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The synthesis of oligomers related to nylon 4 6 and nylon 6 6

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Abstract

A series of end-capped oligomers **17**, **21**, **25** and **28** related to nylon 4 6, and **39**, **43**, **47** and **50** related to nylon 6 6 have been prepared starting from adipic acid monoethyl ester **6**, the α,ω-di-secondary diamines **8** and **29** and their mono end-protected derivatives **7** and **30**, respectively, using the reactions of polypeptide chemistry. The formation of N-protected *secondary* amide bonds bearing the *N-p*-methoxybenzyl group ensured the solubility of all intermediates in common organic solvents and enabled purification by chromatography; boiling trifluoroacetic acid removed the protecting group in the final stage of the synthesis. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Oligomers; Nylon 4 6; Nylon 6 6

1. Introduction

The polydispersity of synthetic polymers is the scourge of scientists wanting to study physical properties (e.g., crystallisation processes and crystal morphology) since the results are inevitably blunted by the inhomogeneity of the material. We have reported the preparation of some monodisperse linear long-chain alkanes [1] which are now being actively investigated as models for commercial polythene [2], and we have described the synthesis of some end-capped oligoamides related to nylon 6 for analogous studies [3]. The crucial feature in the synthesis of these oligoamides was the formation of the *secondary amides* -NR(C=O)- (where R = 4-$MeOC_6H_4CH_2$-) in the chain-extension reactions, which were soluble in common organic solvents because of the absence of inter-chain hydrogen-bonding effects; they were purified by preparative-scale chromatography and their purity monitored by analytical h.p.l.c. and ^1H n.m.r. spectroscopy. Replacement of the *protecting group* R by H was the final stage in the synthetic procedure.

In his pioneering work on polyamides, Carothers described the first use of a *di*secondary diamine MeNH $(CH_2)_5NHMe$ to make $-[N(Me)(CH_2)_5N(Me)\ (C=O)\ (CH_2)_2\ (C=O)]_n-$, a nylon 5 4 derivative which exhibited rubbery properties [4]. Other workers later prepared nylon 6 6 compounds containing different levels of *N*-methyl groups from the corresponding diamines [5], the fully methylated material being a viscous liquid/gum at room temperature, with increased solubility in organic solvents. Other 1,6-dialkyl groups incorporated into the hexamethylene diamine moiety included ethyl, 2-methylpropyl and benzyl [6]. In this article, we report the synthesis of pure oligomers of nylon 4 6 and of nylon 6 6; some derivatives of the latter were described by German workers over 35 years ago [7], but because of their poor solubility in common organic solvents, their *precise* purity is unknown.

2. Synthetic work

In the recent work on the synthesis of oligomers of nylon 6 [3] starting from the fully protected 6-aminohexanoic acid **1** and utilising the methods developed in polypeptide chemistry, removal of the Boc protecting group [8] with trifluoroacetic acid at room temperature [9] produced the secondary amine derivative **2**, while treatment of **1** with alkali gave the acid **3**. Condensation of **2** and **3** using dicyclohexylcarbodiimide (DCC)/1-hydroxybenzotriazole [10] gave **4** containing the first secondary amide group, and the process was repeated in turn to form the chain-doubled product **5** and higher homologues (Scheme 1). Removal of the *N*-Boc protecting group and ethanoylation, was followed by conversion of the ester end group into the *N*-propylamide [11] and the synthesis of the end-group protected oligomers completed by removal of the secondary amide protecting groups with boiling trifluoroacetic acid [12].

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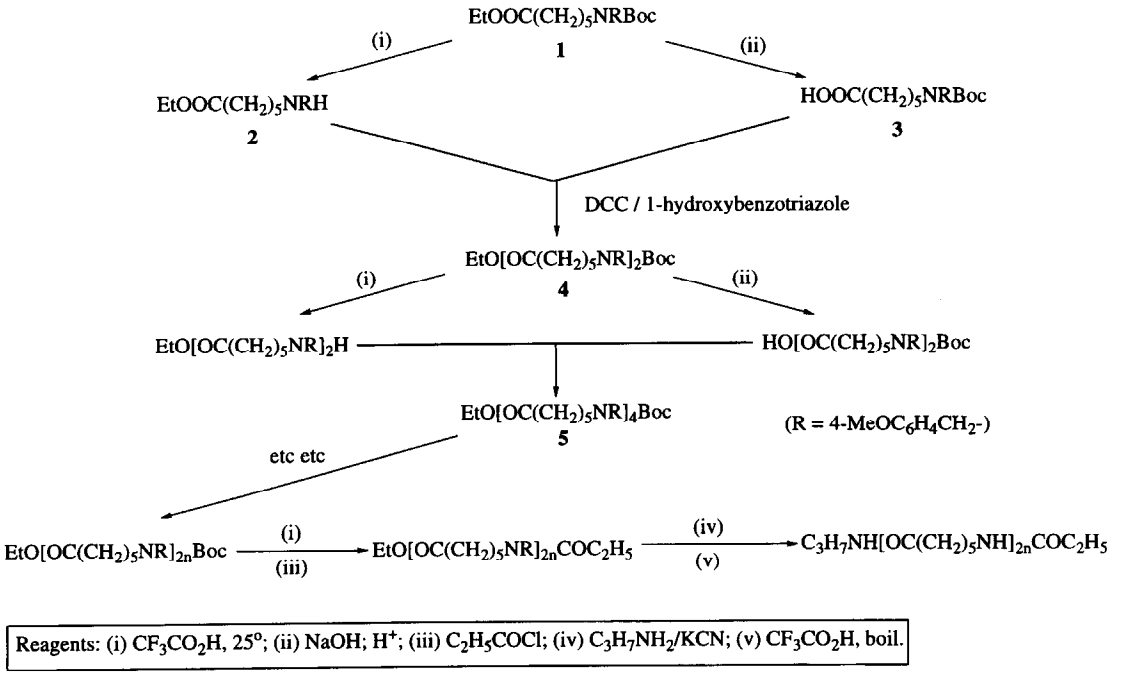
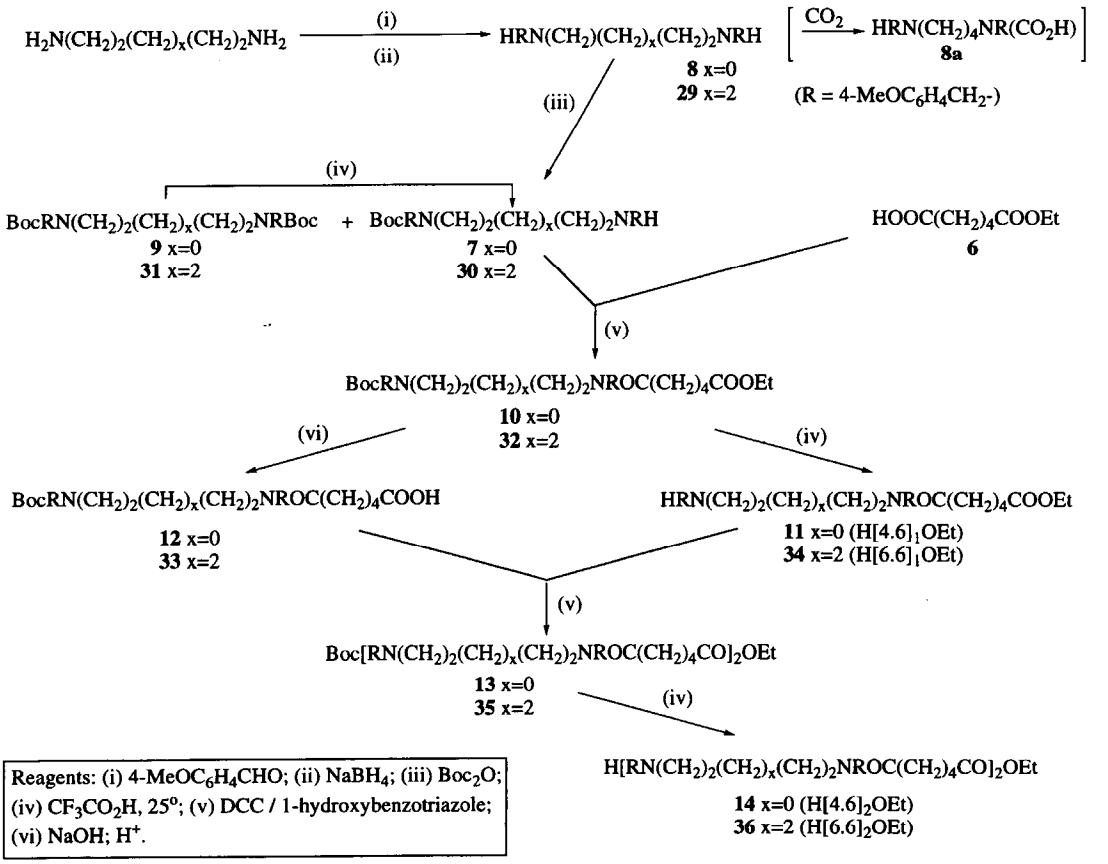


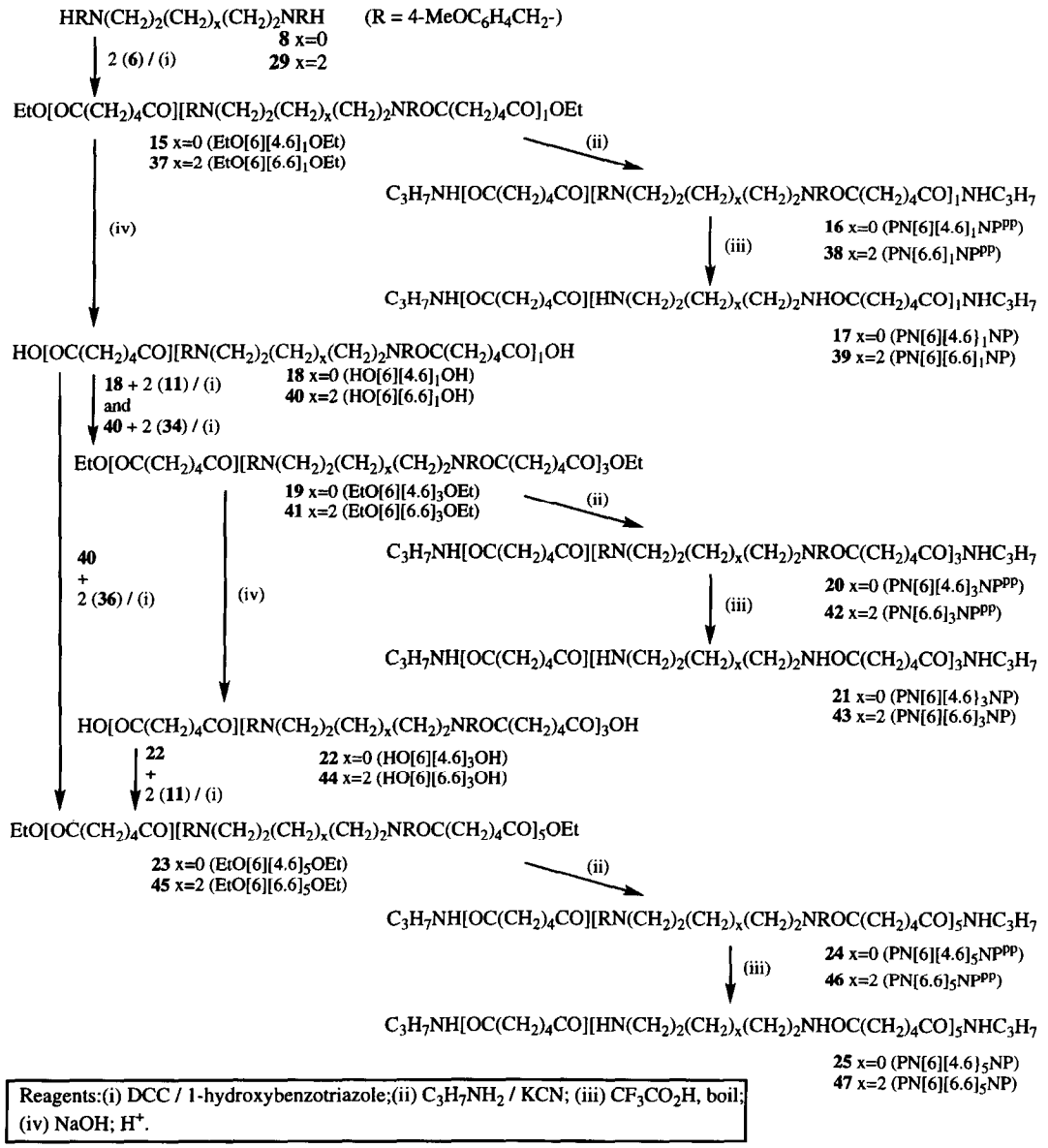
Scheme 1.



