Kinetics and Thermodynamics of the Inclusion of Ionene-6,10 in α-Cyclodextrin in an Aqueous Solution

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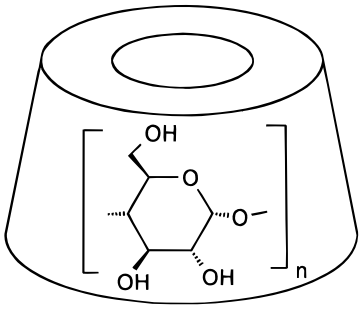
ABSTRACT: The kinetics of the inclusion of ionene-6,10 (**3b**) dibromide and of its monomeric model, 1,10-bis(trimethylammonium)decane (**5**) diiodide, by α-cyclodextrin (**1a**) were investigated by ^{1}H NMR spectroscopy in an aqueous solution. The inclusion of the monomer **5** is unusually slow and shows a high activation energy, $E_a = 63$ kJ mol^{-1}, which was attributed to a high steric hindrance for the threading caused by the terminal trimethylammonium groups. Microcalorimetric titration of **5** with **1a** revealed a stability constant, $K_S = 1540$ M^{-1}, of the inclusion compound. Because of its high kinetic stability, **5·1a** was termed a rotaxane. The inclusion of the ionene polymer by α-cyclodextrin takes days, months, or even years depending on the temperature. The kinetics could be described quantitatively by a *Monte Carlo* type of computer simulation of a consecutive hopping process of the rings along the polymer chain. The rate constants and activation energies for the polymer **3b** were found to be similar to those for the monomer **5**. A very high occupation of the polymer **3b** (95% of the repeat units) was reached by the thermally induced threading of **1a**. The resulting supramolecular structure of one polymer chain and about 65 rings was termed a polyrotaxane, as it can be isolated by GPC or dialysis.

Introduction

Threading rings onto linear polymer chains is an interesting area of research, as it provides a new principle for creating new polymeric materials from known polymers. The types of rings commonly used for threading include crown ethers,[1] cyclic paraquat derivatives,[2] and cyclodextrins.[3−6]

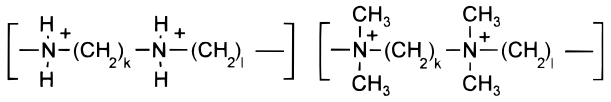
Cyclodextrins **1**, cyclic oligomers of glucose, are well-known to include monomeric hydrophobic guest molecules in aqueous solution.[4] The stability constant of these inclusion compounds increases with increasing length of the hydrophobic part of the guest, reaching values of $K_S = 20\,000$ M^{-1} and more.[7] The major driving force for the inclusion is the hydrophobic interaction.[8] α-Cyclodextrin **1a** is well suited to incorporate linear alkyl chains,[9−11] the larger cyclodextrins **1b** and **1c** also include benzene[12] and naphthalene[13] moieties and even larger molecules, such as steroids[14] and buckminster fullerene C_{60}.[15]

For the axial inclusion of a polymer by cyclodextrins, hydrophobic binding sites have to be part of the main chain and some solubility in water is also required. Thus, poly(ethylene glycol) can be included in **1a**, poly-

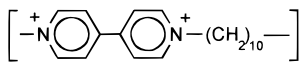


1a, b, c n=6,7,8

(propylene glycol) in **1b**, and poly(isobutene) and poly(methyl vinyl ether) in **1c** to form inclusion compounds which are insoluble in water.[16] Water-soluble inclusion compounds are formed from **1a** and poly(iminooligomethylene)s (**2**)[5,17] or ionenes **3** and **4**[18,19] containing



2 **3a** k=l=10 **3b** k=6 l=10



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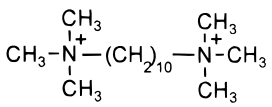
alkyl segments longer than seven methylene groups. The high solubility of these polymeric inclusion compounds allows the investigation of the kinetics of the threading process. We found that threading **1a** onto polymers **2**−**4** was quite slow, possibly because of some steric hindrance between the bulky cationic groups of the polymers and the cyclodextrin rings.

In this paper, we report the kinetics and temperature dependence of threading **1a** on the ionene polymer **3b** and its monomeric model **5**. These kinetic results are



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rationalized by a simple *Monte Carlo* type simulation model based on a consecutive hopping process.

Experimental Section

Materials. α-Cyclodextrin (Wacker-Chemie GmbH, München Germany, pharmaceutical grade, 99%) was dried for 16 h at 100 °C *in vacuo*. Unless specified otherwise, reagent-grade reactants and solvents were used as received from chemical suppliers.

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Measurements. ^{1}H NMR spectra were obtained on a 400 MHz Bruker spectrometer at 25 °C in a D_2O solution, reported in ppm and referenced to HOD (4.800 ppm) as the internal standard. Threading kinetics were run in a 12.2 mM solution of D_2O in NMR test tubes immersed in a water thermostat with temperatures 25, 60, and 80 ± 0.5 °C. The microcalorimetric titrations were performed with an Omega calorimeter (MicroCal Inc., Northampton, MA) using 1.336 mL sample and reference cells.[20] The reference cell was filled with pure solvent. The sample cell was filled with a 1.99 mM solution of **5** in 0.1 M phosphate buffer with pH 7.2. The 46.69 mM solution of **1a** in buffer was added automatically by a syringe with 20 portions of 5 μL.

