Carbohydrate-Based Poly(ester-urethane)s: A Comparative Study Regarding Cyclic Alditols Extenders and Polymerization Procedures

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ABSTRACT: A set of segmented poly(ester-urethane)s were prepared from diisocyanates HDI or MDI and using 1,4-butanediol and D-glucose-derived cyclic diols (1,4 : 3,6-dianhydro-D-glucitol (isosorbide) or 2,4;3,5-di-O-methylidene-D-glucitol (gludioxol) or mixtures of them) as extenders. Hydroxyl end-capped polycaprolactone with a molecular weight of 3000 g·mol^{-1} was used as soft segment. Two polymerization methods, in solution and in bulk, were applied for the synthesis of these poly(ester-urethane)s. The influence of the preparation procedure and composition in cyclic extender on synthesis results, structure, and properties of the novel poly(ester-urethane)s was comparatively evaluated and discussed. The effect of replacement of 1,4-butanediol by isosorbide or gludioxol on hydrodegradability was also assessed; the hydrolysis rate increased noticeably with the presence of glucitol derived units, although degradation of the polymers took place essentially by hydrolysis of the polyester soft segment. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3723–3736, 2009

Key words: degradation; hydrophilic polymers; polyurethanes; renewable resources; structure-property relations

INTRODUCTION

Segmented polyurethanes constitute a large family of high-performance materials, with a wide variety of properties that are tunable by an appropriate molecular design.[1] These linear thermoplastics usually exhibit elastomeric behavior at room temperature. Segmented polyurethanes are usually obtained by the reaction of two diols, a macroglycol (precursor of the soft segment) and a short diol (which leads to the hard segment), with a diisocyanate. Different macroglycols are suitable for this synthesis, the most frequently used being hydroxyl end-capped polyesters of low molecular weight.[2] Although the poly(ester-urethane)s resulting from these synthesis display an excellent thermal and environmental stability, they are vulnerable to hydrolysis, their hydrodegradability being mainly decided by the chemical structure of the polyester segment.[3] Polycaprolactone, polylactides, and aliphatic polyesters derived from alkanediols and dicarboxylic acids, such as succinic and adipic acids, are polyesters commonly found as soft segments of industrial thermoplastic polyurethanes. The use of these materials range from adhesives and coatings to high-performance engineering parts; they also offer a great potential for biomedical applications as biocompatible biodegradable materials.[4]

A growing interest currently exists for chemicals derived from renewable resources as an alternative to oil-based monomers for the production of well-established industrial polymers. Specifically, utilization of carbohydrate derivatives for polymer synthesis has attracted much attention not only because of the huge abundance of these resources but also because of the degradable and biocompatible behavior that can be expected for such polymers.[5,6] Moreover, carbohydrates stand out as very convenient raw materials because they are inexpensive, readily available, and provide great functional diversity. In recent years, several notable examples of carbohydrate-based polymers have been reported in the literature.[7–10]

A highly promising carbohydrate derivative for the development of sustainable polymeric materials is the cyclic compound 1,4 : 3,6-dianhydro-D-glucitol, also known as isosorbide. This carbohydrate-based diol is a potentially useful monomer for the synthesis of polyesters, poly(ester-amide)s, and polycarbonates.[11] It has been proved that polyesters, poly(ester-amide)s, polycarbonates, and poly(ester-carbonate)s derived from isosorbide are more or less biodegradable depending on the structures, as judged from

degradation tests performed in activated sludge, in soil, and in the presence of hydrolytic enzymes.[12] The use of other cyclic diols derived from sugars as monomers for the synthesis of polycondensates has been scarcely explored. Nevertheless, several optically active polyamides derived from 2,3-O-methylidene L-tartaric acid have been described in the old and more recent literature.[13–15]

The main purpose of this work was to study comparatively the effect of the preparation method and composition on the structure and some properties of new thermoplastic segmented poly(ester-urethane)s in which the hard segment is made of D-glucitol-derived extenders. These PURs are prepared from 1,6-hexamethylene diisocyanate (HDI) or 4,4′-methylene-bis(phenyl isocyanate) (MDI) and polycaprolactone diol (PCL) with a molecular weight of 3000 g·mol^{-1} as soft segment. The diols chosen to be used as extenders are the habitual 1,4-butanediol (BD) and the cyclic glucitols, isosorbide and gludioxol (2,4;3,5-di-O-methylidene-D-glucitol). Two polymerization methods, in solution and in bulk, are used for the preparation of these poly(ester-urethane)s and results obtained from each method are compared. The influence of the selected extender, isosorbide or gludioxol, on the properties of the resulting segmented PURs is also evaluated and discussed.

EXPERIMENTAL

Materials and methods

Common reagents and solvents were purchased from Aldrich and used as received. N,N-dimethylformamide (DMF) and tetrahydrofuran (THF) solvents were dried under inert atmosphere before use by distillation. 1,4-Butanediol and polycaprolactone with a number-average molecular weight of 3000 were donated by Merquinsa (Mercados Químicos S.L.), and 1,4 : 3,6-dianhydro-D-glucitol (isosorbide, Is) was a gift from Roquette Freres S.A. This cyclic dianhydride was prepared from corn starch following the route depicted in Scheme 1. Diols and reagents for polymerization were stored in a desiccator under vacuum until used. 1,6-Hexamethylene diisocyanate was vacuum distilled before use, and together with 4,4′-methylene-bis(phenyl isocyanate), stored at 4°C. Both compounds were invariably handled under inert atmosphere.

Viscosities were measured in dichloroacetic acid at 25.0 ± 0.1°C, using an Ubbelohde microviscometer at concentrations ranging from 5 to 10 mg·mL^{-1}. Gel permeation chromatograms (GPC) were acquired at 35°C on a Waters equipment provided with a refractive index detector. The samples were chromatographed with 0.05 M sodium trifluoroacetate-hexafluoroisopropanol (NaTFA-HFIP) at a flow rate
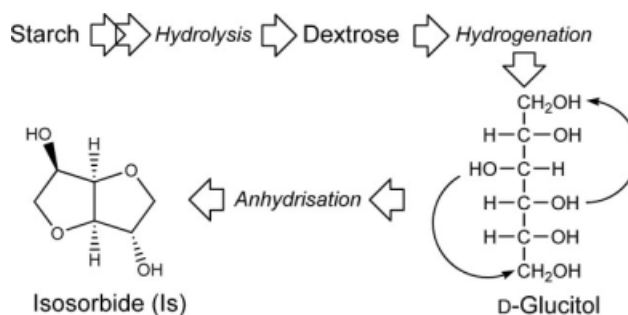
Scheme 1　Synthetic route to isosorbide from corn starch.

of 0.5 mL·min^{-1}, using a polystyrene-divinylbenzene packed linear column. Chromatograms were calibrated against poly(methyl methacrylate) (PMMA) monodisperse standards. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AMX-300 spectrometer operating at 300.1 and 75.5 MHz for ^{1}H and ^{13}C, respectively, and using TMS as internal reference. Sample concentrations within the 1–5% (w/v) range were used for these analyses. The spectra were acquired with 64 scans and 1000–10,000 scans for ^{1}H and ^{13}C{^{1}H}, respectively, and relaxation delays of 1 and 2 s. Differential scanning calorimetry (DSC) experiments were performed at heating/cooling rates of 10°C·min^{-1} on a Perkin-Elmer Pyris 1 instrument calibrated with indium. All the experiments were performed with sample amounts of 3–4 mg within a range of temperatures from 0°C to 200 or 250°C, and under a 20 mL·min^{-1} nitrogen flow to minimize possible oxidative degradations. Glass transition data were obtained by DSC with a Thermal Analysis instrument TA-Q100 equipped with a refrigerated cooling system. These experiments were conducted under a flow of dry nitrogen (50 mL·min^{-1}) with sample weights of around 5 mg, and calibration was performed with indium and sapphire. Determinations were made at a heating rate of 20°C·min^{-1} on samples quenched to −70°C from samples melt at temperatures between 200 and 250°C. Thermogravimetry analysis (TGA) was performed under inert atmosphere at a heating rate of 10 °C·min^{-1} and within a temperature range of 30 to 600°C, using a Mettler TA4000 thermobalance. Sample weights of about 15 mg were used in these experiments. Wide-angle X-ray scattering was performed on a Philips automatic horizontal axis diffractometer using Cu K$_\alpha$ Ni-filtered radiation. Spectra were taken at room temperature with the scattering angle 2θ varying from 3 to 50°. Films for mechanical properties of selected polyurethanes with a thickness of ∼ 300 μm were prepared by hot-press molding at 10–20°C above the melting temperature. The tensile strength (σ), elongation at break (ε), and Young's modulus (E) were measured at a stretching rate of 20 mm·min^{-1} on a Zwick 2.5/
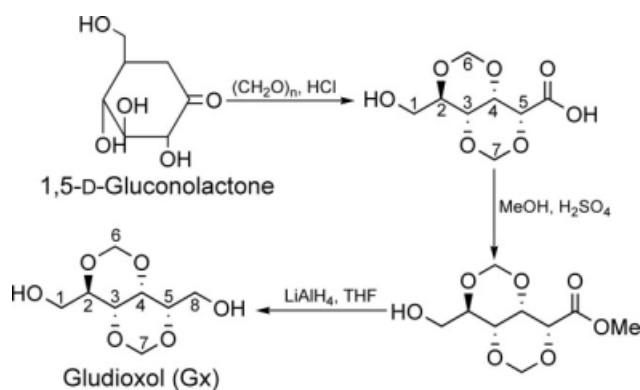
Scheme 2 Synthetic route to gludioxol from gluconolactone.