Scheme 2.

The exploitation of this methodology for the preparation of oligomers of nylon 4 6 required the half ester of adipic acid **6** and the mono-protected *N,N'*-bis(alkyl)-1,4-diamine **7** and is shown in Scheme 2. The former compound is commercially available while the latter was prepared via treatment of 1,4-butanediamine with *p*-methoxybenzaldehyde and reduction of the crude di-imine with sodium borohydride to the *N,N'*-bis(alkyl)-1,4-diamine derivative **8**. Compound **8** (which had a propensity to absorb CO_2 from the atmosphere to form the carbamic acid **8a**) was converted with one equivalent of Boc_2O into the mono Boc derivative **7** (39%) and 1,4-di-Boc derivative **9**, which in turn was converted into further compound **7** (19%) by half deprotection with trifluoroacetic acid at room temperature. The condensation of **6** with **7** gave **10** which was separately deprotected to the secondary amine **11** (abbreviated H $[4.6]_1$OEt) and the acid **12**. One more condensation between **11** and **12** yielded the fully protected compound **13**, which was finally deprotected at the terminal nitrogen to form **14** ($H[4.6]_2OEt$). Compounds **11** and **14** were key reactants for the preparation of the longer oligomers of nylon 4 6 in this work. Repetition of the chain-doubling process would lead to a geometrical series of oligomers having one amino and one carboxyl termini, like those related to nylon 6[3]. However, there were advantages in preparing oligomers with two identical end-groups with a centre of symmetry, since some compounds in the nylon 6 6 series (see later) had been made before [7]. We therefore decided to synthesise α,ω-di-*n*-propylamide 'end-capped' derivatives of oligomers of nylon 4 6, so that the corresponding α,ω-di-ethyl esters were required as intermediates.

Condensation of the *N,N'*-bis(alkyl)-1,4-diamine **8** with two equivalents each of adipic acid monoethyl ester /DCC



Scheme 3.

/1-hydroxybenzotriazole gave the α,ω-di-ester **15** (EtO[6][4.6]$_1$OEt) which with two equivalents of *n*-propylamine and a catalytic amount of potassium cyanide gave the partially protected oligoamide **16** (abbreviated PN [6][4.6]$_1$NP^{PP}). Treatment of **16** with TFA at reflux temperature resulted in the formation of the first 'end-capped' oligoamide of nylon 4 6, compound **17** (PN[6][4.6]$_1$NP), possessing four amide linkages (Scheme 3).

The di-ester **15** was hydrolysed to the di-acid **18** which was reacted with two equivalents of the terminal secondary amine **11** to give the α,ω-di-ester **19** (EtO[6][4.6]$_3$OEt). Reaction of **19** with two equivalents of *n*-propylamine and a catalytic amount of potassium cyanide gave the partially protected oligoamide **20** (PN[6][4.6]$_3$NP^{PP}) which with TFA at reflux temperature gave the second 'end-capped' oligoamide of nylon 4 6, compound **21** (PN[6][4.6]$_3$NP), possessing eight amide linkages.

In an analagous sequence of reactions, the di-ester **19** was converted into the di-acid **22**, which with **11** again, gave the α,ω-di-ester **23** (EtO[6][4.6]$_5$OEt); **23** was transformed into **24** which was deprotected to the third 'end-capped' oligoamide of nylon 4 6, compound **25**, (PN[6][4.6]$_5$NP), possessing 12 amide linkages.

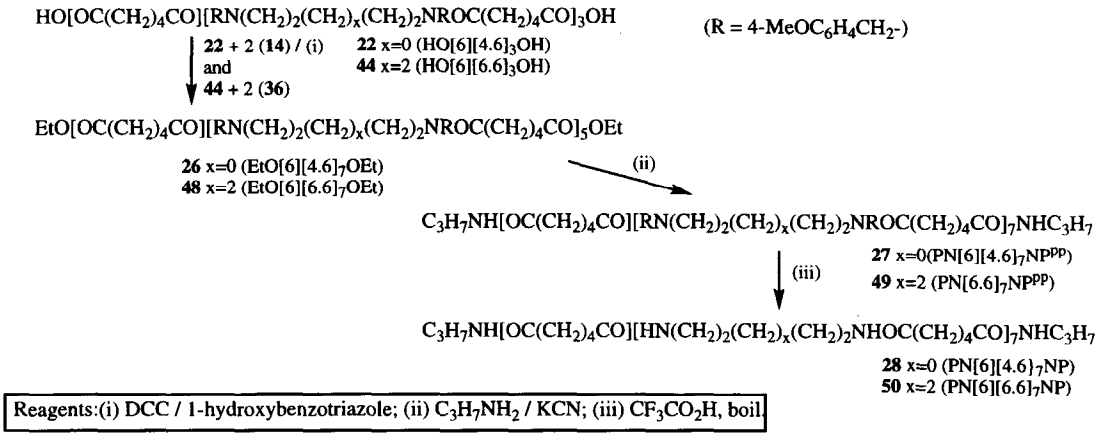
Finally, the di-acid **22** was reacted with the longest terminal secondary amine prepared in this work, compound **14**, to give the the α,ω-di-ester **26** (EtO [6] [4.6]$_7$ OEt); **26** was converted into **27** which was deprotected to the fourth 'end-capped' oligoamide of nylon 4 6, compound **28**, (PN[6][4.6]$_7$NP), possessing 16 amide linkages (Scheme 4).

Repeated addition of the two two-residue components, derived from compound **14**, would lead to oligomers with *n*, *n* + 4, *n* + 8 residues etc., i.e., an arithmetical series; for longer chains the geometrical progression involved in chain-doubling the asymmetrical component **14** before reaction with component **22** would be preferable [13].

Oligomers of nylon 6 6 (**39**, **43**, **47** and **50**) were prepared in essentially the same way as for the nylon 4 6 compounds (Scheme 3, Scheme 4). In addition to **6**, crucial materials were **29**, **30**, **34** and **36** (Scheme 2); surprisingly, no carbamic acid analogous to **8a** was observed from **29**. A more efficient route to the derivative **45** (EtO[6][6 6]$_5$OEt than the one used for the corresponding compound **23** (EtO[6][4 6]$_5$OEt was achieved by reacting **40** with **36**.

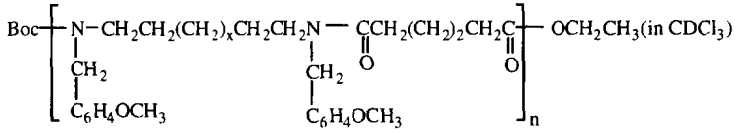
The structures of *all* the compounds described in this paper were established by ^{1}H n.m.r. spectroscopy, chemical shifts being assigned using standard tables of data [14]. Data are tabulated for both the nylon 4 6 and the nylon 6 6 series: for the α,ω-Boc ethyl ester compounds **10** and **13**, and **32** and **35** and the products of their deprotection at the terminal nitrogen (**11** and **14**, and **34** and **36**) in Table 1, Table 2, respectively; for the α,ω-diethyl esters (**15**, **19**, **23** and **26**) and (**37**, **41**, **45** and **48**) in Table 3; for the α,ω-diacids **18** and **22**, and **40** and **44**, in Table 4; and for the α,ω-di-*n*-propylamides fully protected on internal amide groups (**16**, **20**, **24** and **27**) and (**38**, **42**, **46** and **49**), in Table 5. The most significant data concerning the *chain lengths* of the various molecules are the excellent values found for the relative intensities expected for specific signals due to *terminal* compared to internal *repeating* groups. Thus the intensity of the signal due to the $-CH_2-$ group (*ca.* 4.1 ppm) in the *terminal* $-CO_2CH_2CH_3$ functionality can be compared with that of adjacent signals due to the *p*-CH_3O- substituents on the protecting group on the secondary amide in the *repeating* group in the compounds listed in Tables 1–3; in Table 5 the CH_3- (*ca.* 0.9 ppm) in the *terminal n*-propylamido groups can be compared with the *p*-CH_3O- substituents in the *repeating* group once more. Overlapping quartets due to the $-CH_2-$ group in the *terminal* $-CO_2CH_2CH_3$ functionality were observed previously in the nylon 6 oligomers[3] and is accounted for on the basis of E/Z isomerism in amides which occurs because of partial double bond character between the C–N bond [15]. The protons in the extra central $-C_2H_4-$ between the two nitrogens in the α,ω-diamine moiety in the nylon 6 6 series compared with the corresponding nylon 4 6 compounds were nicely resolved in the compounds shown in Table 4 Table 5 Table 6.

The structures of the final end-capped oligoamides (**17**,



Scheme 4.