GPC analysis of the polymer **3b** was performed with a setup from Waters Chromatography Division (Millipore Corp., Milford, MA) equipped with a HEMA 100 Bio column (Polymer Standards Service, Mainz, Germany) and elution with a mixture of 30 vol % of acetonitrile and 70 vol % of an aqueous solution of 0.5 M sodium acetate and 0.5 M acetic acid (flow rate 1 mL/min). Calibration was performed with narrow poly-[N-(methylvinyl)pyridinium iodide] standards (Polymer Standards Service, Mainz, Germany).

GPC analysis of the inclusion compound **3b·1a** was performed at room temperature with a setup consisting of a Gynkothek HPLC pump (flow rate 1 mL/min), a Rheodyne injection valve (injection volume 20 μL), a HEMA Bio column (Polymer Standards Service, Mainz, Germany; 1000 DEAE, 8 × 300 mm), and a continuous-flow polarimeter detector (Chiralizer, IBZ-Messtechnik, Hannover, Germany, cuvette length 10 cm, $\lambda = 589$ nm). Degassed water/acetonitrile/acetic acid (80:20:0.1) was used as the eluent.

The intrinsic viscosity of polymer **3b** was determined with an Ubbelode viscometer (type 50101, capillary 0a, Schott, Mainz, Germany) at 35 °C.

Kinetics of the dissociation were measured in a continuous dialysis apparatus which consisted of a circular array of a hollow fiber module (ALWALL GFE 12, Gambro GmbH, Hechingen, Germany), a peristaltic pump (MASTERFLEX, Barnant Co., Barrington, IL, flow 630 mL/h), a solution reservoir (stopped round bottom flask, 50 mL), and a continuous-flow polarimeter detector (Polarmonitor, IBZ Messtechnik, Hanover, Germany, $\lambda = 589$ nm) at room temperature. The digital value of the polarimeter angle α was recorded by a personal computer.

Poly[(*N*,*N*-dimethylammonio)hexamethylene-(*N*′,*N*′-dimethylammonio)-decamethylene dibromide] (3b Br$_2$).[21,22] A solution of 39.00 g (130.0 mmol) of 1,10-dibromodecane (Aldrich) and 22.40 g (130.0 mmol) of *N*,*N*,*N*′,*N*′-tetramethyl-1,6-diaminohexane (Aldrich) in 130 mL of a mixture of *N*-methylformamide/methanol (1:1) was heated to 50 °C for 14 days. Afterward the reaction mixture was added to 3 L of *tert*-butyl methyl ether. The precipitate was filtered, rinsed with *tert*-butyl methyl ether, and dried *in vacuo*. The aqueous solution of the crude product was dialyzed by a hollow fiber module (ALWALL GFE 12, Gambro GmbH, Hechingen, Germany) for 24 h to remove the fraction of low molecular weight. The retantate was freeze-dried to afford 37.3 g (78.9 mmol, 61%) of a white hygroscopic foam (**3b**). ^{1}H NMR (D_2O): δ 1.24−1.35 (m, 16 H, H-c-e, C), 1.67 (bs, 8 H, H-b, B), 2.96 (s, 12 H, Me), 3.18−3.22 (m, 8 H, H-a, A). The molecular weight, $M_w = 34\,000$, equivalent to a degree of polymerization $P_w = 68$, was determined by GPC. The intrinsic viscosity in 0.4 M KBr was $[\eta] = 18.95$ mL g^{-1}.

Polyrotaxane 3b·1a Br$_2$. A solution of 0.40 g (0.84 mmol) of **3b** and 145 g (149 mmol) of **1a** in 1 L of water was stirred for 35 days at 60 °C. The free cyclodextrin rings were removed by ultrafiltration. Freeze-drying afforded 1.20 g (0.82 mmol, 98%) of a white powder (**3b·1a**). ^{1}H NMR (D_2O): δ 1.23−1.51 (m, 16.0 H, H-c′-e′,c″-e″, C), 1.67, 1.75, 1.83 (bs, 8.0 H, H-b′,b″, B), 3.01 (s, 6.0 H, Me″), 3.06 (s, 6.0 H, Me′), 3.20−3.37 (m, 8 H, H-a′,a″,A), 3.60 (Ψ−t, $J = 4.3$ Hz, 6.0 H, H-4′), 3.67 (dd, $J = 9.7$ and 3.0 Hz, 6.0 H, H-2′), 3.75−3.86 (m, 24.0 H, H-3′,5′,6′), 5.05 (d, $J = 3.5$ Hz, 0.4 H, H-1), 5.08 (d, $J = 3.0$ Hz, 5.6 H, H-1′); the letters a, b, etc. indicate the decamethylene segment starting from the cationic group, A, B, and C, the hexamethylene segment. Signals of included repeating units are labeled with single and double primes.

