Research Article

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Synthesis of ω-amino-α-phenylcarbonate alkanes and their polymerization to [*n*]-polyurethanes

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Abstract

Aliphatic [*n*]-polyurethanes have recently been synthesized from ω-isocyanato-α-alkanols or, more traditionally, by cationic ring-opening polymerization of cyclourethanes or by the $Bu_2Sn(OMe)_2$-promoted polycondensation of ω-hydroxy-α-*O*-phenylurethane alkanes. For the latter procedures, the conditions employed do not seem to be suitable for highly functionalized monomers. In contrast, the polymerization of ω-amino-α-phenylcarbonate alkanes is expected to occur under milder conditions. ω-Amino-α-phenylcarbonate alkanes have been synthesized from 6-aminohexanol (1) and 3-aminopropanol (6). The procedure involves the *N*-Boc protection of the amino group, followed by activation of the alcohol. Removal of the *N*-Boc affords the corresponding ω-amino-1-*O*-phenyloxycarbonyloxyalkane hydrochlorides. Other oligomeric comonomers between 1 and 6 have been prepared. The polymerization of these precursors takes place in the absence of metal catalysts to afford the corresponding linear and regioregular [*n*]-polyurethanes. The procedure described is useful for the preparation of stable ω-amino-α-phenylcarbonate alkane derivatives, which possess varied chain lengths between the terminal functions. These monomers yield [*n*]-polyurethanes having various structures starting from just two aminoalkanols. The polyurethanes were obtained in high yields, with reasonable molecular weight and polydispersity values, and they were characterized spectroscopically and thermally. These studies reveal constitutionally uniform structures that are free of carbonate or urea linkages.

Keywords: aminoalkanols; ω-amino-α-phenylcarbonate alkanes; polymerization; polyurethanes

INTRODUCTION

Polyurethanes are produced in the form of foamed plastics, structural elastomers, adhesives and auxiliary agents. They generally offer advantageous performance properties, ease of processing and good resistance to water, oils, greases, organic solvents and diluted acids and alkalis. Therefore, polyurethanes are applied in the fields of technology and commerce and in everyday life.[1,2] Their wide range of application is continuously expanding. The newer trends include the development of high-performance polyurethanes[3] and biodegradable ionomers,[4] and their combination with other polymers to yield interpenetrating networks.[5] Furthermore the good physical properties and hydrolytic stability of polyurethanes as well as their low *in vitro* absorption of proteins and adhesion to platelets enables some medical applications, mainly when contact of the polymer with body fluids is required.[6]

Linear [*m*,*n*]-polyurethanes are usually prepared by reaction of diisocyanates with diols. To avoid the use of toxic diisocyanates, which are usually derived from the even more toxic phosgene, novel routes to polyurethanes avoiding the use of diisocyanates and phosgene have been reported. Some such routes include the reaction of adiponitrile carbonate with diols or polyols,[7] the polymerization of cyclic carbonates with amines[8,9] and melt transurethane polycondensation under solvent-free conditions.[10] Also, the enzymatic synthesis of polyurethanes has been attempted as a green and sustainable strategy.[11]

The synthesis of [*n*]-polyurethanes from α-hydroxy-ω-isocyanate alkanes has not been described in the literature up to recently, due to the difficulty of preparing such monomers.[12] Alternatively, aliphatic [*n*]-polyurethanes have been synthesized by cationic ring-opening polymerization of cyclourethanes,[13,14] or by the $Bu_2Sn(OMe)_2$-promoted polycondensation of α-hydroxy-ω-*O*-phenylurethane alkanes,[15] which requires heating at high temperature (100–120 °C) and the use of a vacuum, for the removal of phenol by distillation to shift the equilibrium to the product side. These conditions do not seem to be appropriate for the polymerization of sugar-derived monomers, the subject of our present investigations.[16–21] These highly functionalized molecules are rather unstable to temperature and catalysts. We reasoned that the use of catalysts could be avoided by replacing α-hydroxy-ω-*O*-phenylurethane alkanes by ω-amino-α-phenylcarbonate alkane derivatives as more reactive monomeric precursors. Milder reaction conditions were also expected as the amine function of the latter monomers is a stronger nucleophile than the hydroxyl group of the α-hydroxy-ω-*O*-phenylurethane alkanes. Therefore, we report here a convenient procedure for the synthesis of

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ω-amino-α-phenylcarbonate alkanes and their polycondensation to linear [*n*]-polyurethanes. Their molecular weights were estimated using gel permeation chromatography (GPC) and they were characterized spectroscopically and thermally. The surfaces of the materials were examined using SEM.

EXPERIMENTAL

General

3-Amino-1-propanol (>99%) and 6-amino-1-hexanol (97%) were purchased from Aldrich Chemical Company Inc., and used without further purification. Melting points were determined with a Fisher–Johns apparatus and were uncorrected.

Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F254 (E Merck) aluminium-supported plates (layer thickness of 0.2 mm). Visualization of the spots was effected by exposure to UV light or by charring with a solution of 5 vol% sulfuric acid in EtOH, containing 0.5 vol% *p*-anisaldehyde; for compounds having a free amino group, the plates were heated after immersion in a solution of ninhydrin in acetone or in a 5 wt% NaOH aqueous solution followed by ninhydrin in acetone. Column chromatography was carried out with silica gel 60 (230–400 mesh; E Merck). GPC was carried out using Styragel columns (HR-3 and HR-4) from Waters, with tetrahydrofuran (THF) as solvent at a flow rate of 1.0 mL min^{-1}. The calibration was performed using polystyrene standards.

NMR spectra were recorded with a Bruker AMX 500 instrument (^{1}H NMR: 500 MHz; ^{13}C NMR: 125.7 MHz) in $CDCl_3$ solutions (tetramethylsilane as internal standard) unless otherwise indicated. The assignments were assisted by 2D COSY, DEPT and HSQC techniques. Fourier transform infrared (FTIR) spectra (films or KBr pellets) were recorded with a Nicolet 510P FTIR spectrometer. Electron-impact mass spectrometry (MS) was carried out with a Shimadzu QP5050A mass spectrometer, operating at 70 eV.

DSC was conducted with a DSC Q20 TA instrument. Samples of about 2 mg were heated from −50 to 200 °C at a rate of 20 °C min^{-1}, then cooled at 5 °C min^{-1} to −50 °C (isothermic 5 min) and finally heated at 10 °C min^{-1} to 200 °C. TGA was performed using a Shimadzu TGA-51 instrument. Samples of about 2 mg were heated at a rate of 10 °C min^{-1}.

The surface morphology of the polyurethanes was analyzed using SEM with a Zeiss Supra 40 instrument with an in-lens secondary detector.

Synthesis of 6-(*N*-Boc)-amino-1-hexanol (2)

A solution of Boc_2O (0.56 g, 2.59 mmol) and 6-amino-1-hexanol (**1**; 0.300 g, 2.56 mmol) in acetonitrile was stirred at room temperature (RT) for 45 min. The mixture was concentrated to yield crude **2** (0.556 g, quantitative), which was employed for the next reaction without further purification.

^{1}H NMR (500 MHz, $CDCl_3$; δ, ppm): 4.55 (bs, 1H, NH), 3.63 (dd, $J_{1,2}$ = 6.7 Hz, 2H, CH_2O), 3.12 (bs, 2H, CH_2N), 1.57 (m, 2H, CH_2-2), 1.53 (m, 2H, CH_2-5), 1.43 (s, 9H, $(CH_3)_3C$), 1.36 (m, 4H, CH_2-3,4). ^{13}C NMR (125.7 MHz, $CDCl_3$; δ, ppm): 156.1 (NCO_2), 85.2 ($(CH_3)_3C$), 62.6 (C-1), 40.3 (C-6), 28.4 ($(CH_3)_3C$), 30.0, 27.4, 26.3, 25.2 (C-2–C-5).