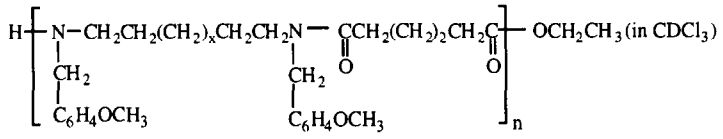
Table 1
^{1}H n.m.r. of :



Chemical shifts at 500 MHz; data refer to the protons underlined

	-$C_6\underline{H}_4$-	-$CH_2CON(C\underline{H}_2Ar)$-	$BocN(C\underline{H}_2Ar)$-	-$CO_2C\underline{H}_2CH_3$	-$OC\underline{H}_3$	-$CH_2CON(CH_2Ar)C\underline{H}_2$-; $BocN(CH_2Ar)C\underline{H}_2$-	-$C\underline{H}_2COOC_2H_5$ -$C\underline{H}_2CON(CH_2Ar(CH_2)$	-$COCH_2(C\underline{H}_2)_2CH_2CO$- -$NRCH_2C\underline{H}_2(CH_2)_x$ CH_2CH_2NR- $(CH_3)_3C$	-$CH_2CH_2C\underline{H}_3$ -$(C\underline{H}_2)_x$
10 x = 0, n = 1	6.8-7.2	4.47(s), 4.40(s)	4.31(bs)	4.10 (overlapping q)	3.7-3.8 (overlapping s)	3.30(bs); 3.0-3.25 (overlapping bs)	2.35-2.38(m)	1.55-1.75(m); 1.3-1.53(m)	1.23(overlapping t)
Integrations (required)	8.0(8)	2.0(2)	2.0(2)	2.0(2)	6.000(6)	4.0(4)	4.0(4)	18.5(17)	3.0(3)
13 x = 0, n = 2	6.78-7.2	4.36-4.5(m)	4.3(bs)	4.1 (overlapping q)	3.7-3.8 (overlapping s)	3.29(bs); 3.0-3.2 (overlapping bs)	2.24-2.40(m)	1.55-1.75(m); 1.3-1.5(m)	1.23 (overlapping t)
Integrations (required)	16.1(6)	6.0(6)	2.0(2)	2.0(2)	12.000(12)	8.0(8)	8.0(8)	25.6(25)	3.1(3)
32 x = 2, n = 1	6.8-7.2	4.7(s), 4.40(s)	4.31(bs)	4.10 (overlapping q)	3.7-3.8 (overlapping s)	3.29 (overlapping d); 3.0-3.2(b)	2.25-2.38(m)	1.55-1.75(m); 1.35-1.55(m)	1.16-1.28 (overlapping m)
Integrations (required)	8.0(8)	2.0(2)	2.0(2)	2.0(2)	6.000(6)	4.0(4)	4.0(4)	17.2(17)	7.0(3 + 4)
35 x = 2, n = 2	6.79-7.2	4.39-4.55(m)	4.3(b)	4.10 (overlapping q)	3.7-3.8 (overlapping s)	3.28(bs); 3.0-3.2(b)	2.25-2.43(m)	1.56-1.75(m); 1.40-1.55(m)	1.16-1.28 (ovelapping m)
Integrations (required)	16.1(16)	6.1(6)	2.0(2)	2.0(2)	12.000(12)	8.1(8)	8.0(8)	25.6(25)	11.0(3 + 8)

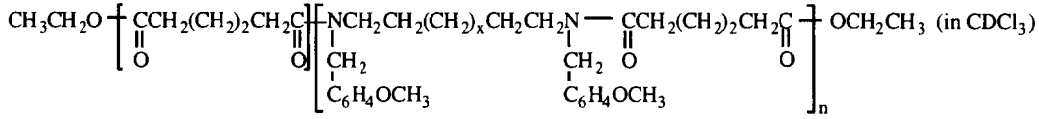
Table 2
^{1}H n.m.r. of :



Chemical shifts at 500 MHz; data refer to the protons underlined

	-C$_6$H$_4$-	-CH$_2$CON (CH$_2$AR)-	HN(CH$_2$Ar)-	-CO$_2$CH$_2$CH$_3$	-OCH$_3$	-H$_2$CON(CH$_2$Ar)CH$_2$-		HN(CH$_2$Ar)CH$_2$-	-CH$_2$COOC$_2$H$_5$ -CH$_2$CON (CH$_2$Ar)	-COCH$_2$(CH$_2$)$_2$ CH$_2$CO- -NRCH$_2$CH$_2$ (CH$_2$)$_x$CH$_2$ CH$_2$NR-	-CH$_2$CH$_2$CH$_3$ -(CH$_2$)$_x$
11 x = 0, n = 1	6.79-7.25	4.42(s) 4.49(s)	3.70(s) 3.73(s)	4.10 (overlapping q)	3.76-3.79 (overlapping q)	3.15(t) 3.31(t)	2.8(b)	2.59(t) 2.64(t)	2.25-2.38(m)	1.40-1.58(m) 1.59-1.75(m)	1.23 (overlapping t)
Integrations (required)	7.9(8)	2.0(2)	2.000(2)	2.0(2)	6.000(6)	2.0(2)	(NH)	2.0(2)	4.0(4)	8.1(8)	3.0(3)
14 x = 0, n = 2	6.78-7.3	4.37-4.5(m)	3.7	4.09 (overlapping q)	3.75-3.83 (overlapping q)	3.13(b) 3.28(b)		2.62(b) 2.73(b)	2.24-2.4(m)	1.37-1.75(m)	1.23 (overlapping t)
Integrations (required)	16.3(16)	5.9(6)	2.000(2)	2.0(2)	12.000(12)	5.9(6)		1.9(2)	8.1(8)	16.1(16)	3.0(3)
34 x = 2, n = 1	6.79-7.25	4.43(s) 4.50(s)	3.70(s) 3.71(s)	4.10 (overlapping q)	3.76-3.79 (overlapping q)	3.12(t) 3.30(t)	2.35(b) (overlapping NH)	2.58(m)	2.25-2.38(bm) overlapping with NH	1.42-1.53(m) 1.56-1.75(m)	1.19-1.34 (overlapping m)
Integrations (required)	7.9(8)	2.0(2)	2.0(2)	2.0(2)	6.000(6)	1.9(2)		2.0(2)	5.1(4 + 1)	7.9(8)	6.9(3 + 4)
36 x = 2, n = 2	6.79-7.25	4.38-4.53(m)	3.72(s)	4.10 (overlapping q)	3.76-3.79 (overlappins s)	3.10(b) 3.29(b)	2.5(vb) (overlapping NH)	2.59(b)	2.25-2.42(bm) overlapping NH(vvb)	1.42-1.55(m) 1.56-1.78(m)	1.17-1.35 (overlapping m)
Integrations (required)	15.8(16)	5.9(6)	2.0(2)	2.0(2)	12.000(12)	5.9(6)		2.2(2)	8.3(8)	16.3(16)	11.1(3 + 8)

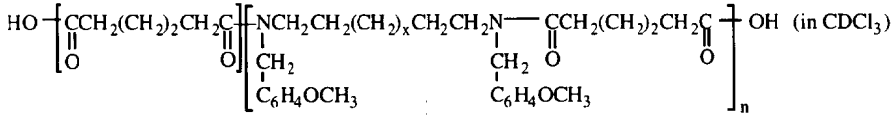
Table 3
^{1}H n.m.r. spectra of :



Chemical shifts at 500 MHz; data refer to the protons underlined

	-$C_6\underline{H}_4$-	-$CH_2CON(C\underline{H}_2Ar)$-	-$COOC\underline{H}_2CH_3$	-$OC\underline{H}_3$	-$CH_2CON(CH_2Ar)C\underline{H}_2$-;	-$C\underline{H}_2COOC_2H_5$ -$C\underline{H}_2CON(CH_2Ar)$	-$COCH_2(C\underline{H}_2)_2CH_2CO$- -$NRCH_2CH_2(CH_2)_xC\underline{H}_2CH_2NR$-	-$(C\underline{H}_2)_x$ -$CO_2CH_2C\underline{H}_3$
15 x = 0, n = 1	6.78-7.16	4.40(s), 4.41(s) 4.47(s)	4.10 (overlapping q)	3.76-3.79 (overlapping s)	3.29(b), 3.15(b)	2.25-2.38(m)	1.57-1.75(m); 1.38-1.5(m)	1.23 (overlapping t)
Integrations (required)	8.0(8)	4.0(4)	4.0(4)	6.000(6)	4.0(4)	8.1(8)	8.1 + 4.0(12)	6.0(6)
19 x = 0, n = 3	6.78-7.18	4.41-4.50(m)	4.10(m) (overlapping q)	3.76-3.79 (overlapping s)	3.30(b), 3.13(b)	2.25-2.43(b)	1.57-1.77(m); 1.3-1.51(m)	1.23 (overlapping t)
Integrations (required)	24.3(24)	12.0(12)	3.9(4)	18.000(18)	12.1(12)	16.2(16)	16.4 + 12.1(28)	6.1
23 x = 0, n = 5	6.76-7.16	4.38-4.47(m)	4.09 (overlapping q)	3.74-3.78 (overlapping s)	3.28(b), 3.12(b)	2.13-2.4(m)	1.56-1.77(m); 1.35-1.52(m)	1.23 (overlapping t)
Integrations (required)	40.3(40)	20.0(20)	4.0(4)	30.000(30)	20.1(20)	24.3(24)	24.5 + 20.2(44)	6.1(6)
26 x = 0, n = 7	6.76-7.16	4.35-4.5(m)	4.09 (overlapping q)	3.74-3.77 (overlapping s)	3.27(b), 3.11(b)	2.23-2.4(m)	1.55-1.77(m); 1.34-1.5(m)	1.22 (ovelapping t)
Integrations (required)	56.3(56)	27.8(28)	3.9(4)	42.000(42)	27.6(28)	31.9(32)	32.4 + 27.9(60)	6.1(6)
37 x = 2, n = 1	6.78-7.17	4.42(d), 4.49(d)	4.10 (overlapping q)	3.76(s), 3.78(s)	3.11(m); 3.28(m)	2.24-2.40(m)	1.57-1.76(m); 1.43-1.53(m)	1.18-1.28 (overlapping m)
Integrations (required)	8.0(8)	4.0(4)	4.0(4)	6.000(6)	4.0(4)	8.0(8)	8.1 + 4.0(12)	9.9(6 + 4)
41 x = 2, n = 3	6.78-7.17	4.4-4.53	4.10 (overlapping q)	3.76-3.79 (overlapping s)	3.12(m); 3.28(m)	2.25-2.45(m)	1.57-1.78(m); 1.4-1.55(m)	1.17-1.28 (overlapping m)
Integrations (required)	23.9(24)	11.9(12)	3.9(4)	18.000(18)	11.9(12)	16.1(16)	1.59 + 11.6(28)	17.6(6 + 12)
45 n = 2, n = 5	6.78-7.17	4.4-4.53(m)	4.10 (overlapping q)	3.76-3.79 (overlapping s)	3.12(m); 3.23(m)	2.25-2.45(m)	1.57-1.79(m); 1.4-1.55(m)	1.17-1.29 (overlapping m)
Integrations (required)	40.0(40)	19.8(20)	4.0(4)	30.000(30)	19.7(20)	24.0(24)	23.6 + 19.1(44)	25.2(6 + 20)
48 x = 2, n = 7	6.78-7.17	4.39-4.5(m)	4.09 (overlapping q)	3.75-3.78 (overlapping s)	3.27(m); 3.11(m)	2.25-2.45(m)	1.57-1.78(m); 1.4-1.55(m)	1.15-1.28 (overlapping m)
Integrations (required)	56.4(56)	28.0(28)	4.2(4)	42.000(42)	27.7(28)	32.3(32)	3.25 + 28.0(60)	33.9(6 + 28)

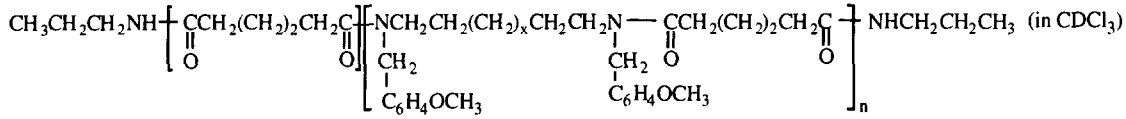
Table 4
^{1}H n.m.r. of :