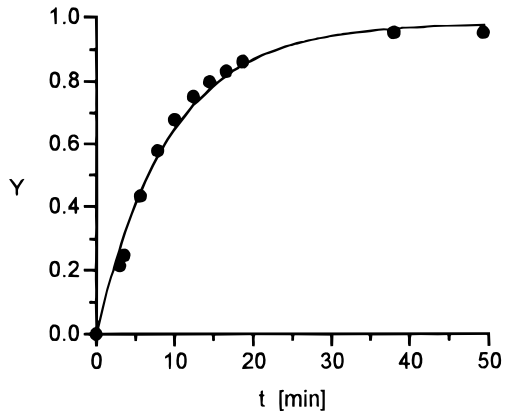

Figure 1. Kinetics of the inclusion of 49.7 mM **5** in 10.3 mM **1a** in D_2O at 25 °C.

***N*,*N*,*N*′,*N*′,*N*′-Hexamethyl-1,10-diaminodecane (5)** was synthesized according to the literature procedure.[23]

Results and Discussion

1. Kinetics of the Inclusion of the Monomeric Guest 5. 1,10-Bis(trimethylammonio)decane diiodide (**5**) was chosen as a monomeric model for ionenes **3**. The bulky trimethyammonium groups with a diameter of about 4−5 Å were expected to hinder threading of **1a** which has an internal diameter of about 5 Å.[24] The decamethylene chain of compound **5** was assumed to be long enough to provide an effective binding site for **1a**.

The inclusion of guest **5** in host **1a** was investigated by ^{1}H NMR spectroscopy in an aqueous solution. Similar to the inclusion of 1,10-diammoniodecane[25,26] and 1,10-bis(1-pyridinio)decane[11] by **1a**, new separate signals arose due to the formation of the inclusion compound. Signals of external protons of **1a** (H-1, H-2, H-4) were shifted downfield, while internal protons (H-3, H-5) were shifted upfield due to inclusion of **5**. The effect on the external protons seemed peculiar as there are no close contacts to the guest. This effect may be caused by guest induced conformational changes of the cyclodextrin from a cone toward a cylindrical form. The signals of the anomeric protons H-1 of **1a** are especially well-suited to detect the inclusion: the signal at 5.06 ppm was assigned to H-1 of free **1a**, the signal at 5.14 ppm was assigned to H-1′ of occupied **1a**. The yield y (based on **1a**) of inclusion was calculated from the integrals of both signals.

The inclusion process was slow enough that it could be directly monitored. The inclusion kinetics (Figure 1) were fitted to the function $y = y_\infty(1 - \exp(k_f[G]_0 t))$ for a pseudo-first-order rate law, as the initial concentration of the guest **5**, $[G]_0$, was in large excess to the concentration of **1a**. The second-order rate constant for the formation of the inclusion compound was $k_f = 0.036$ s^{-1} M^{-1}. From the limiting value of the yield, $y_\infty = 98\%$, a binding constant of $K_S = 1540 \int 400$ M^{-1} can be estimated.

2. Activation Energy of the Inclusion Process. The observed rate constant k_f for the formation of the inclusion compound is unusually small.[11,27,28] This low rate is likely caused by a high activation energy. For the determination of the activation energy of threading E_a, we measured the temperature dependence of the threading rate constants k_f of **5** in **1a** (Table 1). The Arrhenius plot revealed an activation energy of $E_a = 63 \pm 4$ kJ mol^{-1}. This high activation energy is most

Table 1. Stability and Rate Constants for the Inclusion of Guest 5 in Host 1a As Determined by ^{1}H NMR Spectroscopy

T [°C]	K_S [M^{-1}]	k_f [10^{-2} s^{-1} M^{-1}]	k_d [10^{-5} s^{-1}]	τ [10^3 s]
25	1540	3.6	2.4	28.8
35	700[a]	7.5	10.7	6.5
50	450[a]	25.9	57.6	1.1

[a] Determined by microcalorimetric titration (Table 2).

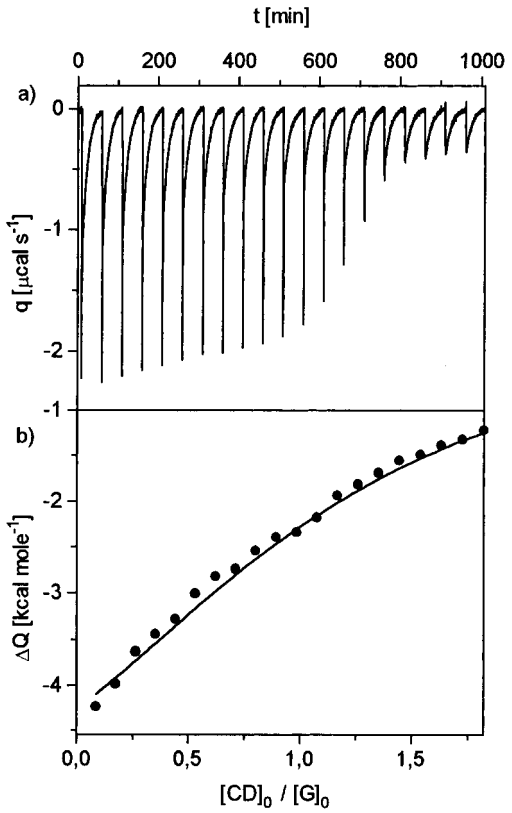

Figure 2. Microcalorimetric titration of 2.66 μmol **5** with 20 portions of 0.233 μmol **1a** each in phosphate buffer: (a) heat flow $q = dQ/dt$ vs time t; (b) heat of inclusion $\Delta Q = \int q\, dt - Q0$ vs the molar ratio of the total concentrations of cyclodextrin and guest $[CD]_0/[G]_0$. (—) Calculated for $K_S = 700$ M^{-1} and $\Delta H°_m{}' = -30$ kJ/mol.

