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Versatile syntheses of oligomers related to nylon 6, nylon 4 6 and nylon 6 6

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Abstract

End-capped oligomers **16**, **24** and **8** of nylon 6 (having 10, 12 and 33 amide bonds, respectively), **32** and **38** of nylon 4 6 (having 9 and 13 amide bonds, respectively), and **43** of nylon 6 6 having 3 amide bonds, have been synthesised using *N*-protected *secondary* amides and the reactions of polypeptide chemistry.

Keywords: Oligomers; Nylon 6; Nylon 4 6

1. Introduction

In earlier papers, the syntheses of oligomers related to nylon 6 [1], nylon 4 6 [2], and nylon 6 6 [2] were described, compounds of high purity able to provide physical data not blunted by inhomogeneity, the serious short-coming which is present in the study of commercial polymers. We now describe extensions to this work which demonstrate the facility to provide chains containing essentially *any* prescribed number of amide linkages.

2. Synthetic work

The original work on nylon 6 derivatives allowed the sythesis of a series of end-capped oligomers by a process of chain-doubling reactions giving compounds containing 1, 2, 4, 8 and 16 of the 6-aminohexanoic acid residues in the chain [1]. The strategic feature of this work was that in addition to using the chain-end protecting groups found in peptide chemistry, the maintainance of the solubility at room temperature in organic solvents of all intermediates was ensured using *secondary amides* –NR(CO)– (where $R = 4\text{–}MeOC_6H_4CH_2$–) to avoid the effects of inter-chain hydrogen-bonding, thereby allowing purifications by solid–liquid chromatography to be carried out. We have now performed one further doubling reaction to give a 32 amino acid-containing oligomer; the reactions involved are shown in Scheme 1.

The fully protected *N*-boc ester 16-mer **1** [1] was deprotected by hot aqueous alkali to give the carboxylic acid **2**, and by trifluoroacetic acid (TFA) at room temperature to give the secondary amine **3** [1]; coupling of **2** and **3** using dicyclohexylcarbodiimide and 1-hydroxybenzotriazole produced the fully protected boc ester **4** which was tailored to the end-capped 33-amide material **8** in four steps: (i) deprotection of the *N*-terminus as before to **5**; (ii) propanoylation of the nitrogen to **6**; (iii) amide formation at the ester-protected carboxylic acid terminus with *n*-propylamine catalysed by KCN to give **7**; and finally (iv) removal of the 4-methoxybenzyl-protecting group from the secondary amide functionality with TFA at reflux temperature to give **8**, the longest chain nylon 6 oligomer (231 atoms) which has been produced to date.

Close collaboration with the physicists using these oligomers for crystallisation studies showed the urgent requirement for end-capped oligomers having specifically 10 and 12 amides in the chain—i.e. derivatives **16** and **24** having 9 and 11 of the 6-aminohexanoic acid residues, respectively, incorporated. The former was prepared starting from carboxylic acid **10** [1] prepared by deprotection of the 8-mer boc ester **9**, which was then coupled to the monomer amine unit **11** [1]; the product **12** was subjected to the four steps described above to give in turn the secondary amine **13** followed by the *N*-propanoylated derivative **14**, the *C*-terminus protected amide of *n*-propylamine **15** and finally the target molecule **16**.

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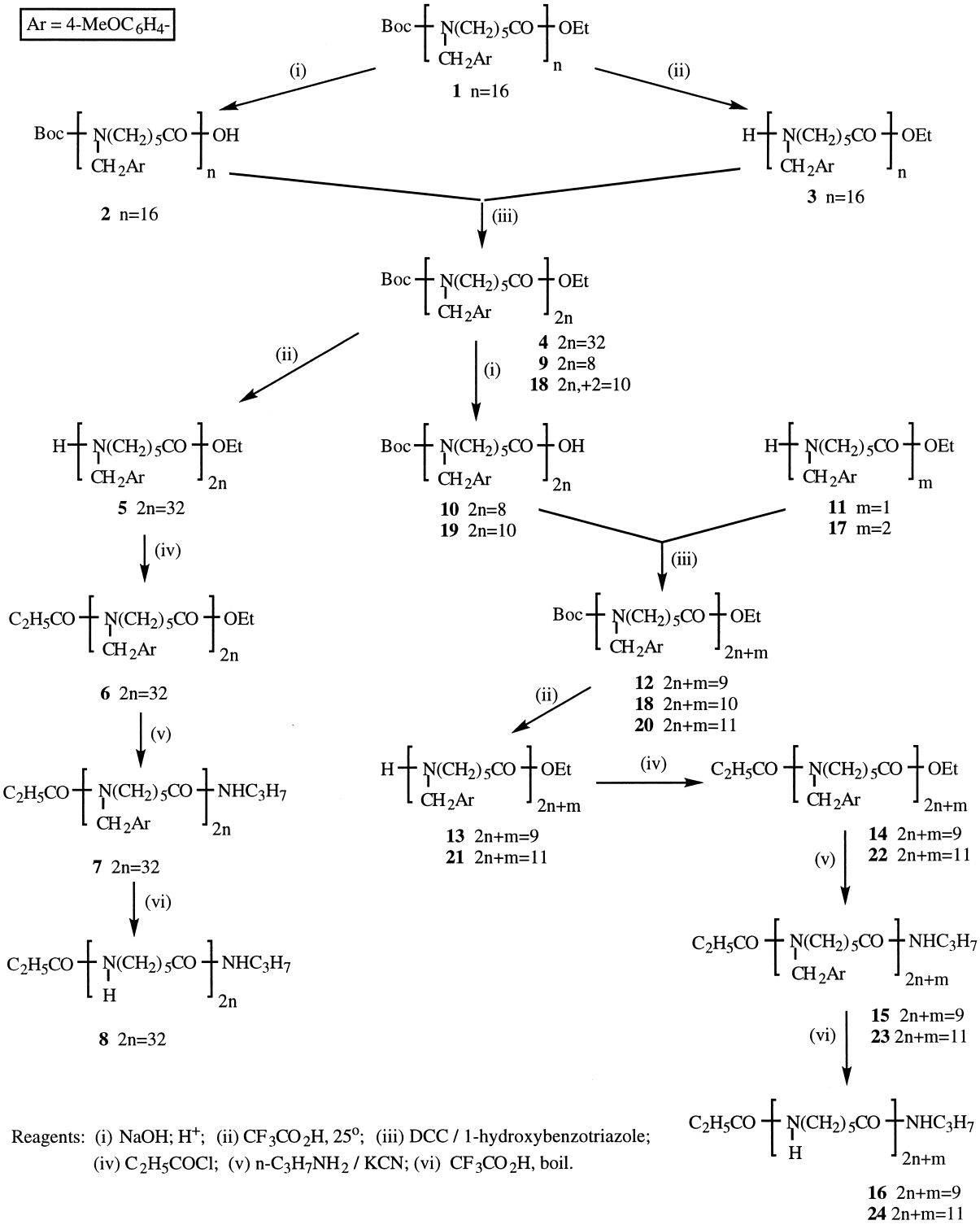


Scheme 1.

The end-capped 11-mer derivative **24** synthesis started again from the 8-mer derivative **10** which was coupled to the 2-mer secondary amine derivative **17** [1] to form the 10-mer boc ester **18**; compound **18** was hydrolysed to the acid **19** which was coupled with the 1-mer amine **11**. The resulting 11-mer boc ester **20** was then converted in turn to **21**, **22**, **23** and finally **24** as before. The integrity of all the materials was determined by the ^{1}H nmr spectroscopy, the data for the different classes of compounds being presented in Tables 1–6.

The earlier work with nylon 4 6 oligomers protected at both ends as *n*-propylamine derivatives of α,ω-dicarboxylic

Table 1
^{1}H nmr of Boc–[N(CH$_2$)$_5$CO–]$_{2n+m}$ with CH$_2$ and C$_6$H$_4$OMe and OCH$_2$CH$_3$ (in $CDCl_3$): chemical shifts at 500 MHz refer to protons in italics