Chemical Shifts at 500 MHz; data refer to the protons underlined

	-$C_6\underline{H}_4$-	-$CH_2CON(C\underline{H}_2Ar)$-	-$OC\underline{H}_3$	-$CH_2CON(CH_2Ar)C\underline{H}_2$-	-$C\underline{H}_2CON(CH_2Ar)$- -$C\underline{H}_2CO$-OH	-$COCH_2(C\underline{H}_2)_2CH_2CO$- -$NRCH_2C\underline{H}_2(CH_2)_xC\underline{H}_2CH_2NR$-	-$(CH_2)_x$
18 x = 0, n = 1	6.78-7.16	4.41(s), 4.43(s) 4.47(s)	3.75-3.79 (overlapping s)	3.16(b); 3.31(b)	2.25-2.45(m)	1.55-1.80(m); 1.35-1.55(m)	
Integrations (required)	8.1(8)	4.0(4)	6.000(6)	4.0(4)	8.0(8)	8.1 + 4.0(12)	
22 x = 0, n = 3	6.77-7.16	4.37-4.53(m)	3.75-3.78 (overlapping s)	3.30(b) 3.15(b)	2.27-2.45(m)	1.57-1.8(m); 1.36-1.53(bs)	-
Integrations (required)	24.0(24)	11.9(12)	18.000(18)	12.0(12)	16.1(16)	16.3 + 12.1(28)	
40 x = 2, n = 1	6.78-7.18	4.44(s), 4.50(s)	3.76-3.79 (overlapping s)	3.13(b) 3.30(b)	2.25-2.45(b)	1.56-1.8(m); 1.42-1.55(m)	1.22(bs)
Integrations (required)	8.1(8)	4.0(4)	6.000(6	4.0(4)	8.0(8)	8.2 + 4.0(12)	4.0(4)
44 x = 2, n = 3	6.77-7.17	4.42-4.49(b)	3.74-3.78 (overlapping s)	3.10(b) 3.30(b)	2.2-2.45(m)	1.53-1.8(m); 1.4-1.53(bs)	1.21(bs)
Integrations (required)	24.2(246)	12.0(12)	18.000(18)	12.0(12)	16.1(16)	15.7 + 11.5(28)	11.4(12)

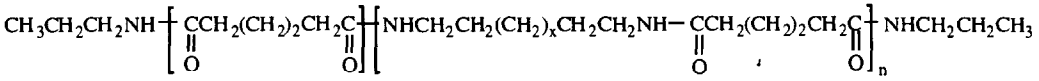
Table 5
^{1}H n.m.r. spectra of :



Chemical shifts at 500 MHz; data refer to the protons underlined

	-$C_6\underline{H}_4$-	-CON$\underline{H}$-	-CH_2CON ($C\underline{H}_2$Ar)-	-OCH_3	-$N(CH_2Ar)C\underline{H}_2$- -$NHC\underline{H}_2CH_2CH_3$ -$NHC\underline{H}_2CH_2CH_3$	-$C\underline{H}_2$CON (CH_2Ar)-	-$C\underline{H}_2$CONH-	-$NHCH_2C\underline{H}_2CH_3$ -$COCH_2(C\underline{H}_2)_2CH_2CO$- -$NRCH_2C\underline{H}_2(CH_2)_xCH_2C\underline{H}_2NR$-	$(C\underline{H}_2)_x$-	-$NHCH_2CH_2C\underline{H}_3$
16 x = 0, n = 1	6.79-7.15	5.98-6.22 (three bs)	4.48(s) 4.415(s) 4.405(s)	3.77-3.80 (overlapping s)	3.10-3.23(m) 3.28-3.35(m)	2.30-2.40(m)	2.17(m); 2.22(m)	1.57-1.76(m)	1.18-156(m)	-	0.90 (overlapping t)
Integrations (required)	8.0(8)	1.8(2)	4.0(4)	6.000(6)	8.1(8)	4.0(4)	4.0(4)	8.1 +	8.2(16)		6.0(6)
20 x = 0, n = 3	6.77-7.16	6.0-6.34 (three b)	4.36-4.52(m)	3.75-3.79 (overlapping s)	3.23-3.36(b) 3.07-3.23(m)	2.25-2.43(b)	2.17(m); 2.21(m)	1.56-1.76(m)	1.36-1.56(m)	-	0.89 (overlapping t)
Integrations (required)	24.1(24)	1.9(2)	12.0(12)	18.000(18)	16.1(16)	12.0 +	4.0(16)	16.2 +	16.1(32)		6.0(6)
24 x = 0, n = 5	6.77-7.16	6.0-6.34 (three b)	4.35-4.52(m)	3.75-3.78 (overlapping s)	3.23-3.37(b) 3.07-3.23(m)	2.24-2.43(b)	2.16(m); 2.21(m)	1.56-1.76(m)	1.35-1.56(m)	-	0.89 (overlapping t)
Integrations (required)	40.4(40)	1.9(2)	20.0(20)	30.000(30)	24.1(24)	20.1 +	4.2(24)	24.5 +	24.2(48)		5.9(6)
27 x = 0, n = 7	6.76-7.17	6.0-6.34 (three b)	4.34-4.52(m)	3.74-3.78 (overlapping s)	3.23-3.37(b) 3.06-3.23(m)	2.24-2.43(b)	2.16(m); 2.20(m)	1.55-1.77(m)	1.33-1.55(m)	-	0.89 (overlapping t)
Integrations (required)	56.4(56)	1.9(2)	28.0(28)	42.000(42)	31.9(32)	28.0 +	4.1(32)	32.3 +	32.3(64)		5.9(6)
38 x = 2, n = 1	6.79-7.17	6.0-6.26 (four b)	4.42(d), 4.49(d)	3.77(s) 3.79(s)	3.12(m) 3.19(m), 3.28(m)	2.30-2.40(m)	2.16(t); 2.22(t)	1.57-1.76(m)	1.42-1.57(m)	1.22(bs)	0.90 (overlapping t)
Integraitons (required)	8.0(8)	1.9(2)	4.0(4)	6.000(6)	8.1(8)	4.0 +	4.0(8)	8.0 +	8.0(16)	3.9(4)	5.6(6)
42 = 2, n = 3	6.77-7.17	6.06-6.32 (three b)	4.42(m), 4.48(m)	3.75-3.78 (overlapping s)	3.11(m) 3.18(m), 3.28(m)	2.26-2.43(m)	2.16(t); 2.21(t)	1.57-1.77(m)	1.40-1.57(m)	1.21(bs)	0.89 (overlapping t)
Integrations (required)	24.2(24)	1.9(2)	12.0(12)	18.000(18)	16.1(16)	12.1 +	4.1(16)	16.0 +	15.7(32)	11.6(12)	5.9(6)
46 = 2, n = 5	6.77-7.17	6.02-6.28 (three b)	4.42(m), 4.48(m)	3.75-3.78 (overlapping s)	3.10(b) 3.18(m), 3.27(b)	2.25-2.43(bm)	2.16(t); 2.20(m)	1.57-1.78(m)	1.40-1.57(m)	1.21(bs)	0.90 (overlapping t)
Integrations (required)	40.4(40)	1.9(2)	20.2(20)	30.000(30)	24.2(24)	20.1 +	4.2(24)	24.0 +	23.5(48)	19.4(20)	5.9(6)
49 n = 2, n = 7	6.77-7.17	6.02-6.28 (three b)	4.41(m), 4.48(m)	3.75-3.78 (overlapping s)	3.10(b) 3.18(m), 3.27(b)	2.25-2.43(bm)	2.16(t); 2.21(t)	1.57-1.78(m)	1.40-1.57(m)	1.21(bs)	0.90 (overlapping t)
Integrations (required)	55.8(56)	1.9(2)	28.2(28)	42.000(42)	32.2(32)	28.3 +	4.2(32)	32.5 +	32.4(64)	28.3(28)	6.1(6)

Table 6
^{1}H n.m.r. spectra of :



Chemical shifts at 500 MHz; data refer to the protons underlined

	$CH_3CH_2C\underline{H}_2NH$- -$NHC\underline{H}_2(CH_2)_2C\underline{H}_2NH$-	$C_3H_7NHCOC\underline{H}_2$;	-$CH_2C\underline{H}_2CONH$-	-$COCH_2(C\underline{H}_2)_2CH_2CO$-	$NHCH_2C\underline{H}_2CH_3$ $NHCH_2(C\underline{H}_2)_2CH_2NH$-	-$(C\underline{H}_2)_x$-	-$NHCH_2CH_2C\underline{H}_3$
17 x = 0, n = 1	3.56(m) (overlapping m)	2.82	2.77	1.94(b)	1.77(m)	-	1.05(t)
Integrations (required)	8.2(8)	4.05 + 4.05(8)		8.1(8)	8.1(8)		6.000(6)
In CD_3CO_2D (70°C)	3.25(bt); 3.19(t)	2.36(b)	2.27(b)	1.65(b)	1.53 (overlapping pks.)	-	0.90(t)
Integrations (required)	4.1(4); 4.2(4)	0.34	8.0(8)	8.3(8)	8.4(8)		6.000(6)
21 x = 0, n = 3	3.57 (overlapping m)	2.81	2.77	1.93(b)	1.77(m)	-	1.05(t)
Integrations (required)	16.8(16)	4.05 + 12.1(16)		16.0(16)	16.3(16)		6.000(6)
25 x = 0, n = 5	3.57 (overlapping m)	2.80	2.77	1.93(b)	1.77(m)	-	1.05(t)
Integrations (required)	24.2(24)	4.0 + 20.4(24)		24.6(24)	24.1(24)		6.000(6)
28 x = 0, n = 7	3.60(b)	2.77 (unresolved)		1.93(b)	1.81(b)	-	1.05(t)
Integrations (required)	32.7(32)	32.5(32)		32.6(32)	32.6(32)		6.000(6)
39 x = 2, n = 1	3.57(m)	2.81(bs)		1.95(m)	1.77(m)	1.49(bs)	1.05(t)
Integrations (required)	8.0(8)	8.0(8)		8.0(8)	8.1(8)	4.0(4)	6.000(6)
43 x = 2, n = 3	3.58(m)	2.81(bs)		1.95(bs)	1.76(m)	1.49(bs)	1.05(t)
Integrations (required)	16.3(16)	16.3(16)		16.3(16)	16.3(16)	12.0(12)	6.000(6)
47 x = 2, n = 5	3.59(bs)	2.82(bs)		1.95(bs)	1.76(bs)	1.50(bs)	1.05(t)
Integrations (required)	24.1(24)	23.8(24)		24.1(24)	24.0(24)	19.9(20)	6.000(6)
50 x = 2, n = 7	3.58(m)	2.81(bs)		1.95(bs)	1.76(bs)	1.50(bs)	1.05(t)
Integrations (required)	32.2(32)	32.3(32)		32.7(32)	32.3(32)	28.3(28)	6.000(6)

21, **25** and **28**) and (**39**, **43**, **47** and **50**) were determined by ^{1}H n.m.r. spectroscopy at room temperature in CF_3CO_2D–TMS, the COSY spectrum of **17** (and of **39**) allowing the assignment of all the protons in both series of oligomers. There was no chemical shift evidence for the presence of amide–iminol tautomerism which had been observed in perdeuteroacetic acid with the oligomers of nylon 6[3], but this could have been due either to the eclipsing of the iminol absorption ($-CH_2C(OH)=N-$) by the amide ($-CH_2CONH-$) or due to the very rapid exchange of these protons (on an n.m.r. timescale) in the stronger acid rendering them unobservable. However, compound **17** was reasonably soluble in CD_3CO_2D at 70°C and did show an absorption at 2.36 ppm close to that due to $-CH_2CONH-$ at 2.27 ppm, in the ratio 4:96, respectively, typical of the iminol–amide tautomerism found before. The COSY spectrum gave the same assignments to the protons as in CF_3CO_2D–TMS.

In the present work terminal NH compounds **7**, **11**, **14**, **30**, **34** and **36** could not be obtained free from residual solvent since heating in vacuo led to decomposition (presumably polymerisation); consequently, no elemental analysis data are given.

