Kinetics of Threading α-Cyclodextrin onto Cationic and Zwitterionic Poly(bola-amphiphiles)

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ABSTRACT: The amphiphilic polymers, poly(iminoundecamethylene), poly((*N*-methylimino)undecamethylene), poly((*N*,*N*-dimethylammonio)undecamethylene), and poly((*N*-methylimino)undecamethylene-*N*-oxide) were synthesized from nylon-11 by BH_3 reduction of amide groups to amino groups and subsequent methylations. The poly(*N*-oxide) was obtained by H_2O_2 oxidation of the polymeric tertiary amine. Since the polymers and their inclusion compounds were water-soluble, threading kinetics of α-cyclodextrin rings onto these polymers could be investigated by ^{1}H NMR. Kinetics were fitted by an empirical root exponential association function $Y = Y_\infty(1 - \exp(-\mathrm{sqrt}(5.3t/t_{90})))$. The time t_{90}, necessary to reach 90% completion of the threading process, was taken as a measure of the steric hindrance exerted by the hydrophilic groups along the polymer chain. The vaIues of t_{90} decreased by more than 3 orders of magnitude as the diameters of the hydrophilic groups decreased from 5.5 to 4.3 Å.

Introduction

Pseudopolyrotaxanes are supramolecular structures consisting of many rings threaded on a polymer chain, where dissociation of the rings from the chain is significantly sterically hindered by substituents at the polymer.[1] Pseudopolyrotaxanes are distinct from similar molecular species, called polyrotaxanes, where dissociation is completely blocked by large bulky substituents, the "stoppers"[2] attached either to the ends of the chain or along the chain.[3] Both polyrotaxanes and pseudopolyrotaxanes, assembled by the template approach, are of increasing relevance, as they give rise to new polymeric materials with interesting properties in a straightforward and modular way from known building blocks.[4−6] The detailed nomenclature of polyrotaxane is referred to in recent publications.[7,8]

Among a great variety of ring-shaped molecules, such as crown ethers,[9−11] or cucurbiturils,[12,13] the cyclodextrins (CDs) have been used most commonly for the construction of (pseudo)-polyrotaxanes as they are readily available and can be functionalized in well-defined ways.[14,15] CDs are 1→4 α-linked cyclic oligomers of anhydrogluose. Those CDs consisting of six, seven, or eight anhydroglucose entities are called α-, *β*-, or *γ*-CD, respectively.[16,17]

CDs rapidly thread onto many linear polymers, such as polyethers,[18−22] polyamines,[23] or polyesters,[24−27] to form channel type inclusion compounds, in which threaded CDs are densely packed along the polymer chain (see Figure 1a).[28] Threading kinetics were already investigated by turbidity measurements.[29] In general, these channel type inclusion compounds are insoluble in water, and dissociate as soon as they are dissolved in organic solvents like DMSO. Only after their conversion to polyrotaxanes they are soluble without decomposition.[30] After derivatization of the threaded CD rings, these polyrotaxanes became water soluble.[31,32]

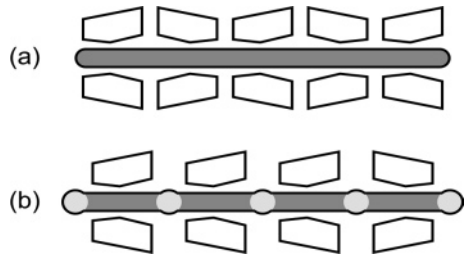

Figure 1. Schematic drawing of cyclodextrin pseudopolyrotaxanes: (a) channel type; (b) poly(bola-amphiphile) type. Hydrophobic parts of the polymer are marked in gray and hydrophilic ones in white. Reprinted from ref 15. Copyright 1997 American Chemical Society.

