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Polyrotaxanes and pseudopolyrotaxanes of polyamides and cucurbituril[1]

Claudia Meschke, Hans-Jürgen Buschmann*, Eckhard Schollmeyer

Deutsches Textilforschungszentrum Nord-West e. V., Frankenring 2, D-47798 Krefeld, Germany

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Abstract

Pseudopolyrotaxanes and polyrotaxanes of polyamide and the macrocycle cucurbituril are synthesized easily by interfacial polycondensation. With different diammonium ions and diacid chlorides a great variety of poly(amide rotaxane)s is obtained. The structure of the diacid chloride influences the possible motion of cucurbituril on the polymer chain. First attempts to characterize these polyrotaxanes using IR, DTA, ^{1}H-NMR and elemental analyses are reported. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Polyrotaxanes; Polyamides; Cucurbituril

1. Introduction

Polyrotaxanes possess special properties because of the physical linkage of the macrocycles and the linear chain [1]. Polyrotaxanes consisting of different macrocyclic and linear species are known from the literature [2,3]. For macrocyclic species, crown ether [4,5] and cyclodextrin [6,7] have been used for the syntheses. The macrocyclic species have been threaded on the main or on the side chain [8] of different polymers. The properties of the polyrotaxanes have been compared with their pure polymers [9]. Using polyamide and β-cyclodextrin the water sorption of the polyrotaxane is higher than that of the pure polyamide [10]. Steinbrunn and Wenz have obtained an inclusion polyamide with α-cyclodextrin which is soluble in water [11]. Cucurbituril as a macrocyclic ligand (Fig. 1) possesses a rigid cavity for host–guest reactions [12] similar to cyclodextrins. With diamines and their ions cucurbituril forms very stable complexes [13]. Kim and coworkers used the *N,N′*-bis(4-pyridylmethyl)-1,4-diaminebutane dihydrochloride complex with cucurbituril to form insoluble aggregates by coordination with $Cu(NO_3)_2$ and $AgNO_3$ [14,15]. They also synthesized a helical one-dimensional coordination polymer with threaded cucurbituril in the solid state [16]. The stable complex with cucurbituril and 1,6-hexanediammonium ion [17] has been used for the synthesis of mono-, oligo- and polyrotaxanes with cucurbituril [18]. Further results of the syntheses and properties of the polyrotaxanes and pseudopolyrotaxanes derived from polyamides and cucurbituril are reported in this paper.

A typical feature of polyrotaxanes is the motion of the threaded macrocyclic molecule relative to the linear chain [2]. The motion of the macrocyclic molecule depends on the interactions between the cyclic and the linear component and the structure of the linear polymer chain itself. The motion of cucurbituril may be inhibited or allowed by diacid chlorides that are used for the synthesis of the poly(amide rotaxane)s.

2. Results and discussion

The stable complex of cucurbituril with the 1,6-hexanediammonium ion is used as a preorganized structure for the syntheses of poly(amide rotaxane)s by interfacial polycondensation. The diacid chlorides can act as bulky groups to prevent cucurbituril from dethreading from the chain. As a result cucurbituril is not able to move along the polymer chain. Different diacid chlorides are used for the syntheses and studies are reported of the resulting pseudorotaxanes, polyrotaxanes and copolymer polyrotaxanes with cucurbituril. The polymer structures of the poly(amide rotaxane)s (PAR6.Z) and their abbreviations are given in Table 1.

2.1. Pseudopolyrotaxanes

If aliphatic diacid chlorides are used with the complex of cucurbituril and 1,6-hexanediammonium ion in the

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* Corresponding author.

[1] Dedicated to Professor Hartwig Höcker on occasion of his 60th birthday.

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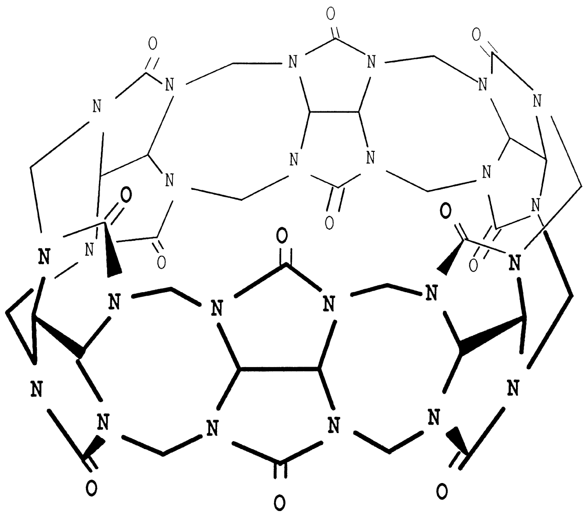