likely due to the steric repulsion between the bulky trimethylammonium group and the interior of the α-cyclodextrin ring. For a guest with other bulky terminal groups, 1,10-bis(1-pyridinio)decane, a lower activation energy, $E_a = 51.9$ kJ mol^{-1}, was found for the threading process.[11] The pyridinium group appears to exert a smaller steric hindrance than the trimethylammonium group, as **1a** may adopt an elliptical shape to overcome the flat pyridinium group. This deformation of **1a** would not help to overcome the trimethylammonium group.

3. Thermodynamics of the Inclusion of 5 in 1a. The threading process was assumed to be driven by a gain of hydrophobic interactions between the decamethylene segment of the guest and the interior of the host **1a**. To reach a better understanding of this driving force, we measured the inclusion enthalpy, $\Delta H°_m{}'$, free enthalpy, $\Delta G°_m{}'$, and entropy by microcalorimetric titration of the guest **5** with the host **1a** in aqueous solution at 35 °C. We found exothermic signals of the heat flow, q, with every addition of **1a** (Figure 2a). Each of those peaks was integrated, $Q = \int q\, dt$, and corrected for the corresponding heat of dilution Q_0 of **1a**. The corrected heats, $\Delta Q = Q - Q_0$, were plotted as a function

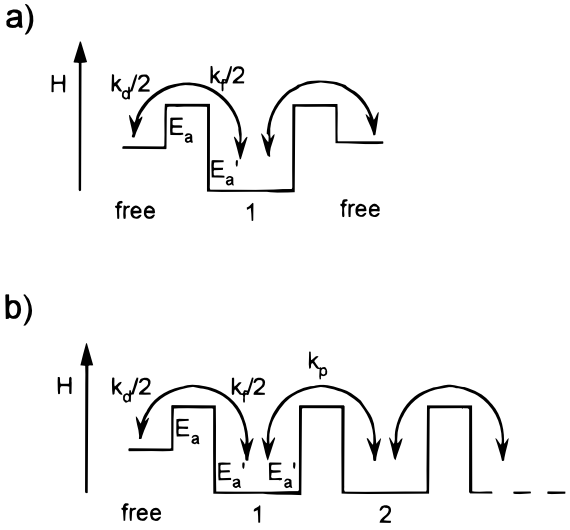

Figure 3. Schematic representation of the energy profile of the inclusion of (a) the monomer **5** in **1a** ($E_a = 63$, $E_a{}' = 93$ kJ mol^{-1}) and (b) the polymer **3b** in **1a** ($E_a{}' = 88$ kJ mol^{-1}).

Table 2. Thermodynamic Parameters for the Inclusion of 3b in 1a As Determined by Microcalorimetric Titration

T [°C]	K_S [M^{-1}]	$\Delta G°_m{}'$ [kJ mol^{-1}]	$\Delta H°_m{}'$ [kJ mol^{-1}]	$T\Delta S°_m{}'$ [kJ mol^{-1}]
35	700	−16.50	−30.00	13.57
50	450	−16.41	−34.53	18.12

of the ratio of the total concentrations of host and guest $[CD]_0/[G]_0$ (Figure 2b). These data were fitted by the curve calculated for the 1:1 complex with the parameters $K_S = 700 \pm 43$ M^{-1} and $\Delta H°_m{}' = -30 \pm 0.7$ kJ/mol (Table 2).

The highly exothermic value of $\Delta H°_m{}'$ implies that not only hydrophobic but also van der Waals interactions are responsible for this inclusion. The values of the binding constants, K_S were in a good agreement with those obtained directly from the yield of **1a·5** determined by ^{1}H NMR spectroscopy. Microcalorimetric titrations at 25 °C were rather inaccurate since the rate of inclusion was too small to measure any heat evolution. Therefore the data obtained by ^{1}H NMR spectroscopy are preferable in this case. Binding constants are somewhat smaller than the binding constants of other decane derivatives ($NH_3^+(CH_2)_{10}NH_3^+$, $K_S = 1960$ M^{-1}; $HO(CH_2)_{10}OH$, $K_S = 7100$ M^{-1}),[10,26] but in contrast to these guests, the inclusion of **5** in **1a** is accompanied by a significant loss of entropy of $T\Delta S°_m{}' > 10$ kJ mol^{-1}. This loss of entropy might be due to a highly restricted mobility of the host **1a** trapped between the bulky end groups at the guest **5**.