On the other hand, highly water-soluble polymers with sufficiently long hydrophobic spacer groups, so-called poly-(bola-amphiphiles),[15] allow threading of CD rings under homogeneous conditions in aqueous solution.[33−37] In particular for the smallest ring, α-CD, threading is so slow that it can be followed in real time in solution by methods such as ^{1}H NMR. While threading α-CD onto the secondary polyamines, poly-(iminoundecamethylene) **1** was already completed after about 1 h at room temperature,[33] threading onto the quaternary polyamine, poly((*N*,*N*-dimethylammonio)hexamethylene(*N*′,*N*′-dimethylammonio)decamethylene), took more than 2 years.[36] A maximal coverage of nearly one α-CD ring per polymer repeat unit was reached, which means that threaded CDs are separated from each other by the bulky hydrophilic amino groups of the polymer backbone, as shown in Figure 1b. The resulting lower packing density of threaded CD rings compared to the packing density of channel inclusion compounds might be the reason for their better water solubility, because the polymer chain retains some conformational flexibility.

The kinetic stability of the α-CD inclusion compounds of poly(bola-amphiphiles) depends on the size of the hydrophilic groups within the polymer chain. The α-CD inclusion compound

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of the secondary polyamine, **1**·α-CD, immediately dissociated as soon as residual free CDs had been removed by dialysis. The attachment of bulky side groups at the polymer was necessary to keep threaded CD rings on the polymer chain.[33] Conversely, the inclusion compound of α-CD and poly((*N*,*N*-dimethylammonio)hexamethylene(*N*′,*N*′-dimethylammonio)-decamethylene) was almost kinetically stable.[36] Since a mixture of α-CD and this polymer just had to be heated, the assembly of the pseudopolyrotaxane was straightforward, but threading times of 35 days are too long for practical application. Consequently, we looked for poly(bola-amphiphiles), which allow faster formation of pseudopolyrotaxanes sufficiently stable to be isolated. In the following we describe threading kinetics of a series of poly(bola-amphiphiles) composed of a undecamethylene spacer and various hydrophilic groups such as $-^{+}NMe_2-$, −NMe−, −NOMe−, and −NH−.

Experimental Section

Materials. α-CD (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. Aqueous solutions (10−20 mg/mL) of the polymers were submitted to continuous ultrafiltration using a stirred filtration autoclave GH-100 (Berghof, Germany) equipped with P005F (cutoff molecular weight 5 kDa, Celgard, Mirodyn-Nadir, Germany) membranes for the removal of low molecular impurities and salts. The 10-fold volume of solvent relative to the volume of the sample solution was passed through the membrane to affirm completeness of purification.

Measurements. Gel permeation chromatography (GPC) was performed as follows. Samples of the polymers were dissolved in the eluent (2 mg/mL), shaken for 16 h and injected by a 50 μL sample loop into the GPC system with a flow rate of 1.00 mL/min. For water soluble samples, Novema 30 and Novema 300 columns (PSS, Mainz, Germany), a LR40 laser refractive index detector (λ = 670 nm, Viscotec, Weingarten, Germany), and a SLD 7000/BI-M_wA light scattering detector (λ = 670 nm, PSS, Mainz, Germany) were used. Data evaluation was performed by WingPC 7 software (PSS, Mainz, Germany). For GPC in organic solvents, a Breeze instrument equipped with RI detector (Waters) was used with Nucleogel 103−5 colums (Machery Nagel, Düren, Germany). Calibration was performed with narrow polystyrene standards using Breeze (Version 3.2) software (Waters).