Fig. 1. Structure of cucurbituril.

polycondensation reaction, an aliphatic polyamide is obtained with threaded cucurbituril molecules. The aliphatic acid chlorides do not build a steric barrier so that a pseudopolyrotaxane is obtained. The dethreading process of cucurbituril in concentrated sulfuric acid solution is slow because of the interactions between the protonated amide nitrogen atoms and the carbonyl groups of cucurbituril which hinder the dethreading from the polymer chain [19].

In Fig. 2, the ^{1}H-NMR spectrum of the pseudopoly(amide rotaxane) PAR6.S is given. Between 0 and 1 ppm, the ^{1}H-NMR spectrum of the pseudopolyrotaxane shows new signals for the diamine methylene protons where cucurbituril is located if it is threaded [20]. At 0.8 ppm and 2.6 ppm the signals belong to the uncomplexed diamine component of the amide unit. Elemental analysis confirmed that not every amid unit is complexed by cucurbituril. The content of threaded cucurbituril molecules on the polymer can be calculated from the C/N ratio which is clearly changed if cucurbituril is threaded on the polyamide (Table 2). The dethreading process and the motion of cucurbituril is slow on the NMR time scale because no averaged NMR-signal is observed. Additionally the resonances between 0.4 and 1.0 ppm of the methylene protons of the diamine and the diacid component (Fig. 2b) have changed compared with the pure polyamide (Fig. 2c). These different resonances indicate the motion of cucurbituril along the polyamide chain. It is also observed that cucurbituril shows a new peak at 3.8 ppm (Fig. 2a) because the magnetic environment for the nearby methylene protons at the portals is changed by threading on the polymer chain.

The thermal behaviour of the pseudopolyrotaxanes PAR6.A was studied with differential thermal analysis (DTA). The cucurbituril complex of the 1,6-hexanediammonium ion and adipoyl chloride is used for the two-phase polycondensation reaction. The syntheses with different molar ratios of cucurbituril to diamine are carried out in order to examine the influence of threaded cucurbituril on the polymer. The DTA-curves of the pseudopolyrotaxanes PAR6.A synthesized with different concentrations of cucurbituril are shown in Fig. 3. The curve for the pure polyamide without cucurbituril which is synthesized under the same reaction conditions shows a desorption of water molecules at 80°C and a melting peak at 260°C. The melting peak of the polymer is shifted to lower temperatures with increasing cucurbituril content. This indicates reduced crystallinity. The threaded cucurbituril influences the formation of the crystalline regions of the polymer matrix during the synthesis. The peak of the dehydration process of the free amide units between 20–80°C decreases with increasing content of cucurbituril. Cucurbituril does not decompose below 400°C. Cucurbituril contains up to 13 water molecules which are more or less strongly bonded. During the threading process, cucurbituril obviously does not loosen all water molecules. Therefore, the peak for the dehydration process at 120°C increases with increasing content of cucurbituril.

Until now, only concentrated sulfuric acid has been found to be a solvent for these pseudopolyrotaxanes. The acid dissolves the polyamide as well as cucurbituril. Because of the possible threading and dethreading process of cucurbituril from the polymeric chain in sulfuric acid, no viscosities are measured. The IR-spectra of the pseudopoly

Table 1
Abbreviations for the poly(amide rotaxane)s PAR6.Z and the structures of their polyamide backbones (as diamine component in the polyrotaxane syntheses 1,6-hexane diamine (6) is always used and the diacid chloride component (Z) is varied)