2.1. Experimental

N.m.r. spectra were recorded on a Bruker AMX 500 ^{1}H (500.139 MHz). Absorption multiplicities have been abreviated 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 Analyical 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°C under high vacuum.

2.2. Preparative chromatography and h.p.l.c. analysis

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

2.2.1. N,N′-Bis(p-methoxybenzyl)-1,4-butanediamine **8**

A solution of 1,4-butanediamine (99.8g, 1.13 mol) and *p*-methoxybenzaldehyde (412.6 g, 3.0 mol) in ethanol (200 ml) was heated at reflux temperature for 15 h and cooled to 25°. The solid which separated was filtered and washed with a mixture of ethanol (700 ml) and water (140 ml) and the crude 1,4-di-imine (356 g, 1.1 mol) in methanol (800 ml) was treated with sodium borohydride (90.8 g, 2.4 mol), added at such a rate as to maintain the internal temperature of the mixture at ≥ 50°. The solvent was evaporated in vacuo, the residue extracted with ether, the extracts dried (Na_2SO_4) and the solvent evaporated to give *N,N′*-bis(*p*-methoxybenzyl)-1,4-butanediamine **8** (267 g, 72%), mp 49.5–50.5°C (recrystallised from ether at 0°) (Found: C, 72.86; H, 8.55; N, 8.39. $C_{20}H_{28}N_2O_2$ requires C, 73.14; H, 8.59; N, 8.53%; δ_H ($CDCl_3$) 7.22, 7.21, 6.86 and 6.84 (2 × C_6H_4), 3.78 (s, 2 × OCH_3), 3.70 (s, 2 × $C\underline{H}_2Ar$), 2.61 (m, 2 × $NC\underline{H}_2CH_2$) and 1.53 (m, overlapping 2 × $NCH_2C\underline{H}_2$ and vb 2 × NH), in the ratio 7.9:6.00:4.0:4.0:5.9, respectively. Compound **8** absorbed CO_2 from the atmosphere to give 4-(*p*-methoxybenzylamino)butylcarbamic acid **8a** (insoluble in ether), mp 109–113°C (Found: C, 67.39; H, 7.65; N, 7.60. $C_{21}H_{28}N_2O_2$ requires C, 67.72; H,7.58; N, 7.52%).

2.2.2. N-tert-Butoxycarbonyl-N,N′-bis(p-methoxybenzyl)-1,4-butanediamine **7** *and N,N′-bis-(tert-butoxycarbonyl)-N,N′-bis(p-methoxybenzyl)-1,4-butanediamine* **9**

A solution of the diamine **8** (198.5 g, 0.61 mol) in methanol (270 ml) and triethylamine (66 g, 0.65 mol) was treated at 0–5°C with di-t-butyl dicarbonate (145.3 g, 0.67 mol) and the mixture was stirred at 25°C for 15 h. A small amount of the carbamic acid **8a** was filtered off and the solvents evaporated in vacuo from the filtrate. Chromatography of the residue on silica using dichloromethane–methanol (95:5, v/v) gave two products: *N,N′*-bis-(*tert*-butoxycarbonyl)-*N,N′*-bis(*p*-methoxybenzyl)-1,4-butanediamine **9**, a viscous liquid (Found: C, 68.10; H, 8.42; N, 5.25. $C_{30}H_{44}N_2O_6$ requires C, 68.15; H, 8.39; N, 5.30%; δ_H ($CDCl_3$) 7.13 (bs) and 6.84 (d) (2 × C_6H_4), 4.33 and 4.30 (overlapping bs, 2 × $C\underline{H}_2Ar$), 3.78 (s, 2 × OCH_3), 3.15 and 3.06 (overlapping bs, 2 × $BocNC\underline{H}_2CH_2$) and 1.55–1.3 (b, overlapping 2 × $NCH_2C\underline{H}_2$ and 2 × Me_3C) in the ratio 8.0:4.0:6.00:4.0:22.4, respectively; followed by *N*-tert-butoxycarbonyl-*N,N′*-bis(*p*-methoxybenzyl)-1,4-butanediamine **7** (100.1 g, 39%) δ_H ($CDCl_3$) 7.28, 7.13 and 6.84 (2 × C_6H_4), 4.25–4.7 (overlapping bs, NH and two bs 1 × $BocNC\underline{H}_2Ar$), 3.77 and 3.76 (s, 2 × OCH_3 overlapping b, 1 × $HNC\underline{H}_2Ar$), 3.15 and 3.07 (overlapping bs, 1 × $BocNC\underline{H}_2CH_2$), 2.65 and 2.60 (overlapping bs, 1 × $HNC\underline{H}_2CH_2$) and 1.62–1.35 (b, overlapping 2 × $NCH_2C\underline{H}_2$ and 1 × Me_3C), in the ratio 8.1:3.1:8.00:2.0:2.0:13.3, respectively. Compound **9** was treated with trifluoroacetic acid (5 equiv.) at 25°C, and when the fully deprotected diamine **8** first began to appear (monitored by TLC on silica using dichloromethane–methanol (95:5, v/v)), the reaction mixture was carefully quenched with saturated sodium bicarbonate solution, extracted with dichloromethane, and a further amount of **7** (48.9 g, 19%) isolated by chromatography as before.

2.2.3. Condensation of adipic acid monoethyl ester **6** *with the secondary amine* **7** *to give* **10**

The carboxylic acid **6** (42.73 g, 0.245 mol) in dichloromethane (500 ml) at 0–5°C was treated with dicyclohexylcarbodiimide (DCC) (50.6 g, 0.245 mol) followed

by 1-hydroxy-benzotriazole (33.15 g, 0.245 mol). A white solid appeared in the solution which was stirred for 1 h, the secondary amine **7** (100.0 g, 0.233 mol) in dichloromethane (70 ml) was added at 0–5°C and the mixture stirred for 15 h. The solid was filtered, washed with dichloromethane (2 × 50 ml) and the combined filtrate after washing in turn with water (100 ml), saturated sodium bicarbonate (3 × 100 ml) and saturated brine (100 ml), was dried (Na_2SO_4). Evaporation of the solvent in vacuo and chromatography of the oily residue on silica (1 kg loaded with 30–35 g batches at a time of crude product) using ether–light petroleum [bp 40–60°] (80:20 v/v). The combined fractions of the major component in ether contained a small amount of insoluble material which was filtered off and the solvent evaporated to give ethyl *N*-{4-[(*tert*-butoxycarbonyl) (*p*-methoxybenzyl) amino] butyl} -*N* -(*p*-methoxybenzyl) adipamate **10** (Boc[4.6]$_1$OEt) (114.1 g, 83%) a clear oil (Found: C, 67.63; H, 8.62; N, 4.87. $C_{33}H_{48}N_2O_7$ requires C, 67.78; H,8.27; N, 4.79%); ^{1}H n.m.r. data in Table 1.

2.2.4. N,N'-Bis(p-methoxybenzyl)-1,6-hexanediamine **29**

An experiment similar to the one described for the preparation of **8** was carried out using 1,6-hexanediamine to give *N,N'*-bis(*p*-methoxybenzyl)-1,6-hexanediamine **29** (71%), mp 69.3–70.5°C (recrystallised from ether at 0°) (Found: C, 74.25; H, 9.14; N, 8.07. $C_{22}H_{32}N_2O_2$ requires C, 74.12; H, 9.05; N, 7.86%; δ_H ($CDCl_3$) 7.23, 7.21, 6.86 and 6.84 (2 × C_6H_4), 3.78 (s, 2 × OCH_3), 3.70 (s, 2 × CH_2Ar), 2.58 (t, 2 × NCH_2CH_2), 1.49 (m, overlapping 2 × NCH_2CH_2 and vb 2 × NH) and 1.32 (m, 2 × $N(CH_2)_2CH_2$–) in the ratio 8.0:6.00:4.0:4.0:6.2:4.2, respectively.

2.2.5. N-tert-Butoxycarbonyl-N,N'-bis(p-methoxybenzyl)-1,6-hexanediamine **30** *and N,N'-bis-(tert-butoxycarbonyl)-N,N'-bis(p-methoxybenzyl)-1,6-hexanediamine* **31**

A mixture of these compounds was prepared from **29** in an experiment similar to the one for the preparation of **7** and **9**. Chromatography of the mixture on silica using first diethyl ether–light petroleum (bp 40–60°) (70:30, v/v) gave **31** (38%) and then followed by dichloromethane–methanol (90:10, v/v) gave **30** (41%): *N,N'*- bis-(*tert*-butoxycarbonyl)-*N,N'*-bis(*p*-methoxy-benzyl)-1,6-hexanediamine **31**, a viscous liquid (Found: C, 69.08; H, 8.78; N, 5.02. $C_{32}H_{48}N_2O_6$ requires C, 69.04; H, 8.69; N, 5.03%; δ_H ($CDCl_3$) 7.14 (bs) and 6.84 (d) (2 × C_6H_4), 4.34 (bs, 2 × CH_2Ar), 3.79 (s, 2 × OCH_3), 3.13 and 3.05 (overlapping bs, 2 × Boc NCH_2CH_2), 1.33–1.57 (b, overlapping 2 × NCH_2CH_2 and 2 × Me_3C) and 1.20 (bs, $N(CH_2)_2(CH_2)_2(CH_2)_2N$) in the ratio 8.1:4.0:6.00:3.9:19.5:3.9, respectively; followed by *N-tert*-butoxycarbonyl-*N,N'*-bis(*p*-methoxybenzyl)-1,6-hexanediamine **30**, δ_H ($CDCl_3$) 6.8–7.26 (2 × C_6H_4), 4.34 (two bs 1 × BocCH_2Ar), 3.78 (s, 2 × OCH_3), 3.72 (s,1 × $HNCH_2Ar$), 3.16 and 3.06 (overlapping bs, 1 × BocNCH_2CH_2), 2.59 (t, 1 × $HNCH_2CH_2$), 2.1–2.5 (vb, NH), 1.46 (overlapping 1 × Me_3C and 2 × NCH_2CH_2) and 1.23–1.29 (overlapping bs, $N(CH_2)_2(CH_2)_2(CH_2)_2N$), in the ratio 8.25:2.0:6.0:1.9:2.1:1.9:1.5:13.2:4.2.

2.2.6. Condensation of adipic acid monoethyl ester **6** *with the secondary amine* **30** *to give* **32**

The carboxylic acid **6** was reacted with the amine **30** as it was with **7** (above). The crude product was worked up as before and purified by chromatography on silica using ether–light petroleum (bp 40–60°C) (70:30, v/v) followed by pure ether to give ethyl *N*-{6-[(*tert*-butoxycarbonyl) (*p*-methoxybenzyl) amino] hexyl} -*N*- (*p* - methoxybenzyl) adipamate **32** (Boc[6.6]$_1$OEt) (81%) a clear oil (Found: C, 68.36; H, 8.58; N, 4.71. $C_{35}H_{52}N_2O_7$ requires C, 68.60; H, 8.55; N, 4.57%); ^{1}H n.m.r. data in Table 1.

2.2.7. Three-stage process for the formation of the chain-doubled products **13** *and* **35** *from fully protected derivatives*

2.2.7.1. Selective removal of the Boc group from **10**. The fully protected compound **10** (41.33 g) at 0–5°C was reacted with trifluoroacetic acid (40 ml), the mixture stirred for 7 h and diluted with dichloromethane (250 ml). The solution was washed with saturated sodium bicarbonate solution (3 × 150 ml) and water (100 ml), the organic phase dried (Na_2SO_4) and the solvent evaporated. Chromatography of the residue on silica (1 kg) using dichloromethane–methanol (95:5 v/v ⇒ 80:20 v/v) gave ethyl *N*-[4-(*p*-met hoxybenzylamino) -butyl]-*N'*-(*p*-methoxybenzyl) adipamate **11** (H[4.6]$_1$OEt) (30.3 g, 88%) a clear oil; ^{1}H n.m.r. data in Table 2.