4. Rate and Activation Energy of the Dissociation Process of the Inclusion Compound 1a·5. From the kinetic and thermodynamic data, the energy profile of the inclusion was derived as shown in Figure 3a. The activation energy of the dissociation process, E'_a, was calculated from the activation energy of the formation, E_a, and the inclusion enthalpy, $\Delta H°_m{}'$, according to $E'_a = E_a - \Delta H°_m{}' = 93$ kJ/mol. This high activation barrier for the dissociation process explains the high kinetic stability of the inclusion compound **1a·5** with a half-life of $\tau = \ln 2/k_d = 8$ h at 25 °C. Since this inclusion compound can be separated by chromatographic methods, it was classified as a [2]rotaxane. The formation of [2]rotaxane **1a·5** is a new example for the so-called "slipping approach" according to the terminology of Stoddart.[29]

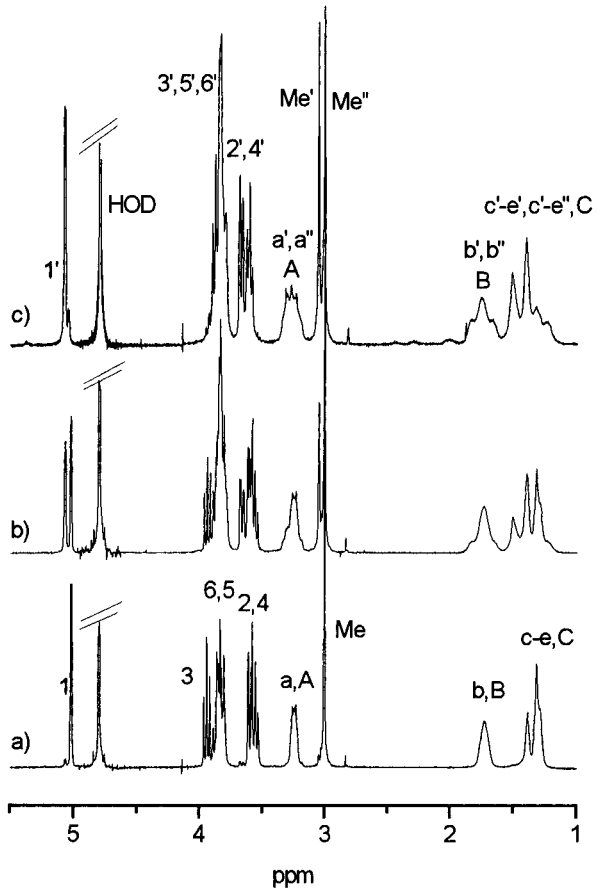

Figure 4. ^{1}H NMR spectra of a mixture of 12.2 mM **3b** and 12.2 mM **1a** in D_2O (a) after 3 h and (b) after 2 yr at 25 °C, conversion 55%, and (c) of the polyrotaxane **3b·1a**, conversion 95%.

5. Kinetics of the Inclusion of Ionene 3b by Host 1a. The inclusion of a long polymer chain, e.g., **3b**, with many bulky dimethylammonium groups along the chain should even be much slower than the inclusion of the monomeric model **5**, because one cyclodextrin ring has to overcome many activation barriers instead of one.

At room temperature the inclusion of **3b** in **1a** takes days before a noticeable change in the ^{1}H NMR spectrum occurs and 2 yr (!) to come close to completion (Figure 4). New characteristic signals were obtained for the threaded cyclodextrins at 5.08 (H-1′) and 3.69 ppm (H-2′) and the included methylene groups of the polymer **3b** at 3.30 (H-a′), 1.83 (H-b′) and 1,5 ppm (H-c′). The yield *y* of inclusion, equal to the fraction of the cyclodextrin rings bound to the polymer chain **1a,** was determined most accurately from the integrals of the ^{1}H NMR signals of H-1′ and H-1, in analogy with the monomeric system composed of **1a** and **5**.

The kinetics of the inclusion of **3b** by **1a** (Figure 5a) is relatively fast in the beginning and slows down significantly after a conversion of 10%. After 2 yr a conversion of 55% was reached. As the formation of the inclusion compound **3b·1a** was much too slow at 25 °C for any further investigation, we repeated the experiment at 60 and 80 °C (Figure 5b,c). The rate of inclusion rose tremendously with increasing temperature, and the inclusion process was finished after about 4 days at 80 °C. Despite the dramatic changes in the inclusion rates, the shapes and limiting conversions of these three kinetics remained very similar. This result suggested to us the possibility of a simple mathematical description of the inclusion process.