Abbreviations of the poly(amide rotaxane)s PAR6.Z	Diacid chloride component (Z) and its abbreviation	Structure of the polyamide backbone
PAR6.A	Adipoyl chloride (A)	$[-NH-(CH_2)_6-NH-CO-(CH_2)_4-CO-]_n$
PAR6.S	Suberoyl chloride (S)	$[-NH-(CH_2)_6-NH-CO-(CH_2)_6-CO-]_n$
PAR6.T	Terephthaloyl chloride (T)	$[-NH-(CH_2)_6-NH-CO-(C_6H_4)-CO-]_n$
PAR6.N(1,4)	1,4-Naphthalene diacid chloride (N(1,4))	$[-NH-(CH_2)_6-NH-CO-(C_{10}H_6)-CO-]_n$
PAR6.N(2,6)	2,6-Naphthalene diacid chloride (N(2,6))	$[-NH-(CH_2)_6-NH-CO-(C_{10}H_6)-CO-]_n$
PAR6.ST S:T[a]	Suberoyl chloride (S), terephthaloyl chloride (T)	$[(-NH-(CH_2)_6-NH-CO-(CH_2)_6-CO-)_x-(-NH-(CH_2)_6-NH-CO-(C_6H_4)-CO-)_y]_n$
PAR6.DN(1,4) D:N[a]	1,12-Dodecane diacid chloride (D), 1,4-naphthalene diacid chloride (N(1,4))	$[(-NH-(CH_2)_6-NH-CO-(CH_2)_{10}-CO-)_x-(-NH-(CH_2)_6-NH-CO-(C_{10}H_6)-CO-)_y]_n$

[a] Different molar ratios of the two diacid chlorides are used in the syntheses.

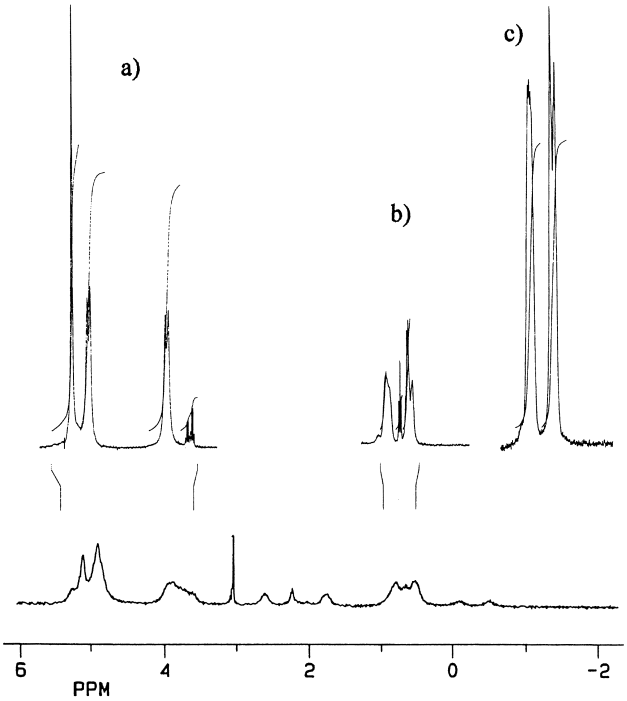

Fig. 2. The ^{1}H-NMR spectrum of the pseudopolyrotaxane PAR6.S with (a) the cucurbituril resonances, (b) the resonances between 0.4 and 1.0 ppm of the methylene protons of the diamine and the diacid component and (c) for comparison a part of the ^{1}H-NMR spectrum of the pure polyamide with the resonances between 0.4 and 1.0 ppm of the methylene protons of the diamine and the diacid component.

(amide rotaxane)s and the poly(amide rotaxane)s show peaks of the polyamide and cucurbituril. Other indications cannot be drawn from the IR-spectra because of the intensive and broad peaks of cucurbituril.

2.2. Polyrotaxanes

If a poly(amide rotaxane) PAR6.N is synthesized with 1,4- or 2,6-naphthalene dicarboxylic acid chloride, the diacid chlorides can act as stopper groups and cucurbituril does not possess the possibility to move along the polymer chain. At room temperature, no dethreading process should exist. The cucurbituril molecules are permanently fixed on the diamine component of the polymer.

The ^{1}H-NMR-spectrum of the polyrotaxane PAR6.N, measured in sulfuric acid shows that the methylene protons of the rotaxaned amide units are shifted to higher fields in the spectrum. The resonances of the original methylene protons of the diamine component have not changed in contrast to the pseudopolyrotaxanes. This observation indicates that cucurbituril is really fixed on the diamine component. Cucurbituril also shows a new resonance as host species.

The DTA-curves of the polyrotaxane PAR6.N and its corresponding pure polyamide do not show a melting peak in the measured temperature range. The decomposition of the polyamide takes place above 300°C. If cucurbituril is threaded on the polyamide, this decomposition could not be observed. So cucurbituril stabilizes the polyamide backbone.