TN1S testing machine coupled with a compressor Dalbe DR 150. The tested samples were cut into rectangular strips with a width of 3 mm and a distance between testing marks of 10 mm. Measurements were made in triplicates.

Synthesis of monomers

The cyclic diol 2,4 : 3,5-di-*O*-methylidene-D-glucitol (gludioxol, Gx) was prepared following the chemical synthetic route depicted in Scheme 2. Compounds 2,4 : 3,5-di-*O*-methylidene-D-gluconic acid and methyl 2,4 : 3,5-di-*O*-methylidene-D-gluconate were synthesized from commercial 1,5-D-gluconolactone as described elsewhere.[17]

2,4 : 3,5-di-*O*-methylidene-D-gluconic acid

A mixture of 30 g (0.168 mol) of 1,5-D-gluconolactone, 30 g of paraformaldehyde, and 42 mL of concentrated hydrochloric acid was refluxed at 110°C for 1 h. The product precipitated from the solution on cooling. Yield: 80%. ^{1}H NMR (DMSO, 300 MHz): δ (ppm) 4.99–4.69 (2 dd, 4H, CH$_2$-6 and CH$_2$-7), 4.34 (m, 1H, CH-5), 4.04 (m, 1H, CH-4), and 3.73–3.61 (m, 4H, CH-3, CH-2 and CH$_2$-1). ^{13}C{^{1}H} NMR (DMSO, 75.5 MHz): δ (ppm) 170.02 (C=O), 92.42 (C-7), 88.72 (C-6), 77.31 (C-5), 76.65 (C-1), 71.29 (C-3), 69.11 (C-4), and 59.72 (C-2).

Methyl 2,4 : 3,5-di-*O*-methylidene-D-gluconate

A mixture of 30 g (0.136 mol) of di-*O*-methylidene-D-gluconic acid, 250 mL of methanol and 0.75 mL of concentrated sulfuric acid was refluxed until complete dissolution. The product precipitated from the solution on cooling; additional crops were obtained on concentrating the mother liquors. Yield: 70%. ^{1}H NMR (DMSO, 300 MHz): δ (ppm) 5.01–4.71 (2 dd, 4H, CH$_2$-6 and CH$_2$-7), 4.52 (m, 1H, CH-5), 4.06 (m, 1H, CH-4), 3.75–3.65 (m, 4H, CH-3, CH-2 and CH$_2$-1), and 3.62 (s, 3H, CH$_3$). ^{13}C{^{1}H} NMR (DMSO, 75.5 MHz): δ (ppm) 169.05 (C=O), 92.36 (C-7), 88.66 (C-6), 77.26 (C-5), 76.72 (C-1), 71.10 (C-3), 68.94 (C-4), 59.78 (C-2), and 52.90 (CH$_3$).

2,4 : 3,5-di-*O*-methylidene-D-glucitol

To a dispersion of 20 g (0.085 mol) of methyl 2,4 : 3,5-di-*O*-methylidene-D-gluconate in 100 mL of dry tetrahydrofuran, 6.8 g (0.179 mol) of LiAlH4 (97%) in 150 mL of dry tetrahydrofuran were added at 0°C under nitrogen atmosphere. The mixture was refluxed for 24 h and then cooled to 0°C. H$_2$O (25 mL), NaOH (15% w/v, 25 mL), and H$_2$O (75 mL) were sequentially and slowly added, and the mixture was then filtrated and concentrated to a ∼ 20 mL oily residue from which a white solid crystallized. Yield: 60%. ^{1}H NMR (DMSO, 300 MHz): δ (ppm) 4.96–4.67 (2 dd, 4H, CH$_2$-6 and CH$_2$-7), 4.63 and 4.40 (2 t, 2H, OH), 3.74 (m, 1H, CH-5), 3.64 (m, 3H, CH$_2$-1 and CH-2), 3.60 (m, 1H, CH-3), 3.54 (m, 1H, CH-5), and 3.42 (m, 2H, CH$_2$-8). ^{13}C{^{1}H} NMR (DMSO, 75.5 MHz): δ (ppm) 93.00 (C-7), 88.52 (C-6), 79.22 (C-5), 77.23 (C-1), 71.51 (C-3), 67.80 (C-4), 60.64 (C-8), and 59.44 (C-2).

Synthesis of polymers

Polymerization in solution

For the synthesis of segmented polyurethanes by polymerization in solution, PCL (1 mmol) and the extender or a mixture of extenders in the chosen ratio (1,4-butanediol or/and isosorbide, 5 mmol) were charged in a round bottom flask saturated with inert gas. *N,N*-dimethylformamide (40 mL) was then added and the mixture stirred at room temperature until homogenization. Six millimoles of diisocyanate, HDI, or MDI, followed by 20 ppm of dibutyltin dilaurate catalyst, were then added, and the mixture was stirred for 24 h at room temperature. The reaction mixture became rapidly homogeneous and remained clear for the whole reaction period except for PUR-(PCL-BD-HDI) that precipitated spontaneously after 2 h of reaction, allowing direct recovery of the polymer. In all other cases, the reaction mixture was added dropwise into cold diethyl ether (250 mL) to precipitate the polymer. Purification was done by redissolution of the polymer in the minimum volume of tetrahydrofuran followed by reprecipitation into diethyl ether. All the polymers were white powders that were dried under vacuum and stored in a desiccator until needed.

Polymerization in bulk

For the synthesis of segmented polyurethanes in bulk, the following one-step procedure was followed: PCL (5 mmol), the extender or combination

Scheme 3 Chemical structures of segmented poly(ester-urethane)s.

of extenders (1,4-butanediol or/and isosorbide or/ and gludioxol, total of diols 25 mmol), and Metatin catalyst (dioctyl tin mercaptide ester, 20 ppm) were mechanically stirred and heated to 130°C. At this temperature, 30 mmol of diisocyanate, HDI, or MDI, were added. The reactants were totally miscible and the reaction was left to proceed until the viscosity increased to the point that the mechanical stirring became severely hindered. At this point, the reaction mass was placed in a heated chamber at 120°C and for 3 h. PURs made from 1,4-butanediol and isosorbide were perfectly white, whereas those produced from gludioxol developed a slightly yellow color.

PUR-(PCL-BD-HDI). ^{1}H NMR (DMSO, 300 MHz): δ (ppm) 6.54 (bs, 2H, N-H), 3.96 (m, 4H, H-1(BD); and m, 2H, PCL), 2.91 (m, 4H, H-a), 2.22 (m, 2H, PCL), 1.52 (m, 4H, H-2(BD); and 4H, PCL), 1.29 (m, 4H, H-b; and 2H, PCL), and 1.20 (m, 4H, H-c). ^{13}C{^{1}H} NMR (DMSO, 75.5 MHz): δ (ppm) 173.24 (C=O PCL), 156.92 (C=O urethane), 64.14 (C-1(BD)), 63.95 (PCL), 40.04 (C-a), 34.17 (PCL), 29.06 (C-b), 28.51 (PCL), 26.60 (C-c), 26.17 (C-2(BD)), 25.61 (PCL), and 24.74 (PCL).