	$-C_6H_4-$	$-CH_2CONCH_2Ar$ BocNCH_2Ar	$-CO_2CH_2CH_3$	$-OCH_3$	$-CH_2CON(CH_2Ar)CH_2-$ BocN$(CH_2Ar)CH_2-$	$-CH_2CO-$	$-NCH_2(CH_2)_3CH_2CO-$ $(CH_2)_3OCO-$–$CO_2CH_2CH_3$
4 ($2n + m = 32$, $m = 0$)	6.75–7.2	4.25–4.55	4.10 (overlapping q)	3.7–3.8 (overlapping s)	3.12 (bs)	2.27 (m)	1.15–1.7
Integrations (required)	126.8 (128)	62.9 (62 + 2)	2.0 (2)	96.000 (96)	3.29 (bs)	63.8 (64)	205.6 (192 + 9 + 3)
					63.3 (62 + 2)		
12 ($2n + m = 9$)	6.78–7.17	4.26–4.52	4.10 (overlapping q)	3.74–3.8 (overlapping s)	3.12 (bs)	2.27 (m)	1.16–1.7
Integrations (required)	35.8 (36)	18.1 (16 + 2)	2.0 (2)	27.000 (27)	3.29 (bs)	18.1 (18)	67.2 (54 + 9 + 3)
					18.1 (16 + 2)		
18 ($2n + m = 10$)	6.75–7.2	4.25–4.55	4.10 (overlapping q)	3.7–3.8 (overlapping s)	3.12 (bs)	2.27 (m)	1.15–1.7
Integrations (required)	39.3 (40)	19.7 (18 + 2)	2.0 (2)	30.000 (30)	3.30 (bs)	19.9 (20)	72.0 (60 + 9 + 3)
					19.8 (18 + 2)		
20 ($2n + m = 11$)	6.75–7.2	4.25–4.55	4.10 (overlapping q)	3.7–3.8 (overlapping s)	3.12 (bs)	2.27 (m)	1.15–1.7
Integrations (required)	43.3 (44)	21.9 (20 + 2)	1.9 (2)	33.000 (33)	3.30 (bs)	22.0 (22)	78.7 (66 + 9 + 3)
					21.9 (20 + 2)		

acids produced chains containing 4, 8, 12 and 16 amide bonds [2]. Two further requirements were for materials with 9 and 13 amide bonds. The strategy for synthesising these two compounds followed closely that employed in the nylon 6 series in that the products have end-capped amino and carboxylic acid groups, and is shown in Scheme 2. The starting material was the *N*-boc ester **25**, the 2-mer of the tetramethylenediamine-dicarboxylic acid unit [2]. Hydrolysis by alkali gave the acid **26** and removal of the boc group with TFA gave the secondary amine **27**. Coupling of **26** with **27** with DCC/1-hydroxybenzotriazole produced the 4-mer **28** which in turn was treated consecutively with the four reagents as before starting with TFA to yield **29**, **30**, **31** and finally the 9-amide molecule **32**.

Deprotection of the ester terminus of **28** gave **33** which was coupled with the 2-mer amine unit **27** using DCC/1-hydroxybenzotriazole to form the fully protected 6-mer boc ester **34**. Again, four stage reaction sequence progressed via **35**, **36**, **37** to the 13-amide target molecule **38**.

Finally, we report the synthesis of a 3 amide derivative of nylon 6 6, **43**, shown in Scheme 3; some of the physics has been reported already [3]. The fully protected boc ester of the 1-mer of the hexamethylenediamine-dicarboxylic acid unit **39** [2] was subjected to the four stage series of reactions described above to give **40** [2], **41**, **42** and the desired 1-mer derivative **43**.

The supporting ^{1}H nmr data for all the nylon 4 6 and the nylon 6 6 compounds are presented in Tables 7–12. The most significant feature of all the ^{1}H nmr data was that the length of the chains could be monitored accurately from the ratio of the integrals of the $-CH_2$-group in compounds containing a terminal $-CO_2CH_2CH_3$ function and the 4–CH_3O-substituent on the protecting groups on the secondary amide in the repeating unit.

3. Experimental

NMR spectra were recorded on a Bruker AMX 500 ^{1}H (500.139 MHz). Absorption multiplicities have been abbreviated as follows: s (singlet), d (doublet), t (triplet), m (multiplet), b (broad). All chemical shifts are given in ppm with respect to TMS, present in $CDCl_3$ used as solvent unless stated otherwise. Elemental analyses were performed on an Exeter Analytical Inc CE440 elemental analyser. Melting points were determined on a Gallenkamp melting point apparatus. In the majority of reactions, the products were viscous oils or gums from which last traces of solvents were removed by heating the sample at 80–100° under high vacuum; however, this treatment could not be applied to any of the secondary amines which were prepared as polymerisation was induced. Consequently, no chemical analyses are reported for these compounds.

Table 2
^{1}H nmr of Boc–[N(CH$_2$)$_5$CO(CH$_2$C$_6$H$_4$OMe)]$_k$–OH (in $CDCl_3$): chemical shifts at 500 MHz refer to protons in italics

	$-C_6H_4-$	$-CH_2CONCH_2Ar$ $BocNCH_2Ar$	$-OCH_3$	$-CH_2CON(CH_2Ar)CH_2-$ $BocN(CH_2Ar)CH_2-$	$-CH_2CO-$	$-NCH_2(CH_2)_3CH_2CO-$ $(CH_3)_3OCO-$
2 ($k = 16$)	6.7–7.2	4.3–4.6	3.7–3.8 (overlapping s)	3.1 (bs) 3.3 (bs)	2.27 (m)	1.1–1.7
Integrations (required)	63.0 (64)	31.6 (30 + 2)	48.000 (48)	31.5 (30 + 2)	31.3 (32)	104.5 (96 + 9)
19 ($k = 10$)	6.8–7.2	4.3–4.6	3.7–3.8 (overlapping s)	3.1 (bs) 3.3 (bs)	2.28 (m)	1.1–1.7
Integrations (required)	39.6 (40)	19.8 (19 + 2)	30.000 (30)	19.9 (18 + 2)	19.8 (20)	70.2 (60 + 9)

4. Preparative chromatography and HPLC analysis

After each reaction, the product was purified by preparative chromatography on Merck silica gel F60 (230–400 mesh) and in many cases the effectiveness of the separation was assessed by HPLC on a Varian Star 5065 instrument fitted with Hypersil 5 ODS 25 cm × 4.6 mm C_{18} reverse phase column.

4.1. Three stage process for formation of fully protected oligomeric derivatives of nylon 6

A(i) *Selective hydrolysis of the ethyl ester in the hexadecamer* **1**. Compound **1** (1.26 g) in hot ethanol (1.2 m) was added to NaOH (33 mg) in water (0.6 ml) and the mixture boiled under reflux for 2 h, cooled, diluted with dichloromethane (30 ml) and shaken with a mixture of hydrochloric acid (1 M, 50 ml) and saturated brine (50 ml). The organic layer was separated, washed again with brine and dried (Na_2SO_4). Evaporation of the solvent in vacuo and chromatography of the residue on silica using dichloromethane–methanol (95:5 v/v) gave α-*tert*-butoxy-ω-carboxyhexadeca[carbonyl(*p*–methoxybenzylimino)pentamethylene] **2**.(1.10 g, 88%) as a clear viscous resin (found: C, 71.01; H, 8.33; N, 5.84. $C_{229}H_{314}O_{35}N_{16}$ requires, C, 71.42; H, 8.22; N, 5.82%; ^{1}H nmr data are given in Table 2.

(ii) *Selective removal of the Boc group from the hexadecamer* **1** to give **3** was described in an earlier paper [1].

(iii) *Chain-doubling reaction to form the dotriacontamer* **4**. The carboxylic acid **2** (2.77 g, 7.2×10^{-4} mol) in a mixture of acetonitrile (14 ml) and dichloromethane (6 ml) was stirred in an ice bath for 0.5 h and dicyclohexylcarbodiimide (164 mg, 7.95×10^{-4} mol) followed by 1-hydroxybenzotriazole (109 mg, 8.0×10^{-4} mol) were added. After a further 1 h at 0°C, the secondary amine **3** (2.88 g, 7.62×10^{-4} mol) in a mixture of the same solvents (12 and 6 ml, respectively) was added, the solution stirred at room temperature for 92 h, and the precipitated dicyclohexylurea filtered off. The filtrate was washed in turn with brine (200 ml, 10% saturated), hydrochloric acid (1 M, 2 × 30 ml), saturated sodium hydrogen carbonate (30 ml) and saturated brine (50 ml) and dried (Na_2SO_4). The solvent was evaporated in vacuo, the residue dissolved in dichloromethane–methanol (98:2 v/v) and passed through a column of Merck Alumina 90 (60 g) using the same solvent mixture (150 ml). Evaporation of the solvent and chromatography of the residue on silica using ethyl acetate–methanol (95:5 ⇒ 80:20 v/v) gave α-*tert*-butoxy-ω-(ethoxycarbonyl)-dotriacontama[carbonyl(*p*–methoxybenzylimino)pentamethylene] **4**, a clear resin (4.26 g, 78%) (found: C, 71.99; H, 8.31; N, 5.90. $C_{455}H_{622}N_{32}O_{67}$ requires C, 71.79; H, 8.24; N, 5.89%); ^{1}H nmr data are given in Table 1.

B(i) *Selective hydrolysis of the ethyl ester in the octamer* **9** to give the carboxylic acid **10** was described in an earlier paper [1].

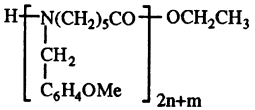
(ii) *Selective formation of the amine* **11** was described in an earlier paper [1].

(iii) *Chain-coupling of* **10** *with* **11** *to form the nonamer* **12**. The carboxylic acid **10** [1] (6.82 g, 3.44×10^{-3} mol)0 in acetonitrile (60 ml) was treated with dicyclohexylcarbodiimide (0.78 g, 3.78×10^{-3} mol) and 1-hydroxybenzotriazole (0.51 g, 3.77×10^{-3} mol) in acetonitrile (10 ml) at 0° for 1 h. The amine **11** [1] (1.05 g, 3.76×10^{-3} mol) in acetonitrile (10 ml) was added and the mixture allowed to warm to room temperature, with stirring, over 18 h. The crude product was isolated as in **A(iii)** and purified by chromatography on silica using ethyl acetate–methanol (95 : 5 ⇒ 85 : 15 v/v) to give α-*tert*-butoxy-ω-(ethoxycarbonyl)-nona[carbonyl(*p*–methoxybenzylimino)pentamethylene] **12**, a viscous oil (5.8 g, 75%) (found: C,70.95; H, 8.30; N, 5.68. $C_{133}H_{185}N_9O_{21}$ requires C, 71.13; H, 8.30; N, 5.61%); ^{1}H nmr data are given in Table 1.

