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Stereocontrolled synthesis of stereoregular, chiral analogs of nylon 5, 5 and nylon 5,6 †

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Abstract: L-glutamic acid (**1**) was employed as a chiral template in the preparation of the pentachlorophenyl ester of (4*S*)-carboxy-1,4-butirolactone (**3**), a key precursor of chiral analogs of nylon 5,5 and nylon 5,6. Stereocontrol in the synthesis of these polymers was achieved by chemoselective condensation of the ester group of **3** with aminoalcohols. The alcohol function of the resulting *N*-(hydroxyalkyl)amides (**4** and **9**) was converted into amine by tosylation, azide substitution and hydrogenolysis. The amino lactones **7** and **12** thus obtained were conveniently functionalized for the polycondensation, which led to the stereoregular, crystalline polyamides **8** and **13**. © 1997 Elsevier Science Ltd

Introduction

In recent years, some procedures have been described for the synthesis of hydroxylated, chiral nylons (polyhydroxypolyamides). Aldaric[1] and tartaric[2] acids as well as carbohydrates[3] and hydroxy amino acids derived from sugars[4,5] have been employed as monomers for the synthesis of such polyamides. Besides their potential as biodegradable and biocompatible materials, useful for medical applications, it has been reported that the presence of a stereocenter in the polyamide chain may promote their arrangement to helical conformations in the solid state, similar to those found for biopolymers.[6] These helical nylons displayed particular properties such as liquid crystals formation and piezoelectricity.[7,8]

A severe limitation encountered in the synthesis of stereoregular polyamides is the control of an ordered spatial configuration, which must be the same in every repeating unit. Otherwise, random orientation of the chiral unit will lead to a non stereoregular polymer. This problem may be overcome only when the monomeric chain possesses a stereoregular arrangement of chiral centers, for example all *S*, as happens in the polyamides derived from methylene-L-tartaric acid.[2]

We wish to report here a stereocontrolled procedure for the synthesis of polyhydroxy, chiral analogs of nylon 5,5 and nylon 5,6, from commercially available and inexpensive L-glutamic acid. The key chiral intermediate in the synthesis of both polyamides was the (4*S*)-carboxy-1,4-butyrolactone (**2**). Stereocontrol in the polymerization was achieved by intermolecular condensation of an "amino lactone" precursor.

Results and discussion

Nitrous acid deamination[9] of L-glutamic acid (**1**) gave crystalline (4*S*)-carboxy-1,4-butyrolactone (**2**), having two carboxylic groups available for the polymerization with diamines. As lactones readily react with amines,[10] we assumed that the lactone function of **2** was suitable for the polymerization. However, the carboxylic acid group required further activation for that purpose. Therefore, the conveniently activated pentachlorophenyl ester **3** was prepared by treatment of **2** with pentachlorophenol in the presence of dicyclohexylcarbodiimide. Compound **3** was obtained crystalline, and could be easily purified by recrystallization (90% yield). The ^{1}H NMR spectrum of **3** (Table 1)

† Dedicated to Professor Dr. Hans Paulsen on the occasion of his 75th birthday.

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Table 1. ^{1}H NMR Data for Compounds **3–13**

Comp.	δ (ppm)								
	H-2a,2b	**H-3a**	**H-3b**	**H-4**	**CONH**	**CH_2-1'**	**CH_2-2'-4'**	**CH_2-5'**	**CH_2-6'**
3	2.84 - 2.59			5.31					
4	2.54	2.57	2.37	4.83	6.47	3.27	1.53 - 1.36		3.62
5[a]	2.66 - 2.43		2.28	4.79	6.54	3.19	1.61 - 1.24		3.95
6	2.45	2.56	2.30	4.78	6.56	3.22	1.57 - 1.27		3.20
7[b,c]	2.45	2.42	2.07	4.89	8.34	3.09	1.60 - 1.28		2.74
8[b]	2.13	1.85	1.65	3.82	7.77, 7.66	3.02	1.39 - 1.23		3.02
9	2.53	2.59	2.35	4.83	6.63	3.27	1.54 - 1.33	3.60	
10[d]	2.66 - 2.46		2.32	4.81	6.56	3.22	1.70 - 1.23	3.98	
11	2.56	2.60	2.32	4.82	6.50	3.27	1.66 - 1.23	3.25	
12[b,e]	2.49	2.42	2.08	4.90	8.37	3.09	1.66 - 1.25	2.72	
13[b]	2.11	1.83	1.65	3.80	7.77, 7.65	3.01	1.39 - 1.23	3.01	