PUR-(PCL-Is-HDI). ^{1}H NMR (DMSO, 300 MHz): δ (ppm) 6.99 (bs, 2H, N-H), 4.92 (m, 1H, H-2(Is)), 4.82 (m, 1H, H-5(Is)), 4.61 (m, 1H, H-4(Is)), 4.34 (m, 1H, H-3(Is)), 3.94 (m, 2H, PCL), 3.85–3.76 (m, 4H, H-1(Is) and H-6(Is)), 2.92 (m, 4H, H-a), 2.23 (m, 2H, PCL), 1.51 (m, 4H, PCL), 1.28 (m, 4H, H-b; and 2H, PCL), and 1.21 (m, 4H, H-c). ^{13}C{^{1}H} NMR (DMSO, 75.5 MHz): δ (ppm) 173.44 (C=O PCL), 156.10 (C=O urethane), 86.54 (C-2(Is)), 81.50 (C-5(Is)), 78.56 (C-4(Is)), 74.23 (C-3(Is)), 73.70 (C-1(Is)), 70.76 (C-6(Is)), 64.05 (PCL), 41.13 (C-a), 34.25 (PCL), 30.04 (C-b), 28.62 (PCL), 26.69 (C-c), 25.73 (PCL), and 24.87 (PCL).

PUR-(PCL-Gx-HDI). ^{1}H NMR (DMSO, 300 MHz): δ (ppm) 6.94 (bs, 2H, N-H), 4.97–4.66 (2 dd, 4H, H-6(Gx) and H-7(Gx)), 3.94 (m, 2H, PCL), 3.98–3.53 (m,

8H, H-1,2,3,4,5,8(Gx)), 2.89 (m, 4H, H-a), 2.22 (m, 2H, PCL), 1.47 (m, 4H, PCL), 1.25 (m, 4H, H-b; and 2H, PCL), and 1.18 (m, 4H, H-c). ^{13}C{^{1}H} NMR (DMSO, 75.5 MHz): δ (ppm) 173.33 (C=O PCL), 156.30 (C=O urethane), 92.74 and 88.47 (C-6,7 (Gx)), 75.79, 74.63, 71.76, 67.41, 58.75, and 57.15 (C-1,2,3,4,5,8 (Gx)), 64.03 (PCL), 41.07 (C-a), 34.07 (PCL), 30.09 (C-b), 28.41 (PCL), 26.60 (C-c), 25.51 (PCL), and 24.64 (PCL).

PUR-(PCL-BD-MDI). ^{1}H NMR (DMSO, 300 MHz): δ (ppm) 9.11 (bs, 2H, N-H), 7.31–7.00 (dd, 8H, Ar), 4.06 (m, 4H, H-1(BD)), 3.97 (m, 2H, PCL), 3.75 (bs, 2H, Ph-CH_2-Ph from MDI), 2.22 (m, 2H, PCL), 1.67 (m, 4H, H-2(BD)), 1.53 (m, 4H, PCL), and 1.30 (m, 2H, PCL). ^{13}C{^{1}H} NMR (DMSO, 75.5 MHz): δ (ppm) 173.29 (C=O PCL), 154.43 (C=O urethane), 137.70, 137.86, 129.44, 119.53 (Ar), 64.48 (C-1(BD)), 64.19 (PCL), 40.92 (Ph-CH_2-Ph from MDI), 34.20 (PCL), 29.56 (PCL), 26.09 (C-2(BD)), 25.65 (PCL), and 24.79 (PCL).

PUR-(PCL-Is-MDI). ^{1}H NMR (DMSO, 300 MHz): δ (ppm) 9.37 (bs, 2H, N-H), 7.31–7.05 (dd, 8H, Ar), 5.10 (m, 1H, H-2(Is)), 5.05 (m, 1H, H-5(Is)), 4.75 (m, 1H, H-4(Is)), 4.45 (m, 1H, H-3(Is)), 3.97 (m, 2H, PCL), 3.88–3.67 (m, 6H, H-1(Is) and H-6(Is)), 3.77 (bs, 2H, Ph-CH_2-Ph from MDI), 2.23 (m, 2H, PCL), 1.53 (m, 4H, PCL), and 1.30 (m, 2H, PCL). ^{13}C{^{1}H} NMR (DMSO, 75.5 MHz): δ (ppm) 173.24 (C=O PCL), 153.55 (C=O urethane), 137.61, 136.38, 129.62, 119.57 (Ar), 86.35 (C-2(Is)), 81.43 (C-5(Is)), 79.18 (C-4(Is)), 74.66 (C-3(Is)), 73.22 (C-1(Is)), 70.15 (C-6(Is)), 64.19 (PCL), 40.90 (Ph-CH_2-Ph from MDI), 34.06 (PCL), 28.52 (PCL), 25.65 (PCL), and 24.83 (PCL).

PUR-(PCL-Gx-MDI). ^{1}H NMR (DMSO, 300 MHz): δ (ppm) 9.42 (bs, 2H, N-H), 7.33–7.05 (dd, 8H, Ar), 5.01–4.71 (2 dd, 4H, H-6(Gx) and H-7(Gx)), 4.03–3.55 (m, 8H, H-1,2,3,4,5,8(Gx)), 3.97 (m, 2H, PCL), 3.79 (s, 2H, Ph-CH_2-Ph from MDI), 2.25 (m, 2H, PCL), 1.54 (m, 4H, PCL), and 1.30 (m, 2H, PCL). ^{13}C{^{1}H} NMR

(DMSO, 75.5 MHz): δ (ppm) 173.13 (C=O PCL), 153.90 (C=O urethane), 137.71, 136.07, 129.29, 119.39 (ar), 92.74 and 88.47 (C-6,7 (Gx)), 75.79, 74.63, 71.76, 67.41, 58.75, and 57.15 (C-1,2,3,4,5,8 (Gx)), 64.03 (PCL), 40.86 (Ph-CH$_2$-Ph from MDI), 34.07 (PCL), 28.41 (PCL), 25.51 (PCL), and 24.64 (PCL).

Hydrolytic degradation assays

For hydrolytic degradation studies, films of selected polyurethanes with a thickness of ∼ 300 μm were prepared by hot-press molding. The films were cut into 10-mm diameter, 20- to 30-mg weight disks, which were dried in vacuum at 30°C to constant weight. The degradation study was performed by placing the disks into vials and adding 10 mL of buffered solutions at the selected pH. Parallel experiments were performed with samples immersed in sodium phosphate buffer (pH 7.4), sodium carbonate buffer (pH 10), and citric acid buffer (pH 2) at temperatures of 37 and 60°C. Vials were sealed to avoid partial evaporation of the fluids in the heated chamber. After immersion for the scheduled period of time, the samples were rinsed thoroughly with water and dried to constant weight. Sample weighing, GPC measurements, and NMR spectroscopy were used to follow the evolution of the hydrodegradation process.

RESULTS AND DISCUSSION

Compared synthesis

The segmented polyurethanes were prepared in parallel by polymerization in solution (sPUR) and polymerization in bulk (bPUR), using both HDI and MDI as diisocyanates and PCL as soft segment. Isosorbide and gludioxol were the cyclic chain extenders used to replace 1,4-butanediol, either totally or partially. The chemical structures of all the segmented PURs studied in this work are depicted in Scheme 3. The constitution and composition of all the synthesized PURs were assessed by ^{1}H and ^{13}C{^{1}H} NMR; signal data and assignments are given in full detail in the Experimental Section.

Data and results pertaining to polymerization in solution are given in Table I. PURs containing Gx extender could not be synthesized by this method because of the insolubility of gludioxol in DMF. Yields of isosorbide-containing sPURs were around 80%, and the polymers were found to be enriched in the diols used as extenders compared to the composition used for the feed. These results indicate some loss of PCL along the preparation procedure, most probably by failing in the precipitation step because either it remained unreacted or it was located in a PCL-enriched PUR fraction of higher solubility in

TABLE I
Polymerization Results and Some Properties of Poly(ester-urethane)s Prepared by Polymerization in Solution

sPUR	Reaction					Molecular size[d]			Solubility[e]					
	PCL : Ext[a]	Solvent	Yield (%)	PCL : Ext[b]	Hard[c] (%)	[η] (dL·g⁻¹)	M_n (g·mol⁻¹)	M_w/M_n	H$_2$O	DMSO	CHCl$_3$	THF	EtOH	AcOH
PCL-BD-HDI	(1 : 5)	DMF	79[f]	(1 : 7)	36.3	0.50	23,200	2.1	−	+	+	+	−	−
PCL-Is-HDI	(1 : 5)	DMF	80	(1 : 7)	41.0	0.46	21,500	2.1	−	+	+	+	−	−
PCL-BD-MDI	(1 : 5)	DMF	77	(1 : 7)	42.3	0.55	20,900	2.1	−	+	+/−	+	−	−
PCL-Is-MDI	(1 : 5)	DMF	81	(1 : 7)	46.0	0.50	19,700	2.1	−	+	+/−	+	−	−