2.3. Copolymer polyrotaxanes

By the choice of the diacid chloride for the poly(amide rotaxane) synthesis, the motion of cucurbituril on the polymer chain can be controlled. The linear aliphatic diacid chlorides allow a motion of cucurbituril. Aromatic diacid chlorides hinder the motion of cucurbituril. If linear aliphatic diacid chlorides and aromatic diacid chlorides are used simultaneously during polyrotaxane synthesis, a copolymer polyrotaxane would be obtained where cucurbituril molecules could move along the aliphatic part of the polyamide. Initial experiments were carried out with suberoyl chloride and terephthaloyl chloride. It is necessary that the diacid chlorides possess the same number of carbon atoms to calculate the content of threaded cucurbituril from elemental analysis. The copolymer polyrotaxane PAR6.ST is synthesized with the molar ratio of suberoyl chloride and terephthaloyl chloride (S:T) 1:1, 5:1 and 1:5. From the determined C/N-ratio of PAR6.ST the amount of threaded cucurbituril can be calculated (Table 2). For comparison, the cucurbituril contents of the polyrotaxane PAR6.T and the pseudopolyrotaxane PAR6.S synthesized with only one of the diacid chlorides are also shown in Table 2. Under identical reaction conditions the content of threaded cucurbituril increases with increasing concentration of the suberoyl chloride. The DTA-curves show clear differences

Table 2
The elemental analyses of the polyrotaxanes and their threaded content of cucurbituril, calculated from the C/N-ratio

Polyrotaxane	C in%		H in %		N in %		C/N		Threaded content of cucurbituril (%)
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	
PAR 6.S	48.00	48.31	5.00	4.38	29.12	29.34	1.65	1.65	95
PAR 6.ST 5:1	35.21	58.91	4.98	6.51	21.11	13.58	1.67	4.34	84
PAR 6.ST 1:1	48.05	50.16	4.89	4.37	29.14	28.16	1.65	1.78	18
PAR 6.ST 1:5	37.14	49.35	5.04	5.05	21.69	22.26	1.71	2.22	84
PAR 6.T	48.15	50.16	4.69	4.37	29.20	28.16	1.65	1.78	5
PAR6.N(2,6)	50.15	47.84	4.37	5.07	28.16	23.06	1.78	2.07	60
PAR6.N(1,4)	50.15	49.35	4.37	5.05	28.16	22.26	1.78	2.22	49
PAR6.DN(1,4) 1:1	49.88	51.92	4.88	5.69	28.01	20.66	1.78	2.51	35

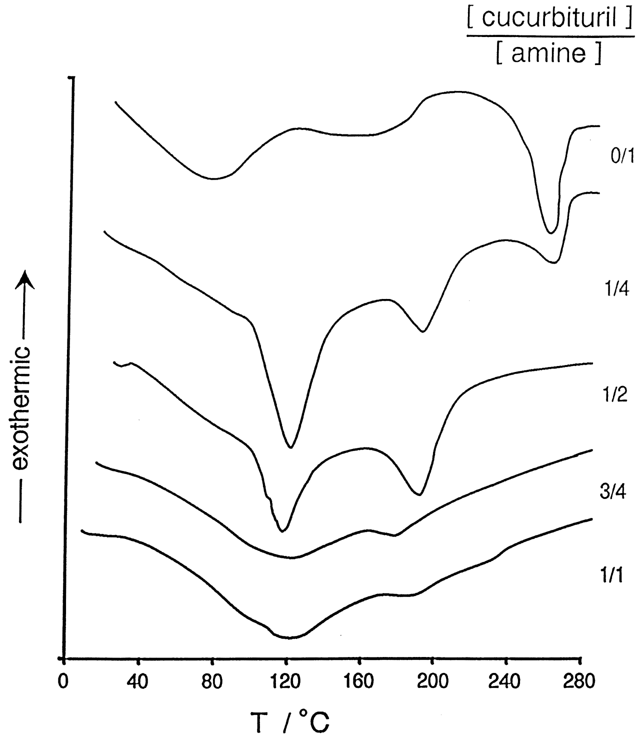

Fig. 3. DTA-curves of the pseudopoly(amide rotaxane)s PAR6.A with different ratios of cucurbituril to amine.

between the copolymer polyrotaxanes PAR6.ST S:T with varying ratios of the two diacid chlorides and their corresponding pure copolymers. The possible motion of cucurbituril along the polymer chain and the copolymerisation influences the crystallization process of the polymer. Therefore, different crystalline regions are formed.