[a] $CH_3C_6H_4SO_2$ δ: 7.72, 7.30 (*J* 8.3 Hz), 2.39. [b] In DMSO d_6. [c] NH_3 δ: 8.07 [d] $CH_3C_6H_4SO_2$ δ: 7.74, 7.32 (*J* 8.3 Hz), 2.42. [e] NH_3 δ:7.91

Table 2. ^{13}C NMR Data for Compounds **3–13**

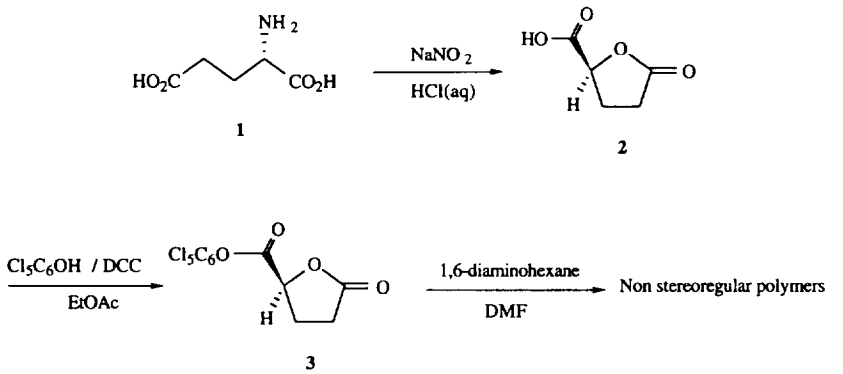
Comp.	δ (ppm) (50.3 MHz)										
	C-1	**C-4**	**C-5**	**C-1'**	**C-6'***	**C-2,3 and C-2'-5'@**					
3	175.1	74.9	169.1			25.9	26.4				
4	175.9	77.5	169.3	39.2	62.6	25.3	25.8	26.4	27.6	29.3	32.5
5	175.8	77.3	169.1	38.8	70.2	24.7	25.6	25.8	27.4	28.4	28.9
6	175.7	77.3	169.1	38.9	51.1	25.6	26.1(2)	27.4	28.5	29.0	
7[a]	177.1	77.1	169.4	38.8#	38.4#	25.6	25.8	25.9	27.0	27.3	28.8
8[a]	173.3	70.6	171.8	38.8#	38.5#	25.9(2)	28.9	29.0	30.4	31.2	
9	176.0	77.6	169.5	39.2	62.4	23.0	25.9	27.6	29.0	32.1	
10	175.8	77.3	169.2	38.7	70.1	22.5	25.7	27.5	28.2	28.5	
11	175.6	77.4	169.3	39.0	51.2	23.9	25.6	27.5	28.4	28.9	
12[a]	176.9	76.8	169.2	38.0#	38.4#	23.0	25.6	26.4	27.1	28.1	
13[a]	173.5	70.7	172.1	38.9#	38.2#	23.9	28.9	29.0	30.6	31.5	

*It corresponds to C-5' in compounds **9-13**. @C-5' corresponds to C-4' in compounds **9-13**. [a]In DMSO d_6 #Signals may be interchanged.

showed the H-4 signal as a multiplet at low fields (5.31 ppm) and in its ^{13}C NMR spectrum (Table 2) two resonances were observed due to the ester (169.1 ppm) and lactone (175.1 ppm) carboxyl groups.

The activated monomer **3** possesses an asymmetric center at C-4, which makes difficult the construction of polyamides of the -ABBA- type with ordered spatial configurations. For example, the reaction of **3** with 1,6-diaminohexane afforded a non-stereoregular polymer, formed by a random combination of the reacting units, due to the lack of regiochemical order (Scheme 1).

The construction of an stereoregular polyamide could be achieved by a regiochemically controlled condensation of an amine to one of the carboxyl functions of **3**. In order to examine if the lactone



Scheme 1.