Synthesis of 6-(*N*-Boc)-amino-1-*O*-phenyloxycarbonyloxyhexane (3)

To a solution of crude compound **2** (0.52 g, 2.4 mmol) in dry pyridine (5 mL) was added phenylchloroformate (0.374 g, 2.39 mmol). The mixture was stirred at RT for 1.5 h. After subsequent addition of MeOH and toluene, the mixture was concentrated and purified by column chromatography (hexane/EtOAc 4 : 1) to yield **3** (0.675 g, 84%), m.p. = 41 °C.

MS (70 eV): *m/z* = 338 (M + H), 282 (M + H − C_4H_8), 264 (M + H − C_4H_9OH), 237 (M + H − C_4H_9 − CO_2), 144 (M + H − PhOH − CO_2 − C_4H_8), 126 (264 − PhOH − CO_2), 100 (M + H − PhOH − CO_2 − C_4H_8 − CO_2), 94 (PhOH), 74 (C_4H_9OH), 57 ($C_4H_9^+$). ^{1}H NMR (200 MHz, $CDCl_3$; δ, ppm): 7.46–7.18 (5H, H-aromatic), 4.25 (q, $J_{5,6}$ = 6.6 Hz, 2H, CH_2O), 3.13 (q, $J_{5,6}$ = $J_{6,NH}$ = 6.6 Hz, 2H, CH_2N), 1.45 (s, 9H, $(CH_3)_3C$), 1.84–1.38 (m, 8H, CH_2-2–CH_2-5). ^{13}C NMR (50.3 MHz, $CDCl_3$; δ, ppm): 156.0 (NCO_2), 153.8 (OCO_2), 151.1, 129.5, 126.0, 121.1 (C-aromatic), 79.2 ($(CH_3)_3C$), 68.8 (C-1), 40.6 (C-6), 28.4 ($(CH_3)_3C$), 30.0, 28.5, 26.4, 25.4 (C-2-C-5). $C_{18}H_{27}NO_5$ (337.19): calcd C 64.07, H 8.07, N 4.15; found C 63.84, H 8.12, N 4.28.

Synthesis of 6-amino-1-*O*-phenyloxycarbonyloxyhexane hydrochloride (4)

Compound **3** (0.168 g, 0.50 mmol) was dissolved in EtOAc saturated with hydrogen chloride (10 mL). The solution was stirred at RT for 20 h, and compound **4** precipitated upon external cooling. The solid was collected by centrifugation (0.130 g, 96%) and was washed with EtOAc (3 × 4 mL), m.p. = 92 °C.

^{1}H NMR (200 MHz, DMSO-d_6; δ, ppm): 8.22 (bs, 3H, NH_3), 7.44–7.20 (m, 5H, H-aromatic), 4.20 (t, $J_{1,2}$ = 6.5 Hz, 2H, CH_2O), 2.75 (t, $J_{5,6}$ = 7.6 Hz, 2H, CH_2N), 1.63, 1.35 (2 m, 8H, CH_2-2–CH_2-5). ^{13}C NMR (50.3 MHz, DMSO-d_6; δ, ppm): 153.1 (OCO_2), 150.7, 129.6, 120.1, 121.2 (C-aromatic), 68.3 (C-1), 38.50 (C-6), 27.8, 26.7, 25.4, 24.6 (C-2-C-5). $C_{13}H_{20}ClNO_3$ (273.11): calcd C 57.04, H 7.36, N 5.12; found C 56.85, H 7.34, N 5.30.

Synthesis of 3-(*N*-Boc)-amino-1-(phenyloxycarbonyloxy)propane (7)

To a solution of Boc_2O (3.09 g, 14.15 mmol) in acetonitrile (15 mL) was added 3-amino-1-propanol (**6**; 1.06 g, 14.15 mmol). The mixture was stirred at RT for 75 min, when TLC (hexane/EtOAc 3 : 7) showed a single spot of R_f = 0.39, moving faster than **6** (R_f = 0). The solution was concentrated and the crude *N*-Boc derivative (2.63 g) was dissolved in dry pyridine (12 mL). Upon addition of phenylchloroformate (2.22 g, 14.15 mmol) the mixture was stirred at RT for 20 h, then diluted with MeOH and toluene, and concentrated. Purification by column chromatography (toluene/EtOAc 4 : 1) afforded **7** (4.11 g, 98%), m.p. = 39 °C.

MS (70 eV): *m/z* = 295 (M), 239 (M − C_4H_8), 222 (M − C_4H_9O), 202 (M − PhO), 178 (M − $C_4H_9OCONH_2$), 150 (M − $C_4H_9OCONH_2$ − C_2H_4), 102 ($C_4H_9OCOH^+$), 94 ($PhOH^+$), 77 ($C_6H_5^+$), 57 ($C_4H_9^+$). ^{1}H NMR (200 MHz, $CDCl_3$; δ, ppm): 7.44–7.16 (5H, H-aromatic), 4.75 (bs, 1H, NH), 4.32 (t, $J_{1,2}$ = 6.2 Hz, 2H, CH_2O), 3.28 (q, $J_{2,3}$ = 6.4 Hz, 2H, CH_2N), 1.94 (m, $J_{1,2}$ = $J_{2,3}$ = 6.4 Hz, 2H, CH_2-2), 1.45 (s, 9H, $(CH_3)_3C$). ^{13}C NMR (50.3 MHz, $CDCl_3$; δ, ppm): 155.9 (NCO_2), 153.8 (OCO_2), 151.1, 129.5, 126.1, 121.0 (C-aromatic), 79.4 ($(CH_3)_3C$), 66.3 (C-1), 37.1 (C-3), 29.2 (C-2), 28.4 ($(CH_3)_3C$). ($C_{15}H_{21}NO_5$) (295.14): calcd C 61.00, H 7.17, N 4.74; found C 61.16, H 7.17, N 4.74.

Synthesis of 3-*N*-(3′-*N*′-Boc-aminopropyloxycarbonyl)amino-1-propanol (8)

Compound **7** (0.958 g, 3.24 mmol) and 3-amino-1-propanol (0.244 g, 3.24 mmol) were dissolved in THF (10 mL) and the solution was stirred at RT for 36 h. After concentration, it was purified by column chromatography (toluene/EtOAc 1 : 1) to give compound **8** (0.835 g, 93%) as a syrup.

MS (70 eV): m/z = 277 (M + H), 221 (M − C_4H_8), 177 (M + H − C_4H_8 − CO_2), 120 ($HOC_3H_6NHCO_2H$ + H), 101 ($C_4H_9OCO^+$), 76 (120 − CO_2), 56 ($C_4H_8^+$). ^{1}H NMR (200 MHz, $CDCl_3$; δ, ppm): 5.26, 4.87 (2 bs, 1H each, NH), 4.12 (t, $J_{1',2'}$ = 6.0 Hz, 2H, CH_2-1′), 3.68 (t, $J_{1,2}$ = 6.0 Hz, 2H, CH_2-1), 3.32, 3.18 (2 q, $J_{2,3}$ = $J_{3,NH}$ = $J_{2',3'}$ = $J_{3',NH}$ = 6.1 Hz, 4H, CH_2-3,3′), 1.79 (q, $J_{1',2'}$ = $J_{2',3'}$ = 6.0 Hz, 2H, CH_2-2′), 1.68 (q, $J_{1,2}$ = $J_{2,3}$ = 6.0 Hz, 2H, CH_2-2), 1.43 (s, 9H, $(CH_3)_3C$). ^{13}C NMR (50 MHz, $CDCl_3$; δ, ppm): 156.6, 156.5 (NCO_2), 79.4 ($(CH_3)_3C$), 62.3 (C-1′), 59.6 (C-1), 37.8, 37.2 (C-3,3′), 32.5 (C-2′), 29.6 (C-2), 28.4 ($(CH_3)_3C$). ($C_{12}H_{24}N_2O_5$) (276.17): calcd C 52.16, H 8.75, N 10.14; found C 51.91, H 8.57, N 9.94.