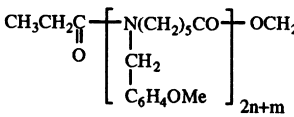
C(i) *Selective hydrolysis of the ethyl ester in the octamer* **9** to give the carboxylic acid **10** was described in an earlier paper [1].

(ii) *Selective formation of the amine* **17** was described in an earlier paper [1].

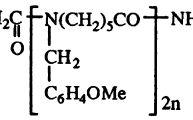
(iii) *Chain-coupling of* **10** *with* **17** *to form the decamer* **18**.

Table 3
^{1}H nmr of  (in $CDCl_3$): chemical shifts at 500 MHz refer to protons in italics

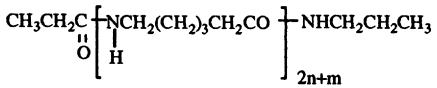
	$-C_6H_4-$	$-CH_2CONCH_2Ar$	$-CO_2CH_2CH_3$	$-OCH_3$ + $-NHCH_2Ar$	$-CON(CH_2Ar)CH_2-$	$HN(CH_2Ar)CH_2-$	$-CH_2CO-$	$-NCH_2(CH_2)_3CH_2CO-$ $CO_2CH_2CH_3$
5 ($2n + m = 32,\ m = 0$)	6.7–7.3	4.4–4.5	4.10 (overlapping q)	3.7–3.8 (overlapping q)	3.12 (bs) 3.29 (bs)	2.6 (m) 2.65 (m)	2.27 (m)	1.15–1.75
Integrations (required)	133.3 (128)	61.4 (62)	1.8 (2)	98.000 (96 + 2)	65.0 (62)	1.8 (2)	64.6 (64)	211.8 (192 + 3)
13 ($2n + m = 9$)	6.78–7.32	4.38–4.52 (m)	4.10 (overlapping q)	3.73–3.84 (overlapping s)	3.12 (bs) 3.29 (bs)	2.66 (m) 2.71 (m)	2.29 (m)	1.17–1.71
Integrations (required)	35.6 (36)	15.8 (16)	1.9 (2)	29.000 (27 + 2)	16.3 (16)	2.1 (2)	18.1 (18)	57.8 (54 + 3)
21 ($2n + m = 11$)	6.74–7.34	4.4–4.5	4.10 (overlapping q)	3.7–3.8 (overlapping singlets)	3.12 (bs) 3.30 (bs)	2.67 (m) 2.73 (m)	2.28 (m)	1.15–1.75
Integrations (required)	44.0 (44)	19.7 (20)	1.9 (2)	35.000 (33 + 2)	19.6 (20)	1.8 (2)	22.0 (22)	69.3 (66 + 3)

Table 4
^{1}H nmr spectra of  (in $CDCl_3$): chemical shifts at 500 MHz refer to protons in italics

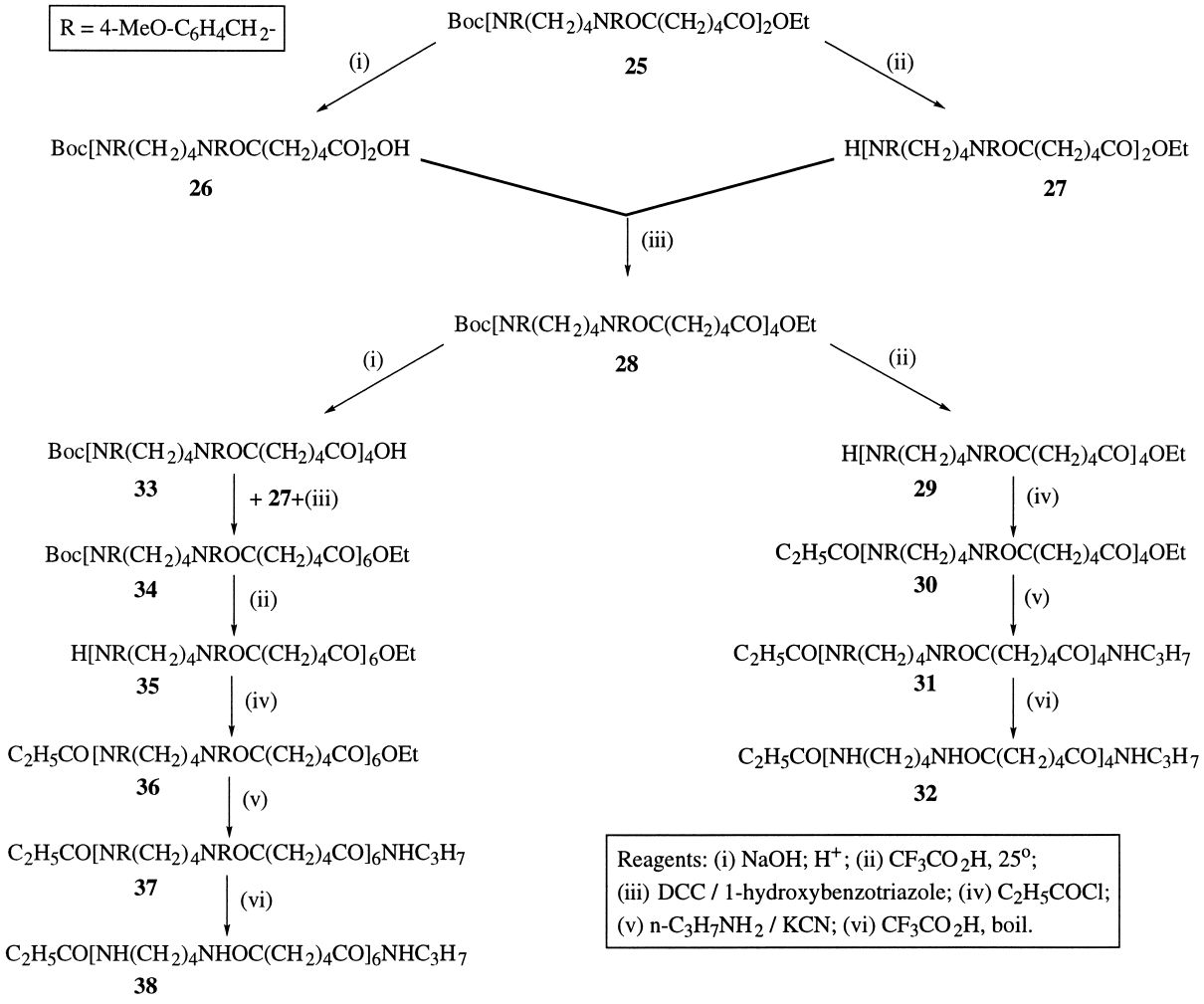
	$-C_6H_4-$	$-CH_2CONCH_2Ar$	$-CO_2CH_2CH_3$	$-OCH_3$	$-CH_2CON(CH_2Ar)CH_2-$	$-CH_2CON(CH_2Ar)-$ CH_3CH_2CON- $CH_2COOCH_2CH_3$	$-NCH_2(CH_2)_3CH_2CO$ CH_3CH_2CON- $CO_2CH_2CH_3$
6 ($2n + m = 32,\ m = 0$)	6.7–7.2	4.35–4.6	4.10 (overlapping q)	3.65–3.9 (overlapping s)	3.12 (bs) 3.30 (bs)	2.28 (m)	1.1–1.75
Integrations (required)	118.7 (128)	56.7 (64)	2.0 (2)	96.000 (96)	60.4 (64)	59.8 (62 + 2 + 2)	190.3 (192 + 3 + 3)
14 ($2n + m = 9$)	6.76–7.18	4.36–4.56	4.09 (overlapping q)	3.70–3.84 (overlapping s)	3.11 (bs) 3.29 (bs)	2.29 (m)	1.06–1.72
Integrations (required)	35.9 (36)	17.9 (18)	1.9 (2)	27.000 (27)	18.1 (18)	20.1 (16 + 2 + 2)	61.2 (54 + 3 + 3)
22 ($2n + m = 11$)	6.7–7.2	4.35–4.55	4.10 (overlapping q)	3.7–3.85 (overlapping s)	3.12 (bs) 3.30 (bs)	2.28 (m)	1.06–1.72
Integrations (required)	43.4 (44)	21.8 (22)	1.9 (2)	33.000 (33)	21.8 (22)	24.0 (20 + 2 + 2)	72.3 (66 + 3 + 3)

Table 5
^{1}H nmr spectra of  (in $CDCl_3$): chemical shifts at 500 MHz refer to protons in italics