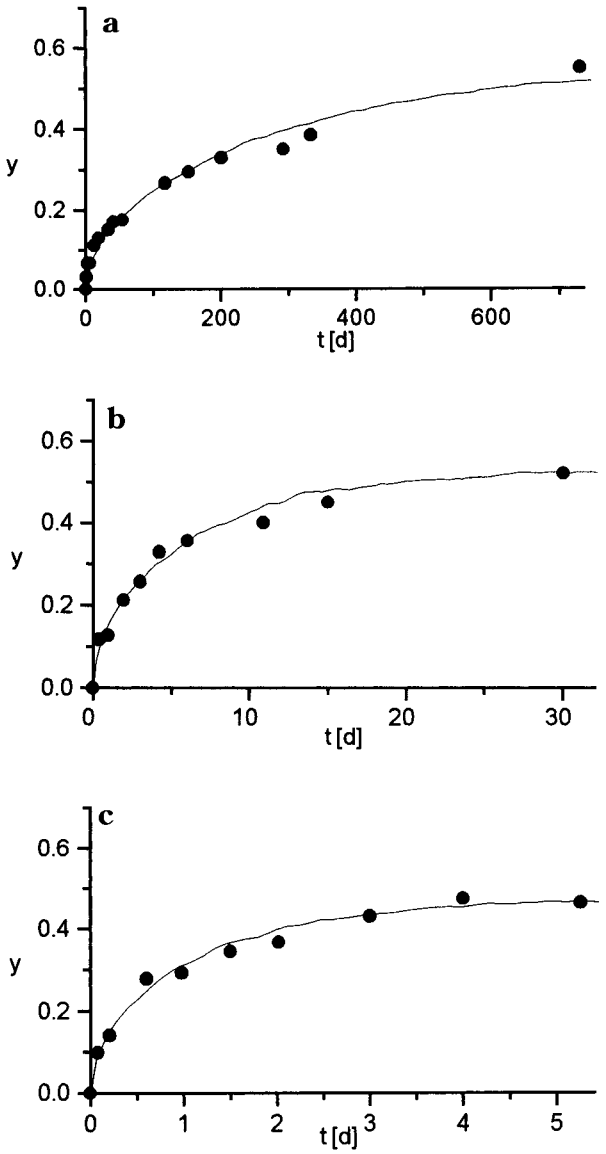

Figure 5. Kinetics of the inclusion of polymer **3b** in **1a** at (a) 25, (b) 60, and 80 °C. (—) Calculated by ABAKUS for the values in Table 3.

6. Quantitative Description of the Threading Process of the Polymer 3b. First, attempts to quantitatively describe the inclusion process of a polymer chain were performed using the equations for a continuous one-dimensional diffusion.[18] Later, we chose another description, which takes the very special molecular circumstances better into account. We assumed a consecutive hopping process which already described the kinetic data for the inclusion of poly(iminooligomethylene)s (**2**) in **1a** very well.[25] For the purpose of simplification the following assumptions were made in this model:

(1) Per polymer repeat unit there is one discrete binding site which can bind one cyclodextrin ring. The enthalpy of a bound cyclodextrin is lower by $\Delta H°_m'$ than the enthalpy of a free one (Figure 3b).

(2) Every binding site is surrounded by one activation barrier at each end. The activation energy for the translation of **1a** from one binding site to the next is E_a'. The activation energy between the free state and the first binding site is $E_a = E_a' + \Delta H°_m'$.

(3) The activation energies E_a', and inclusion enthalpies, $\Delta H°_m'$, for all binding sites are equal in the first approximation.

(4) Any interaction between threaded cyclodextrin rings is neglected in the first approximation. This assumption appeared reasonable, as the threaded rings are separated by high activation barriers.

(5) A cyclodextrin ring can migrate in both directions along the polymer with the same probability, but it can only occupy a free binding site.

Taking these five assumptions into account, we wrote the computer simulation program ABAKUS[30] to quantitatively describe the threading kinetics of one polymer chain with P repeat units by xP rings, where $x = [CD]_0/[G]_0$ is the molar ratio of the total concentrations of cyclodextrin $[CD]_0$ and the polymer repeat units $[G]_0$. The individual binding sites of the polymer chain are labeled $i = 1, 2, 3, ..., P$ from one end to the other. The occupation of a certain binding site i is named $y(i)$ with $y(i) = 0$ for the free state and $y(i) = 1$ for the occupied state. The occupation of site i averaged over many chains is denoted as $\bar{y}(i)$.

A cyclodextrin ring can be (a) free, (b) threaded at a chain end, or (c) threaded elsewhere at the chain at site i. The corresponding concentrations are abbreviated as (a) [CD], (b) $[CD]_{end}$, and (c) $[CD]_i$. Rate constants were related to one chain with two chain ends.

The *free rings* thread onto the free polymer chain ends according to the second order rate equation (eq 1). The

$$-\frac{d[CD]}{dt} = \frac{k_f}{2}[CD][\text{free chain ends}] = k_f[CD]\frac{[G]_0}{P}(1 - \bar{y}(1)) \quad (1)$$

corresponding probability, w_f, of the formation of an inclusion compound at the first or last site of a polymer chain within a time interval, Δt, is given by eq 2.

$$w_f = -\frac{\Delta[CD]}{[CD]} = k_f\frac{[G]_0}{P}\Delta t \quad \text{if} \quad \{y(1) = 0 \text{ or } y(P) = 0\} \quad (2)$$