2.2.7.2. Selective hydrolysis of the ethyl ester in compound **10**

Compound **10** (39.3 g, 6.70 × 10^{-2} mol), ethanol (15 ml) and a solution of sodium hydroxide (2.96 g, 7.4 × 10^{-2} mol) in water (10 ml) were heated under reflux for 30 min. The ethanol was evaporated from the solution in vacuo, the residual paste cooled to 0°C and sulphuric acid (2 M) added to slight excess (universal indicator). The mixture was extracted with dichloromethane (250 ml), washed with water and the aqueous extracts re-extracted with dichloromethane. The combined organic phases were dried (Na_2SO_4) and the residue purified by chromatography on silica (1 kg) using dichloromethane–methanol (94:6 v/v ⇒ 80:20 v/v)to give *N*-{4-[(*tert*-butoxycarbonyl)(*p*-methoxybenzyl) amino]-butyl} -*N*- (*p* -methoxybenzyl) adipamic acid **12** (Boc[4.6]$_1$OH) (34.7 g, 92%) a clear oil; (Found: C, 66.81; H, 8.12; N, 5.13. $C_{31}H_{44}N_2O_7$ requires C, 66.88; H,7.97; N, 5.03%); δ_H ($CDCl_3$) 6.78–7.2 (2 × C_6H_4), 4.47 (s), 4.41 (s) and 4.30 (b) (2 × CH_2Ar), 3.77–3.79 (overlapping s, 2 × OCH_3), 3.15 (b) and 3.30 (b) (2 × NCH_2CH_2), 2.30–2.39 (m, CH_2CO), 1.55–1.8 (m) 1.3–1.5 (m) [overlapping 2 × NCH_2CH_2, 2 × CH_2CH_2CO and $(CH_3)_3C$], in the ratio 7.8:4.00:6.0:4.0:4.0:17.2.

2.2.7.3. Chain-doubling reaction to form **13**. The carboxylic acid **12** (30.7 g, 55.1 × 10^{-3} mol) in dichloromethane (200 ml) was treated with DCC (11.96 g, 58.0 × 10^{-3} mol) in dichloromethane (20 ml) and 1-hydroxybenzotriazole (7.83 g, 57.7 mol) at 0°C and the mixture stirred for 1 h at room temperature. The secondary amine **11** (28.06 g, 57.9 × 10^{-3} mol) in dichloromethane (20 ml) was added and the mixture stirred for 5 h at room temperature. The crude product was isolated as in the preparation of **10** and purified by chromatography on silica (1 kg) using ethyl acetate–methanol (100:0 ⇒ 90:10 v/v) initially, followed by recycling of the material three times further to give α-(*tert*- butoxycarbonyl) -ω -ethoxydi[(*p* - methoxybenzyl)-iminotetramethylene(*p*-methoxybenzyl)iminoadipoyl] **13** (Boc[4.6]$_2$OEt) (42.2 g, 75%) a clear oil (Found: C, 68.95; H, 8.11; N, 5.58. $C_{59}H_{82}N_4O_{11}$ requires C, 69.25; H, 8.07; N, 5.47%); ^{1}H n.m.r. data in Table 1.

Deprotection of the terminal nitrogen in **13** (41.0 g) with trifluoroacetic acid (35 ml) and work-up as in Section 2.2.7.1 gave ω-ethoxydi[(*p*-methoxybenzyl)iminotetramethylene(*p*-methoxybenzyl)-iminoadipoyl] **14** (H[4.6]$_2$ OEt) (33.5 g, 91%) a clear oil; ^{1}H n.m.r. data in Table 2.

2.2.7.4. Selective removal of the Boc group from **32**. The fully protected compound **32** was deprotected as in Section 2.2.7.1 and the product purified by chromatography on silica using dichloromethane–methanol (95:5 v/v ⇒ 85:15 v/v) to give ethyl *N*-[6-(*p*-methoxybenzylamino)hexyl]-*N*-(*p*-methoxybenzyl)adipamate **34** (H[6.6]$_1$OEt) (91%) a clear oil; ^{1}H n.m.r. data in Table 2.

2.2.7.5. Selective hydrolysis of the ethyl ester in compound **32**

The ester **32** was saponified as in Section 2.2.7.2 and the product purified by chromatography on silica using dichloromethane–methanol (95:5 v/v ⇒ 85:15 v/v) to give *N*-{6-[(*tert*-butoxycarbonyl)(*p*-methoxybenzyl) amino]hexyl}-*N*-(*p*-methoxybenzyl)adipamic acid **33** (Boc[6.6]$_1$OH) (89%) a clear oil (Found: C, 67.78; H, 8.45; N, 4.95. $C_{33}H_{48}N_2O_7$ requires C, 67.78; H, 8.27; N, 4.79%); δ_H ($CDCl_3$) 6.8–7.2 (2 × C_6H_4), 4.50 (s), 4.44 (s) and 4.32 (b) (2 × CH_2Ar), 3.77–3.80 (overlapping s, 2 × OCH_3), 3.10 (b) and 3.0–3.2 (b) (2 × NCH_2CH_2), 2.30–2.40 (m, CH_2CO), 1.57–1.8 (m) 1.35–1.57 (m) [overlapping 2 × NCH_2CH_2, 2 × CH_2CH_2CO and $(CH_3)_3C$] and 1.22 (overlapping bs, $N(CH_2)_2(CH_2)_2(CH_2)_2N$) in the ratio 8.0:4.0:6.00:4.0:4.0:17.1:4.0, respectively.

2.2.7.6. Chain-doubling reaction to form **35**. The carboxylic acid **33** was reacted with the amine **34** as in Section 2.2.7.3 and the product purified by chromatography on silica using ethyl acetate–light petroleum (bp 40–60°) (65:35 ⇒ 100:0 v/v) to give α- (*tert*- butoxycarbonyl) -ω- ethoxydi [(*p*- methoxybenzyl) iminohexamethylene (*p*-methoxybenzyl) iminoadipoyl] **35** (Boc[6.6]$_2$OEt) (81%) a clear oil (Found: C, 70.01; H, 8.47; N, 5.34. $C_{63}H_{90}N_4O_{11}$ requires C, 70.10; H, 8.40; N, 5.19%); ^{1}H n.m.r. data in Table 1.

Deprotection of the terminal nitrogen in **35** with trifluoroacetic acid and work-up as in Section 2.2.7.1 gave ω-ethoxydi [(*p*-methoxybenzyl) iminohexamethylene (*p*-methoxybenzyl)iminoadipoyl] **36** (H[4.6]$_2$OEt) (92%) a clear oil; ^{1}H n.m.r. data in Table 2.

2.2.7.7. Synthesis of α,ω-diesters EtO[OC(C H_2)$_4$ CORN(CH_2)$_2$ (CH_2)$_x$(CH_2)$_2$NR]$_n$OC(CH_2)$_4$CO OEt and the conversion of some to α,ω-dicarboxylic acids

2.2.7.7.1. x = 0, n = 1. Adipic acid monoethyl ester **6** (27.2 g, 0.156 mol) in dichloromethane (300 ml) at room temperature was treated with DCC (30.75 g, 0.149 mol) in dichloromethane (20 ml) followed by 1-hydroxybenzotriazole (20.14 g, 0.149 mol). A white solid appeared in the solution which was stirred for 1 h, the secondary amine **8** (23.28 g, 0.071 mol) in dichloromethane (50 ml) was added at 0–5°C and the mixture stirred for 5 h. The solid was filtered off, washed with dichloromethane (3 × 50 ml) and the combined filtrate after washing in turn with water (100ml), saturated sodium bicarbonate (3 × 100 ml) and saturated brine (100 ml), was dried (Na_2SO_4). Evaporation of the solvent in vacuo and chromatography of the oily residue on silica (1 kg) using ether–methanol (98:2 ⇒ 95:5 v/v) gave the major component which in ether contained a small amount of insoluble material; this was filtered off and the solvent evaporated to give diethyl 7,12-bis(*p*-methoxybenzyl)-6,13-dioxo-7,12-diazaoctadecanedioate **15** (EtO[6][4.6]$_1$ OEt) (35.18 g, 77%) a clear oil (Found: C, 67.33; H, 8.37; N, 4.44. $C_{36}H_{52}N_2O_8$ requires C, 67.48; H, 8.18; N, 4.37%); ^{1}H n.m.r. data in Table 3.

The diester **15** (29.62 g, 4.62 × 10^{-2} mol) was heated under reflux with sodium hydroxide (3.88 g, 9.7 × 10^{-2} mol) in water (20 ml) for 25 m and the product, isolated as in Section 2.2.7.2, was purified by chromatography on silica (1 kg) using dichloromethane–methanol (95:5 v/v ⇒ 75:25 v/v) to give 7,12-bis(*p*-methoxybenzyl)-6,13-dioxo-7,12-diazaoctadecanedioic acid**18** (HO[6][4.6]$_1$OH) (18.35 g, 68%) a clear oil (Found: C, 65.46; H, 7.65; N, 4.73. $C_{32}H_{44}N_2O_8$ requires C, 65.73; H, 7.59; N, 4.79%); ^{1}H n.m.r. data in Table 4.

2.2.7.7.2. x = 2, n = 1. Adipic acid monoethyl ester **6** was reacted with the secondary amine **29** as in Section 2.2.7.7.1 and the product purified by chromatography on silica using first diethyl ether followed by dichloromethane–methanol (85:15 v/v) to give diethyl 7,14-bis(*p*-methoxybenzyl)-6,15-dioxo-7,14-diazacosanedioate **37** (EtO[6][6.6]$_1$OEt) (80%) a clear oil (Found: C, 68.28; H, 8.46; N, 4.28. $C_{38}H_{56}N_2O_8$ requires C, 68.24; H, 8.44; N, 4.19%); ^{1}H n.m.r. data in Table 3.

The diester **37** was saponified as in Section 2.2.7.2 and the product purified by chromatography on silica using dichloromethane–methanol (93:7 v/v ⇒ 85:15 v/v) to give 7,14-bis(*p*-methoxy-benzyl)-6,15-dioxo-7,14-diazacosanedioic acid **40** (HO[6][6.6]$_1$OH) (95%) a clear oil

(Found: C, 66.38; H, 7.87; N, 4.68. $C_{34}H_{48}N_2O_8$ requires C, 66.64; H, 7.90; N, 4.57%); ^{1}H n.m.r. data in Table 4.