NMR spectra were recorded by a Varian VXR-300 spectrometer (^{1}H: 299.969 MHz, ^{13}C: 100.62 MHz) and a Bruker Avance 500 spectrometer (^{1}H: 500.00 MHz, ^{13}C: 125.71 MHz). The following internal standards were used for ^{1}H NMR: for D_2O HOD 4.75 ppm, for $CDCl_3$ $CHCl_3$ 7.25 ppm; for ^{13}C NMR: for D_2O CH_3CN 1.30 ppm, for $CDCl_3$ $CDCl_3$ 77.0 ppm. The following abbreviations were used: s singlet, d doublet, t triplet, m multiplet, br broad signal. The atoms of the anhydroglucose units were labeled 1, 2, ..., 6. Polymer chain atoms were labeled as a, b, c, d, ... Threading kinetics have been run in 12.2 mM solution in D_2O in standard NMR test tubes immersed in water thermostats with temperatures of 25 and 60 ± 0.5 °C. ^{1}H NMR signals of H-1 of free (5.00 ppm) and occupied CDs (5.05 ppm) were integrated after Gauss multiplication resolution enhancement. The program Origin 7.0 was used for curve fitting.

The binding constant K_S of α-CD and 1,11-diaminoundecane was calculated according to eq 4 from the yield of complexation Y_∞ of a 1.0 mM equimolar mixture of host and guest. Y_∞ = 0.48 had been determined before from the integrals of the ^{1}H NMR signals of H-1 of free (5.00 ppm) and occupied CDs (5.05 ppm) in 0.1 M acetate buffer pH 4.6 in D_2O at 25 °C.

Poly(iminoundecamethylene) (1) was synthesized by reduction of poly(11-undecaneamide) (Degussa, Marl, Germany, P_n = 140, determined by acidimetric end group titration, P_w = 315 determined by GPC in THF after trifluoroacetylation[38]) as described previously.[33]

Poly((*N*,*N*-dimethylammonio)undecamethylene chloride) (2). A mixture of 5.00 g (29.6 mmol) **1**, 7.8 g (74 mmol) Na_2CO_3 and 4.6 g (74 mmol) methyl iodide in 250 mL methanol was stirred for 1 d at 80 °C. Afterward, 25 mL of concentrated ammonium hydroxide solution was added to the clear reaction mixture, stirred overnight at room temperature, and then neutralized with HCl. This solution was ultrafiltrated first with methanol/water 1:1 v/v, then 70 mL 1 M HCl was added for ion exchange, and finally it was ultrafiltrated with water. The product **2** (9.9 g, 57%) was obtained as a white foam after lyophilization. ^{1}H NMR (D_2O): δ 1.33 (br, 6 H, H−e,f), 1.38 (br, 8 H, H−c,d), 1.76 (m, 4 H, H−b), 3.06 (s, 6 H, *N*-methyl), 3.28 (m, 4 H, H−a). ^{13}C NMR (DMSO-d_6/D_2O 1:1 v/v): δ 23.5 (C−e,f), 27.2 (C−d), 30.0 (C−c), 30.3 (C−b), 52.1 (*N*-methyl), 66.7 (C−a).

Poly((*N*-methylimino)undecamethylene) (3). After dissolution of 5.00 g (25.5 mmol) of **1** in 90 mL of formic acid, 3.4 mL of a 36 wt % solution of formaldehyde in H_2O was added and stirred for 2 d at room temperature. Furthermore, 1.0 mL of formaldehyde solution was added and stirred for another 2 d. The reaction mixture was diluted with 100 mL methanol and ultrafiltrated with methanol. Afterward, the residual solution was reduced to one-half and dropped into 500 mL of a 25 wt % solution of NH_3 in H_2O. The residual solution was decanted from the white slimy precipitate. The precipitate was washed twice with water and taken up in CH_2Cl_2. The organic phase was separated by centrifugation, concentrated and dried in vacuo to afford the product **3** (5.24 g, 97%) as a gluey yellow residue. ^{1}H NMR ($CDCl_3$): δ 1.24 (br, 14H, H−c,d,e,f), 1.42 (br, 4H, H−b), 2.17 (s, 3H, *N*-methyl), 2.27 (t, J = 5.5 Hz, 4H, H−a). ^{13}C NMR ($CDCl_3$): δ 25.88 (C−e), 27.28 (C−c,d,f), 29.4 (C−b), 41.3 (CH_3), 57.1 (C−a). M_w = 35 000 g mol^{-1}; P_w = 190 by GPC in THF/triethylamine 100:1 v/v (see Supporting Information).