	$-C_6H_4-$	$-CONH-$	$-CH_2CONCH_2Ar$	$-OCH_3$	$-CON(CH_2Ar)CH_2$ + $-CONHCH_{2-}$	$-CH_2CO-$	CH_3CH_2CO-	$-NCH_2(CH_2)_3CH_2CO-$, CH_3CH_2CO- $HNCH_2CH_2CH_3$	$-NCH_2CH_2CH_3$
7 ($2n + m = 32,\ m = 0$)	6.7–7.2	5.7 (b)	4.35–4.6 (m)	3.65–3.95 (overlapping s)	3.13 (bs) 3.30 (bs)	2.28 (m)	2.11 (m)	1.05–1.75 (m)	0.89 (overlapping t)
Integrations (required)	120.4 (128)	1.1 (1)	57.7 (64)	96.000 (96)	61.8 (64 + 2)	62.7 (overlapping signals)	(64 + 2)	190.0 (192 + 2 + 3)	2.7 (3)
15 ($2n + m = 9$)	6.77–7.18	5.77 (b)	4.37–4.55 (m)	3.73–3.8 (overlapping s)	3.13 (bs) 3.29 (bs)	2.28 (m)	2.11 (m)	1.07–1.72 (m)	0.89 (overlapping t)
Integrations (required)	35.9 (36)	1.0 (1)	18.1 (18)	27.000 (27)	20.1 (18 + 2)	18.2 (18)	2.1 (2)	60.1 (54 + 2 + 3)	3.0 (3)
23 ($2n + m = 11$)	6.75–7.20	5.7 (b)	4.35–4.55 (m)	3.70–3.85 (overlapping s)	3.14 (bs) 3.30 (bs)	2.28 (m)	2.11 (m)	1.07–1.72 (m)	0.89 (overlapping t)
Integrations (required)	43.2 (44)	0.9 (1)	21.7 (22)	33.000 (33)	23.7 (22 + 2)	21.9 (22)	2.0 (2)	71.5 (66 + 2 + 3)	2.9 (3)

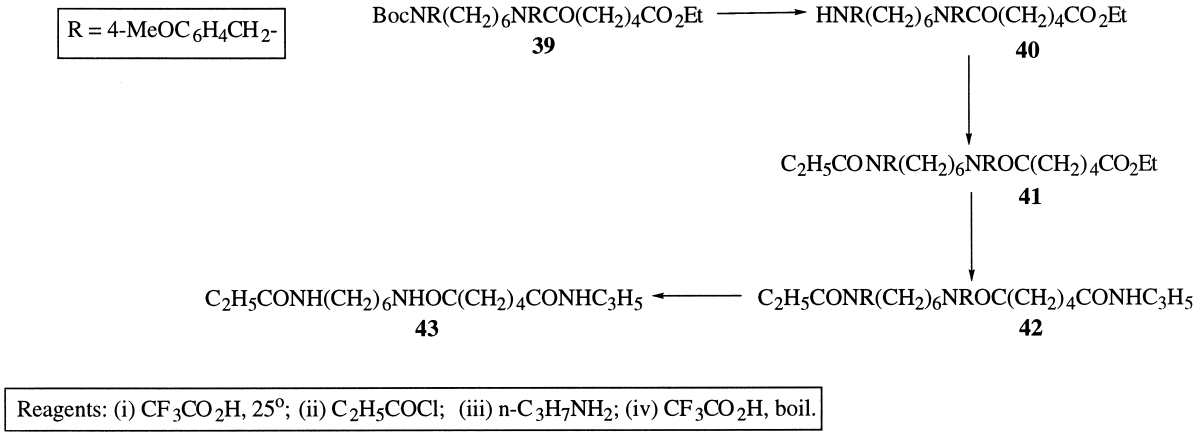
Table 6
^{1}H nmr of  (in CF_3CO_2D): chemical shifts at 500 MHz refer to protons in italics

	$-CONHCH_2-$	$-CH_2CONH-$	$-CH_2CH_2CONH-$	$-NHCH_2CH_2-$	$-NH(CH_2)_2CH_2(CH_2)_2CO-$	CH_3CH_2CONH-	$-NHCH_2CH_2CH_3$
8 ($2n + m = 32,\ m = 0$)	3.60 (m)	2.78 (m)	1.87 (m)	1.80 (m)	1.56 (m)	1.41 (t)	1.06 (t)
Integrations (required)	63.3 (64 + 2)	60.6 (64 + 2)	120.9 (some overlapping signals) (64 + 64 + 2)		62.9 (overlapping signals) (64 + 3)		3.000 (3)
16 ($2n + m = 9$)	3.61 (m)	2.78 (m)	1.88 (m)	1.81 (m)	1.56 (m)	1.41 (t)	1.06 (t)
Integrations (required)	20.3 (18 + 2)	20.3 (18 + 2)	18.1 (18)	20.6 (18 + 2)	18.2 (18)	3.21 (3)	3.000 (3)
24 ($2n + m = 11$)	3.61 (m)	2.78 (m)	1.89 (m)	1.80 (m)	1.56 (m)	1.42 (t)	1.06 (t)
Integrations (required)	24.1 (22 + 2)	23.8 (22 + 2)		70.5 (some overlapping signals) (22 + 22 + 2 + 22 + 3)			3.000 (3)



Scheme 2.

The carboxylic acid **10** [1] (3.08 g, 1.55×10^{-3} mol) in acetonitrile (20 ml) and dichloromethane (10 ml) was treated with dicyclohexylcarbodiimide (0.35 g, 1.71×10^{-3} mol), and 1-hydroxybenzotriazole (0.23 g, 1.71×10^{-3} mol) at 0° for 1 h. The amine **17** [1] (0.80 g, 1.56×10^{-3} mol) in acetonitrile (6 ml) was added and the mixture allowed to warm to room temperature, with stirring, over 117 h. The crude product was isolated as in



Scheme 3.

Table 7
^{1}H nmr of Boc–[N(–$CH_2CH_2CH_2CH_2$N(–CH_2Ar)–CH_2–$C_6H_4OCH_3$)–CH_2–CH_2–CH_2–CH_2–C(=O)–]$_n$–OCH_2CH_3 (in $CDCl_3$): chemical shifts at 500 MHz refer to protons in italics

	$-C_6H_4-$	$-CH_2CON(CH_2Ar)-$ $BocN(CH_2Ar)-$	$-CO_2CH_2CH_3$	$-OCH_3$	$-CH_2CON(CH_2Ar)CH_2-$;$BocN(CH_2Ar)CH_2-$	$-CH_2CON(CH_2Ar)-$ $-CH_2COOCH_2CH_3$	$-COCH_2(CH_2)_2CH_2CO-$ $-NRCH_2(CH_2)_2CH_2NR$ $(CH_3)_3COCO-$	$-CO_2CH_2CH_3$
28 ($n = 4$)	6.7–7.2	4.25–4.55	4.08 (m)	3.7–3.85 (overlapping s)	3.12 (bs) 3.27 (bs)	2.30 (m)	1.3–1.8 (m)	1.22 (m)
Integrations (required)	31.3 (32)	15.9 (14 + 2)	1.8 (2)	24.000 (24)	16.0 (14 + 2)	16.0 (14 + 2)	41.8 (16 + 16 + 9)	3.1 (3)
34 ($n = 6$)	6.75–7.2	4.25–4.6	4.09 (m)	3.7–3.9	3.12 (bs) 3.28 (bs)	2.30 (m)	1.3–1.8 (m)	1.22 (m)
Integrations (required)	47.5 (48)	23.8 (22 + 2)	1.9 (2)	36.000 (36)	23.9 (22 + 2)	24.0 (24)	58.0 (24 + 24 + 9)	3.0 (3)

A(iii) and purified by filtration through Merck Alumina 90 (72 g) with dichloromethane–methanol (500 ml, 99:1 v/v) evaporation of the solvent in vacuo and chromatography of the residue on silica using dichloromethane–methanol (97 : 3 ⇒ 95 : 5 v/v) to give α-*tert*-butoxy-ω-(ethoxycarbonyl)-deca[carbonyl(*p*–methoxybenzylimino)pentamethylene] **18**, a viscous oil (3.23 g, 84%) (found: C, 71.21; H, 8.42; N, 5.63. $C_{147}H_{204}N_{10}O_{23}$ requires C, 71.20; H, 8.29; N, 5.65%); ^{1}H nmr data are given in Table 1.

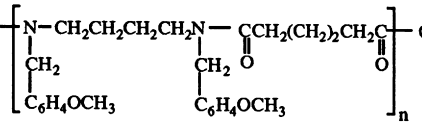
D(i) *Selective hydrolysis of the ethyl ester in the decamer* **18**. Compound **18** (3.10 g) was hydrolysed in a mixture of ethanol (40 ml), water (2 ml) and NaOH (97 mg) by the method described in A(i) and the crude product was chromatographed on silica using dichloromethane–methanol (97 : 3 ⇒ 94 : 6 v/v) to give α-*tert*-butoxy-ω-carboxydeca[carbonyl(*p*–methoxybenzylimino)pentamethylene] **19**.(2.53 g, 83%) (found: C, 70.78; H, 8.25; N, 5.70.$C_{145}H_{200}N_{10}O_{23}$ requires C, 71.05; H, 8.22; N, 5.71%); ^{1}H nmr data are given in Table 2.

(ii) *Selective formation of the amine* **11** was described in an earlier paper [1].