[a] PCL : BD or PCL : Is molar ratio in the feed.
[b] PCL : BD or PCL : Is molar ratio in the resulting polyurethane determined by ^{1}H NMR.
[c] Content in hard segment in the sPUR.
[d] Intrinsic viscosity measured in DCA and average molecular weights determined by GPC in HFIP against PMMA standards.
[e] Solubility at 20 ± 5°C at sample concentration of 1 g·L⁻¹: +, soluble; +/−, partially soluble; −, insoluble.
[f] Precipitated after 2 h of reaction

TABLE II
Results and Some Properties of Segmented Poly(ester-urethane)s Obtained by Polymerization in Bulk

bPUR	Reaction					Molecular Size[d]			Solubility[e]						Appearance
	PCL : Ext[a]	(BD : I or Gx)	Yield (%)	PCL : Ext[b]	Hard[c] (%)	$[\eta]$ (dL·g^{-1})	M_n (g·mol^{-1})	M_w/M_n	H$_2$O	EtOH	AcOH	DMSO	CHCl$_3$	THF	
PCL-BD-HDI	(1 : 5)	(1 : 0)	100	(1 : 5)	29.0	1.23	56,200	2.2	−	−	−	+	+	+	Translucent
PCL-2BD/1Is-HDI	(1 : 5)	(2 : 1)	100	(1 : 5)	30.4	0.97	41,000	1.8	−	−	−	+	+	+	Translucent
PCL-1BD/1Is-HDI	(1 : 5)	(1 : 2)	100	(1 : 5)	31.8	0.88	38,000	2.0	−	−	−	+	+	+	Translucent
PCL-Is-HDI	(1 : 5)	(0 : 1)	100	(1 : 5)	33.1	0.75	36,700	2.1	−	−	−	+	+/−	+/−	Translucent
PCL-2BD/1Gx-HDI	(1 : 5)	(2 : 1)	100	(1 : 5)	31.9	0.93	37,600	2.0	−	−	−	+	+/−	+/−	Translucent
PCL-1BD/2Gx-HDI	(1 : 5)	(1 : 2)	100	(1 : 5)	34.6	0.78	32,200	1.9	−	−	−	+	+/−	+/−	Opaque
PCL-Gx-HDI	(1 : 5)	(0 : 1)	100	(1 : 5)	37.1	0.69	29,000	1.9	−	−	−	+	−	+	Opaque
PCL-BD-MDI	(1 : 5)	(1 : 0)	100	(1 : 5)	34.4	1.18	46,200	2.2	−	−	−	+	−	+	Opaque
PCL-2BD/1Is-MDI	(1 : 5)	(2 : 1)	100	(1 : 5)	35.6	1.06	37,800	1.8	−	−	−	+	−	+	Opaque
PCL-1BD/2Is-MDI	(1 : 5)	(1 : 2)	100	(1 : 5)	36.7	0.99	36,000	1.9	−	−	−	+	−	+	Opaque
PCL-Is-MDI	(1 : 5)	(0 : 1)	100	(1 : 5)	37.9	0.97	33,100	2.0	−	−	−	+	−	+	Opaque
PCL-2BD/1Gx-MDI	(1 : 5)	(2 : 1)	100	(1 : 5)	36.9	1.04	34,100	2.1	−	−	−	+	+/−	+/−	Opaque
PCL-1BD/2Gx-MDI	(1 : 5)	(1 : 2)	100	(1 : 5)	39.1	0.91	31,900	2.0	−	−	−	+	−	+/−	Opaque
PCL-Gx-MDI	(1 : 5)	(0 : 1)	100	(1 : 5)	41.2	0.83	31,700	2.0	−	−	−	+	−	+/−	Opaque

[a] Molar relation of (PCL : total of extenders used) in reaction solution.
[b] Molar relation of (PCL : total of extenders used) in final polyurethane, determined by ^{1}H RMN.
[c] Content in hard segment in the bPUR.
[d] Intrinsic viscosity measured in DCA and average molecular weights determined by GPC in HFIP against PMMA standards.
[e] Solubility at 20 ± 5°C at sample concentration of 1 g·L^{-1} : +, soluble; +/−, partially soluble; −, insoluble.

diethyl ether. The molecular weights of these sPURs are around 20,000 g·mol^{-1} with polydispersities about 2 and intrinsic viscosities near 0.5 g·dL^{-1}. All they display a largely restricted solubility that was not significantly affected by composition. It can be concluded, therefore, that substitution of 1,4-butanediol by isosorbide in the polymerization of these poly(ester-urethane)s does not modify substantially the synthesis results.

The polymerization in bulk for the synthesis of the segmented polyurethanes was performed at 130°C, with a molar ratio of PCL to extender of 1 to 5 and using Metatin as catalyst. The initially transparent mobile reaction mixture was losing clarity and increasing viscosity as the reaction advanced so it had to be stopped when the mechanical stirring became severely hindered. At this point the temperature was reduced to 120°C, and the reaction left to proceed for further 3 h. The appearance of the resulting bPURs was dependent on both the extender and the diisocyanate that were used for the synthesis; all the aromatic bPURs without exception were opaque, whereas aliphatic bPURs made from 1,4-butanediol and/or isosorbide were translucent.

The data and results obtained in the polymerization carried out in bulk are given in Table II. Contrary to what happens in the polymerization in solution, the PCL to extender ratio used in the feed was almost exactly maintained in the resulting polymer (which was proven by NMR to be completely exempted from free PCL). The molecular sizes of both aliphatic and aromatic bPURs obtained in bulk were noticeably higher than those obtained in solution and their polydispersities oscillated between 1.8 and 2.2, i.e., an average value similar to that found for sPURs. With regard to the kind of extender used, 1,4-butanediol provided the highest molecular weights, whereas bPURs made from gludioxol had
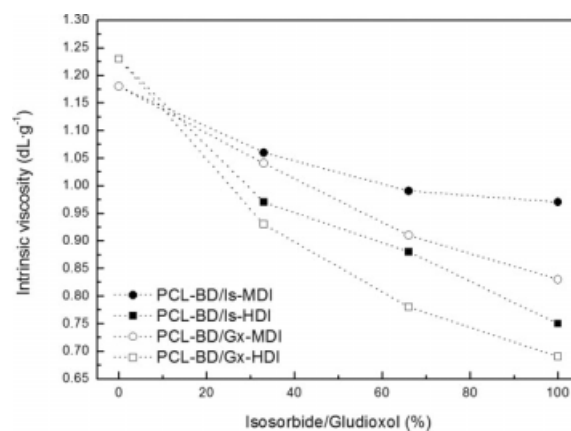

Figure 1 Intrinsic viscosity of aliphatic and aromatic bPUR as a function of the extender composition.

TABLE III
Compared Thermal Properties of Poly(ester-urethane)s

		Soft Segment[a]						Hard Segment[b]								
		1st Heating		Cooling		2nd Heating		1st Heating		Cooling		2nd Heating		Annealing[c]		
	T_g[c] (°C)	T_m (°C)	ΔH_m (J·g^{-1})	T_c (°C)	ΔH_c (J·g^{-1})	T_m (°C)	ΔH_m (J·g^{-1})	T_m (°C)	ΔH_m (J·g^{-1})	T_c (°C)	ΔH_c (J·g^{-1})	T_m (°C)	ΔH_m (J·g^{-1})	T_a (°C)	T_m (°C)	ΔH_m (J·g^{-1})
PCL	−63	58	85	33	72	50	72	—	—	—	—	—	—	—	—	—
sPUR																
PCL-BD-HDI	−54	54	37	21,24	23	47,51	28	152,165	25	130,145	26	162	26	155	174	18
PCL-Is-HDI	−49	51	17	—	—	43	16	151,172,191	6	—	—	—	—	170	215	6
PCL-BD-MDI	−26	52,57	3	—	—	54	2	176,204	7	—	—	—	—	190	220	6
PCL-Is-MDI	−4	46	8	—	—	44	2	226	4	—	—	—	—	170	242	4
bPUR																
PCL-BD-HDI	−60	47	2	—	—	46	2	159,165	25	112	22	156,168	22	160	179	25
PCL-2BD/1Is-HDI	−59	45	2	—	—	43	2	140	14	42	4	142	7	130	157	10
PCL-1BD/2Is-HDI	−59	43	2	—	—	41	2	133,147	5	79	3	146	3	130	161	4
PCL-Is-HDI	−57	45	7	—	—	40	3	188	3	140	3	193	2	180	234	15
PCL-2BD/1Gx-HDI	−50	42,51	4	—	—	49	4	145	1	—	—	—	—	135	148	2
PCL-1BD/2Gx-HDI	−43	50	4	—	—	48	3	—	—	—	—	—	—	—	—	—
PCL-G-HDI	−38	44	4	—	—	43	3	—	—	—	—	—	—	—	—	—
PCL-BD-MDI	−36	54	2	—	—	53	2	188,204	12	137	13	196,216,230	12	190	224	25
PCL-2BD/1Is-MDI	−35	51	2	—	—	49	2	190,203	9	72	3	162	6	195	229	8
PCL-1BD/2Is-MDI	−34	42	3	—	—	49	3	203,225	2	118	2	192	2	195	232	2
PCL-Is-MDI	−31	43	5	—	—	42	2	220,227	4	181	4	231	4	220	260	13
PCL-2BD/1Gx-MDI	−19	46	2	—	—	45	1	162	2	—	—	—	—	—	—	—
PCL-1BD/2Gx-MDI	−8	45	2	—	—	44	1	176	9	—	—	—	—	—	—	—
PCL-Gx-MDI	−3	45	2	—	—	44	1	176	12	—	—	—	—	—	—	—