Poly((*N*-methylimino)undecamethylene-*N*-oxide) (4). After dissolution of 2.00 g (10.9 mmol) of **3** in 40 mL of methanol and cooling to 0 °C, 4.0 mL of a 35 wt % solution of H_2O_2 was added and stirred for 3 d. Excess H_2O_2 was destroyed afterward by addition of 50 mg of 5 wt % Pd on charcoal. The filtrate was ultrafiltrated with water and lyophilized afterward to afford the product **4** (1.63 g, 75%) as a white foam. ^{1}H NMR (D_2O): δ 1.03−1.29 (br, 14H, H−c,d,e,f), 1.43−1.65 (br, 4H, H−b), 2.66 (br, 3H, *N*-methyl), 2.89−3.01 (m, 4H, H-1). ^{13}C NMR (D_2O/CD_3OD): δ 24.22 (C−d), 27.35 (C−e,f), 30.06 (C−c), 30.28 (C−a), 56.91 (*N*-methyl), 68.46 (C−a). M_w = 2800 g mol^{-1}; P_w = 140 by GPC in water/methanol/acetic acid 70:30:1 v/v/v; absolute calibration by light scattering.

Results and Discussion

1. Synthesis of the Poly(bola-amphiphiles). Poly(iminoundecamethylene) **1** was synthesized by polymer analogous reduction of polyamide-11 with BH_3·SMe_2 as already described.[33] The resulting poly(iminoundecamethylene) was further methylated in two ways. First, it was methylated completely by methyl iodide to the ionene poly((*N*,*N*-dimethylammonio)-undecamethylene) **2** in 57% yield (see Figure 2). Because iodide counterions lead to precipitation of ionene **2**, they have to be replaced by chloride ions using ultrafiltration. The ionene chloride **2**·Cl was readily soluble in water. Second, the secondary polyamine **1** was partially methylated to the tertiary polyamine **3**. While partial methylation with a stoichiometric amount of methyl iodide leads to undesirable statistically substituted products, Eschweiler−Clark methylation was the method of choice. This specific reaction was already successfully applied for the methylation of poly(ethylene imine) to poly(*N*-methylethylene imine).[39] Polyamine **1** was reacted with formaldehyde in formic acid solution. A totally regular polymer **3** was obtained in 97% yield, as demonstrated by the ^{1}H NMR, shown in Figure 3a.

Oxidation of a polymeric tertiary amine, such as poly(4-vinylpyridine), was already performed by H_2O_2 at 75−80 °C

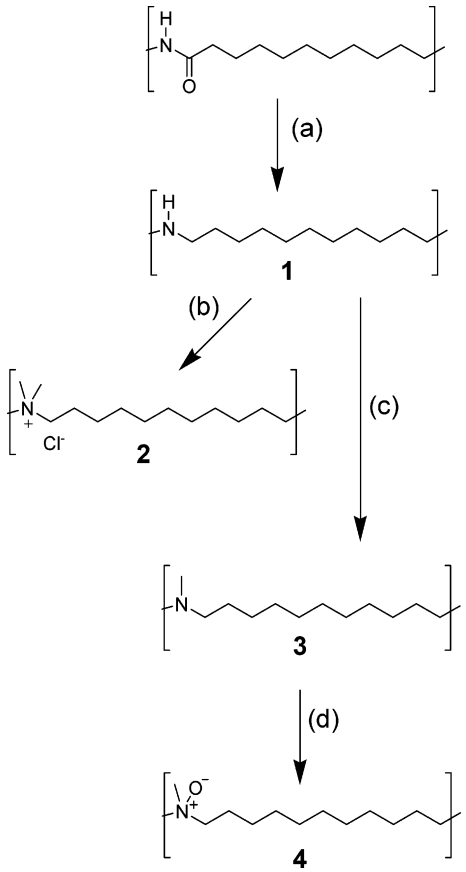

Figure 2. Synthesis of poly(bola-amphiphiles) from poly(11-undecaneamide): (a) $BH_3 \cdot Me_2S$; (b) MeI, K_2CO_3; (c) HCOOH, HCHO; (d) H_2O_2.