(iii) *Chain-coupling of* **19** *with* **11** *to form the undecamer* **20**. The carboxylic acid **19** (2.49 g, 1.02×10^{-3} mol) in a mixture of acetonitrile (18 ml) and dichloromethane (9 ml) was treated with dicyclohexylcarbodiimide (0.23 g, 1.12×10^{-3} mol) and 1-hydroxybenzotriazole (0.15 g, 1.11×10^{-3} mol) at 0° for 1 h. The amine **11** [1] (0.32 g, 1.12×10^{-3} mol) in acetonitrile (1.5 ml) was added and the mixture allowed to warm to room temperature, with stirring, over 137 h. The crude product was isolated as in A(iii) and purified by chromatography firstly on alumina using dichloromethane–methanol (100 : 0 ⇒ 99 : 1 v/v) and then on silica using dichloromethane–methanol (97 : 3 ⇒ 96 : 4 v/v) to give α-*tert*-butoxy-ω-(ethoxycarbonyl)-undeca[carbonyl(*p*–methoxybenzylimino)pentamethylene] **20**, a viscous oil (2.52 g, 92%) (found: C, 71.43; H, 8.47; N, 5.80. $C_{161}H_{223}N_{11}O_{25}$ requires C, 71.29; H, 8.29; N, 5.68%); ^{1}H nmr data are given in Table 1.

4.2. Four stage process leading to the formation of 'end-capped' oligomers of nylon 6

E(i) *Selective removal of Boc group from dotriacontamer* **4**. Compound **4** (1.90 g, 2.5×10^{-4} mol) in dichloromethane (4.3 ml) was stirred in an ice bath for 20 m and treated dropwise with trifluoroacetic acid (4.3 ml) over 30 m, and after a further 30 m was allowed to warm to room temperature over 6 h. The solution was diluted with dichloromethane (100 ml), poured into water (200 ml) and the organic phase washed with saturated sodium hydrogen carbonate (100 ml) and saturated brine (180 ml), dried (Na_2SO_4) and the solvent

Table 8
^{1}H nmr of  (in $CDCl_3$): chemical shifts at 500 MHz refer to protons in italics

	$-C_6H_4-$	$-CH_2CON(CH_2Ar)-$ BocN(CH_2Ar)	$-OCH_3$	$-CH_2CON(CH_2Ar)CH_2$; BocN(CH_2Ar)CH_2-	$-CH_2CON(CH_2Ar)$ $-CH_2COOH$	$-COCH_2(CH_2)_2CH_2CO-$ $NRCH_2(CH_2)_2CH_2NR-$ $(CH_3)_3COCO-$
26 ($n = 2$)	6.76–7.2	4.25–4.52	3.7–3.84 (overlapping s)	3.14 (bs) 3.30 (bs)	2.33 (m)	1.3–1.8
Integrations (required)	15.9 (16)	8.0 (6 + 2)	12.000 (12)	8.1 (6 + 2)	8.1 (6 + 2)	25.4 (8 + 8 + 9)
33 ($n = 4$)	6.7–7.2	4.25–4.55	3.7–3.9 (overlapping s)	3.14 (bs) 3.28 (bs)	2.34 (m)	1.35–1.8
Integrations (required)	31.5 (32)	15.9 (14 + 2)	24 000 (24)	16.0 (14 + 2)	16.3 (14 + 2)	41.1 (16 + 16 + 9)

evaporated in vacuo. The residue was chromatographed on silica using ethyl acetate–methanol (86 : 14 ⇒ 75 : 25 v/v) to give ω-ethoxydotriaconta[(*p*–methoxybenzyl)imino(6–oxohexamethylene)] **5** (1.24 g, 66%): ^{1}H nmr data are given in Table 3.

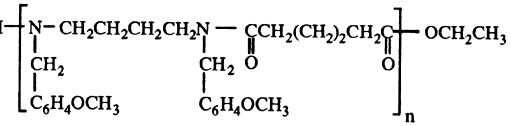
(ii) *Propanoylation of terminal NH of dotriacontamer* **5**. Compound **5** (1.32 g, 2.5×10^{-4} mol) in a mixture of dichloromethane (20 ml) and triethylamine (0.2 ml, *d* 0.726, 1.44×10^{-3} mol) was treated dropwise at 0° with propanoyl chloride (0.16 ml, *d* 1.065, 1.84×10^{-3} mol), and after stirring for 3 h, the solvent was removed in vacuo and the residue dissolved in dichloromethane (65 ml). The solution was washed with hydrochloric acid (1 M, 2×25 ml) and saturated brine (30 ml), and dried (Na_2SO_4). The solvent was removed in vacuo and the crude residue purified by chromatography on silica using dichloromethane–methanol (97 : 3 ⇒ 93 : 7 v/v) to give α-ethyl-ω-(ethoxycarbonyl)dotriaconta[carbonyl(*p*–methoxybenzyl)iminopentamethylene] **6** (1.23 g, 93%) (found: C, 71.68; H, 8.28; N, 5.87. $C_{453}H_{618}N_{32}O_{66}$ requires C, 71.89; H, 8.23; N, 5.92%); ^{1}H nmr data are given in Table 4.

(iii) *n-Propylamide formation from dotriacontamer* **6**. Compound **6** (1.13 g) in methanol (6 ml) was heated under reflux with *n*-propylamine (12 ml) and potassium cyanide (12 mg) for 96 h and the all volatile components evaporated in vacuo. The residue was dissolved in dichloromethane (40 ml) and the solution washed with hydrochloric acid (1 M, 25 ml) and saturated brine (25 ml) and dried (Na_2SO_4). The solvent was removed in vacuo and the crude residue purified by chromatography on silica using dichloromethane–methanol (96:4 v/v) to give α-ethyl-ω-(*N*-*n*-propylcarbamoyl)dotriaconta[-carbonyl(*p*–methoxybenzyl)iminopentamethylene] **7** a glass (0.69 g, 61%) (found: C, 71.67; H, 8.33; N, 6.03. $C_{454}H_{621}N_{33}O_{65}$ requires C, 71.93; H, 8.26; N, 6.10%); ^{1}H nmr data are given in Table 5.

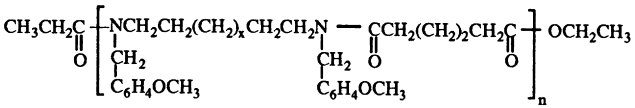
(iv) *Final deprotection of secondary amides in* **7** *to give* **8**, *an end-capped dotriacontamer of nylon* **6**. The end-capped dotriacontamer **7** (0.68 g) and trifluoroacetic acid (3 ml) were heated under reflux for 1 h and the excess reagent removed in vacuo. The treacly residue was triturated with saturated sodium hydrogen carbonate (5 ml) and the resulting solid was washed with water (4×4 ml) and toluene (5×3 ml) and dried under high vacuum. Recrystallisation from acetic acid with filtration of the hot solution through Hyflo gave α-ethyl-ω-(*N*-*n*-propylcarbamoyl)dotriaconta(carbonyliminipentamethylene) **8** (0.29 g, 87%) m.p. 188–191° (found: C, 63.35; H, 9.80; N, 12.08. $C_{198}H_{365}N_{33}O_{33}$ requires C, 63.65; H, 9.85; N, 12.37%); ^{1}H nmr data are given in Table 6.

F(i) *Selective removal of Boc group from nonamer* **12**. Compound **12** (4.2 g) was stirred at 0–5° with trifluoroacetic acid (6 ml) and allowed to warm to room temperature over 5 h. after which the mixture was diluted with dichloromethane (ca. 40 ml). The solution was washed with saturated sodium bicarbonate solution (3×20 ml) and water (50 ml), the organic phase dried (Na_2SO_4) and the solvent evaporated. Chromatography of the residue on silica using dichloromethane–methanol (95:5 v/v) gave ω-ethoxynona[(*p*–methoxybenzylimino)(6–oxohexamethylene)] **13** (3.2 g, 80%), a clear oil; ^{1}H nmr data are given in Table 3.

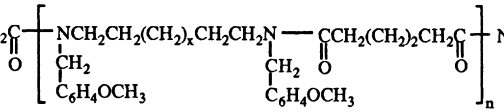
(ii) *Propanoylation of terminal NH of nonamer* **13**. Compound **13** (2.9 g, 1.35×10^{-3} mol) in a mixture of acetonitrile (20 ml) and triethylamine (0.37 ml, *d* 0.726, 2.7×10^{-3} mol) was treated dropwise at 0–5° with propanoyl chloride (0.23 ml, *d* 1.065, 2.6×10^{-3} mol), and after stirring for 2 h, the solvent removed in vacuo and the residue dissolved in dichloromethane (100 ml). The solution was washed in turn with HCl (1 M, 30 ml), water (30 ml) and saturated brine (30 ml), and dried (Na_2SO_4). The solvent was removed in vacuo and the crude residue

Table 9
^{1}H nmr of  (in $CDCl_3$): chemical shifts at 500 MHz refer to the protons in italics

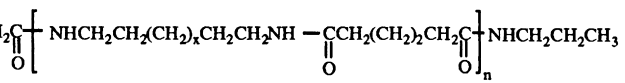
	$-C_6H_4-$	$-CH_2CON(CH_2Ar)-$	$-CO_2CH_2CH_3$	$-OCH_3$ + $HN(CH_2Ar)-$	$-CON(CH_2Ar)CH_2-$	$HN(CH_2Ar)CH_2-$	$-CH_2CON(CH_2Ar)--CH_2COOCH_2CH_3$	$-COCH_2(CH_2)_2CH_2CO-$ $-NRCH_2(CH_2)_2CH_2NR-$	$-CO_2CH_2CH_3$
29 ($n = 4$)	6.75–7.25	4.34–4.52	4.09 (m)	3.66–3.84 (overlapping s)	3.13 (bs) 3.28 (bs)	2.58 (m) 2.63 (m)	2.31 (m)	1.34–1.78	1.22 (overlapping t)
Integrations (required)	31.8 (32)	13.9 (14)	1.9(2)	26.000 (24 + 2)	14.0 (14)	1.9 (2)	17.0 (14 + 2)	32.5 (32)	3.2 (3)
35 ($n = 6$)	6.75–7.25	4.3–4.55	4.09 (m)	3.65–3.85 (overlapping s)	3.13 (bs) 3.28 (bs)	2.55–2.65 (m)	2.30 (m)	1.35–1.8	1.22 (overlapping t)
Integrations (required)	47.4 (48)	21.8 (22)	1.9 (2)	38.000 (38)	22.0 (22)	2.0 (2)	24.6 (22 + 2)	49.7 (48)	3.4 (3)