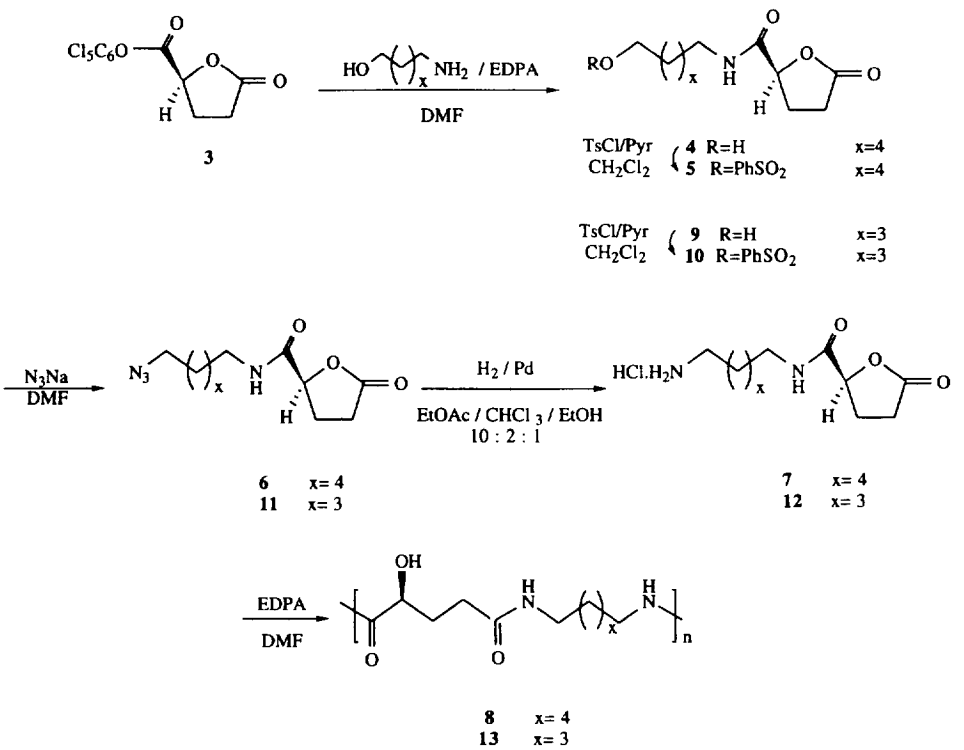
and ester groups of **3** may be chemoselectively differentiated, the condensation of this compound with an amine was attempted. 6-Amino-1-hexanol was selected as nucleophile, since it contains an hydroxyl group as a further precursor of the second amino group required for the polymerization. The condensation was conducted in the presence of ethyldiisopropylamine (EDPA) as a basic catalyst. The reaction was highly regioselective affording the amido derivative **4** in 90% yield (Scheme 2). The ^{13}C NMR spectrum of this product showed the signals for the amido (175.9 ppm) and lactone (169.3 ppm) carbonyl carbons, and the resonances of the carbons bonded to oxygen at 77.5 and 62.6 ppm. Compound **4** arises from the selective attack of the amino group of 6-amino-1-hexanol (no ester formation was detected) to the activated pentachlorophenyl carboxylate of **3**. The formation of the other regioisomer, which results from the attack of the amino group to the lactone function, was observed in a small proportion (about 5%) by NMR inspection of the reaction mixture.

Compound **4** was purified by recrystallization and its primary hydroxyl group was converted into an amino group in order to obtain an "amino acid dimer" precursor of the stereoregular polyamide. Tosylation of **4** gave **5**, which underwent nucleophilic substitution by sodium azide (DMF, 60 °C, 1 h) to afford the azide derivative **6** (90% yield from **4**). When the hydrogenolysis of the azide was conducted with 10% Pd/C in aqueous hydrochloric acid, the expected hydrochloride amino derivative **7** was impure due to the presence of a considerable amount of the product resulting from the hydrolysis of the lactone. However, the hydrogenolysis was successfully accomplished when the HCl was generated from chloroform–ethanol, as previously described.[11] Under these anhydrous conditions the crystalline hydrochloride derivative **7** was obtained in 95% yield.