Synthesis of 3-(3′-*N*-Boc-aminopropyl-1′-oxycarbonyl)amino-1-phenyloxycarbonyloxypropane (9)

To a solution of **8** (0.356 g, 1.29 mmol) in dry pyridine (2 mL) was added phenylchloroformate (0.202 g, 1.29 mmol). The mixture was stirred at RT for 22 h, when an additional amount of phenylchloroformate (0.100 g, 0.638 mmol) was added. The stirring was continued for 26 h, and then the mixture was diluted with toluene and concentrated. Purification by column chromatography (toluene/EtOAc 9 : 1 v/v) afforded **9** (0.491 g, 96%) as a syrup.

MS (70 eV): m/z = 397 (M + H), 341 (M − C_4H_8), 297 (M − C_4H_8 − CO_2), 240 ($PhOCO_2C_3H_6NHCO_2H$ + H), 196 (240 − CO_2), 185 (M + H − $PhOCO_2H$ − C_4H_9OH), 102 ($C_4H_9OCOH^+$), 94 ($PhOH^+$), 74 (C_4H_9OH + H), 57 ($C_4H_9^+$). ^{1}H NMR (200 MHz, $CDCl_3$; δ, ppm): 7.40–7.15 (m, 5H, H-aromatic), 5.00, 4.80 (2 bs, 1H each, NH), 4.34 (t, $J_{1,2}$ = 6.2 Hz, 2H, CH_2-1), 4.13 (t, $J_{1',2'}$ = 6.2 Hz, 2H, CH_2-1′), 3.34, 3.19 (2 q, $J_{2,3}$ = $J_{3,NH}$ = $J_{2',3'}$ = $J_{3',NH}$ = 6.4 Hz, 4H, CH_2-3,3′), 1.96 (m, $J_{1,2}$ = $J_{2,3}$ = 6.4 Hz, 2H, CH_2-2), 1.79 (m, $J_{1',2'}$ = $J_{2',3'}$ = 6.2 Hz, 2H, CH_2-2′), 1.44 (s, 9H, $(CH_3)_3C$). ^{13}C NMR (50 MHz, $CDCl_3$; δ, ppm): 156.5, 156.4 (NCO_2), 153.2 (OCO_2), 121.0, 126.1, 129.5 (C-aromatic), 66.1 (C-1), 62.2 (C-1′), 37.6, 37.2 (C-3,3′), 29.5 (C-2′), 29.0 (C-2), 28.4 ($(CH_3)_3C$). ($C_{19}H_{28}N_2O_7$) (396.19): calcd C 57.56, H 7.12, N 7.07; found C 57.11, H 7.20, N 7.24.

Synthesis of 3-(3′-aminopropyl-1′-oxycarbonyl)amino-1-phenyloxycarbonyloxypropane hydrochloride (10)

Compound **9** (0.478 g, 1.21 mmol) was dissolved in a saturated solution of hydrogen chloride in EtOAc (20.4 mL). The mixture was stirred at RT for 24 h, and then concentrated. To complete the removal of the *N*-Boc group, an additional amount of HCl/EtOAc (10 mL) was added and the stirring was continued for 24 h. After concentration, the residue was washed with EtOAc to yield compound **10** as a syrup (0.37 g, 91%).

^{1}H NMR (200 MHz, DMSO-d_6; δ, ppm): 7.96 (bs, 3H, N′H_3), 7.47–7.10 (m, 6H, H-aromatic + NH), 4.21 (t, $J_{1,2}$ = 6.3 Hz, 2H, CH_2-1), 4.01 (t, $J_{1',2'}$ = 6.0 Hz, 2H, CH_2-1′), 3.10 (q, $J_{2,3}$ = $J_{3,NH}$ = 6.1 Hz, 2H, CH_2-3), 2.82 (bs, 2H, CH_2-3′), 1.82 (m, 4H, CH_2-2,2′). ^{13}C NMR (50.3 MHz, DMSO-d_6; δ, ppm): 156.2 (NCO_2), 153.0 (OCO_2), 150.8, 129.6, 126.2, 121.3 (C-aromatic), 66.2, 61.1 (C-1,1′), 36.8, 36.2 (C-3,3′), 28.5, 26.7 (C-2,2′). ($C_{14}H_{20}N_2O_5$) · (1.2 HCl): calcd C 49.45, H 6.28, N 8.24; found C 49.10, H 6.34, N 8.05.

Synthesis of 6-(3′-*N*-Boc-aminopropyl-1′-oxycarbonyl)amino-1-phenyloxycarbonyloxyhexane (12)

A solution of **1** (0.122 g, 1.041 mmol) and **7** (0.30 g, 1.03 mmol) in THF (3 mL) was stirred at RT for 23 h. The mixture was concentrated and the residue was dissolved in pyridine (2.8 mL). Upon addition of phenylchloroformate (0.286 g, 1.827 mmol), the suspension was stirred at RT for 5 h. An additional amount of phenylchloroformate (0.142 g, 0.909 mmol) was added and the stirring was continued for 72 h. The mixture was diluted with toluene, concentrated and purified by column chromatography (hexane/EtOAc 7 : 3) to give compound **12** (0.35 g, 87%), m.p. = 69 °C.

MS (70 eV): m/z = 439 (M + H), 383 (M + H − C_4H_8), 339 (M + H − C_4H_8 − CO_2), 238 (M + H − $C_3H_5NHCO_2C_4H_9$ − CO_2), 201 (M + H − $PhOCO_2C_4H_9$ − C_4H_8 − CO_2), 144 ($C_6H_{11}NHCO_2H$), 126 (144 − H_2O), 101 ($C_4H_9OCO^+$), 94 (PhOH), 56 ($C_4H_8^+$). ^{1}H NMR (500 MHz, $CDCl_3$; δ, ppm): 7.42–7.17 (m, 5H, H-aromatic), 4.80, 4.73 (2 bs, 1H each, NH), 4.25 (t, $J_{1,2}$ = 6.6 Hz, 2H, CH_2-1), 4.12 (t, $J_{1',2'}$ = 6.0 Hz, 2H, CH_2-1′), 3.20 (m, 2H, CH_2-3′,6), 1.79 (m, 2H, CH_2-2′), 1.76 (m, 2H, CH_2-2), 1.53 (m, $J_{3,4}$ = $J_{4,5}$ = 7.2 Hz, 2H, CH_2-4), 1.46 (m, 2H, CH_2-3), 1.44 (s, 9H, $(CH_3)_3C$), 1.39 (m, 2H, CH_2-5). ^{13}C NMR (125.7 MHz, $CDCl_3$; δ, ppm): 156.7, 155.9 (NCO_2), 153.7 (OCO_2), 151.1, 129.4, 126.0, 121.0 (C-aromatic), 79.2 ($(CH_3)_3C$), 68.7 (C-1), 62.0 (C-1′), 40.8, 37.2 (C-3′,6), 29.8 (C-4), 29.6 (C-2′), 28.5 (C-2), 28.4 ($(CH_3)_3C$), 26.3 (C-5), 25.4 (C-3). ($C_{22}H_{34}N_2O_7$) (438.24): calcd C 60.26, H 7.82, N 6.39; found C 60.44, H 7.87, N 6.46.

Synthesis of 6-(3′-aminopropyl-1′-oxycarbonyl)amino-1-phenyloxycarbonyloxyhexane hydrochloride (13)

Compound **12** (0.247 g, 0.56 mmol) was dissolved in a saturated solution of HCl in EtOAc (15 mL) and stirred at RT for 24 h. The reaction mixture was concentrated and the solid residue was washed with EtOAc to yield compound **13**, which was recrystallized from EtOAc (0.172 g, 82%), m.p. = 87 °C.