Table 10
^{1}H nmr spectra of  (in $CDCl_3$): chemical shifts at 500 MHz (or at 400 MHz)* refer to the protons in italics

	$-C_6H_4-$	$-CH_2CON(CH_2Ar)-$	$-COOCH_2CH_3$	$-OCH_3$	$-CH_2CON(CH_2Ar)CH_2-$	$-CH_2CON(CH_2Ar)-CH_3CH_2CO-$	$-COCH_2(CH_2)_2-CH_2CO-$; $-NRCH_2CH_2(CH_2)_xCH_2CH_2NR$	$-(CH_2)_x-$;CH_3CH_2CO- $-CO_2CH_2CH_3$
30 $x = 0$, $n = 4$	6.75–7.2	4.3–4.55	4.09 (m)	3.65–3.85 (overlapping s)	3.14 (bs) 3.29 (bs)	2.32 (m)	1.35–1.8	1.08–1.27 (m)
Integrations (required)	32.0 (32)	15.5 (16)	1.8 (2)	(24)	15.7 (16)	17.7 (16 + 2)	31.1 (32)	5.7 (6)
36 $x = 0$, $n = 6$	6.75–7.2	4.3–4.55	4.09 (m)	3.65–3.85 (overlapping s)	3.12 (bs) 3.28 (bs)	2.32 (m)	1.35–1.8	1.07–1.27 (m)
Integrations (required)	47.3 (48)	23.4 (24)	1.7 (2)	36.000 (36)	24.0 (24)	26.2 (24 + 2)	48.4 (48)	6.2 (6)
41* $x = 0$, $n = 1$	6.75–7.2	4.35–4.58	4.10 (m)	3.65–3.85 (overlapping s)	3.12 (bs) 3.29 (bs)	2.35 (m)	1.35–1.8	1.07–1.30 (m)
Integrations (required)	8.1 (8)	4.0 (4)	1.9(2)	6.000 (6)	4.0 (4)	5.8 (4 + 2)	7.6 (8)	8.5 (4 + 3 + 3)

Table 11
^{1}H nmr of  (in $CDCl_3$): chemical shifts at 500 MHz (or at 400 MHz*) refer to the protons in italics

	$-C_6H_4-$	$-CH_2CON(CH_2Ar)-$	$-OCH_3$	$-CH_2CON(CH_2Ar)CH_2-$ $-CONHCH_2CH_2CH_3$	$-CH_2CONH-$ $CH_2CON(CH_2Ar)-$ CH_3CH_2CO-	$-COCH_2(CH_2)_2CH_2CO-$ $-NRCH_2\ (CH_2)_2CH_2NR-$ $NHCH_2CH_2CH_3$	$-(CH_2)_x-$;CH_3CH_2CO-	$-NHCH_2CH_2CH_3$
31 $x = 0,\ n = 4$	6.75–7.2	4.35–4.55	3.7–3.85 (overlapping s)	3.13 (overlapping bs) 3.28 (bs)	2.31 (m)	1.35–1.8	1.07–1.20 (overlapping q)	0.90 (t)
Integrations (required)	32.1 (32)	15.9 (16)	24.000 (24)	18.2 (16 + 2)	18.2 (16 + 2)	33.9 (16 + 16 + 2)	3.0 (3)	3.0 (3)
37 $x = 0, n = 6$	6.75–7.2	4.35–4.55	3.7–3.9 (overlapping s)	3.12 (overlapping bs) 3.28 (bs)	2.16 (m); 2.21 (m); 2.32 (m)	1.35–1.78	1.07–1.20 (overlapping q)	0.90 (t)
Integrations (required)	47.4 (48)	23.8 (24)	36.000 (36)	25.8 (24 + 2)	26.0 (24 + 2)	50.5 (24 + 24 + 2)	3.0 (3)	3.0 (3)
42* $x = 2,\ n = 1$	6.75–7.2	4.35–4.55	3.7–3.9 (overlapping s)	3.11 (m); 3.19 (m); 3.30 (m)	2.16 (t); 2.21 (m); 2.34 (m)	1.35–1.78	1.07–1.28	0.90 (t)
Integrations (required)	7.9 (8)	4.0 (4)	6.000 (6)	6.0 (4 + 2)	5.8 (4 + 2)	8.8 (4 + 4 + 2)	5.9 (4 + 3)	2.3 (3)

Table 12
^{1}H nmr spectra of  (in CF_3CO_2D/TMS or CD_3CO_2D*); chemical shifts at 500 MHz refer to the protons in italics

	$-NHCH_2(CH_2)_2$ CH_2NH- $-NHCH_2CH_2CH_3$	$-CH_2CH_2CONH-$ CH_3CH_2CONH-	$-COCH_2(CH_2)_2CH_2CO-$	$-NHCH_2(CH_2)_2CH_2NH-$ $NHCH_2CH_2CH_3$	$-(CH_2)_x-$	CH_3CH_2CO-	$-NHCH_2CH_2CH_3$
32 $x = 0,\ n = 4$	3.6 (overlapping m)	2.76 (overlapping bs)	1.93 (bs)	1.70–1.88 (overlapping bs)		1.41 (t)	1.05 (t)
Integrations (required)	18.4 (16 + 2)	18.6 (16 + 2)	16.5 (16)	18.4 (16 + 2)		3.0 (3)	3.000 (3)
38 $x = 0,\ n = 6$	3.60 (overlapping m)	2.77 (bs)	1.93 (bs)	1.70–1.88 (overlapping bs)		1.41 (t)	1.05 (t)
Integrations (required)	25.2 (24 + 2)	24.7 (24 + 2)	23.2 (24)	25.2 (24 + 2)		3.1 (3)	3.000 (3)
43* $x = 2,\ n = 1$	3.21 (overlapping m)	2.37 (m) 2.28 (m)	1.63 (m)	1.51 (m)	1.33 (bs)	1.12 (t)	0.90 (t)
Integrations (required)	6.3 (4 + 2)	0.25 + 6.07 (4 + 2)	4.3 (4)	6.2 (4 + 2)	4.1 (4)	3.1 (3)	3.000 (3)

purified by chromatography on silica using ethyl acetate–methanol (92:8 v/v) to give α-ethyl-ω-(ethoxycarbonyl)-nona[carbonyl(*p*–methoxybenzyl)iminopentamethylene] **14** (2.71 g, 91% (found: C, 71.21; H, 8.26; N, 5.86. $C_{131}H_{181}N_9O_{20}$ requires C, 71.46; H, 8.29; N, 5.72; ^{1}H nmr data are given in Table 4.

(iii) *n-Propylamide formation from nonamer* **14**. Compound **14** (2.12 g), methanol (10 ml), *n*-propylamine (20 ml) and potassium cyanide (20 mg) were heated together under reflux for 4 d and the solvents evaporated in vacuo. The residue was dissolved in dichloromethane (100 ml), the solution washed with water (30 ml), saturated brine (30 ml) and dried (Na_2SO_4). Removal of the solvent in vacuo and chromatography of the residue on silica using dichloromethane–methanol (95:5 v/v) gave α-ethyl-ω-(*N*-*n*-propylcarbamoyl)nona[carbonyl(*p*–methoxybenzyl)iminopentamethylene] **15** a viscous liquid (1.84 g, 86%) (found: C, 71.48; H, 8.39; N, 6.33. $C_{132}H_{184}N_{10}O_{19}$ requires C, 71.58; H, 8.37; N, 6.32%); ^{1}H nmr data are given in Table 5.

(iv) *Final deprotection of secondary amides in* **15** *to give* **16**, an end-capped nonomer of nylon **6**. The end-capped nonamer **15** (1.84 g) and trifluoroacetic acid (6 ml) were heated under reflux for 40 m and the excess reagent removed in vacuo. The residue was dissolved in dichloromethane (100 ml), saturated sodium bicarbonate (10 ml) added and the mixture stirred for 10 min during which a white solid was precipitated: this was filtered off, washed with water (2 × 10 ml) and dichloromethane (8 × 100 ml), and dried in vacuo. Recrystallisation from butan-1,4-diol gave α-ethyl-ω-(*N*-*n*-propylcarbomoyl)nona(carbonyliminipentamethylene) **16** (0.796 g, 84%) mp 204–205° (found: C, 63.37; H, 10.11; N, 12.32. $C_{60}H_{112}N_{10}O_{10}$ requires C, 63.57; H, 9.96; N, 12.36%); ^{1}H nmr data are given in Table 6.