The same synthetic sequence (Scheme 2) was employed to prepare the hydrochloride derivative **12**, an analog of **7** having one less carbon in the *N*-aminoalkyl chain. In this case, compound **3** was regioselectively condensed with 5-amino-1-pentanol to give the amide **9**, a direct precursor of **12**. The "amino acid dimers" **7** and **12** possess the carbonyl group activated for the polymerization, and the amino function blocked as the hydrochloride derivative. As these reacting groups for the polymerization are located in the same molecule, an exact stoichiometric ratio is provided, and hence the highest degree of polymerization should be expected.[12]

The polymerization of **7** and **12** took place after releasing the amino function with EDPA. We found that DMF was an appropriate solvent for this reaction as **7** and **12** were readily dissolved (in the presence of EDPA) in small volumes of the solvent, affording concentrated solutions which facilitated the intermolecular condensation. The EDPA hydrochloride generated during the polymerization tended to be retained persistently by the polyamide. To remove it completely the crude polymer recovered from the polycondensation mixture was subjected to repeated solution–precipitation sequences, employing DMSO (solvent)–methanol:ether (non solvent).

The IR spectra of polymers **8** and **13** were in full agreement with those expected for a polyamide.



Scheme 2.

For example, **8** gave the characteristic bands for the amide group at 1654, 1622 and 1535 cm^{-1}. The ^1H NMR spectrum of **8** showed two amide protons at 7.77 and 7.66 ppm, and the H-4 signal which appeared shifted upfield (3.82 ppm) with respect to the corresponding resonance in **7** (4.89 ppm), due to the opening of the lactone ring. The 2H-signals of the methylene groups bonded to amino (2.74 ppm) and to amido (3.09 ppm) in the latter, collapsed into a complex multiplet centered at 3.01 ppm in **8**. In the ^{13}C NMR spectrum of **8** were observed the signals for two amide carbons (173.3 and 176.8 ppm), the carbons bonded to oxygen and nitrogen (70.6 and 38.8, 38.5 ppm, respectively), and the resonances for the methylene groups between 31.2 and 25.9 ppm. The analogous polyamide **13** showed a similar spectroscopic behavior.

As observed for other stereoregular polymers[13], compounds **8** and **13** displayed relatively high optical rotation values, compared with those of the monomers. In a preliminary study, the powder X-ray diffraction of polyamides **8** and **13** revealed that these are highly crystalline products, since well defined diagrams were obtained. The differential scanning calorimetry (DSC) analysis of **8** and **13** showed broad endotherms corresponding to melting transitions, during the first heating cycle. Both polyamides also gave an endothermic peak, produced by moisture evaporation, at approximately 50 °C. The molecular weights estimated by size exclusion chromatography (SEC) are in agreement with those found for polymers prepared by polycondensation of activated esters with amines[1]. Further studies are being conducted in order to gain insight into the crystal structure and crystallization kinetics of **8** and **13**.

Experimental

General

Solvents were dried and purified when necessary, by appropriate standard procedures. TLC was performed on silica gel 60 F_{254} (Merck) with detection by UV light or by heating after immersion in a

solution of anisaldehyde (5% v/v) in 95% ethanol containing 5% H_2SO_4. Column chromatography was performed with silica gel 60 (200–400 mesh, Merck). Optical rotations were measured with a Perkin-Elmer 343 polarimeter. FT IR spectra (KBr disks) were recorded with a Nicolet 510P spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded in a Bruker AC 200 spectrometer. Differential scanning calorimetry (DSC) was carried out on a Mettler DSC 20 instrument. Samples (5–10 mg) were heated at a rate of 15 °C/min and cooled to room temperature at high rates. Peaks were taken as melting temperatures. Size exclusion chromatography (SEC) analyses were performed with polymers modified as trifluoroacetyl derivatives, in a Shimadzu L 6A apparatus with a column shim-pack series GPC 80 - 801 and 802, calibrated with polystyrene samples of narrow molecular weight distribution, with THF as solvent (flow rate 1 mL/min). X-Ray diffraction patterns were recorded in a Siemens D5000 using a nickel-filtered Cu–Kα radiation 1.542 Å.

(2S)-2-Hydroxypentanedioic acid 5,2-lactone (2)

It was prepared from (*S*)-(+)-glutamic acid (**1**) as previously described.[9]

Pentachlorophenyl 2(S)-2-hydroxypentanedioic acid ester 5,2-lactone (3)

To a solution of **2** (0.5 g, 3.85 mmol) in dry ethyl acetate (10 mL), pentachlorophenol (1.19 g, 4.42 mmol) and dicyclohexylcarbodiimide (0.925 g, 4.42 mmol) were added. After stirring at room temperature for 24 h, the suspension was filtered and the solid washed with ethyl acetate. The combined filtrate and washings were concentrated, and the residue was suspended in dichloromethane and extracted several times with saturated aqueous $NaHCO_3$. The organic layer was dried ($MgSO_4$) and concentrated under diminished pressure. The residue crystallized from ethanol to give **3** (1.31 g, 90%); mp 157–159 °C; $[\alpha]_D$ +27 (*C* 1, $CHCl_3$). Anal. Calcd for $C_{11}H_5O_4Cl_5$: C, 34.91; H, 1.33. Found: C, 35.26; H, 1.57.