[a] First heating up to 100°C, cooling to room temperature, and reheating.
[b] First heating up to 250°C, cooling to room temperature, and reheating.
[c] Annealing at the indicated temperatures T_a for a period of 12 h, except for PCL-Is-HDI and PCL-Is-MDI from solution, which was 6 h.

the lowest values; accordingly, *b*PURs containing Is or Gx units in addition to BD showed intermediate molecular weights. The intrinsic viscosity values of *b*PURs as a function of the content of the polyurethane in diols derived from the cyclic extenders are plotted in Figure 1. For both isosorbide and gludioxol, [η] was found to decrease with the degree of replacement of 1,4-butanediol, such decreasing being slightly less pronounced for the case of isosorbide. A first interpretation would be related to the lower reactivity of the glucitol derived diols compared with 1,4-butanediol because of the sterical hindrance caused by the relative bulky cyclic structure. Nevertheless, the detrimental effect on the polyaddition reaction exerted by small amounts of residual water, which is extremely difficult to remove completely, cannot be fully excluded. This would also explain the even lower viscosity values attained for *b*PURs made from gludioxol; the results obtained with this diol are inconsistent because a higher reactivity in the addition to the isocyanate group should be expected for primary hydroxyl groups. As far as solubility is concerned, the replacement of 1,4-butanediol by isosorbide did not change significantly the solubility of *b*PURs, *i.e.*, the aromatic series is soluble in DMSO and THF and the aliphatic series is in addition soluble in CHCl₃. Conversely, all the *b*PURs containing gludioxol displayed a much more restricted solubility, DMSO being the only solvent known for these polymers.

Structure and compared thermal and mechanical properties

All the segmented PURs obtained either in solution or in bulk were semicrystalline regardless of their composition; their DSC data are compared in Table III. A common feature to all of them, without exception, is the occurrence of an endothermic peak within the 40–60°C range, which is interpreted as arising from the melting of the crystalline domains made of PCL soft segments. All PURs made from 1,4-butanediol or/and isosorbide displayed also melting of the hard segment at temperatures above 140°C regardless of the method used for synthesis. Conversely, PUR containing Gx units displayed hard segment melting for the whole aromatic series but not for the aliphatic series, except for the polymer with a Gx to BD units ratio of 2 : 1. For the study of the crystallizability of the individual segments in segmented poly(ester-urethane)s, samples were heated to maximum temperatures of 100°C and 200–250°C for the soft and hard segment, respectively. A selection of representative DSC traces registered for both *s*PURs and *b*PURs are depicted in Figures 2 and 3. In these figures, polymerization methods and compositional effects on melting and

crystallization behavior associated to both soft and hard segments are compared.

A close comparison between PURs with the same composition but differing in the method of synthesis, in solution or in bulk, leads to the following conclusions:

1. PURs obtained in solution display higher T_g than PUR obtained in bulk, which is most likely due to the greater contents in extender resulting in the former method.
2. Melting and enthalpy values found for both soft and hard segments are very similar for the two series of PURs.
3. Crystallization of the hard segment on cooling from the melt takes place in PURs obtained in
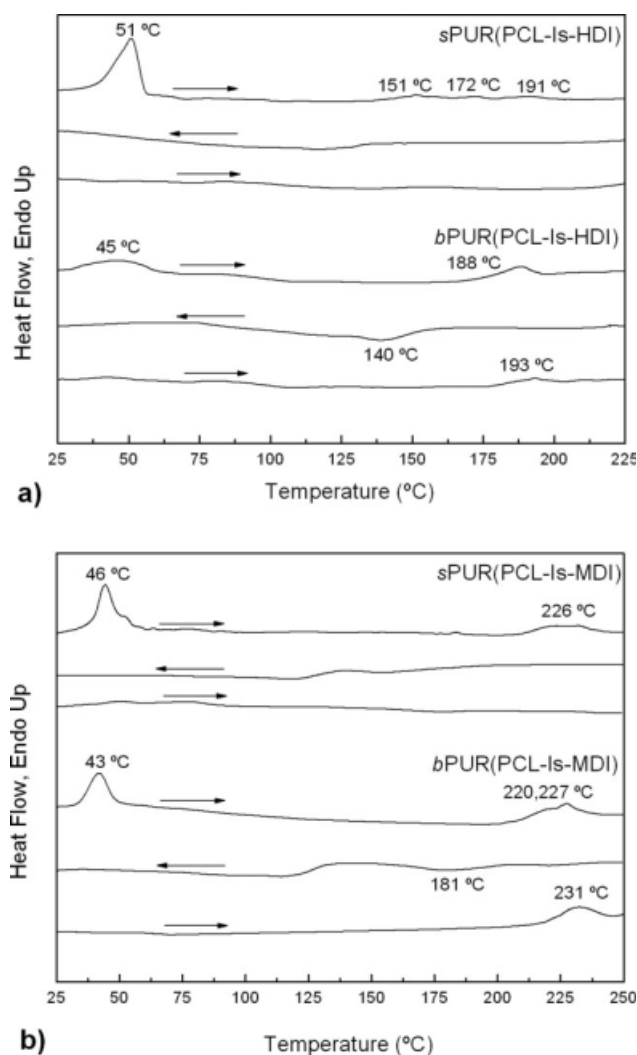

Figure 2 Comparative DSC traces of segmented *s*PUR and *b*PUR. (a) PCL-Is-HDI from solution: first heating (i), cooling (ii), and second heating (iii); PCL-Is-HDI from bulk: first heating (iv), cooling (v), and second heating (vi). (b) PCL-Is-MDI from solution: first heating (i), cooling (ii), and second heating (iii); PCL-Is-MDI from bulk: first heating (iv), cooling (v), and second heating (vi).
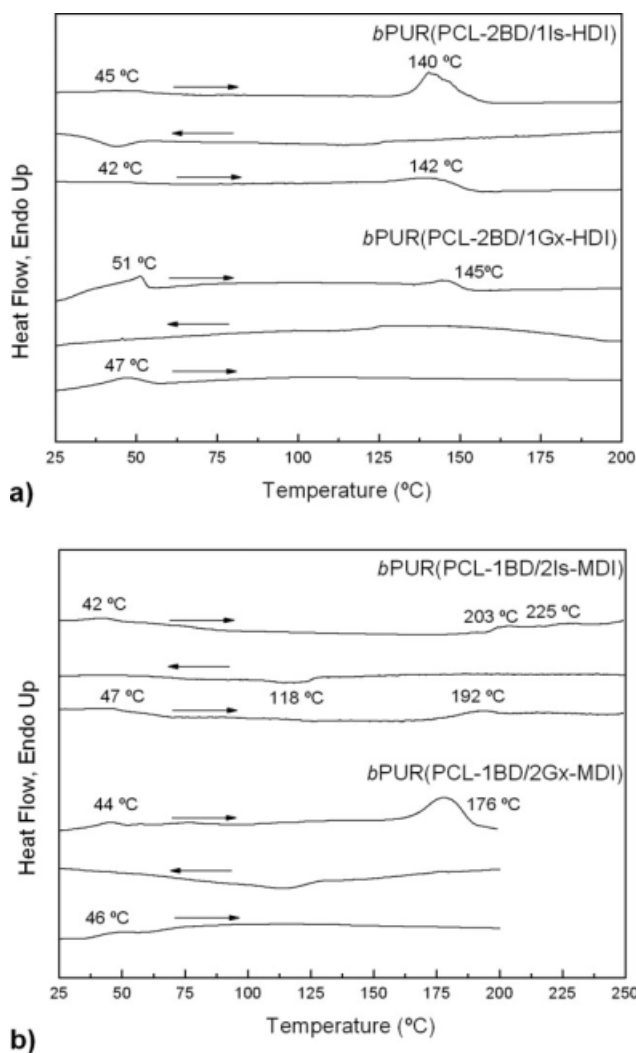
Figure 3 Comparative DSC traces of segmented *b*PUR. (a) PCL-2BD/1Is-HDI: first heating (i), cooling (ii), and second heating (iii); PCL-2BD/1Gx-HDI: first heating (iv), cooling (v), and second heating (vi). (b) PCL-1BD/2Is-MDI: first heating (i), cooling (ii), and second heating (iii); PCL-1BD/2Gx-MDI: first heating (iv), cooling (v), and second heating (vi).

bulk but it is not observed in those obtained in solution except for the case of the PURs made entirely of 1,4-butanediol i.e., PUR-(PCL-BD-HDI). Such differences may be attributed again to the differences in extender content between the two series or/and in its distribution along the polymer chain.