^{1}H NMR (500 MHz, DMSO-d_6; δ, ppm): 8.0 (bs, 3H, NH_3), 7.44–7.19 (m, 5H, H-aromatic), 4.19 (m, $J_{1,2}$ = 6.6 Hz, 2H, CH_2-1), 3.99 (m, $J_{1',2'}$ = 6.2 Hz, 2H, CH_2-1′), 2.97 (m, J = 6.7 Hz, 2H, CH_2-6), 2.82 (m, 2H, CH_2-3′), 1.85 (m, $J_{1',2'}$ = $J_{2',3'}$ = 5.9 Hz, 2H, CH_2-2′), 1.65 (m, $J_{1,2}$ = $J_{2,3}$ = 6.8 Hz, 2H, CH_2-2), 1.41 (m, $J_{4,5}$ = $J_{5,6}$ = 7.2 Hz, 2H, CH_2-5), 1.34 (m, 4H, CH_2-3,4). ^{13}C NMR (125.7 MHz, DMSO-d_6; δ, ppm): 156.1 (NCO_2), 153.1 (OCO_2), 150.8, 129.6, 126.1, 121.3 (C-aromatic), 68.5 (C-1), 60.9 (C-1′), 40.1 (C-6), 36.2 (C-3′), 29.3 (C-5), 28.0 (C-2′), 26.9 (C-2), 25.8, 24.9 (C-3,4). ($C_{17}H_{27}ClN_2O_5$) (374.16): calcd C 54.47, H 7.26, N 7.47; found C 54.29, H 7.26, N 7.42.

Synthesis of 6-[3′-(3″-*N*-Boc-aminopropyl-1″-oxycarbonyl)aminopropyl-1′-oxycarbonyl] aminophenyloxycarbonyloxyhexane (15)

To a solution of **2** (0.047 g, 0.40 mmol) and **9** (0.158 g, 0.40 mmol) in THF (1.2 mL) was added *N*,*N*-diisopropylethylamine (DIPEA; 0.136 mL, 0.80 mmol). The mixture was stirred at RT for 24 h and then concentrated. The residue was dissolved in pyridine (0.93 mL) and, after addition of phenylchloroformate (0.094 g, 0.60 mmol), the suspension was stirred at RT for 48 h. The mixture was diluted with toluene, concentrated and purified by column chromatography (hexane/EtOAc 3 : 7 v/v) to give compound **15** (0.178 g, 83%), m.p. = 70 °C.

^{1}H NMR (500 MHz, $CDCl_3$; δ, ppm): 7.41–7.17 (m, 5H, H-aromatic), 5.05, 4.80 (2 bs, 3 NH), 4.26 (t, $J_{1,2}$ = 6.6 Hz, 2H, CH_2-1), 4.13 (m, 4H, CH_2-1′,1″), 3.25 (m, $J_{2',3'}$ = $J_{3',NH}$ = 6.2 Hz, 2H, CH_2-3′), 3.19 (m, 4H, CH_2-3′,6), 1.81–1.73 (m, 6H, CH_2-2,2′,2″), 1.54 (m, $J_{3,4}$ = $J_{4,5}$ = 7.2 Hz, 2H, CH_2-4), 1.48–1.37 (m, 4H, CH_2-3,5), 1.44 (s, 9H, $(CH_3)_3C$). ^{13}C NMR (125.7 MHz, $CDCl_3$; δ, ppm): 156.7, 156.6, 156.0 (NCO_2), 153.8 (OCO_2), 150.9, 129.5, 126.0, 121.1 (C-aromatic), 79.3 ($(CH_3)_3C$), 68.7 (C-1), 62.0 (C-1′, C1″), 40.9, 37.2, 37.3 (C-3′,3″,6), 29.9 (C-4), 29.6 (C-2′,C-2″), 28.5 (C-2), 28.4 ($(CH_3)_3C$), 26.3 (C-5), 25.4 (C-3). ($C_{26}H_{41}N_3O_9$) (539.28): calcd C 57.87, H 7.66, N 7.79; found C 57.53, H 7.51, N 7.67.

Synthesis of 6-[3′-(3″-aminopropyl-1″-oxycarbonyl) aminopropyl-1′-oxycarbonyl]aminophenyloxyhexane hydrochloride (16)

Compound **15** (0.136 g, 0.25 mmol) was dissolved in EtOAc saturated with HCl (6.5 mL) and the solution was stirred at RT overnight. The reaction mixture was concentrated, and the solid residue was washed with EtOAc to yield hydrochloride **16** (0.120 g, 100%), m.p. = 93 °C.

^{1}H NMR (500 MHz, DMSO-d_6; δ, ppm): 7.79 (bs, NH_3), 7.44–7.21 (m, 5H, H-aromatic), 7.20, 7.09 (1H each, NH), 4.18 (t, $J_{1,2}$ = 6.6 Hz, 2H, CH_2-1), 3.99 (t, $J_{1',2'}$ = 6.3 Hz, 2H, CH_2-1′), 3.92 (t, $J_{1'',2''}$ = 6.5 Hz, 2H, CH_2-1″), 3.03 (q, $J_{2'',3''}$ = 6.4 Hz, 2H, CH_2-3″), 2.95 (q, J = 6.8 Hz, 2H, CH_2-6), 2.83 (t, $J_{2',3'}$ = 7.3 Hz, 2H, CH_2-3′), 1.83 (m, $J_{1',2'} = J_{2',3'}$ = 6.9 Hz, 2H, CH_2-2′), 1.67 (m, $J_{1'',2''} = J_{2'',3''}$ = 6.8 Hz, 2H, CH_2-2″), 1.64 (m, $J_{1,2} = J_{2,3}$ = 7.2 Hz, 2H, CH_2-2), 1.39 (m, $J_{4,5} = J_{5,6}$ = 7.0 Hz, 2H, CH_2-5), 1.34 (m, 2H, CH_2-3), 1.29 (m, 2H, CH_2-4). ^{13}C NMR (125.7 MHz, DMSO-d_6; δ, ppm): 156.2, 156.0 (NCO_2), 153.1 (OCO_2), 150.6, 129.5, 126.1, 121.2 (C-aromatic), 68.4 (C-1), 61.3, 60.9 (C-1′,1″), 37.1 (C-6), 36.2 (C-3′,3″), 29.2, 29.1 (C-2″, C-5), 27.9 (C-2), 26.8 (C-2′), 25.7 (C-4), 24.8 (C-3). $C_{21}H_{33}N_3O_7 \cdot 1.2$ HCl (483.26): calcd C 52.19, H 7.13, N 8.70; found C 52.38, H 7.18, N 8.97.

General procedure for the polymerization of 4

A solution of **4** in anhydrous solvent was placed in a screw-cap V-vial, and the organic base (3 molar equivalents) indicated in Table 1 was added. The volume was adjusted to give a 1 mol L^{-1} solution of the monomer, except for entry 4, where the initial concentration of monomer was 0.5 mol L^{-1} because of its low solubility in THF. The vial was flushed with argon, closed and placed in an oil bath heated at the temperature indicated in Table 1. The mixture was stirred for 20 h and then was allowed to reach RT and was subsequently poured into MeOH. The solid was recovered by centrifugation and it was purified three times by suspension in hot MeOH, and isolated by centrifugation. Finally polyurethane **5** was dried in vacuum.

Preparative-scale polymerizations

The ω-amino-α-phenylcarbonate alkane **4,10,13** or **16** (0.30 mmol) was dissolved in anhydrous dimethylformamide (DMF; 0.15 mL) in a V-vial and DIPEA (0.15 mL, 0.9 mmol) was added. The vial was flushed with argon and closed. The mixture was stirred at 100 °C for 24 to 48 h and then was allowed to reach RT. The jelly mass formed was diluted with MeOH and the solid was recovered by centrifugation. The polymer was purified as described above. The isolated yields are reported in Table 1.