*(2S)-2-Hydroxy-1-*N*-(6-hydroxy-n-hexyl)amidopentan-5-oic acid 5,2-lactone (4)*

To a stirred solution of **3** (1 g, 2.64 mmol) in dry DMF (20 mL) and ethyldiisopropylamine (EDPA, 0.4 mL) cooled at 0 °C, 6-amino-1-hexanol (0.30 g, 2.56 mmol) in dry DMF (20 mL) was added dropwise at 0 °C. The solution was stirred at room temperature for 16 h and the solvent was evaporated. The residue was chromatographed on a silica gel column with a mixture of increasing polarity of hexane–ethyl acetate (9:1 to 1:1). Concentration of the fractions having R_f 0.2 (ethyl acetate) afforded **4** (0.53 g, 90%) as a colorless solid. For analytical purposes a sample of **4** was crystallized from ethyl acetate–hexanol. It gave mp 90–92 °C; $[\alpha]_D$ −34.5 (*C* 1, $CHCl_3$). Anal. Calcd for $C_{11}H_{19}NO_4$: C, 57.63; H, 8.35; N, 6.11. Found: C, 57.37; H, 8.21; N, 6.02.

*(2S)-2-Hydroxy-1-*N*-(6-azido-n-hexyl)amidopentan-5-oic acid 5,2-lactone (6)*

To an externally cooled solution of **4** (0.30 g, 1.31 mmol) in dichloromethane (8 mL) containing dry pyridine (0.2 mL, 2.5 mmol) was added tosyl chloride (0.37 g, 1.95 mmol) in small portions. When the addition was completed, the solution was allowed to warm to room temperature and it was stirred for 24 h. The solution was diluted with dichloromethane and washed with saturated aqueous K_2CO_3. The organic layer was dried and concentrated to give the crude tosyl derivative **5**, which was used directly in the next step without further purification. TLC: R_f 0.50 (ethyl acetate). To a solution of crude compound **5** in DMF (10 mL) was added sodium azide (0.25 g, 3.9 mmol) and the mixture was heated at 60 °C for 1 h. The solvent was evaporated under diminished pressure and the residue extracted with dichloromethane. The extract was filtered and concentrated. The resulting syrup was chromatographed on a silica gel column (hexane–ethyl acetate) to give **6** (0.29 g, 90%) as a colorless oil; $[\alpha]_D$ −31 (*C* 1, $CHCl_3$). Anal. Calcd for $C_{11}H_{18}N_4O_3$: C, 51.96; H, 7.13; N, 22.03. Found: C, 51.89; H, 7.03; N, 21.78.

*(2S)-2-Hydroxy-1-*N*-(hydrochloride 6-amino-n-hexyl)amidopentan-5-oic acid 5,2-lactone (7)*

A solution of **6** (0.50 g, 1.97 mmol) in 10:1:2 EtOAc–EtOH–$CHCl_3$ (13 mL) was hydrogenated at 45 psi and room temperature, in the presence of 10% Pd–C (0.07 g). After 4 h, the mixture was filtered

and the catalyst was washed with ethanol. The combined filtrate and washings were concentrated to a syrup, which crystallized from ethanol–ethyl ether to give **7** (0.49 g, 95%); mp 147–149 °C; $[\alpha]_D$ +7 (*C* 1, DMSO). Anal. Calcd for $C_{11}H_{20}N_2O_3.1.1HCl$: C, 49.22; H, 7.92; N, 10.43. Found: C, 48.93; H, 8.16; N, 10.22.