The *rings, threaded at the ends*, can dissociate back to the free state according to the first order rate law (eq 3). The corresponding probability of dissociation of

$$\frac{d[CD]}{dt} = -\frac{\Delta[CD]_{end}}{dt} = \frac{k_d}{2}[CD]_{end} = k_d\frac{[G]_0}{P}\bar{y}(1) \quad (3)$$

a ring at a chain end, w_d, is given by eq 4. In addition,

$$w_d = -\frac{\Delta[CD]_{end}}{[CD]_{end}} = \frac{k_d}{2}\Delta t \quad (4)$$

these rings can also propagate to the next site if this is available. The probability of propagation, w_{pe}, is given by eq 5. For the first approximation and in accordance

$$w_{pe} = -\frac{\Delta[CD]_{end}}{[CD]_{end}} = \frac{k_p}{2}\Delta t = \frac{k_d}{2}\delta t \quad \text{if} \quad \{y(2) = 0 \text{ or } y(P-1) = 0\} \quad (5)$$

with assumption 3, the rate constants k_d and k_p were assumed to be equal.

For *rings threaded on the chain at segment i*, the probability w_p of propagation to next segments $i - 1$ or $i + 1$ is given by eq 6. This probability w_p must be the double of w_{pe}, as there are two directions of propagation possible rather than one.

$$w_p = -\frac{\Delta[CD]_i}{[CD]_i} = k_p\Delta t = k_d\Delta t \quad \text{if} \quad \{y(i-1) = 0 \text{ or } y(i+1) = 0\} \quad (6)$$

Within the program ABAKUS, the state of each of the xP rings was checked and probabilities w_f, w_d, w_{pe}, and w_p were executed by a generator of random numbers and accumulated. Such a simulation run was repeated for at least 100 times to get the average value $\bar{y}(i)$ after a certain run time t. This way, the complete process of threading rings on a polymer chain was simulated, using only two parameters, k_f and k_d. The occupation profile of a polymer chain $\bar{y}(i)$ for several threading times t is represented in Figure 6. Obviously, the chain ends reach their final occupation rather rapidly, while the middle of the chain remains free for a longer period of time.

Finally, the occupation of all segments becomes equal: $\lim t \to \infty\ \bar{y}(i) = y_\infty$. The limiting occupation, y_∞, is related to the rate constants and the thermodynamic binding constant, K_S (eq 7).

$$K_S = \frac{k_f}{k_d} = \frac{y_\infty}{[CD](1 - y_\infty)} = \frac{y_\infty}{[G]_0(x - y_\infty)(1 - y_\infty)} \quad (7)$$

There is thus only one adjustable parameter left (k_d), while the other parameters P, $[CD]_0$, $[G]_0$, K_S, and k_f are known or dependent. The yield of inclusion y as a function of time was calculated from the average value of $\bar{y}(i)$ over i according to eq 8. It was plotted for a given

$$y = \frac{1}{P}\sum \bar{y}(i) \quad (8)$$

set of parameters as a function of time.

The kinetics calculated for $P = 68$ were compared with the measured ones. The parameter k_d was varied until the best fit was obtained. The agreement between this simple theoretical model and the experimental data is fairly good (Figures 5a−c). The values obtained for k_d (Table 3) are in the same range of the corresponding values for the monomer **5**. Kinetic measurements have to be repeated with several ionene **3a** samples with a narrow molecular weight distribution to allow a direct proof of this model. Nevertheless, the assumptions made seem to be valid in the first approximation.

7. Activation Energy of the Threading Process of Polymer 3b by 1a. The Arrhenius plot of k_d yielded an activation energy of $E_a' = 88$ kJ/mol for the migration process. This activation energy is similar to that of the dissociation $E_a' = 93$ kJ/mol for the monomeric inclusion compound **1a·5**. This result corroborates the above made assumptions, especially assumption 3.

8. Thermodynamic Stability of the Polymeric Inclusion Compound 3b·1a. The binding constants, K_S of the host **1a** toward the polymeric guest were calculated from the limiting conversions y_∞ of the threading kinetics (eq 7) and are listed in Table 3. The values of K_S are somewhat lower than the value for the monomeric model **5** with **1a**. It is possible that the decamethylene segment of the polymer **3b** is in an unfavorable, more coiled, conformation than this segment at the monomer **5**. This explanation is supported by the fact that the binding constant K_S increases significantly with decreasing concentration of the polymeric guest **3b** (Figure 7): at low concentrations of **3b** the binding constant is very close to that of the monomeric model. At low concentrations of **3b** the chain is

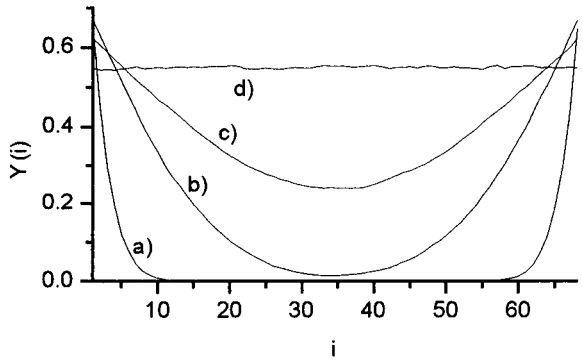

Figure 6. Occupation profile of a polymer chain of $P = 68$, $[G]_0 = [CD]_0 = 12.2$ mM: (a) after 4 days, (b) after 70 days, (c) after 250 days, and (d) after 650 days as simulated by ABAKUS for $K_S = 223\ M^{-1}$ and $k_d = 1.4 \times 10^{-5}\ s^{-1}$.