Polyurethane 5

T_m = 165.7 °C. FTIR (KBr; cm^{-1}): 3318 (s, NH st), 2938 (m, CH), 1686 (s, C=O), 1542 (s, NH δ). ^{1}H NMR (500 MHz, DMSO-d_6; δ, ppm): 7.02 (bs, 0.9 H, NH *trans*), 6.74 (bs, 0.1 H, NH *cis*), 3.90 (t, $J_{1,2}$ = 5.9 Hz, 2H, CH_2O), 2.94 (q, $J_{5,6}$ = 6.4 Hz, 2H, CH_2N), 1.51 (m, $J_{1,2} = J_{2,3}$ = 6.4 Hz, 2H, CH_2-2), 1.38 (m, $J_{4,5} = J_{5,6}$ = 6.5 Hz, 2H, CH_2-5), 1.27 (m, 4H, CH_2-3,4). ^{13}C NMR (50.3 MHz, DMSO-d_6; δ, ppm): 156.3 (NCO_2), 63.4 (C-1), 39.8 (C-6), 29.3, 28.6, 25.8, 25.0 (C-2-C-5). $(C_7H_{13}NO_2)_n$ $(143.18)_n$: calcd C 58.72, H 9.15, N 9.75; found C 58.35, H 8.97, N 9.34.

Polyurethane 11

T_m = 166.6 °C. FTIR (KBr; cm^{-1}): 3302 (s, NH st), 2973 (m, CH), 1677 (s, C=O), 1558 (s, NH δ). ^{1}H NMR (200 MHz, DMSO-d_6; δ, ppm): 7.14 (bs, 0.9 H, NH *trans*), 6.80 (bs, 0.1 H, NH *cis*), 3.92 (t, $J_{1,2}$ = 6.3 Hz, 2H, CH_2-1), 3.01 (q, $J_{2,3} = J_{3,NH}$ = 6.3 Hz, 2H, CH_2-3), 1.66 (m, $J_{1,2} = J_{2,3}$ = 6.3 Hz, 2H, CH_2-2). ^{13}C NMR (50 MHz, DMSO-d_6; δ, ppm): 156.2 (NCO_2), 61.5 (CH_2O), 37.2 (CH_2 NH), 29.2 (C-2). $(C_4H_7NO_2)_n$ $(101.10)_n$: calcd C 47.52, H 6.98, N 13.85; found C 47.44, H 7.11, N 13.33.

Polyurethane 14

T_m = 143.0 °C. FTIR (KBr; cm^{-1}): 3315 (s, NH st), 2939 (m, CH), 1697 (s, C=O), 1552 (s, NH δ). ^{1}H NMR (500 MHz, DMSO-d_6; δ, ppm): 7.07 (bs, 1.7 H, NH *trans*), 6.75 (bs, 0.3 H, NH *cis*), 3.92 (m, 4H, CH_2-1,1′), 3.01 (q, $J_{2',3'} = J_{3',NH}$ = 6.3 Hz, 2H, CH_2-3′), 2.93 (q, $J_{5,6} = J_{6,NH}$ = 6.4 Hz, 2H, CH_2-6), 1.65 (m, $J_{1',2'} = J_{2',3'}$ = 6.6 H, 2H, CH_2-2′), 1.51 (m, $J_{1,2} = J_{2,3}$ = 6.7 Hz, 2H, CH_2-2), 1.37 (m, $J_{4,5} = J_{5,6}$ = 6.7 Hz, 2H, CH_2-5), 1.28 (m, 4H, CH_2-3,4). ^{13}C NMR (125.7 MHz, DMSO-d_6; δ, ppm): 156.6 (NCO_2), 63.6 (CH_2-1), 61.4 (CH_2-1′), 40.1 (CH_2-6), 37.2 (CH_2-3′), 29.3 (CH_2-5), 29.2 (CH_2-2′), 28.6 (CH_2-2), 25.9 (CH_2-3), 25.1 (CH_2-4). $(C_{11}H_{20}N_2O_4)_n$ $(244.14)_n$: calcd C 54.08, H 8.25, N 11.47; found C 53.99, H 8.14, N 11.22.

Polyurethane 17

T_m = 127.9 °C. FTIR (KBr; cm^{-1}): 3315 (s, NH st), 2939 (m, CH), 1697 (s, C=O), 1552 (s, NH δ). ^{1}H NMR (500 MHz, DMSO-d_6; δ, ppm): 7.13–7.07 (bs, 2.7 H, NH *trans*), 6.89–6.73 (bs, 0.3 H, NH *cis*), 3.91 (m, 6H, CH_2-1,1′,1″), 3.01 (q, J = 6.3 Hz, 4H, CH_2-3′,3″), 2.93 (q, $J_{5,6} = J_{6,NH}$ = 6.4 Hz, 2H, CH_2-6), 1.65 (m, J = 6.6 Hz, 4H, CH_2-2′,2″), 1.51 (m, $J_{1,2} = J_{2,3}$ = 6.6 Hz, 2H, CH_2-2), 1.37 (m, $J_{4,5} = J_{5,6}$ = 6.6 Hz, 2H, CH_2-5), 1.26 (m, 4H, CH_2-3,4). ^{13}C NMR (125.7 MHz, DMSO-d_6; δ, ppm): 156.2 (NCO_2), 63.6 (CH_2-1), 61.5, 61.4 (CH_2-1′,1″), 40.1 (CH_2-6), 37.2 (CH_2-3′,3″), 29.3 (CH_2-5), 29.2 (CH_2-2′,2″), 28.6 (CH_2-2), 25.9 (CH_2-3), 25.1 (CH_2-4). ($C_{15}H_{27}N_3O_6$.

Table 1. Polymerization of monomers **4, 10, 13** and **16**

Entry	Monomer	Polymer	Base	Solvent	T^a (°C)	Yield (%)	M_w^b (g mol^{-1})	M_n^b (g mol^{-1})	M_w/M_n
1	**4**	**5**	TEA	THF	80	65	13360	9060	1.47
2	**4**	**5**	DIPEA	THF	80	72	13020	5620	2.32
3	**4**	**5**	TEA	DMF	100	80	9730	7100	1.37
4	**4**	**5**	DIPEA	DMF	100	84	9710	5480	1.77
5	**10**	**11**	DIPEA	DMF	100	83	3680	2940	1.25
6	**13**	**14**	DIPEA	DMF	100	72	11500	6360	1.80
7	**16**	**17**	DIPEA	DMF	100	84	7580	6890	1.34

[a] Temperature of external heating (see Experimental section).
[b] Measured using GPC relative to polystyrene standards.

$(H_2O)_{0.2})_n$ (348.79)$_n$: calcd C 51.62, H 7.91, N 12.04; found C 51.50, H 8.08, N 12.02.

RESULTS AND DISCUSSION

The route for the preparation of [*n*]-polyurethanes here proposed involves ω-amino-α-phenylcarbonate alkanes as monomeric precursors. The synthesis of these compounds requires the following steps: (i) selective protection of the amino group of the ω-aminoalcohol leaving free the hydroxyl group, (ii) activation of the latter as phenylcarbonate and (iii) removal of the amino protecting group. To accomplish this strategy, we explored the use of the *N-tert*-butylcarbonyl (*N*-Boc) group for the selective protection of the amine, as it is known that this group may be selectively introduced in the presence of an alcohol and it is readily hydrolyzed under anhydrous acidic conditions.[22] Thus, reaction of **1** with di-*tert*-butyldicarbonate (Boc_2O) gives the *N*-Boc derivative **2** (Scheme 1). Treatment of crude **2** with phenylchloroformate affords the phenylcarbonate derivative **3** (84% from **1**). The ^{1}H NMR spectrum of **3** shows at lower fields the signals of the aromatic protons (7.18–7.46 ppm) and the triplet of the protons of the methylene bonded to oxygen (4.25 ppm). The methylene vicinal to the *N*-Boc appears as a triplet at 3.13 ppm. The ^{13}C NMR spectrum of **3** shows, as diagnostic signals, those of the carbonyl carbons of carbonate (153.8 ppm) and carbamate (156.0 ppm). Treatment of **3** with a solution of EtOAc saturated with dry hydrogen chloride affords the crystalline hydrochloride derivative **4** (96%). Its ^{1}H NMR spectrum shows the expected aromatic proton signals remain but the singlet of the *tert*-butyl group of *N*-Boc has disappeared. In the ^{13}C NMR spectrum is detected, in the region of the carbonyl carbon, a single signal due to the carbonate carbon (153.1 ppm).