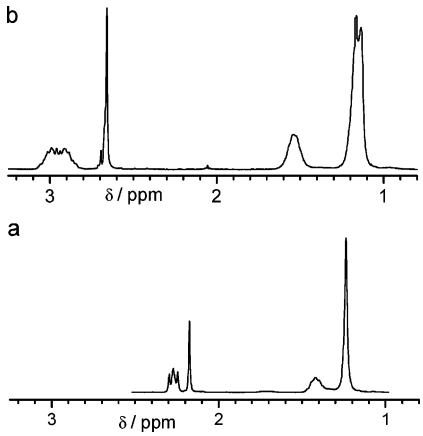

Figure 3. ^{1}H NMR spectra of (a) poly((*N*-methylimino)undecamethylene), **3**, in $CDCl_3$, and (b) poly((*N*-methylimino)undecamethylene *N*-oxide), **4**, in D_2O.

in acetic acid solution leading to the poly(*N*-oxide).[40] We found it already sufficient to oxidize the tertiary polyamine **3** in methanol solution at room temperature by H_2O_2 to the poly(*N*-oxide) **4**. The product was isolated in 75% yield. The ^{1}H NMR signals of both, α-methylene groups and *N*-methyl groups shown in Figure 3b, were shifted downfield due to the electron withdrawing effect of the oxygen. Since the poly(*N*-oxide) **4** was highly soluble in water, it could be purified by aqueous ultrafiltration.

The degrees of polymerization P_w 140−190 of polymers **1** − **4** ought to be similar, because they were all derived from the same starting polymer, poly(11-undecaneamide), by polymer-analogous reactions, and because low molecular weight fractions were removed after every reaction step by ultrafiltration. Molecular weights of the secondary and quaternary polyamines **1** and **2** could not be determined by GPC because interactions between them and the stationary phase could not be excluded.

2. Investigation of the Threading Kinetics by ^{1}H NMR. The polymers **2**, and **4** dissolved clearly in water. Polyamines **1** and **3** required acidic conditions pH ≤ 4.6 for dissolution. Furthermore, no precipitation occurred after addition of an aqueous α-CD solution to solutions of polymers **1**−**4**. Thus, threading kinetics could be studied in situ by ^{1}H NMR in D_2O solution. In all cases, signals of the anomeric protons H-1 of α-CD were shifted downfield by 0.05 ppm due to the incorporation of the polymer chain as described previously.[36] Therefore, the amount of CDs bound to the polymer could be quantified from the integrals of the corresponding signals. If a large excess of α-CD was used, it was difficult to integrate small signals of bound α-CD in the neighborhood of large signals of excess free α-CD. Therefore, highest accuracies were achieved by a 1:1 molar ratio of polymer repeat unit and α-CD. The obtained threading kinetics for polymers **1** and **3** at 25 °C, and for polymers **2** and **4** at 60 °C are depicted in Figure 4.

3. Mathematical Description of Threading Kinetics. The square root of the time was chosen as the abscissa for displaying threading kinetics, because it allowed a much better comparison of the data than a normal linear plot. Plotting vs the root of time was already used for the investigation of simple macroscopic one-dimensional diffusion processes,[41,42] such as the diffusion in a sheet, which are very similar to the threading of rings onto polymers from a phenomenological point of view.