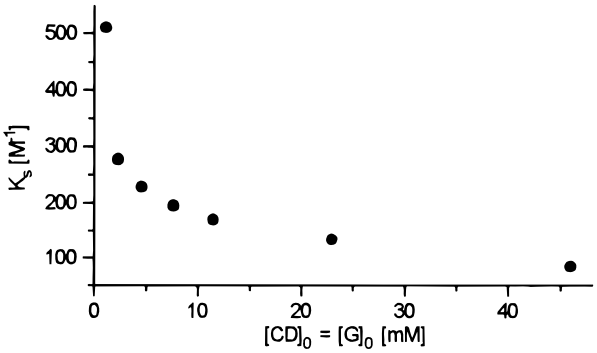

Figure 7. Equilibrium constant K_S for the inclusion of **3b** in **1a** as a function of the concentration $[G]_0 = [CD]_0$ in D_2O at 60 °C.

Table 3. Results of the Simulation of the Threading Process of 1a on Polymer 5

T [°C]	y_∞ [%]	K_S [M^{-1}]	k_d [10^{-5} s^{-1}]
25	55	223	1.4
60	52	185	56
80	47	132	335

expected to be in a more expanded conformation and at high concentration in a more coiled conformation. In the limiting case of low concentration, a polymeric guest can be treated thermodynamically by the law of mass action (eq 7) like a corresponding monomeric guest.

The occupation y_∞ of the polymer chain with rings **1a** can be increased according to eq 7 by the increase of the total concentration of **1a**. A nearly complete (95%) occupation was reached, if a high excess of **1a** was used.

9. Kinetic Stability of the Polymeric Inclusion Compound 3b·1a. The rate of dissociation of **1a·3b** was measured by quantitative dialysis experiments. The solution of **1a·3b** was circulated through a cellulose hollow fiber dialyzer and the cut-off molecular weight of the dialyzer of approximately 10 000 ensured a selective removal of free cyclodextrin rings within 3 h (Figure 8b). Consequently, the inclusion equilibrium should be driven toward the free components **1a** and **3b**. However, after the fast removal of the free rings **1a** nearly no further permeation of **1a**, was observed (Figure 8a). Thus, the rate of dissociation of **1a·3b** is so slow that it was hardly measurable.

This inclusion compound is also stable to gel permeation chromatography as we detect a polarimeter signal for both threaded and free cyclodextrins (Figure 9). The yields of threading derived from the integrals of these GPC peaks are similar to those determined by ^{1}H NMR spectroscopy, suggesting that nearly no dissociation

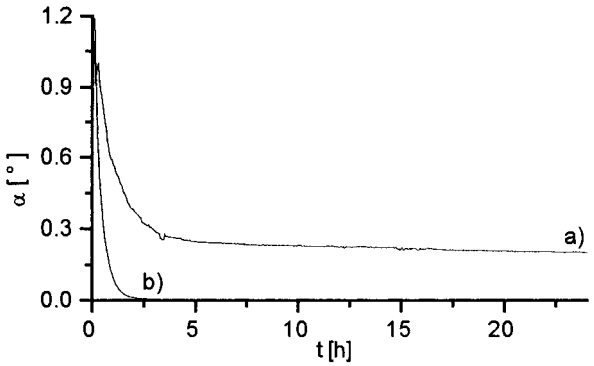

Figure 8. Kinetics of the dialysis of (a) polymeric inclusion compound **3b·1a** and (b) free cyclodextrin **1a** measured by a polarimeter detector.

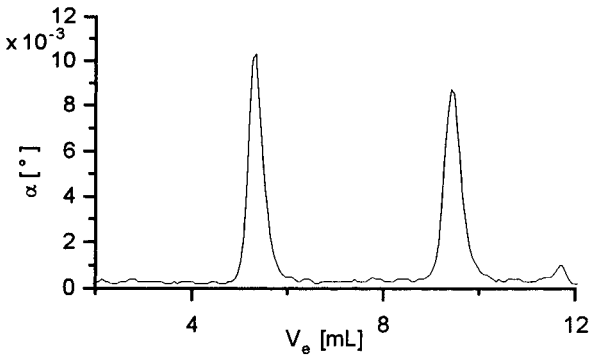

Figure 9. GPC of the polymeric inclusion compound **3b·1a**. The residual free rings were not removed before.

occurs during GPC. The high kinetic stability of **1a·3b** was attributed to the cooperative steric hindrances of the dimethylammonium groups of **3b**. Because of its high kinetic stability, **1a·3b** was termed a polyrotaxane.

Conclusion

Rotaxanes and polyrotaxanes can be created by thermal-induced slippage of α-cyclodextrin rings over quaternary ammonium groups which act as activation barriers. More than 60 rings of **1a** could be strung on a polymer chain this way.

The kinetics of threading of the rings onto the polymer chain can quantitatively be described by a consecutive hopping process. Interactions between the rings at the polymer chain can be neglected.

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