2.2.7.7.3. x = 0, n = 3. The α,ω-dicarboxylic acid **18** (15.74 g, 2.69 × 10^{-2} mol) in dichloromethane (300 ml) at 0–5°C was treated with DCC (11.40 g, 5.52 × 10^{-2} mol) in dichloromethane (25 ml) followed by 1-hydroxybenzotriazole (7.46 g, 5.52 × 10^{-2} mol). A white solid appeared in the solution which was stirred for 1 h, the secondary amine **11** (27.39 g, 5.65 × 10^{-2} mol) in dichloromethane (75 ml) was added at 0–5°C and the mixture stirred for 18 h. The solid was filtered, washed with dichloromethane (3 × 50 ml) and the combined filtrate after washing in turn with saturated sodium bicarbonate (3 × 100 ml) and saturated brine (100 ml), was dried (Na_2SO_4). Evaporation of the solvent in vacuo and chromatography of the oily residue on silica (1 kg) using ethyl acetate–methanol (95:5 ⇒ 85:15 v/v) gave α-[5(ethoxycarbonyl)pentanoyl]-ω-ethoxytri[(*p*-methoxybenzyl)iminotetramethylene (*p*-methoxybenzyl) iminoadipoyl] **19** (EtO[6][4.6]$_3$OEt) (36.02 g, 88%) a clear oil (Found: C, 69.43; H, 8.01; N, 5.54. $C_{88}H_{120}N_6O_{16}$ requires C, 69.63; H, 7.97; N, 5.54%); ^{1}H n.m.r. data in Table 3.

The diester **19** (29.796 g, 1.96 × 10^{-2} mol) in ethanol (10 ml) was heated under reflux with sodium hydroxide (1.64 g, 4.1 × 10^{-2} mol) in water (20 ml) for 30 min and the product, isolated as in Section 2.2.7.2, was purified by chromatography on silica (1 kg) using dichloromethane–methanol (94:6 v/v ⇒ 75:25 v/v) to give α-(5-carboxypentanoyl)-ω-hydroxytri [(*p*-methoxybenzyl)imino-tetramethylene(*p*-methoxybenzyl)iminoadipoyl] **22** (HO[6][4.6]$_3$OH) (21.61 g, 75%) a clear oil (Found: C, 68.81; H, 7.74; N, 5.91. $C_{84}H_{112}N_6O_{16}$ requires C, 69.02; H, 7.72; N, 5.75%); ^{1}H n.m.r. data in Table 4.

2.2.7.7.4. x = 2, n = 3. The α,ω-dicarboxylic acid **40** was reacted with the secondary amine **34** as in Section 2.2.7.7.3 and the product purified by chromatography on silica using ethyl acetate–methanol (100:0 ⇒ 90:10 v/v) to give α-[5-(ethoxycarbonyl) pentanoyl] -ω-ethoxytri [(*p*-methoxybenzyl)imino-hexamethylene (*p*-methoxybenzyl)iminoadipoyl] **41** (EtO[6][6.6]$_3$OEt) (80%) a clear oil (Found: C, 70.47; H, 8.47; N, 5.37. $C_{94}H_{132}N_6O_{16}$ requires C, 70.47; H, 8.30; N, 5.25%); ^{1}H n.m.r. data in Table 3.

The diester **41** was saponified as in Section 2.2.7.2 and the product purified by chromatography on silica using dichloromethane–methanol (93:7 v/v ⇒ 85:15 v/v) to give α-(5-carboxypentanoyl)-ω-hydroxytri[(*p*-methoxybenzyl)iminohexamethylene (*p*-methoxybenzyl) iminoadipoyl] **44** (HO[6][6.6]$_3$OH) (90%) a clear oil (Found: C, 69.68; H, 8.04; N, 5.50. $C_{90}H_{124}N_6O_{16}$ requires C, 69.92; H, 8.08; N, 5.44%); ^{1}H n.m.r. data in Table 4.

2.2.7.7.5. x = 0, n = 5. The α, ω- dicarboxylic acid **22** (6.088 g, 4.16 × 10^{-3} mol) in dichloromethane (150 ml) at 0–5°C was treated with DCC (1.76 g, 8.53 × 10^{-3} mol) in dichloromethane (20 ml) followed by 1-hydroxybenzotriazole (1.15 g, 8.51 × 10^{-3} mol). A white solid appeared in the solution which was stirred for 1 h, the secondary amine **11** (4.23 g, 8.73 × 10^{-3} mol) in dichloromethane (30 ml) was added at 0–5°C and the mixture stirred for 18 h. The solid was filtered, washed with dichloromethane (2 × 50 ml) and the combined filtrate after washing in turn with saturated sodium bicarbonate (2 × 50 ml), water (75 ml) and saturated brine (50 ml), was dried (Na_2SO_4). Evaporation of the solvent in vacuo and chromatography of the oily residue on silica using ethyl acetate–methanol (94:6 ⇒ 85:15 v/v) gave α-[5-(ethoxycarbonyl) pentanoyl] -ω-ethoxypenta [(*p*-methoxybenzyl) iminotetramethylene (*p* - methoxybenzyl) iminoadipoyl] **23** (EtO[6][4.6]$_5$OEt) (8.70 g, 87%) a clear oil (Found: C, 70.01; H, 7.94; N, 5.88. $C_{140}H_{188}N_{10}O_{24}$ requires C, 70 20; H, 7.91; N, 5.85%); ^{1}H n.m.r. data in Table 3.

2.2.7.7.6. x = 2, n = 5. The α,ω-dicarboxylic acid **40** was reacted with the secondary amine **36** as in Section 2.2.7.7.5 and the product purified by chromatography on silica using ethyl acetate–dichloromethane–methanol (75:20:5 ⇒ 70:20:10 v/v) to give α-[5-(ethoxycarbonyl)pentanoyl]-ω-ethoxypenta [(*p*-methoxybenzyl) iminohexamethylene (*p*-methoxybenzyl) iminoadipoyl] **45** (EtO [6] [6.6]$_5$ OEt) (81%) a clear oil (Found: C, 71.03; H, 8.28; N, 5.54. $C_{150}H_{208}N_{10}O_{24}$ requires C, 71.06; H, 8.27; N, 5.52%); ^{1}H n.m.r. data in Table 3.

2.2.7.7.7. x = 0, n = 7. The α,ω-dicarboxylic acid **22** (14.90 g, 1.02 × 10^{-2} mol) in dichloromethane (250 ml) at 0–5°C was treated with DCC (4.31 g, 2.09 × 10^{-2} mol) in dichloromethane (20 ml) followed by 1-hydroxybenzotriazole (2.82 g, 2.09 × 10^{-2} mol). A white solid appeared in the solution which was stirred for 1 h, the secondary amine **14** (19.76 g, 2.14 × 10^{-2} mol) in dichloromethane (40 ml) was added at 0–5°C and the mixture stirred for 18 h. The solid was filtered, washed with dichloromethane (2 × 50 ml) and the combined filtrate after washing in turn with saturated sodium bicarbonate (2 × 50 ml), water (75 ml) and saturated brine (50 ml), was dried (Na_2SO_4). Evaporation of the solvent in vacuo and chromatography of the oily residue on silica (1 kg) using ethyl acetate–methanol (90:10 ⇒ 75:25 v/v) gave α-[5-(ethoxycarbonyl)-pentanoyl]-ω-ethoxyhepta [(*p*-methoxybenzyl) iminotetramethylene (*p*-methoxybenzyl)-iminoadipoyl] **26** (EtO[6][4.6]$_7$OEt) (26.64 g, 80%) a clear oil (Found: C, 70.22; H, 7.85; N, 6.08. $C_{192}H_{256}N_{14}O_{32}$ requires C, 70.48; H, 7.89; N, 5.99%); ^{1}H n.m.r. data in Table 3.

2.2.7.7.8. x = 2, n = 7. The α,ω-dicarboxylic acid **44** was reacted with the secondary amine **36** as in Section 2.2.8.7 and the product purified by chromatography on silica using ethyl acetate–methanol (92:8 ⇒ 80:20 v/v) to give α-[5-(ethoxycarbonyl) pentanoyl]-ω-ethoxyhepta [(*p*-methoxybenzyl) -iminohexamethylene (*p*-methoxybenzyl) iminoadipoyl] **48** (EtO[6][6.6]$_7$OEt) (91%) a clear oil (Found: C, 71.42; H, 8.36; N, 5.62. $C_{206}H_{284}N_{14}O_{32}$ requires C, 71.33; H, 8.25; N, 5.65%); ^{1}H n.m.r. data in Table 3.

2.2.7.8. Preparation of α,ω-di-n-propylamides: n-C_3H_7NH

[OC(CH$_2$)$_4$ CORN(CH$_2$)$_2$ (CH$_2$)$_x$(CH$_2$)$_2$NR]$_n$ OCCH$_2$)$_4$CO NHC$_3$H$_7$-n

2.2.7.8.1. x = 0, n = 1. Compound **15** (5.20 g, 8.1 mmol), methanol (10 ml), *n*-propylamine (15 ml, 180 mmol) and a catalytic amount of potassium cyanide (20 mg) were heated together under reflux for 4 days, and the solvents removed in vacuo. The residue was dissolved in dichloromethane (150 ml) and the solution washed in turn with water (30 ml) and saturated brine (30 ml) and then 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 ⇒ 92:8 v/v) to give 7,12-bis(*p*-methoxybenzyl) -6,13-dioxo- 7,12-diazaoctade canebis(*n*-propylamide) **16** (PN[6][4.6]$_1$NP^{pp}) (5.21 g, 96%) an oil (Found: C, 68.46; H, 8.82; N, 8.56. C_{38} $H_{58}N_4O_6$ requires C, 68.44; H, 8.77; N, 8.40%); ^{1}H n.m.r. data in Table 5.

2.2.7.8.2. x = 2, n = 1. Compound **37** was reacted with *n*-propylamine as in Section 2.2.7.8.1 and the product purified by chromatography on silica using ethyl acetate–dichloromethane–methanol (70:25:5 ⇒ 65:25:10 v/v) to give 7,14-bis *p*-methoxybenzyl)-6,15-dioxo-7,14-diazacosanebis(*n*-propyl-amide) **38** (PN[6][6.6]$_1$NP^{pp}) (88%) an oil (Found: C, 68.75; H, 9.01; N, 8.13. $C_{40}H_{62}N_4O_6$ requires C, 69.13; H, 8.99; N, 8.06%); ^{1}H n.m.r. data in Table 5.

2.2.7.8.3. x = 0, n = 3. Compound **19** (5.49 g, 3.6 mmol), methanol (10 ml), *n*-propylamine (15 ml, 180 mmol) and a catalytic amount of potassium cyanide (20 mg) were heated together under reflux for 4 days, and worked up as in Section 2.2.7.8.1. The crude product was purified by chromatography on silica using ethyl acetate–methanol (89:11 ⇒ 80:20 v/v) to give α-[5-(*n*-propylcarbamoyl) pentanoyl]-ω-*n*-propylaminotri [(*p*-methoxybenzyl) iminotetramethylene(*p*-methoxybenzyl)iminoadipoyl] **20** (PN[6][4.6]$_3$NP^{pp}) (4.73 g, 85%) an oil (Found: C, 69.90; H, 8.33; N, 7.38. $C_{90}H_{126}N_8O_{14}$ requires C, 70.01; H, 8.22; N, 7.26%); ^{1}H n.m.r. data in Table 5.

2.2.7.8.4. x = 2, n = 3. Compound **41** was reacted with *n*-propylamine as in Section 2.2.7.8.3 and the product purified by chromatography on silica using ethyl acetate–methanol (94:6 ⇒ 85:15 v/v) to give α-[5-(*n*-propylcarbamoyl) pentanoyl]-ω-*n*-propylaminotri [(*p*-methoxybenzyl) iminohexamethylene(*p*-methoxybenzyl)iminoadipoyl] **42** (PN[6][6.6]$_3$NP^{pp}) (81%) an oil (Found: C, 70.81; H, 8.71; N, 7.02. $C_{96}H_{138}N_8O_{14}$ requires C, 70.82; H, 8.54; N, 6.88%); ^{1}H n.m.r. data in Table 5.