The threading kinetics of the ionene poly((*N*,*N*-dimethylammonio)hexamethylene(*N*′,*N*′-dimethylammonio)decamethylene) were already fitted by the program ABAKUS, a Monte Carlo type of computer simulation assuming a consecutive hopping process of the CD rings along the polymer chain within a periodic potential as depicted in Figure 5a.[36] This program has provided valuable information about the individual rate constants of the complex threading process, but application is cumbersome, because one has to find parameters by trial and error. Meanwhile we found it more practicable to use an explicit fitting function to describe the kinetic data. We found empirically the exponential association function, using the root of time as the abscissa according to eq 1, fits our kinetic data very well, as demonstrated in Figure 4.

$$Y = Y_\infty(1 - e^{\sqrt{-kt}}) \tag{1}$$

Fitting was performed by standard software after plotting the kinetics vs the square root of time. The limiting conversion Y_∞ and the rate constant k were obtained as fitting parameters. As an intuitive description of the threading process, the threading time t_{90}, necessary for reaching 90% of the limiting conversion, was defined according to eq 2 and listed in Table 1.

$$t_{90} = \frac{(\ln 10)^2}{k} \cong \frac{5.3}{k} \tag{2}$$

4. Dependence of the Threading Time t_{90} on the Structure of the Polymers. As already stated, threading onto the ionene poly((*N*,*N*-dimethylammonio)hexamethylene(*N*′,*N*′-dimethylammonio)decamethylene) is very slow.[36] It takes t_{90} = 57 d = 1370 h at 60 °C to reach 90% of the limiting conversion. The steric hindrance exerted by the two neighboring dimethylammonium groups are responsible for the slowness of threading. The hexamethylene spacer between these two groups is too short

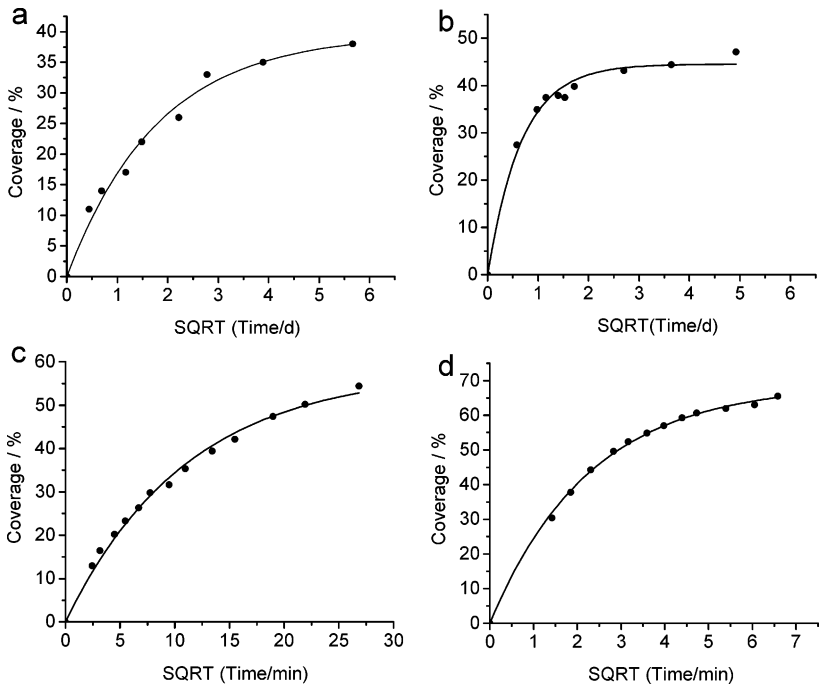

Figure 4. Kinetics of threading α-cyclodextrin on polymer chains: coverage of the polymer Y as a function of the square root of threading time for (a) ionene-11 **2**, and (b) poly(*N*-oxide) **4**, both in 0.1 M NaCl at 60 °C, (c) tertiary polyamine **3**, and (d) secondary polyamine **1** both in 0.1 M sodium acetate pH 4.6 at 25 °C in aqueous solution.

