was annealed in a glastube at 240°C and 0.1 mbar for 5 h. Yield: 196 mg (97.4 %), light brown powder. ^{1}H-NMR (D_2O): δ = 5.08 (s, 12 H, H-1), 4.0 - 3.75 (m, 52 H, H-3,5,6), 3.75 - 3.50 (m, 25, 4 H, H-2,4), 3.0 (m, 2 H, H-a), 2.30 - 2.05 (m, 2 H, H-j), 1.75 - 1.6 (m, 4 H, H-b,i), 1.50 - 1.15 (m, 12 H, H-c-h) ppm. ^{1}H-NMR ([D_6]-DMSO / CD_3COOD 10:1): δ = 4.78 (d, 12 H, ^{3}J (H,H) = 1.73 Hz, H-1), 3.74 (t, 12 H, ^{3}J (H,H) = 8.9 Hz, H-3), 3.62 (m, 36 H, H-5,6), 3.36 (t, 12 H, ^{3}J (H,H) = 8.86 Hz, H-4), 3.26 (dd, 12 H, ^{3}J (H,H) = 1.73 Hz, ^{3}J (H,H) = 8.86 Hz, H-2), 2.98 (t, 1,7 H, ^{3}J (H,H) = 7.38 Hz, H-a), 2.49 (DMSO), 2.13 (t, 1.7H, ^{3}J (H,H) = 7.39 Hz, H-j), 1.44 (m, 3.7 H, H-b,i), 1.35 - 1.15 (m, 12 H, H-c-h) ppm. IR (KBr): ν = 3399 s, 2925 s, 2362 w, 1733 m, 1646 m, 1410 w, 1362 w, 1161 s, 1087 s, 938 m, 862 w, 755 w, 706 w, 703 w, 579 m cm^{-1}. ^{13}C-CP-MAS: δ = 103 C-1, 83 C-4, 71 C-2,3,5, 64 C-6, 39-26 C-a-j ppm. WAXS: 2 Θ = 7.28, 11.93, 12.74, 15.91, 19.68, 22.33, 41.96, 42.92°. EA: calc.: C: 46.83, H: 6.68, N: 0.66, found: C: 46.61, H: 6.96, N: 1.14 %.

p-**2**: 1.172 g p-(**2·1a$_2$**) was stirred in 60 ml of 1% HCl at 80°C for 25 h. The resulting precipitate was filtered and washed three times with 50 ml water and methanol. Yield: 103.1 mg (94 %).

p-(**2**-$COCF_3$) : 90 mg p-**2** (0.49 mmol) was added to 15 ml absolute CH_2Cl_2 and stirred for 16h with trifluoracetic anhydride (0.21 g, 1.0 mmol) at 25°C. After removal of the solvent by destillation, the residue

was dried in vacuum (0.1 mbar) at 80 °C. Yield: 129 mg, 46 mmol (94 %). ^{1}H-NMR ($CDCl_3$): δ = 2.87 (m, 22 H, H-a), 1.96 (m, 2 H, H-j), 1.19 - 1.10 (m, 4 H, H-b, i), 0.82 (m, 12 H, H-c-h) ppm. IR (KBr): ν = 3399 s, 2935 s, 2853 m, 2359 w, 1734 m, 1644 m, 1556 m, 1157 m cm^{-1}.

p-(**2**-**1a**) : in analogy to p-(**2**-**1a**$_2$), yield: 196 mg (97 %), light brown powder: ^{1}H-NMR ([D_6]-DMSO / CD_3COOD 10:1): δ = 4.78 (d, 6 H, ^{3}J (H,H) = 1.73 Hz, H-1), 3.77 (t, 6 H, ^{3}J (H,H) = 8.9 Hz, H-3), 3.63 (m, 18 H, H-5,6), 3.36 (t, 6 H, ^{3}J (H,H) = 8.86 Hz, H-4), 3.26 (dd, 6 H, ^{3}J (H_1,H_2) = 1.73 Hz, ^{3}J (H_2,H_3) = 8.86 Hz, H-2), 2.98 (t, 1.7 H, ^{3}J (H,H) = 7.38 Hz, H-a), 2.14 (t, 1.7 H, ^{3}J (H,H) = 7.39 Hz, H-j), 1.87 (AcOD), 1,44 (m, 4 H, H-b,i), 1.35 - 1.15 (m, 12 H, H-c-h) ppm. IR (KBr): ν = 3367 s, 2927 s, 1733 m, 1630 m, 1560 m, 1408 m, 1361 m, 1329 m, 1152 s, 1078 s, 1030 s, 949 m, 938 m, 703 m, 572 m cm^{-1}. WAXS: 2 Θ = 5.47, 7.28, 11.93, 12.74, 15.91, 19.68, 22.33, 41.96, 42.92°. EA: calc.: C: 48.83, H: 7.06, N: 1.21, found: C: 48.91, H: 7.13, N: 1.54 %.