Comparison among the PUR obtained in bulk allows evaluating the effect of the composition on thermal properties and leads to the following conclusions:

1. The replacement of BD units by either Is or Gx units gives rise to an increase in T_g that is more pronounced in the later case. As usual, the aromatic PUR displays higher T_g than the aliphatic ones; in fact T_g values are found to be within the -40 to $-60°C$ and 0 to $-40°C$ ranges for the two respective series.
2. All *b*PUR display melting of the PCL soft segment at temperatures between 40 and 50°C, with very low enthalpy values (among 2 and 7 $J \cdot g^{-1}$).
3. As it could be reasonably anticipated, the crystallizability of the hard segment is highly depending on its chemical constitution; whereas all PURs made from BD and/or Is display hard segment melting, only aromatic PURs made from gludioxol show melting in the high temperature region.
4. Aromatic *b*PURs display higher hard segment T_m than aliphatic ones; highest T_m values are observed for PURs with hard segments entirely made of isosorbide, whereas *b*PURs containing Gx units display the lowest ones. Melting enthalpies decrease with the degree of replacement of BD by either Is or Gx, revealing that the presence of cyclic extenders repress crystallinity.
5. Only hard segments made of 1,4-butanediol or/and isosorbide are able to crystallize from the melt.

Annealing is the thermal treatment usually applied to polymers to increase the size of crystallites defectively grown in an incomplete crystallization process. Provided that annealing conditions are optimized, the efficiency of such treatment depends on the capability of chains to form large crystallites. The heating DSC traces showing the influence of composition of the annealing treatment on the hard segment melting peak for aliphatic and aromatic *b*PURs made of 1,4-butanediol and isosorbide are displayed in Figure 4(a,b), respectively. A noteworthy shift toward higher temperatures is observed in all cases, but the effect is even greater for *b*PURs containing Is units. In Figure 4(c), the response of PURs containing Gx to the annealing treatment is compared with that given by PURs containing Is units; DSC traces show that on annealing, the hard segment melting peak displayed by PUR-(PCL-2BD/1Is-HDI) shifted from 140°C to 157°C and became much sharper, indicating the high sensitivity of this PURs to the thermal treatment. On the contrary, the result obtained on annealing of PUR-(PCL-2BD/1Gx-HDI) was much poorer; the peak shifted only 3°C upward without significant sharpening. The results of all the annealing treatments applied in this work are listed in Table III, with the indication of the conditions used in every case.

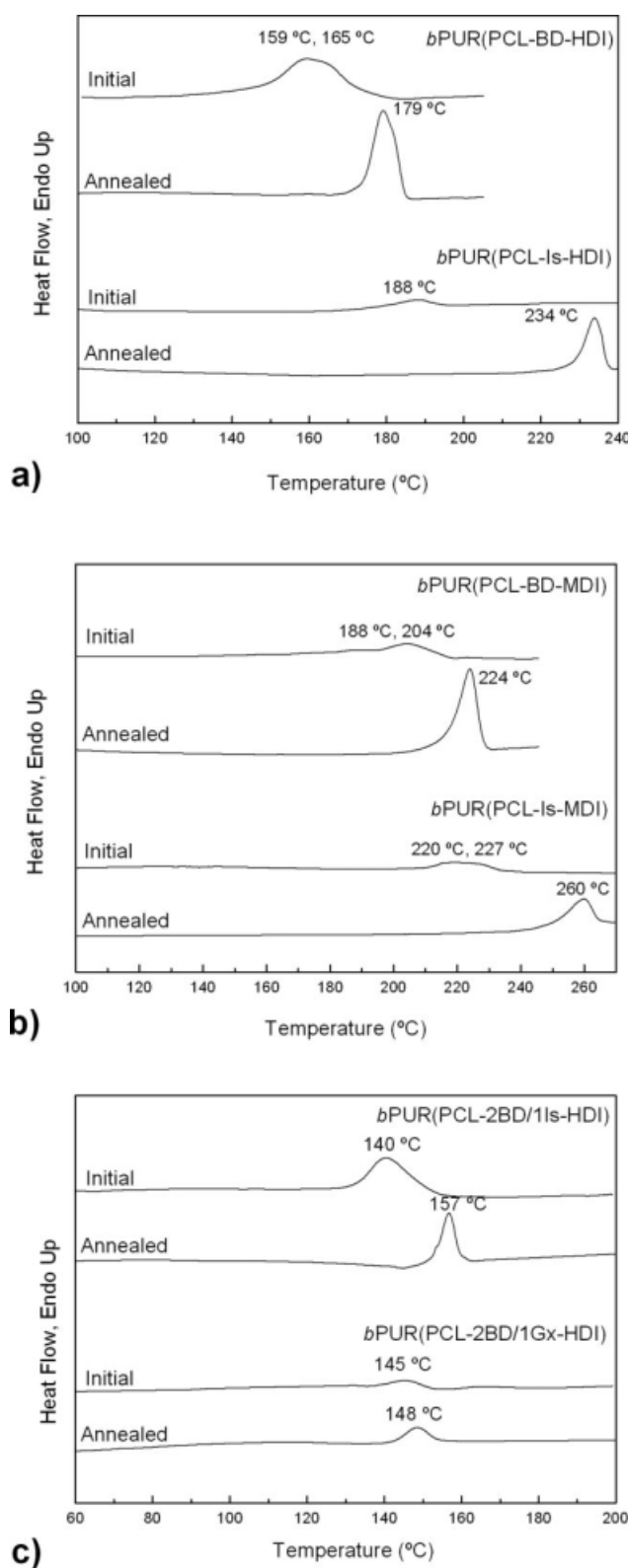The thermal stability of segmented PURs under inert atmosphere was evaluated by TGA. The TGA

Figure 4 Heating DSC traces showing the compositional influence on the annealing treatment on poly(ester-urethane)s synthesized in bulk. (a) Replacement of BD by Is in aliphatic bPUR. (b) Replacement of BD by Is in aromatic bPUR. (c) Replacement of Is by Gx in aliphatic bPUR.

curves of some representative PURs are compared in Figures 5 and 6, and the decomposition parameters measured on such traces are listed in Table IV. Thermal decomposition takes place in one or two steps within the 280–420°C range followed by a final step at temperatures around 450°C. The residue left after heating at 600°C is less than 2% in the case of aliphatic PUR and between 4 and 8% in the case of aromatic ones. It is noteworthy that aromatic PUR display decomposition temperatures in the low temperature region, which are inferior to those displayed by aliphatic PURs, whereas no differences between the two series are appreciated in the high temperature step. Moreover, degradation takes place for sPURs at temperatures lower than for bPURs for both aliphatic and aromatic series. Replacement of 1,4-butanediol by isosorbide was found to produce a light decrease in the thermal stability reflected as a slight decay in both onset and maximum rate decomposition temperatures. Nevertheless, it is the replacement of BD by Gx units that gives place to a
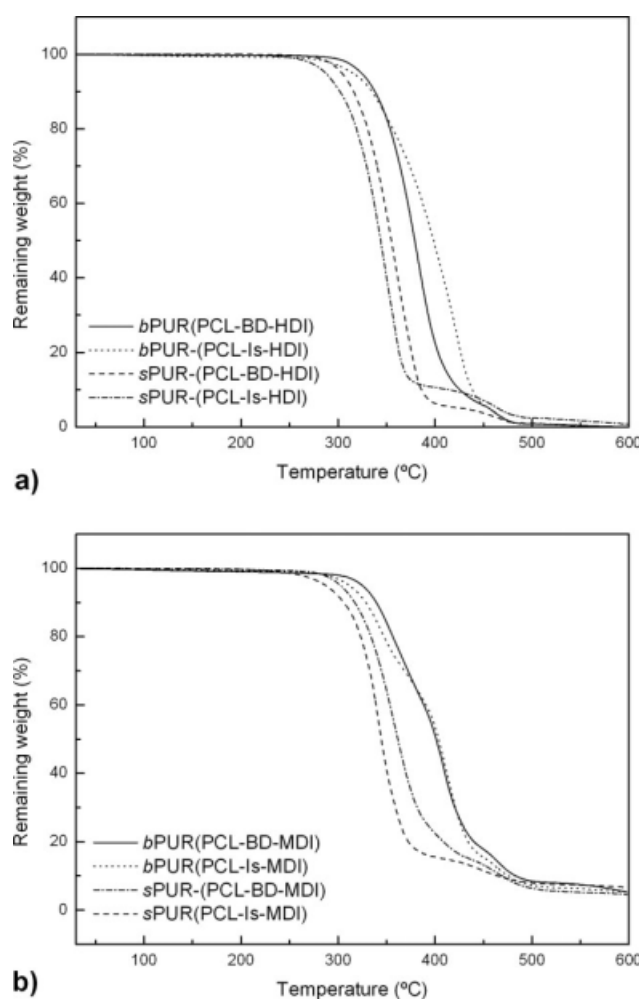