Compound **4** is suitable for the polycondensation as the amine may be readily released from the hydrochloride with an organic base, and the terminal phenylcarbonate is expected to react preferentially or exclusively with the nucleophilic amino end group with elimination of the phenyloxy leaving group.[15,23] Polymerizations of **4** were conducted under varied reaction conditions as shown in Table 1. In first instance (entry 1) THF was used as solvent and triethylamine (TEA) as an organic base. An excess of amine (3 molar equivalents) was employed, as tertiary amines catalyze the aminolysis of carbonates.[24] The advance of the polymerization is evidenced as the mixture becomes progressively more viscous. Polyurethane **5** was recovered by pouring the reaction mixture into MeOH, followed by centrifugation. The solid was washed three times by suspension in hot MeOH, cooled and centrifuged. The polymer was somewhat contaminated by triethylamine hydrochloride, and it was subjected to additional purifications as indicated above, until the ^{1}H NMR spectrum shows no hydrochloride salt. The NMR data for **5** are in good agreement with those previously reported for [7]-polyurethane.[15] The molecular weight of the purified polymer **5** was estimated with GPC, using THF as solvent. The polymer was *N*-trifluoroacetylated, as described for polyamides,[25] to make it soluble in the mobile phase. Polyurethane **5** exhibits molecular weight and polydispersity similar to those of the polymers prepared using previous procedures.[12,15]

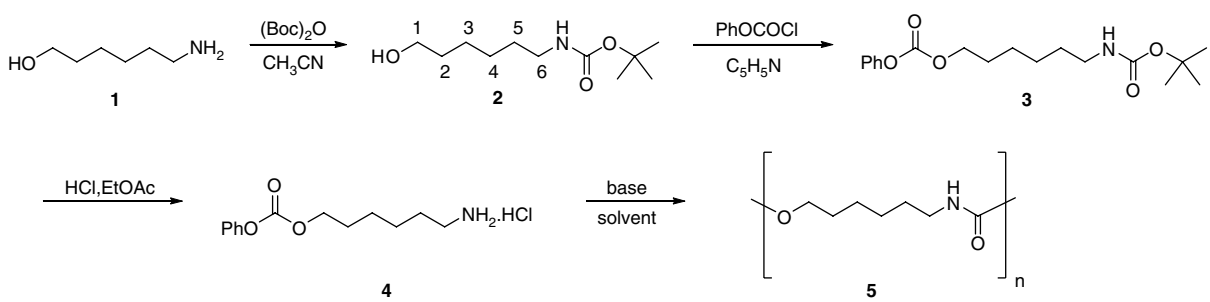
The polymerization of **4** was also conducted using DIPEA instead of TEA (entry 2). In this case, the purification of the resulting polyurethane **5** required several washings with hot MeOH. This material shows a molecular weight and polydispersity similar to those obtained using TEA.

The change of the solvent in the polycondensation of **4** was also examined, and DMF was employed as a polar non-protic solvent. Satisfactory results are obtained using both TEA and DIPEA, as organic bases and the polymer are readily purified by washing with hot MeOH. Polyurethane **5** was obtained in higher yields, but with somewhat lower molecular weights (GPC), compared with those of the preparations using THF. As purification of the THF/polymer requires several washings, polymeric chains of lower molecular weight may be removed, resulting in higher M_w but in a lower yield. The DIPEA/DMF system seems to be more convenient and it was employed for the subsequent polymerizations performed.

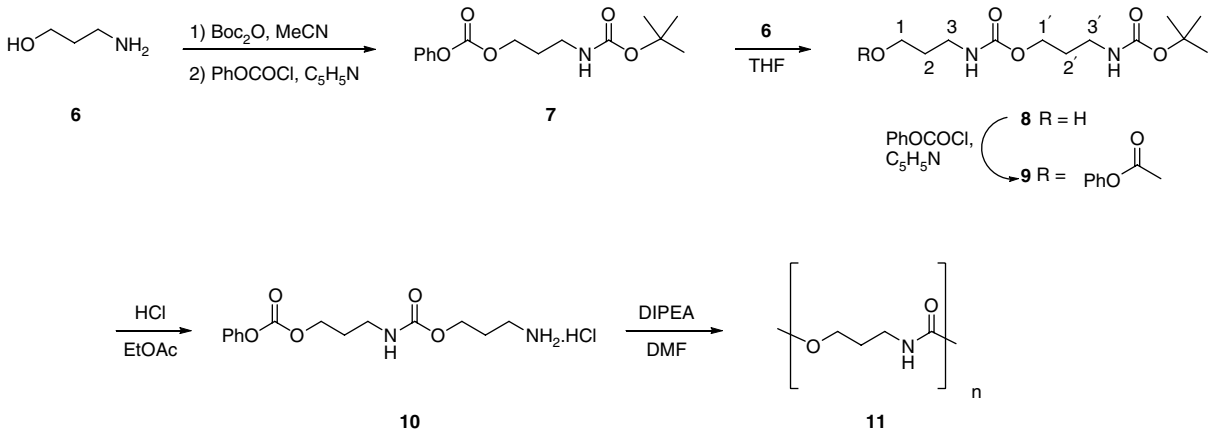
For the synthesis of the polyurethane with three carbon atoms between the functional groups, the linear dimer **10** was prepared as depicted in Scheme 2. The synthesis of this dimer is required in order to prevent the intramolecular cyclization that takes place when formation of five- and six-membered cyclic urethanes is posible.[14,15] Thus, *N*-Boc protection of **6** followed by treatment of the crude compound with phenylchloroformate affords crystalline **7** (98% overall yield). Condensation of **7** with **6** leads to the dimer **8** (93%), which reacts with phenylchloroformate to give the active carbonate **9** (96%). The hydrochloride derivative **10** is obtained in 91% yield by removal of the *N*-Boc protecting group of **9** with HCl/EtOAc.

Polymerization of **10** in DMF and in the presence of DIPEA affords polyurethane **11**, which is readily purified by washing with hot MeOH, as described for **5**. The molecular weight and polydispersity of **11** were determined using GPC (Table 1).

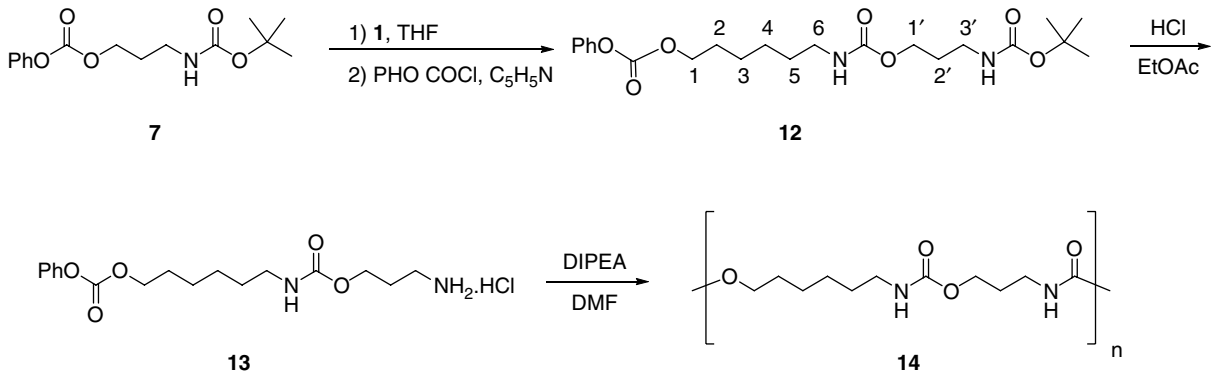
The linear polyurethane having alternate three and six carbon atoms between the carbamate functions was also synthesized. The monomer constituted of aminopropanol and aminohexanol was prepared using as precursor the active carbonate **7** (Scheme 3). Thus, reaction of **7** with **1** followed by treatment with phenylchloroformate gives the phenyloxycarbonate derivative **12** (87%). Standard deprotection of the *N*-Boc of **12** affords the crystalline hydrochloride derivative **13** (82%), as the monomer precursor of polyurethane **14**. Polymerization of **13** under the conditions



Scheme 1. Synthesis of polyurethane 5 from 6-amino-1-hexanol (1).