G(i) *Selective removal of Boc group from undecamer* **20**. Compound **20** (2.23 g) in dichloromethane (7 ml) was treated dropwise with trifluoroacetic acid (2.2 ml), stirred at room temperature for 5.5 h and worked up as in F(i). Chromatography of the crude product on silica using dichloromethane–methanol (95 : 5 ⇒ 85 : 15 v/v) gave ω-ethoxyundeca[(*p*–methoxybenzylimino)(6–oxohexamethylene)] **21** (1.98 g, 89%); ^{1}H nmr data are given in Table 3.

(ii) *Propanoylation of terminal NH of undecamer* **21**. Compound **21** (1.56 g, 6.07×10^{-4} mol) in a mixture of dichloromethane (25 ml) and triethylamine (0.25 ml, *d* 0.726, 2.56×10^{-3} mol) was treated dropwise at 0° with propanoyl chloride (0.20 ml, d 1.065, 2.3×10^{-3} mol), and after stirring for 4 h, the solvent was removed in vacuo and the residue dissolved in dichloromethane (75 ml). The solution was washed in turn with HCl (1 M, 2 × 25 ml) and saturated brine (30 ml), and dried (Na_2SO_4). The solvent was removed in vacuo and the crude residue purified by chromatography on silica using dichloromethane–methanol (97 : 3 ⇒ 96 : 4 v/v) to give α-ethyl-ω-(ethoxycarbonyl)undeca[carbonyl(*p*–methoxybenzylimino)pentamethylene] **22** (1.47 g, 92%) (found: C, 71.28; H, 8.26; N, 5.87. $C_{159}H_{219}N_{11}O_{24}$ requires C, 71.57; H, 8.27; N, 5.78%); ^{1}H nmr data are given in Table 4.

(iii) *n-Propylamide formation from undecamer* **22**. Compound **22** (1.44 g), methanol (8 ml), *n*-propylamine (16 ml) and potassium cyanide (20 mg) were heated together under reflux for 89 d and the solvents evaporated in vacuo. The crude product was isolated as in F(iii) and chromatographed on silica using dichloromethane–methanol (97 : 3 ⇒ 96 : 4 v/v) to give α-ethyl-ω-(*N*-*n*-propylcarbamoyl)undeca[carbonyl(*p*–methoxybenzylimino)pentamethylene] **23** a viscous liquid (1.24 g, 86%) (found: C, 71.53; H, 8.46; N, 6.40. $C_{160}H_{222}N_{12}O_{23}$ requires C, 71.67; H, 8.34; N, 6.27%); ^{1}H nmr data are given in Table 5.

(iv) *Final deprotection of secondary amides in* **23** *to give* **24**, *an end-capped undecamer of nylon* **6**. The end-capped nonamer **23** (1.20 g) in trifluoroacetic acid was kept at room temperature for 2 h, then heated under reflux for 2 h and the excess reagent removed in vacuo. The pink treacly residue was triturated with saturated sodium hydrogen carbonate solution and the resulting solid was washed with the same reagent (2 × 3 ml), water (4 × 5 ml) and toluene (4 × 5 ml) to leave a white powder which was dissolved in boiling acetic acid (12 ml) and filtered hot. The gelatinous solid which had separated after 23 h at room temperature was collected on a No. 3 glass sinter, and washed with toluene followed by water to give α-ethyl-ω-(*N*-*n*-propylcarbamoyl)undeca(carbonyliminipentamethylene) **24** (0.46 g, 76%) m.p. 198–200° (found: C, 62.85 H, 9.86; N, 12.23. $C_{72}H_{134}N_{12}O_{12}.H_2O$ requires C, 62.76; H, 9.95; N, 12.20%); ^{1}H nmr data are given in Table 6.

4.3. Three stage process for the formation of oligomers of nylon 4 6 from fully protected derivatives

H(i) *Selective hydrolysis of the ethyl ester in compound* **25**. Compound **25** [2] (5.652 g, 5.52×10^{-3} mol), ethanol (5 ml), sodium hydroxide (0.24 g, 6×10^{-3} mol) and water (20 ml) were heated together under reflux for 1 h. The ethanol was evaporated from the solution in vacuo, the mixture acidified with sulphuric acid (2 M) and extracted with dichloromethane (4 × 50 ml). The combined organic extracts were dried (Na_2SO_4), the solvent evaporated and the residue purified by chromatography on silica using dichloromethane–methanol (95 : 5 ⇒ 90 : 10 v/v) to give α-(*tert*-butoxycarbonyl-ω-hydroxy*di*[(*p*–methoxybenzyl)iminotetramethylene(*p*–methoxybenzyl)iminoadipoyl] **26**, (4.8 g, 87%) a clear

oil; (found: C, 67.60; H, 7.98; N, 5.65. $C_{57}H_{78}N_4O_{11}.1H_2O$ requires C, 67.56; H, 7.96; N, 5.53%); ^{1}H nmr data are given in Table 8.

(ii) *Selective removal of the Boc group from* **25** to give **27** was described in an earlier paper [2].

(iii) *Chain-doubling reaction to form* **28**. The carboxylic acid **26** (4.3 g, 4.32×10^{-3} mol) in acetonitrile (50 ml) was treated with dicyclohexylcarbodiimide (0.93 g, 4.51×10^{-3} mol) and 1-hydroxybenzotriazole (0.61 g, 4.51×10^{-3} mol) in acetonitrile (5 ml) at 0 to $-5°$ and the mixture stirred for 1 h. The secondary amine **27** (4.18 g, 4.53×10^{-3} mol) in acetonitrile (15 ml) was added and the mixture stirred for 2 d at room temperature. The crude product was isolated by filtering off the DCU which was washed with acetonitrile (60 ml) and the combined filtrate washed with saturated $NaHCO_3$ followed by saturated brine. The organic phase was dried (Na_2SO_4), the solvent evaporated and the residue purified by chromatography on silica using THF/diethyl ether (50 : 50 ⇒ 100 : 0 v/v) to give α-(*tert*-butoxycarbonyl)-ω-ethoxy*tetra*[(*p*−methoxybenzyl)−iminotetramethylene(*p*−methoxybenzyl)iminoadipoyl] **28** (6.138 g, 75%) a clear oil (found: C, 70.25; H, 8.01; N, 5.96. $C_{111}H_{150}N_8O_{19}$ requires C, 70.15; H, 7.96; N, 5.90%); ^{1}H nmr data are given in Table 7.

I(i) *Selective hydrolysis of the ethyl ester in compound* **28**. Compound **28** (1.89 g, 9.95×10^{-4} mol) was hydrolysed in a mixture of ethanol (2 ml), water (1 ml) and NaOH (49 mg) by the method described in A(i) and the crude product was chromatographed on silica using dichloromethane−methanol (95:5 v/v) to give α-(*tert*-butoxycarbonyl-ω-hydroxy*tetra*(*p*-methoxybenzyl)iminotetramethylene(*p*-methoxynenzyl)iminoadipoly] 33, (1.60 g, 86%) a colourless resin (found: C, 69.69; H, 8.03; N,.6.11. $C_{109}H_{146}N_8O_{19}$ requires C, 69.92; H, 7.86; N, 5.99%); ^{1}H nmr data are given in Table 8.

(ii) *Selective removal of the Boc group from* **25** to give **27** was described in a previous paper [2].

(iii) *Chain-coupling of* **33** *with* **27** *to form the hexamer* **34**. The carboxylic acid 33 (1.50 g, 8.0×10^{-4} mol) in acetonitrile (12 ml) and dichloromethane (6 ml) was treated at 0° with dicyclohexylcarbodiimide (0.186 g, 9.0×10^{-4} mol) and 1-hydroxybenzotriazole (0.121 g, 9.0×10^{-4} mol) for 1 h and the amine 27 (0.942 g containing 16% dichloromethane, 8.7×10^{-4} mol) in acetonitrile (5 ml) was added. The mixture was stirred at room temperature for 89 h, and the precipitated DCU filtered off and washed with dichloromethane (50 ml) and the combined filtrate washed successively with a mixture of water (85 ml) and brine (15 ml), hydrochloric acid (1 M, 2×50 ml), saturated sodium hydrogen carbonate (30 ml) and brine (45 ml). The organic phase was dried (Na_2SO_4) and the solvent evaporated in vacuo. The residue was passed through a column of alumina (Merck 90, 26 g) using dichloromethane−methanol (98:2 v/v) and then chromatographed on silica using (97 : 3 ⇒ 94 : 6 v/v) to give α-(*tert*-butoxycarbonyl)-ω-ethoxy*hexa*[(*p*−methoxybenzyl)−iminotetramethylene(*p*−methoxybenzyl) iminoadipoly] 34 (1.83 g, 82%) a clear resin (found: C, 70.41; H, 7.82; N, 6.08. $C_{163}H_{218}N_{12}O_{27}$ requires C, 70.47; H, 7.91; N, 6.08%); ^{1}H nmr data are given in Table 7.

4.4. Four stage process leading to the formation of 'end-capped' oligomers of nylon 4 6

J(i) *Selective removal of Boc group from tetamer* **28**. Compound **28** (1.52 g) in dichloromethane (0.8 ml) was treated dropwise with trifluoroacetic acid (1.2 ml) at 0° and stirred for 5 h at room temperature. The mixture was worked up as in E(i) and the crude product chromatographed on silica using dichloromethane−methanol (96 : 4 ⇒ 80 : 20 v/v) to give ω-ethoxytetra[*p*−methoxybenzyl)−iminotetramethylene(*p*−methoxybenzyl)iminoadipoyl] 29 (1.00 g, 62%) a clear oil; ^{1}H nmr data are given in Table 9.