The ^{1}H-NMR spectra of the copolymer polyrotaxanes PAR6.ST S:T and the pure copolymer polyamides are compared. The methylene protons of the rotaxaned amide units are again shifted to higher fields in the spectrum. The resonances of the original methylene protons of the diamine component have changed. This indicates that cucurbituril can move along the aliphatic part of the polyamide chain. Cucurbituril shows the same new resonance as the host species.

If 1,12-dodecanoyl diacid chloride and 1,4-naphthalene diacid chloride are used for the synthesis of the copolymer polyrotaxane PAR6.DN the ^{1}H-NMR-spectrum shows a similar spectrum as the copolymer polyrotaxane PAR6.ST. The motion of cucurbituril is reduced by the aromatic diacid chloride on the aliphatic part of the polymer. The polycondensation reaction of polyrotaxanes with both, aliphatic and aromatic diacid chlorides makes it possible to control the motion of cucurbituril.

With the pseudopoly(amide rotaxane) PAR6.A and the poly(amide rotaxane) PAR6.T, polymer films are prepared during the interfacial polycondensation by pulling the polymer film from the liquid interface [21]. These polymer films can be dyed using acid dyes. These results will be reported in the near future.

Different poly(amide rotaxane)s with cucurbituril are easily synthesized with high yields. The choice of the diacid chlorides determines the motion and content of threaded cucurbituril. The DTA curves show that the crystallinity of the polyamide has changed if cucurbituril molecules are threaded on the polymer chain. Further studies of the poly(amide rotaxane)s with threaded cucurbituril macrocycles and their properties are in progress.

3. Experimental

3.1. Materials

Cucurbituril was prepared as reported in the literature [22] and recrystallized several times from hydrochloric acid. Amines, diacid chlorides, dicarboxylic acids and solvents were obtained from Fluka and used without further purification. 1,4- and 2,6-naphthalene-dicarboxylic acid chlorides were prepared with PCl_5 as reported in the literature.

3.2. General synthesis for pseudopolyrotaxanes, polyrotaxanes and copolymer polyrotaxanes

Cucurbituril (1 mmol) and 1,6-hexanediamine (1 mmol) are dissolved in 15 ml 16% hydrochloride acid. The diacid chloride (1 mmol) is dissolved in diethylether. Under stirring both solutions are mixed and lithium hydroxide (0.07 mol) is added. The resulting precipitate is filtered and washed with 5 vol% hydrochloride acid, water and diethylether. Yields: 70–80%.

3.3. Characterization of the polyrotaxanes

As an example the characterization of some polyrotaxanes using elemental analysis (Table 2), IR-spectra and ^{1}H-NMR-spectra is given. The values of the elemental analyses are referred to the monomer of the polyamiderotaxanes.

IR (KBr) PAR6.N: $\tilde{\nu} = 2933$ (m), 2860 (s), 1745 (s, C=O, cuc), 1635 (s, amide I), 1545 (m, amide II) cm^{-1}; PAR6.ST (5:1): $\tilde{\nu} = 2933$ (m), 1733 (s, C=O, cuc), 1637 (m, amide I), 1543 (m, amide II) cm^{-1}.

^{1}H-NMR (D_2SO_4, d^6-DMSO): PAR6.ST 5:1 $\delta = -1.07$, -0.66, 0.54 to -0.20 (–CH_2, m), 1.20, 1.67, 2.05, 2.49 (DMSO), 3.62–2.93 (cuc), 4.91–4.13 (cuc), 6.57 (arom, 4H), 9.45 (s, D_2SO_4).

^{13}C-NMR (D_2SO_4, d^6-DMSO): PAR6.ST 5:1 $\delta = 17.62$, 29.94, 30.67, 32.19, 32.78, 47.02, 48.72, 57.46, 58.50, 77.78, 164.50, 184.15.

3.4. Measurements

The IR spectra were recorded with an FT–IR Bio-Rad, the ^{1}H-NMR spectra with a Bruker AM 200 and the DTA measurements with a DTA 2000 TA Instruments.

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