Scheme 2. Synthesis of polyurethane 11 from 3-amino-1-propanol (6).



Scheme 3. Synthesis of polyurethane 14 using aminoalkanols 1 and 6 as comonomers.

described for the preparation of **5** and **11** yields the expected polyurethane **14**. Monomer **13** and polymer **14** aer obtained as highly pure materials, as shown by their respective ^{1}H NMR and ^{13}C NMR spectra. The ^{1}H NMR spectrum of **14** is shown in Fig. 1. The molecular weight of polymer **14** was estimated using GPC (Table 1) as described for the polymers previously obtained.

The synthesis of **14** evidences the usefulness of the procedure here described to construct regioregular polymers starting from just two aminoalcohols. To prove the scope of the synthetic method, we prepared another regioregular polymer also constituted of 3-amino-1-propanol and 6-amino-1-hexanol units. In this case, the polyurethane was designed to have a repeating unit with six–three–three carbon atoms between the carbamate functions. The trimer **16**, precursor of the polymer, was obtained as depicted in Scheme 4. Condensation of the activated dimer **9** with **1**, followed by reaction with phenylchloroformate affords the phenylcarbonate derivative **15** (83%). Removal of the *N*-Boc group of **15** with HCl/AcOEt yields quantitatively the hydrochloride **16**. Polymerization of **16** with DIPEA in DMF, under conditions analogous to those employed for the preparation of the polymers already described, leads to polyurethane **17** (84%). The molecular weight of **17** was estimated using GPC (Table 1). The polyurethanes obtained exhibit moderate molecular weights probably due to their precipitation from the solution during polymerization.

Polymers **5, 11, 14** and **17** are obtained as homogeneous materials of a high degree of purity; their ^{1}H NMR spectra (Fig. 1) show the absence of signals at *ca* 5.60 ppm due to urea linkages.[8,12] In addition, the spectra recorded in DMSO-d_6 reveal the signals of the *trans* (*ca* 7.1 ppm) and *cis* (*ca* 6.8 ppm) forms adopted by the C–N bond of the urethane function, as observed for analogous polymers.[12,15] Also the ^{13}C NMR spectra of the polymers show the resonance for the carbonyl carbon of the carbamate (156.6–156.2 ppm), but no signals for the urea or carbonate carbonyl carbons (*ca* 157.9 and 153.5 ppm, respectively) are observed. In agreement with these results, in the FTIR spectra of the polyurethanes the characteristic absorptions for urea (*ca* 1660 cm^{-1}) or carbonate carbonyl (*ca* 1770 cm^{-1}) are absent.

The thermal behavior of polyurethanes **5, 11, 14** and **17** was studied using DSC (Table 2). The DSC traces for the first heating cycle of polyurethane **5** show a narrow melting transition at 165.7 °C. On cooling the melt, an exotherm due to crystallization is observed with a crystallization temperature (T_{cr}) and an enthalpy of crystallization (ΔH_{cr}) smaller than those of melting. The second heating cycle shows a melting transition at nearly the same temperature of the first heating, preceded by a shoulder. Except for the first heating cycle, which reflects the intrinsic history of the material (synthesis, purification, etc.), the curves for the cooling and second heating are similar to those reported by Höcker and co-workers for [7]-polyurethane.[15] Polyurethane **11** shows, during the first heating, a complex melting pattern with three overlapped peaks, characteristic for three crystalline modifications.[26] On cooling, a glass transition was the only transition detected. During the second heating the glass transition temperature (T_g) appears at almost the same temperature and it is accompanied by a crystallization exotherm followed by a single melting transition.

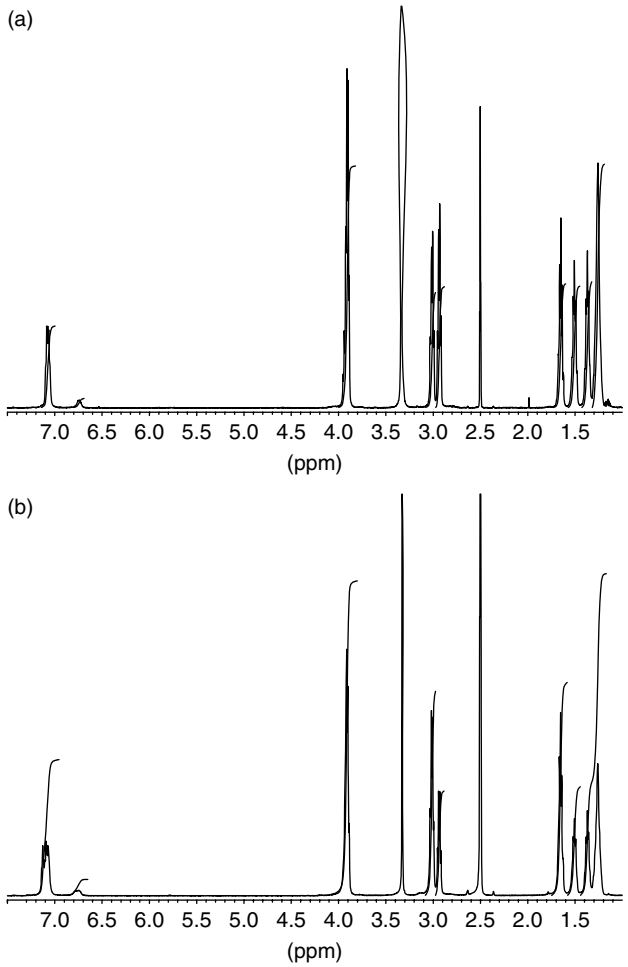


Figure 1. ^{1}H NMR (500 MHz) spectra of polyurethanes (a) **14** and (b) **17**.

Similar ΔH values for the crystallization and melting suggest the melting of the crystallite previously formed. Polyurethane **14** shows a transition with a shoulder during the first heating. On cooling, a broad exotherm is observed at lower temperature and with a smaller ΔH. The second heating cycle shows a melting peak with a maximum close to that of the first melting, although with a smaller ΔH. Polyurethane **17** exhibits a single melting transition during the first heating, associated with a large melting enthalpy (ΔH_m). On cooling, only a broad exotherm is observed at lower temperature and with a smaller ΔH. During the second heating cycle a T_g value is registered followed by a crystallization exotherm and an immediate melting transition at lower temperature than that of the first cycle. The large ΔH_m values during the first heating for polyurethanes **5, 11, 14** and **17** are indicative that they are highly crystalline materials, when precipitated from a solution.