(ii) *Propanoylation of terminal NH of tetramer* **29**. Compound **29** (0.95 g, 5.3×10^{-4} mol) in as mixture of dichloromethane (15 ml) and triethylamine (0.15 ml, d 0.726, 1.5×10^{-3} mol) was treated with propanoyl chloride (0.22 ml, *d* 1.065, 2.5×10^{-3} mol) at 0° and after stirring at room temperature for 2.75 h, the solvent was removed in vacuo and worked up as E(ii). The crude product chromatographed on silica using dichloromethane−methanol (98 : 2 ⇒ 94 : 6 v/v) to give α-*N*-propanoyl-ω-ethoxy*tetra*[(*p*−methoxybenzyl)iminotetramethylene(*p*−methoxybenzyl)−iminoadipoyl] 30 a colourless gum (0.95 g, 98%) (found: C, 70.17; H, 8.04; N, 6.24. $C_{109}H_{146}N_8O_{18}$ requires C, 70.52; H, 7.93; N, 6.04; ^{1}H nmr data are given in Table 10.

(iii) *n-Propylamide formation from tetramer* **30**. Compound **30** (0.89 g) in methanol (5 ml) was heated under reflux with *n*-(propylamine (10 ml) and potassium cyanide (10 mg) for 96 h and worked up as in E(iii). The crude product was chromatographed on silica using 5–20% methanol in a mixture of ethyl acetate and dichloromethane (2:1 v/v) to give α-*N*-propanoyl-ω-*n*-propylamino*tetra*[*p*−methoxybenzyl)iminotetramethylene(*p*−methoxybenzyl)−iminoadipoyl] 31 a hard resin (0.79 g, 88%) (found: C, 70.11; H, 8.10; N, 6.82. $C_{110}H_{149}N_9O_{17}$ requires C, 70.67; H, 8.03; N, 6.79%); ^{1}H nmr data are given in Table 11.

(iv) *Final deprotection of secondary amides in* **31** *to give* **32**, an endcapped tetramer of nylon 4 6. The end-capped tetramer 31 (0.74 g) and trifluoroacetic acid (3 ml) were heated under reflux for 55 m and the excess reagent removed in vacuo. The crude product was worked up as in E(iv) without a hot filtration, and the solid which

separated after 4 d was washed with dichloromethane to give α-*N*-propanoyl-ω-*n*-propylamino*tetra*[iminotetramethylene–iminoadipoyl] 32 (0.31 g, 86%) mp 234–236° (found: C, 60.38; H, 9.66; N, 13.62. $C_{46}H_{85}N_9O_9$ requires C, 60.84; H, 9.43; N, 13.88%); ^{1}H nmr data are given in Table 12.

K(i) *Selective removal of Boc group from hexamer* **34**. Compound **34** (1.80 g) in dichloromethane (5 ml) was treated dropwise with trifluoroacetic acid (1.8 ml) at 0° and stirred for 6 h at room temperature. The mixture was worked up as in E(i) and the crude product chromatographed on silica using dichloromethane–methanol (96 : 4 ⇒ 78 : 22 v/v) to give ω-ethoxy*hexa*[(*p*–methoxybenzyl)iminotetramethylene(*p*–methoxybenzyl)–iminoadipoyl] 35 (1.63 g, 94%) a sticky resin; ^{1}H nmr data are given in Table 9.

(ii) *Propanoylation of terminal NH of the hexamer* **35**. Compound **35** (1.56 g, 5.8×10^{-4} mol) in a mixture of dichloromethane (25 ml) and triethylamine (0.25 ml, *d* 0.726, 2.56×10^{-3} mol) was treated with propanoyl chloride (0.20 ml, *d* 1.065, 2.3×10^{-3} mol) at 0° and after stirring at room temperature for 3.5 h, the solvent was removed in vacuo and worked up as E(ii). The crude product chromatographed on silica using dichloromethane–methanol (97 : 3 ⇒ 94 : 6 v/v) to give α-*N*-propanoyl-ω-ethoxy*hexa*[(*p*–methoxybenzyl)iminotetramethylene(*p*–methoxybenzyl)–iminoadipoyl] 36 (1.45 g, 90%) (found: C, 70.13; H, 7.97; N, 6.10. $C_{161}H_{214}N_{12}O_{26}$ requires C, 70.74; H, 7.89; N, 6.16%; ^{1}H nmr data are given in Table 10.

(iii) *n-Propylamide formation from hexamer* **36**. Compound **36** (1.41 g) in methanol (8 ml) was heated under reflux with *n*-propylamine (16 ml) and potassium cyanide (24 mg) for 74 h and worked up as in E(iii). The crude product was chromatographed on silica using dichloromethane–methanol (97 : 3 ⇒ 94 : 6 v/v) to give α-*N*-propanoyl-ω-*n*-propylamino*hexa*[(*p*–methoxybenzyl)iminotetramethylene(*p*–methoxybenzyl)–iminoadipoyl] 37 a clear glass (1.38 g, 97%) (found: C, 70.84; H, 8.08; N, 6.63. $C_{162}H_{217}N_{13}O_{25}$ requires C, 70.84; H, 7.96; N, 6.63%); ^{1}H nmr data are given in Table 11.

(iv) *Final deprotection of secondary amides in* **37** *to give* **38**, an end-capped hexamer of nylon 4 6. The end-capped tetramer 37 (1.38 g) and trifluoroacetic acid (6 ml) were heated under reflux for 1 h and the excess reagent removed in vacuo. The crude product was worked up as in E(iv) and the solid which separated after 48 h was washed with ethanol to give α-*N*-propanoyl-ω-*n*-propylamino*hexa*[iminotetramethylene–iminoadipoyl] 38 (0.48 g, 73%) mp 248–251° (found: C, 60.44; H, 9.23; N, 13.88. $C_{66}H_{121}N_{13}O_{13}$ requires C, 60.76; H, 9.35; N, 13.96%); ^{1}H nmr data are given in Table 12.

4.5. Four stage process for formation of end-capped monomer of nylon 6 6

L(i) *Selective removal of Boc group from monomer* **39** to give **40** was described in a previous paper [2].

(ii) *Propanoylation of terminal NH of the monomer* **40**. Compound **40**. (9.5 g, 1.86×10^{-2}) in a mixture of dichloromethane (100 ml) and triethylamine (3.8 ml, *d* 0.726, 2.73×10^{-2} mol) was treated dropwise at −5° with propanoyl chloride (3.8 ml, d 1.065, 2.78×10^{-2} mol), and after stirring for 45 m the solvent was removed in vacuo and the residue dissolved in dichloromethane (80 ml). The solution was washed with water, hydrochloric acid (1 M, 30 ml), saturated $NaHCO_3$ (30 ml) and saturated brine (30 ml). The organic phase was dried (Na_2SO_4) the solvent removed in vacuo and the crude residue purified by chromatography on silica using diethyl ether to give ethyl *N*-[6–(*p*–methoxybenzyl)–6–(propanoyl)aminohexyl]-*N′*-(*p*-methoxybenzyl)adipamate 41 an oil (9.422 g, 89%) (found: C, 69.36; H, 8.46; N, 5.09. $C_{33}H_{48}N_2O_6$ requires C, 69.42; H, 8.48; N, 5.08%); ^{1}H nmr data are given in Table 10.

(iii) *n-Propylamide formation from monmer* **41**. Compound **41** (8.866 g), methanol (10 ml), *n*-propylamine (15 ml) and potassium cyanide (20 mg) were heated together under reflux for 48 h, and the solvents removed in vacuo. The residue was dissolved in dichloromethane (50 ml) and the solution washed with water, then with saturated brine and dried (Na_2SO_4). Removal of the solvent in vacuo gave the crude product which was purified by chromatography on silica using ethyl acetate: methanol (96:4 v/v) to give unchanged **41**(1.22 g) and α-propanoyl-ω-*n*-propylamino[(*p*–methoxybenzyl)iminohexamethylene(*p*–methoxybenzyl)iminoadipoyl] 42 (7.312 g, 93%) a viscous liquid (found: C, 69.90; H, 8.89; N, 7.29. $C_{34}H_{51}N_3O_5$ requires C, 70.19; H, 8.84; N, 7.22%); ^{1}H nmr data are given in Table 11.

(iv) *Final deprotection of secondary amides to give* **43**, an end-capped monomer of nylon 6 6. The end-capped monomer **42** (7.312 g) and trifluoroacetic acid (3 ml) were heated under reflux for 1 h and the excess reagent was removed in vacuo. The residue was treated with ethanol and the resulting solid was filtered off and dissolved by washing with hot ethanol (4 × 50 ml). Evaporation of the filtrate and recrystallisation from ethanol gave α-propanoyl-ω-*n*-propylamino[iminohexamethyleneiminoadipoyl] 43 (1.811 g, 42%) m.p. 177° [3] (found: C, 63.25; H, 10.43; N, 12.32. $C_{18}H_{35}N_3O_3$ requires C, 63.31; H, 10.33; N, 12.30%); ^{1}H nmr data are given in Table 12.

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