Figure 5 Comparative TGA traces of aliphatic (a) and aromatic (b) PUR prepared by polymerization in solution and in bulk.
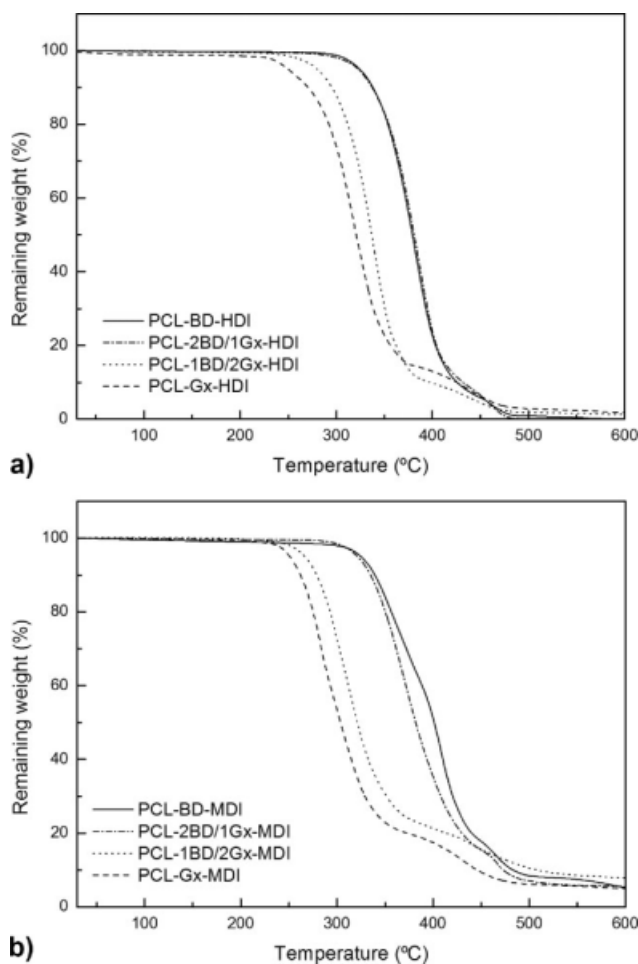
Figure 6 Comparative TGA traces of aliphatic (a) and aromatic (b) gludioxol-derived PUR.

TABLE IV
Compared TGA Results of Poly(ester-urethane)s

PUR	Inert Atmosphere		
	$^{o}T_d$ (°C)	$^{max}T_d$ (°C)	W (%)
PCL	356	379, **420**	0
*s*PUR			
PCL-BD-HDI	315	**362**, 460	0
PCL-Is-HDI	300	**352**, 463	0
PCL-BD-MDI	314	**358**, 465	5
PCL-Is-MDI	304	**346**, 467	7
*b*PUR			
PCL-BD-HDI	334	**381**, 463	0
PCL-2BD/1Is-HDI	336	**384**, 465	0
PCL-1BD/2Is-HDI	334	**390**, 466	0
PCL-Is-HDI	310	355, **417**, 466	0
PCL-2BD/1Gx-HDI	338	**386**, 459	0
PCL-1BD/2Gx-HDI	302	**337**, 443	1
PCL-Gx-HDI	267	**319**, 442	2
PCL-BD-MDI	329	367, **408**, 466	5
PCL-2BD/1Is-MDI	329	**379**, 410, 466	4
PCL-1BD/2Is-MDI	330	**379**, 415, 467	5
PCL-Is-MDI	316	346, **413**, 466	5
PCL-2BD/1Gx-MDI	331	**369**, 467	6
PCL-1BD/2Gx-MDI	275	**313**, 471	8
PCL-Gx-MDI	258	**282**, **306**, 432	5

Onset decomposition temperature ($^{o}T_d$), maximum rate decomposition temperatures ($^{max}T_d$) with main steps indicated in bold, and remaining weight (W).

notable decrease in the thermal stability; such decrease is found to be more accentuated as the content in Gx units is made greater.

Mechanical properties of segmented *b*PURs made from isosorbide were evaluated by stress–strain
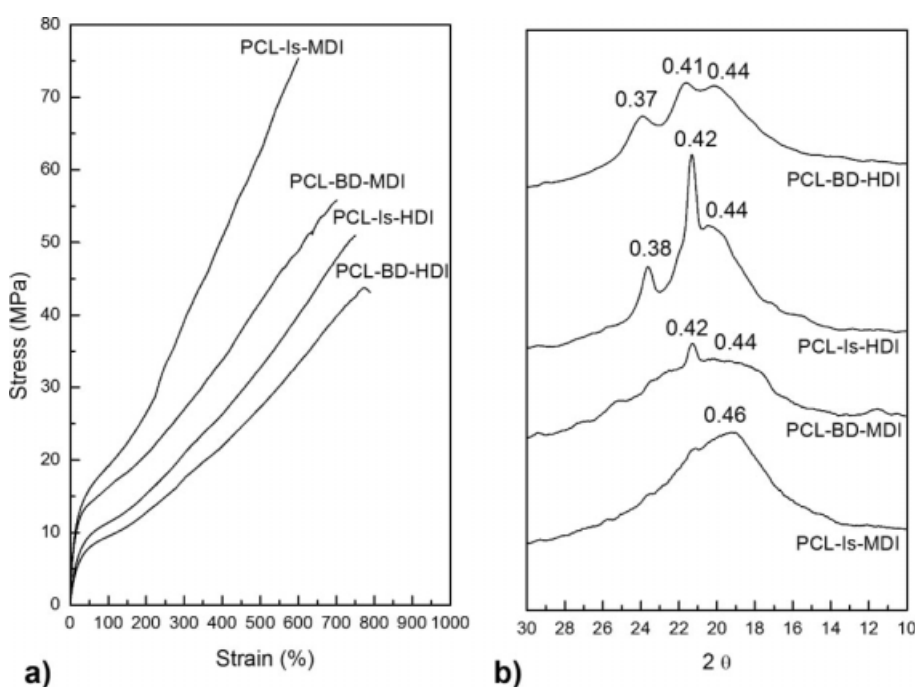

Figure 7 a) Stress–strain plot. (b) WAXS of bulk poly(ester-urethane)s.

TABLE V
Mechanical Properties and Some Structural Data of Bulk Poly(ester-urethane)s
Synthesized in Bulk

| bPUR | Stress–Strain Data | | | X-ray Diffraction[a] |
	E (MPa)	σ_{break} (MPa)	ε_{break} (%)	d_{hkl} (nm)
PCL-BD-HDI	43.6	44	774	0.44s 0.41s 0.37s
PCL-Is-HDI	52.3	51	750	0.44s 0.42s 0.38s
PCL-BD-MDI	113.5	56	700	0.44s 0.42s
PCL-Is-MDI	130.6	75	610	0.46s

[a] Visually estimated intensities denoted as: s, strong; m, medium; w, weak.

assays and compared with those obtained for bPURs made from 1,4-butanediol. Representative stress–strain plots are compared in Figure 7 and data are given in Table V, indicating that significant changes follow substitution of BD by Is. PURs containing Is units display elastic modulus and stress-to-break increments of around 15–20%, whereas the strain-to-break parameter is reduced in 3–15%; such changes are obviously due to the changes in chain stiffness introduced by the incorporation of rigid Is cyclic units. As expected, similar differences were observed when aliphatic and aromatic series are compared due in such case to the rigidity provided by MDI units.