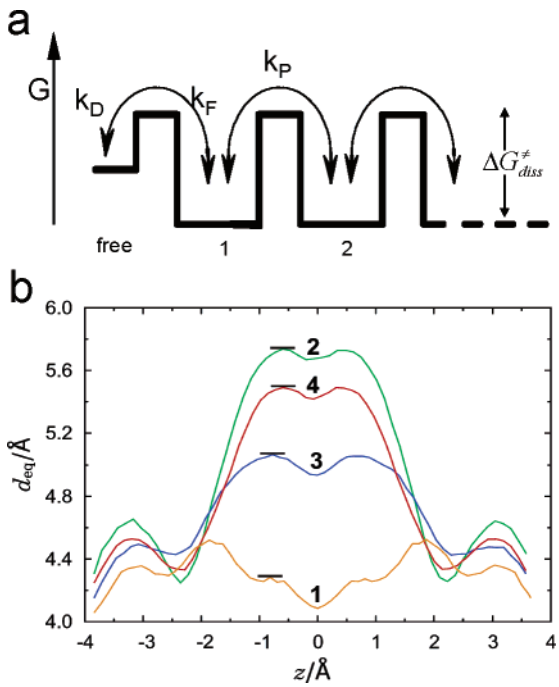

Figure 5. Profiles of the poly(bola-amphiphiles): (a) schematic drawing of the free energy profile (reprinted from ref 36. Copyright 1997 American Chemical Society); (b) thickness profiles of polymers **1**−**4** as calculated by MolShape in this work, (−) maximum diameters.

to accommodate a α-CD ring. Therefore, both dimethylammonium groups count as one steric barrier. Consequently, ionene **2** should be included faster, because it contains only one bulky dimethylammonium group per repeat unit. This is indeed the case, a lower threading time of t_{90} = 413 h was found for **2** at 60 °C, as shown in Table 1. Threading of the poly(*N*-oxide) **4** was still faster taking only t_{90} = 58 h at 60 °C.

For comparison, the slimmer tertiary polyamine **3** is included even faster than the other polymers, showing threading times of t_{90} = 0.16 h at 60 °C, and t_{90} = 10.8 h at 25 °C. One methyl group less at the nitrogen atoms compared to the ionene **2** exerts such an enormous kinetic effect. With the loss of another methyl group in the secondary polyamine **1** threading is faster still with t_{90} = 0.47 h at 25 °C. In the last two cases, mobilities of the α-CD rings on the polymer chains **1** and **3** were too high to allow isolation of the pseudopolyrotaxanes by ultrafiltration.

Table 1. Kinetic Data for the Inclusion of Poly(bola-amphiphiles) in α-CD[a]

polymer	X	T [°C]	t_{90} [H]	$\hat{d}_{eq}$ [Å]	Y_∞ [%]	K_s [M^{-1}]
1	$-^{+}NH_2-$	25	0.47	4.28	69	583
2	$-^{+}NMe_2-$	60	413	5.73	40	163
3	$-^{+}NHMe-$	25	10.8	5.06	58	274
3	$-^{+}NHMe-$	60	0.16	5.06	51	177
4	$-^{+}NO^{-}Me-$	60	58	5.49	45	307

[a] **1** and **3** in 0.1 M acetate buffer pH 4.6; **2** and **4** in 0.1 M NaCl.

Polymers **1**−**3** are cationic at the conditions of the kinetic experiments, while the poly(*N*-oxide) **4** should be zwitterionic at neutral pH. The pK_A values of monomeric and polymeric *N*-oxides are known to be around 4.6.[43,44] Since also the hydrophobic segments of the polymers **1**−**4** are the same, only different repulsive forces due to the different sizes of the hydrophilic groups were made responsible for the marked differences in threading kinetics. Similar strong size effects on the threading kinetics were already found for hydrophilic end groups of monomeric bola-amphiphiles.[15]