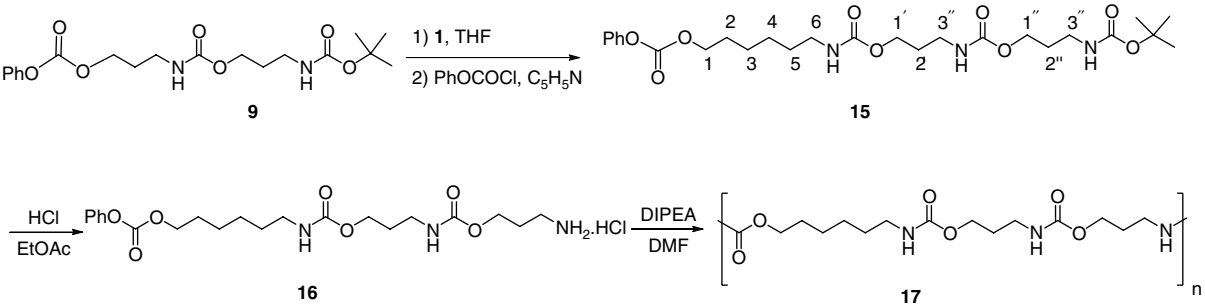
TGA of [*n*]-polyurethanes **5, 11, 14** and **17** reveals a higher thermal stability for **5, 14** and **17**, whereas **11** gives a lower temperature of decomposition. This result could indicate an increased stability of the polyurethane when aminohexanol is a constituent of the polymer chain. The differential curves show for **11** and **17** a single minimum (decomposition temperature (T_d) of 245 and 275.6 °C, respectively), whereas **5** shows two main peaks indicative of a decomposition in two steps. Similar to **5**, the differential TGA curve for polyurethane **14** shows two main peaks at 271.6 and 303.3 °C.

The polymers were analyzed using SEM in order to determine their surface features. The materials were prepared by isolation from the polymerization reaction as already described. It is very clear from the SEM images that the polyurethanes studied have different morphologies. As the isolation process was identical for all the polymers, the difference in SEM morphology seems to arise from the difference in the chemical structure of the polyurethane backbone. In agreement with the DSC analysis, the SEM images reveal the crystalline nature of all the polymers studied.

The surface of polymer **5** resembles that of a sponge (Fig. 2(a)). At higher magnification a lamellar morphology is observed (Fig. 2(b)). The SEM analysis of polyurethane **11** shows a surface constituted of irregular plates that is more discontinuous than that of **5**, although with a similar spongy appearance (Fig. 2(c)). The magnified images of **11** show, compared to those of **5**, elongated superstructures with a rather fibrous arrangement (Fig. 2(d)). Among the polyurethanes, **14** and **17** display a spherulitic-like texture (Figs 2(e) and (g)), although the spherules are smaller for **17**. The average size of these superstructures is in the range 10–35 μm for **14** and the diameter reaches a maximum of 3 μm for **17**. Upon magnification, the spherulites reveal a lamellar morphology (Figs 2(f) and (h)).

CONCLUSIONS

The straightforward synthesis of ω-amino-α-phenylcarbonate alkanes starting from aminoalkanols has been successfully accomplished. The procedure is useful for the preparation of ordered urethane-linked precursors, such as **13** and **16**, which have varied chain lengths between the carbamate linkages. These types of monomers could yield regioregular [*n*]-polyurethanes, with different structures, starting from just a few aminoalkanols. The ω-amino-α-phenylcarbonate alkane hydrochlorides are stable compounds that can be stored at low temperatures for several



Scheme 4. Synthesis of polyurethane 17 using aminoalkanols 1 and 6 as comonomers.

Table 2. Thermal properties of [*n*]-polyurethanes **5, 11, 14** and **17**

Polyurethane	Cycle[a]	T_m (°C)	ΔH_m (J g^{-1})	T_{cr} (°C)	ΔH_{cr} (J g^{-1})	T_g (°C)	T_d (°C)[b]
5	1 H	165.7	85.8				299.8, 321.5
	C			136.6	−59.8		
	2 H	155.1, 165.5	56.3				
11	1 H	166.6, 158.4, 151.0	99.6				245.0
	2 H	159.4	41.7	118.2	−36.6	26.4	
14	1 H	132.8, 143.0	87.9				271.6, 303.3
	C			95.6	−58.6		
	2 H	141.3	54.9				
17	1 H	127.9	92.2				275.6
	C			88.7	−16.0		
	2 H	124.6	50.3	101.7	−18.5	23.1	

[a] Heating/cooling cycle: 1 H, first heating; C, cooling; 2 H, second heating. Values determined using DSC.
[b] Determined using thermogravimetry.

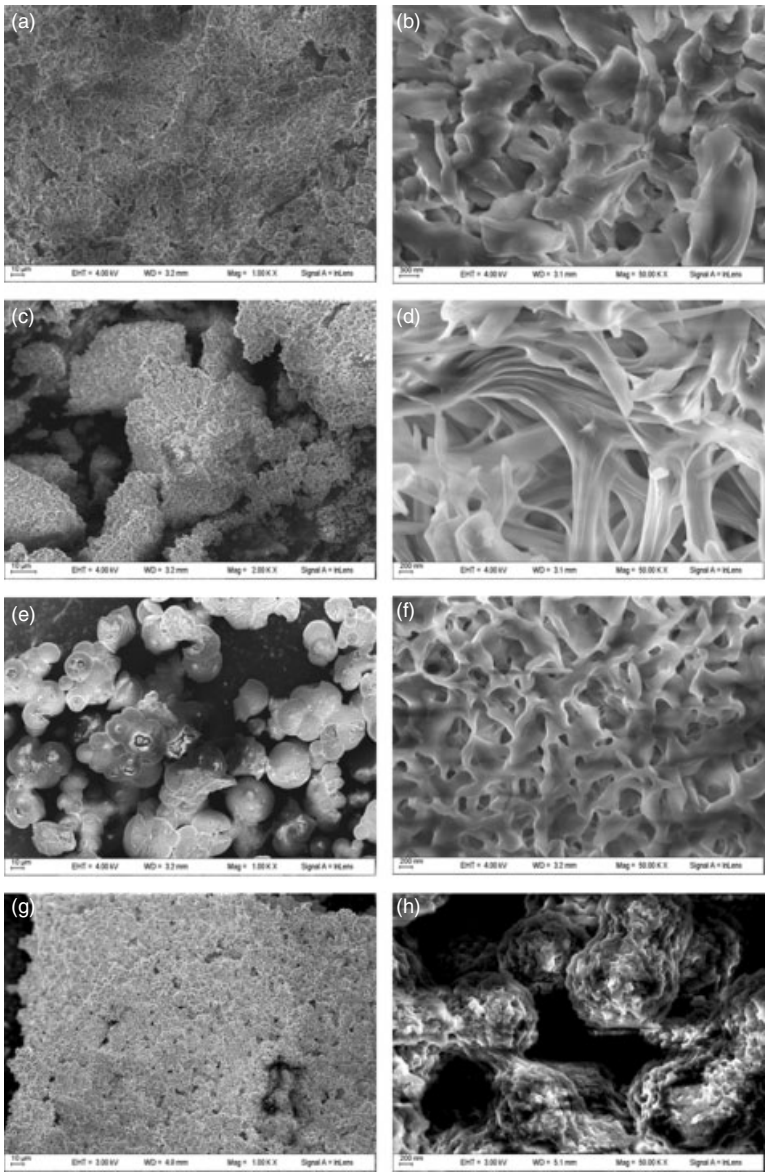


Figure 2. SEM images of polyurethanes: (a, b) **5**; (c, d) **11**; (e, f) **14**; (g, h) **17**.

weeks and they undergo polycondensation under mild reaction conditions. This new route avoiding the use of isocyanates and phosgene does not require melting of the monomer[10] or the use of catalysts.[15] Compared with the straightforward method described by Versteegen *et al*.,[12] our procedure affords higher yields of polymers that in turn have somewhat lower molecular weights. Polyurethanes **5, 11, 14** and **17** possess a constitutionally uniform structure, as only head-to-tail repeating units are observed using NMR analysis and they are free of carbonate or urea linkages. According to the DSC analysis, these materials are highly crystalline and exhibit supramolecular structures as observed using SEM.

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