2.2.7.8.5. x = 0, n = 5. Compound **23** (7.92 g, 3.3 mmol), methanol (15 ml), *n*-propylamine (20 ml, 245 mmol) and a catalytic amount of potassium cyanide (20 mg) were heated together under reflux for 3 days, and worked up as in Section 2.2.7.8.1. The crude product was purified by chromatography on silica using ethyl acetate–methanol (90:10 ⇒ 80:20 v/v) to give α-[5-(*n*-propylcarbamoyl)pentanoyl]-ω-*n*-propylaminopenta [(*p*-methoxybenzyl) iminotetramethylene (*p*-methoxybenzyl)iminoadipoyl] **24** (PN[6][4.6]$_5$NP^{pp}) (7.47 g, 93%) an oil (Found: C, 70.18; H, 8.15; N, 7.07. $C_{142}H_{194}N_{12}O_{22}$ requires C, 70.44; H, 8.08; N, 6.94%); ^{1}H n.m.r. data in Table 5.

2.2.7.8.6. x = 2, n = 5. Compound **45** was reacted with *n*-propylamine as in Section 2.2.7.8.5 and the product purified by chromatography on silica using dichloromthane–methanol (95:5 ⇒ 90:10 v/v) to give α-[5-(*n*-propylcarbamoyl)pentanoyl]-ω-*n*-propylaminopenta [(*p*-methoxybenzyl) imino- hexamethylene (*p*-methoxybenzyl) iminoadipoyl] **46** (PN[6][6.6]$_5$NP^{pp}) (83%) an oil (Found: C, 71.15; H, 8.42; N, 6.47. $C_{152}H_{214}N_{12}O_{22}$ requires C, 71.27; H, 8.42; N, 6.56%); ^{1}H n.m.r. data in Table 5.

2.2.7.8.7. x = 0, n = 7. Compound **26** (6.16 g, 1.9 mmol), methanol (15 ml), *n*-propylamine (20 ml, 245 mmol) and a catalytic amount of potassium cyanide (20 mg) were heated together under reflux for 4 days, and worked up as in Section 2.2.7.8.1. The crude product was purified by chromatography on silica using ethyl acetate–methanol (88:12 ⇒ 75:25 v/v) to give α-[5-(*n*-propylcarbamoyl) pentanoyl] -ω-*n*- propylaminohepta [(*p*-methoxybenzyl) iminotetramethylene(*p*-methoxybenzyl)iminoadipoyl] **27** (PN[6][4.6]$_7$NP^{pp}) (5.357 g, 86%) an oil (Found: C, 70.40; H, 8.02; N, 6.89. $C_{194}H_{262}N_{16}O_{30}$ requires C, 70.65; H, 8.01; N, 6.79%); ^{1}H n.m.r. data in Table 5.

2.2.7.8.8. x = 2, n = 7. Compound **48** was reacted with *n*-propylamine as in Section 2.2.7.8.7 and the product purified by chromatography on silica using dichloromthane–methanol (95:5 ⇒ 90:10, v/v) to give α-[5-(*n*-propylcarbamoyl)pentanoyl]-ω-*n*-propylaminohepta [(*p*-methoxybenzyl) iminohexamethylene (*p*-methoxybenzyl) iminoadipoyl] **49** (PN[6][6.6]$_7$NP^{pp}) (75%) an oil (Found: C, 71.27; H, 8.39; N, 6.53. $C_{208}H_{290}N_{16}O_{30}$ requires C, 71.49; H, 8.36; N, 6.41%); ^{1}H n.m.r. data in Table 5.

2.2.7.9. Formation of oligoamides of nylon 4 6 and nylon 6 6: n-C$_3$H$_7$NH[OC (CH$_2$)$_4$ CORN (CH$_2$)$_2$ (CH$_2$)$_x$ (CH$_2$)$_2$ NR]$_n$OC(CH$_2$)$_4$CONHC$_3$H$_7$-n

2.2.7.9.1. x = 0, n = 1. The end-capped compound **16** (3.14 g) and trifluoroacetic acid (6 ml) were heated under reflux for 40 min, during which an unidentified solid precipitated from a dark purple solution. The excess reagent was removed in vacuo, the semi-solid paste dissolved in dichloromethane (100 ml) and the solution washed with saturated sodium bicarbonate (10 ml). A white solid precipitated which was filtered and washed with dichloromethane (6 × 100 ml) to give 6,13- dioxo-7,12 -diazaoctadecanebis (*n*-propylamide) **17** (PN[6][4.6]$_1$NP) (1.65 g, 82%) mp 230–232°C (from ethanol) (Found: C, 61.81; H, 10.03; N, 13.03. $C_{22}H_{42}N_4O_4$ requires C, 61.94; H, 9.92; N, 13.13%); ^{1}H n.m.r. data in Table 6.

2.2.7.9.2. x = 2, n = 1. The end-capped compound **38** was deprotected with trifluoroacetic acid as in Section 2.2.7.9.1. and the product purified by recrystallisation to give 6,15-dioxo -7,14- diazacosanebis (*n*-propylamide) **39** (PN[6][6.6]$_1$NP) (86%) mp 218–220°C (from ethanol) (lit.[7] mp 229–230°) (Found: C, 63.52; H, 10.32; N, 12.33.

$C_{24}H_{46}N_4O_4$ requires C, 63.40; H, 10.20; N, 12.32%); ^{1}H n.m.r. data in Table 6.

2.2.7.9.3. x = 0, n = 3. The end-capped compound **20** (2.91 g) and trifluoroacetic acid (6 ml) were reacted together and the product isolated as in Section 2.2.7.9.1. to give α-[5-(*n*-propylcarbamoyl) pentanoyl]-ω-*n*-propylaminotri (iminotetramethyleneiminoadipoyl) **21** (PN[6][4.6]$_3$NP) (0.82 g, 53%) mp 268–270° (from acetic acid) (Found: C, 61.15; H, 9.73; N, 13.60. $C_{42}H_{78}N_8O_8$ requires C, 61.29; H, 9.55; N, 13.61%); ^{1}H n.m.r. data in Table 6.

2.2.7.9.4. x = 2, n = 3. The end-capped compound **42** was deprotected with trifluoroacetic acid as in Section 2.2.7.9.3 and the product purified by recrystallisation to give α-[5-(*n*-propylcarbamoyl) pentanoyl] -ω-*n*- propylaminotri (iminohexamethyleneiminoadipoyl)**43** (PN[6][6.6]$_3$NP) (85%) mp 244–246°C (from acetic acid) (lit.[7] 248–250°C) (Found: C, 63.53; H, 9.83; N, 12.09. $C_{48}H_{90}N_8O_8$ requires C, 63.54; H, 10.00; N, 12.35%); ^{1}H n.m.r. data in Table 6.

2.2.7.9.5. x = 0, n = 5. The end-capped compound **24** (4.27 g) and trifluoroacetic acid (10 ml) were reacted together and the product isolated as in Section 2.2.7.9.1 was boiled with toluene in a Dean and Stark apparatus and fitered to give α-[5-(*n*-propylcarbamoyl)pentanoyl]-ω-*n*- propylamino -penta (iminotetramethyleneiminoadipoyl) **25** (PN[6][4.6]$_5$NP) (1.93 g, 90%) mp 276–278°C (from 1,4-butanediol) (Found: C, 60.88; H, 9.53; N, 13.81. $C_{62}H_{114}N_{12}O_{12}$ requires C, 61.06; H, 9.42; N, 13.78%); ^{1}H n.m.r. data in Table 6.

2.2.7.9.6. x = 2, n = 5. The end-capped compound **46** was deprotected with trifluoroacetic acid as in Section 2.2.7.9.5 and the product purified by recrystallisation to give α-[5-(*n*-propylcarbamoyl)pentanoyl]-ω-*n*-propylaminopenta(iminohexamethyleneiminoadipoyl) **47** (PN[6][6.6]$_5$NP) (95%) mp 248–250°C (from 1,4-butanediol) (lit.[7] 258–261°C) (Found: C, 63.32; H, 10.01; N, 12.36. $C_{72}H_{134}N_{12}O_{12}$ requires C, 63.59; H, 9.93; N, 12.36%); ^{1}H n.m.r. data in Table 6.

2.2.7.9.7. x = 0, n = 7. The end-capped compound **27** (2.14 g) and trifluoroacetic acid (8 ml) were reacted together and the product isolated as in Section 2.2.7.9.1 to give α-[5-(*n*-propylcarbamoyl) pentanoyl] -ω-*n*- propylaminohepta (iminotetramethyleneiminoadipoyl) **28** (PN[6][4.6]$_7$NP) (1.02 g, 97%) mp 260–262°C (from 1,4-butanediol) (Found: C, 60.65; H, 9.55; N, 13.87. $C_{82}H_{150}N_{16}O_{16}$ requires C, 60.94; H, 9.36; N, 13.87%); ^{1}H n.m.r. data in Table 6.

2.2.7.9.8. x = 2, n = 7. The end-capped compound **49** was deprotected with trifluoroacetic acid as in Section 2.2.7.9.7 and the product purified by recrystallisation to give α-[5-(*n*-propylcarbamoyl)pentanoyl]-ω-*n*-propylaminohepta(iminohexamethyleneiminoadipoyl) **50** (PN[6][6.6]$_7$NP) (93%) mp 232–234°C (from 1,4-butanediol) (Found: C, 63.50; H, 10.13; N, 12.20. $C_{96}H_{178}N_{16}O_{16}$ requires C, 63.61; H, 9.90; N, 12.36%); ^{1}H n.m.r. data in Table 6.

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References

[1] Brooke GM, Burnett S, Mohammed S, Proctor D, Whiting M. J Chem Soc Perkin Trans 1996;1:958.
[2] Bassett DC, Holley RH, Sutton SJ, Vaughan AS. Macromolecules 1996;29:1852.
[3] Brooke GM, Mohammed S, Whiting M. J Chem Soc Perkin Trans, 1997, 3371.
[4] Carothers WH, US Patent, 2,130,523 (20 September 1938).
[5] Baker WO, Fuller CS. J Am Chem Soc 1943;65:1120.
[6] Wittbecker EL, Houtz RC, Watkins WW. Ind Eng Chem, 1948;40:875; Briggs BS, Frosch CJ, Erickson RH. Ind Eng Chem, 1946;38:1016; Lewis JR, Reynolds RJW. Chem and Ind (London), 1951, 958.
[7] Zahn H, Gleitsman GB. Angew Chem Int Edn 1963;2:410.
[8] Bodanszky M, Bodanszky A. The Practice of Peptide Synthesis, 2nd edn. Springer-Verlag, 1994, p. 15.
[9] Bodanszky M, Bodanszky A. The Practice of Peptide Synthesis, 2nd edn. Springer-Verlag, 1994, p. 142.
[10] Bodanszky M, Bodanszky A. The Practice of Peptide Synthesis, 2nd edn. Springer-Verlag, 1994, p. 119.
[11] Hogberg T, Strom P, Ebner M, Ramsby S. J Org Chem 1987;52:2033.
[12] Brooke GM, Mohammed S, Whiting M. J Chem Soc Chem Commun., 1997, 1511.
[13] Igner E, Paynter OI, Simmonds DJ, Whiting MC. J Chem Soc Perkin Trans 1987;1:2447.
[14] Silverstein RM, Bassler GC, Morrill TC. Spectrometric Identification of Organic Compounds, 4th edn. Wiley, New York, 1981.
[15] March J. Advanced Organic Chemistry, 4th edn. Wiley, New York, 1992, p. 129.