A preliminary approach to the analysis of the crystalline structure of PURs made of Is was made by powder X-ray diffraction analysis. All the samples were subjected to annealing under the conditions indicated in Table III before recording diffraction data. In Figure 7(b), the WAXS profiles of PUR-(PCL-Is-HDI) and PUR-(PCL-Is-MDI) are compared with the their homologues PURs with the hard segment entirely made of 1,4-butanediol. The most outstanding interplanar spacings measured in these profiles are compared in Table V. The characteristic spacings of linear polyurethanes, which are known to appear at approximately 0.44, 0.4,1 and 0.37 nm,[18] corresponds to the main peaks seen on the profiles of the two aliphatic PUR-(PCL-BD-HDI) and PUR-(PCL-Is-HDI), indicating that such scattering must arise from the hard segment crystalline domains. It is worthy to note the coincidence in spacing found between the two profiles despite that all flexible BD units have been totally replaced by cyclic rigid Is units. On the other hand, the two aromatic PUR-(PCL-BD-MDI) and PUR-(PCL-Is-MDI) present similar scattering, although in this case as poorly resolved broad peaks.

Hydrolytic degradation

The hydrolytic degradation experiments were restricted to the aliphatic poly(ester-urethane)s PUR-(PCL-BD-HDI), PUR-(PCL-Is-HDI) and PUR-(PCL-

Gx-HDI) synthesized in bulk because the aim of this study was to evaluate the effect of replacing BD by the cyclic glucitols on hydrolysis rate. Assays were performed in parallel at pH 2, 7.4, and 10 and temperatures of 37°C and 60°C and the evolution of the degradation process was followed along a period of 40 days by weighting and GPC running of the residual samples at regular incubation intervals. The
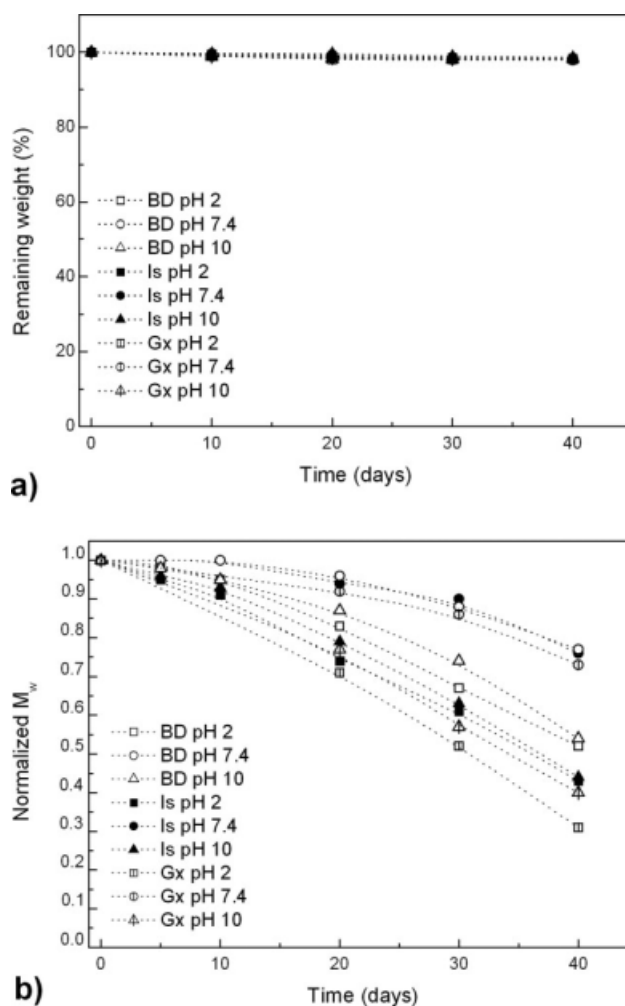

Figure 8 Changes in weight (a) and molecular weight (b) of aliphatic bulk poly(ester-urethane)s PCL-X-HDI$_b$ (X = BD or Is or Gx) at 60°C.

TABLE VI
Hydrolytic Degradation of Aliphatic Poly(ester-urethane)s Synthesized in Bulk

Days		pH 2		pH 7.4		pH 10	
		37 °C	60 °C	37 °C	60 °C	37 °C	60 °C
bPUR-(PCL-BD-HDI)							
0	W (%)	100	100	100	100	100	100
	M_w (g·mol^{-1})	123,600	123,600	123,600	123,600	123,600	123,600
20	W (%)	99.8	98.2	99.8	99.3	99.7	98.0
	M_w (g·mol^{-1})	123,400	102,300	123,600	118,800	123,400	107,400
40	W (%)	99.2	98.2	99.2	97.9	99.1	98.0
	M_w (g·mol^{-1})	123,200	64,200	123,400	95,300	123,400	67,300
bPUR-(PCL-Is-HDI)							
0	W (%)	100	100	100	100	100	100
	M_w (g·mol^{-1})	77,100	77,100	77,100	77,100	77,100	77,100
20	W (%)	99.8	99.6	99.8	99.1	99.8	98.8
	M_w (g·mol^{-1})	77,100	56,900	77,100	72,700	77,100	61,100
40	W (%)	98.8	98.6	99.5	98.1	99.0	98.0
	M_w (g·mol^{-1})	76,400	33,000	76,800	58,600	76,400	34,200
bPUR-(PCL-Gx-HDI)							
0	W (%)	100	100	100	100	100	100
	M_w (g·mol^{-1})	55,100	55,100	55,100	55,100	55,100	55,100
20	W (%)	99.7	98.6	99.6	98.5	99.7	98.5
	M_w (g·mol^{-1})	54,500	39,100	55,100	50,700	54,900	42,400
40	W (%)	98.8	98.3	99.4	98.3	98.4	98.2
	M_w (g·mol^{-1})	54,900	17,000	54,200	40,200	54,400	22,000

changes taking place in the weight and average molecular weight of the three studied PURs as a function of incubation time at 60°C are comparatively plotted in Figure 8(a,b); a numerical account of degradation results for all the experiments that have been carried out is given in full detail in Table VI.

None of the assayed polyurethanes showed appreciable loss of weight after 40 days of incubation under any of the assayed conditions. Conversely, a noticeable decrease in the molecular weight of the three polymers was observed at 60°C whichever was the pH of the incubating medium; nevertheless, higher degradation rates were observed at pH 2 and 10 than at pH 7.4, which is by no means an unexpected result. The fact that such decay in molecular weight was not accompanied by any weight loss of the sample is taken as indicative that the degraded fragments remained insoluble in the aqueous medium. Regarding the extender composition, degradation was found to be faster for PUR containing Gx units than for those made of BD, the polymers made from isosorbide showing intermediate degradation rates. These results evidenced the positive although moderate influence of glucitol units on the hydrodegradability of these segmented PUR. However, parallel experiments carried out on polyurethanes entirely made of Is-HDI hard segment showed total absent of degradation under similar incubation conditions (results not included). Therefore, it seems that degradation must take place by hydrolysis of the polyester segment rather than of the hard seg-

ment; the enhancement of hydrolysis observed for glucitol derived PUR could be therefore interpreted as a consequence of the higher hydrophilicity that the presence of such units confers to the polymer. On the other hand, the ^{1}H NMR spectrum of degraded PUR-(PCL-Gx-HDI) after incubation for 40 days at 60°C did not show signal arising from free hydroxyl group; therefore, it was inferred that the acetal group was unperturbed along the degradation process, which is a result fully consistent with previous observations made on other methylidene acetalized polyurethanes recently reported by us.[19]

CONCLUSIONS

The main conclusion derived from the present study can be summarized as follows:

a. Segmented poly(ester-urethane)s made of PCL soft segment and containing isosorbide in the hard segment could be prepared by polymerization in solution and in bulk with similar synthesis results attained in the two cases.
b. Segmented poly(ester-urethane)s made of PCL soft segment and containing gludioxol in the hard segment could be prepared by polymerization in bulk with results similar to those obtained in the preparation of poly(ester-urethane)s containing isosorbide.
c. The presence of Is or Gx units did not repress totally the crystallinity of the PURs, although

the crystallizability of the hard segment became appreciably hindered; on the other side, the crystal structure did not change significantly.

d. The replacement of BD units by Is or Gx units increased the T_g of the polymer, the increment being larger for the latter. T_m also increased for a complete replacement of the BD units but decreased for intermediate substitution degrees.

e. The hydrolytic degradation of PURs was enhanced by the presence in the chain of Is or Gx units, the effect being more noticeable for the latter. Degradation took place, however, by hydrolysis of the polyester soft segment without apparent breaking of the polyurethane hard segment.

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