p-(**3**-**1a**$_2$): in analogy to p-(**2**-**1a**$_2$), yield: 184 mg (96 %), brown powder. ^{1}H-NMR ([D_6]-DMSO / CD_3COOD 10:1): δ = 4.78 (d, 12 H, ^{3}J (H,H) = 1.73 Hz, H-1), 3.76 (t, 12.76 H, ^{3}J (H,H) = 8.9 Hz, H-3), 3.60 (m, 37.5 H, H-5,6), 3.39 (t, 12.6 H, ^{3}J (H,H) = 8.86 Hz, H-4), 3.28 (dd, 12.8 H, ^{3}J (H,H) = 1,73 Hz, ^{3}J (H,H) = 8.86 Hz, H-2), 3.06 (t, 3.93 H, ^{3}J (H,H) = 4.92 Hz, H-l), 2.56 (m, 3.54 H, H-k), 2.31 (t, 1.8 H, ^{3}J (H,H) = 7.39 Hz, H-j), 2.16 (t, 1.87 H, ^{3}J (H,H) = 7.39 Hz, H-a), 1.46 (m, 3.90 H, H-b,i), 1.35 - 1.15 (m, 12.4 H, H-c-h) ppm. IR (KBr): 3411 s, 2931 s, 1729 m, 1568 m, 1363 m, 1161 s, 1084 s, 937 w, 860 w, 757 w, 707 m, 582 m, 531 m cm^{-1}. WAXS: 2 Θ = 5.11, 10.37, 17.26, 19.47, 22.05, 38.06, 40.02°. EA: calc.: C: 47.54, H: 6.79, N: 1.27, found: C: 47.51, H: 6.85, N: 1.43 %.

p-(**4**-**1a**): in analogy to p-(**2**-**1a**$_2$), afterwards the product was dissolved in 100 ml of water and passed through a nylon filter (pore size 0.45 μm). Then the solution was ultrafiltrated (pore size 4000 Dalton) with 1000 ml of water. The retentate solution was freeze-dried. Yield: 180 mg, (58 %), brown powder: ^{1}H-NMR (D_2O): δ = 4.94 (s, 6 H, H-1), 4.70 (HOD), 3.74 (t, 6, ^{3}J (H,H) = 8.5 Hz, H-3), 3.77 (m, 18 H, H-5,6), 3.54 (m, 12 H, H-2,4), 3.50 - 3.25 (m, 6 H, H-l,m,n,n′), 2.91 (t, 2 H, ^{3}J (H,H) = 7.5 Hz, H-a), 2.19 (t, 2 H, ^{3}J (H,H) = 6.0 Hz, H-j), 1.88 (AcOD), 1.65 - 1.35 (m, 4 H, H-b,i), 1.35 - 1.18 (m, 12 H, H-c-h), 1.24 (d, ^{3}J (H,H) = 3.0 Hz, 3 H, H-p), 1.21 (d, ^{3}J (H,H) = 3.0 Hz, 3 H, H-p′) ppm. IR (KBr): ν = 3342 s, 2928 s, 2890 m, 1735 m, 1706 m, 1656 m, 1153 s, 1080 s, 1040s, 708 m, 578 m, cm^{-1}. WAXS: 2 Θ = 19.63°. EA: calc.: C: 51.26, H: 7.23, N: 2.21, found: C: 51.23, H: 7.28, N: 2.43 %.

p-(**6**-**7**-**1a**$_4$) : in analogy to p-(**2**-**1a**$_2$), yield: 169 mg (97 %), brown powder: ^{1}H-NMR ([D_6]-DMSO / CD_3COOD 10:1): δ = 4.78 (d, 24 H, ^{3}J (H,H) = 1.73 Hz, H-1), 3.74 (t, 24 H, ^{3}J (H,H) = 8.86 Hz, H-3), 3.61 (m, 48 H, H-5,6), 3.36 (t, 24 H, ^{3}J (H,H) = 8.86 Hz, H-4), 3.26 (dd, 24 H, ^{3}J (H_1,H_2) = 1.73 Hz, ^{3}J (H_2,H_3) = 8.86 Hz, H-2), 2.94 (m, 4 H, H-a), 2.49 (AcOD), 2.15 (t, 4 H, ^{3}J (H,H) = 7.39 Hz, H-α), 1.45 (m, 8 H, H-b,β), 1.35 - 1.20 (m, 24 H, H-c-e,γ-ε) ppm. IR (KBr): ν = 3383 s, 2923 s, 1732 m, 1644 m, 1550 w, 1404w, 1361w, 1291w, 1205 w, 1148 s, 1038 s, 938 m, 756 w, 610 w, 570 w cm^{-1}. WAXS: 2 Θ = 5.41, 11.71,

15.77, 17.08, 19.68, 22.57, 33.24°. EA: calc.: C: 46.57, H: 6.62, N: 0.66, found: C: 46.52, H: 6.96, N: 0.94 %.

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