Poly(hexamethylene-(2S)-2-hydroxypentanodiamide) (8)

A solution of **7** (0.40 g, 1.51 mmol) in dry DMF (0.9 mL) containing EDPA (0.6 mL) was stirred under N_2 at room temperature for 5 days. The polymer precipitated out upon addition of 1:3 methanol–ether. The solid was collected by centrifugation and it was purified by dissolution with DMSO and precipitation with methanol–ether. This purification procedure was repeated three times. The solid was washed with ether and dried, to afford **8** (0.29 g, 85%); Tm 183 and 200 °C; $[\alpha]_D$ −14 (*C* 0.1, DMSO); MW 2149 (SEC); ν_{max} 3315 and 3256 cm^{-1} (NH), 1654 and 1622 cm^{-1} (amide I), 1535 cm^{-1} (amide II). Anal. Calcd for $(C_{11}H_{20}N_2O_3.0.4\ H_2O)_n$: C, 56.10; H, 9.04; N, 11.89. Found: C, 56.51; H, 9.57; N, 11.59.

*(2S)-2-Hydroxy-1-*N*-(5-hydroxy-n-pentyl)amidopentan-5-oic acid 5,2-lactone (9)*

It was prepared by the procedure described for **4**, starting from **3** (1.00 g, 2.64 mmol) and 5-amino-1-pentanol (0.272 g, 2.64 mmol). The syrup obtained slowly crystallized at low temperature (−18 °C), to give **9** (0.49 g, 87%); mp 30–32 °C; $[\alpha]_D$ −36 (*C* 1, $CHCl_3$). Anal. Calcd for $C_{10}H_{17}NO_4$: C, 55.80; H, 7.96; N, 6.51. Found: C, 55.60; H, 8.14; N, 6.41.

*(2S)-2-Hydroxy-1-*N*-(5-azido-n-pentyl)amidopentan-5-oic acid 5,2-lactone (11)*

The procedure employed for the synthesis of **6** was applied, starting from **9** (0.35 g, 1.05 mmol), tosyl chloride (0.31 g 1.6 mmol) and pyridine (0.17 mL, 2.12 mmol) in dichloromethane (10 mL). The tosyl derivative **10** showed by TLC R_f 0.5 (ethyl acetate). Crude compound **10** was treated with sodium azide (0.25 g, 3.9 mmol) in the conditions described for **5**, to give **11** (0.33 g, 85%) as a colorless oil; $[\alpha]_D$ −34 (*C* 1, $CHCl_3$). Anal. Calcd for $C_{10}H_{16}N_4O_3$: C, 49.99; H, 6.71; N, 23.32. Found: C, 49.55; H, 6.31; N, 23.44.

*(2S)-2-Hydroxy-1-*N*-(5-hydrochloride amino-n-pentanyl)amidopentan-5-oic acid 5,2-lactone (12)*

It was obtained starting from **11** (0.47 g, 1.97 mmol), following the procedure described above for **7**. Compound **12** crystallized from methanol–ether as a hygroscopic solid, mp 105–107 °C; $[\alpha]_D$ +2 (*C* 1, DMSO). Anal. Calcd for $C_{10}H_{18}N_2O_3$. 1.1HCl. H_2O: C, 44.08; H, 7.80. Found: C, 43.85; H, 7.56.

Poly(pentamethylene-(2S)-2-hydroxypentanodiamide) (13)

A solution of **12** (0.38 g, 1.51 mmol) in dry DMF (0.9 mL) containing EDPA, (0.6 mL) was stirred under N_2 at room temperature for 5 days. The polymer precipitated out upon addition of 1:3 methanol–ether. The solid was collected by centrifugation, and it was purified as described for **8**. Compound **13** (0.27 g, 83%) gave, Tm 200 °C; $[\alpha]_D$ −27 (*C* 0.1, DMSO); MW 2619 (SEC); ν_{max} 3313 and 3257 cm^{-1} (NH), 1654 and 1622 cm^{-1} (amide I), 1535 cm^{-1} (amide II). Anal. Calcd for $(C_{10}H_{18}N_2O_3.0.5\ H_2O)_n$: C, 53.35; H, 8.88; N, 12.63. Found: C, 53.79, H, 8.57; N, 12.55.

Trifluoroacetylation of 8 and 13

In order to facilitate the SEC analysis of polyamides **8** and **13** they were trifluoroacetylated according to the procedure developed by Schulz.[14] To a suspension of the polyamides (20 mg) in dried chloroform (2 mL), was added trifluoroacetic anhydride and the mixture was stirred overnight at room temperature. After removing the solvent and the trifluoroacetic acid generated in the reaction by evaporation under vacuum, a transparent film of the TFA polyamide was obtained. This product was soluble in dry THF.

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