5. Calculation of the Thicknesses of Polymers 1−4. There are several approaches to describe the thickness of a polymer from experimental or theoretical data. Cross-sectional areas of polymers can be estimated by addition of increments[45] or obtained from structural data of polymers in the bulk.[46] In addition, the radius of gyration perpendicular to the chain axis is derivable from X-ray or neutron scattering data.[47] Thus, the cross-sectional area of a linear alkanes and oxyalkanes is around $A \approx 17.6-18.3$ Å^2,[46] which relates to a diameter of $d_{eq} \approx 4.7-4.8$ Å of an equivalent circle, according to eq 3.[46] Since this diameter fits well into the minimal internal width of α-CD of $\check{d}_{eq}$ = 4.4 Å, polymers like poly(oxyethylene) readily form

inclusion compounds with α-CD. The structures of CD inclusion compounds are predictable from the thicknesses of the guest polymers relative to $\breve{d}_{eq}$ of the CD as recently demonstrated.[15]

For the calculation of the thicknesses of the poly(bola-amphiphiles) **1**−**4**, electron density maps of the polymer repeat units were calculated first using the B3LYP/6-31G(d) method executed by the program Gaussian03.[48] In a second step, those area elements Δa_i^* of the cross-section perpendicular to the chain direction *z*, which exceed an electron density of 0.002 au, were added up to the cross-sectional area $A(z)$ using the program MolShape.[49] The equivalent diameter $d_{eq}(z)$ was calculated from $A(z)$ according to eq 3 and plotted as the function of the *z* coordinate as shown in Figure 5b. The different sizes of the hydrophilic groups are clearly visible, maxima of thickness $\widehat{d}_{eq}$ are listed in Table 1. The secondary polyamine **1** does not show any steric barrier at all. This explains why threading time t_{90} is very short, even at room temperature Threading time and necessary threading temperature increase steeply with the thickness of the hydrophilic group thickness $\widehat{d}_{eq}$ (see Table 1). Even the small difference in diameter $\Delta\widehat{d}_{eq} = 0.24$ Å between polymers **2** and **4**, caused a remarkable increase in threading time t_{90} by a factor 7. Consequently, threading time is indeed a very sensitive probe for the chain thickness.

$$d_{eq} = \sqrt{\frac{4A}{\pi}} \tag{3}$$

6. Maximum Coverages of the Polymers by α-CD. The limiting coverages Y_∞ of polymers **1**−**4** by α-CD were in the range of 40−70% (see Table 1). The corresponding binding constants $K_S \approx 150-600\ M^{-1}$, calculated by eq 4 for a 1:1 molar ratio of host and guest and the molar concentration *c*, were slightly lower than those of related monomeric guests, such as 1,11-diaminoundecane with $K_S = 1800\ M^{-1}$.

$$K_S = \frac{Y_\infty}{c(1 - Y_\infty)^2} \tag{4}$$

In previous work a strong decay of the binding constant K_S was found for poly((*N*,*N*-dimethylammonio)hexamethylene-(*N*′,*N*′-dimethylammonio)decamethylene) with increasing concentration of the polymer.[36] This concentration effect might be the case here as well. In addition, weak repulsive forces between threaded CD rings or entropy loss of the polymer chain due to inclusion might also prevent high coverages.

Conclusion

Threading kinetics of α-CD and poly(bola-amphiphiles) were measured by ^{1}H NMR and described by an empirical root exponential association function. Kinetics are very sensitive to the diameter of the polymer backbone. Threading times t_{90} ranged from minutes to weeks. Poly(*N*-oxide) **4** is an interesting example of a new class of neutral poly(bola-amphiphiles), which readily forms pseudopolyrotaxanes by slippage[50] in water within feasible times at neutral pH. They should be very useful for the assembly of polyfunctional pseudopolyrotaxanes, especially for those with attached sugar moieties designed for the specific recognition of lectins.[51]

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Supporting Information Available: Text and tables of chromatographic characterization of the polymers in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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