

Carbohydrate-Based Polyurethanes: A Comparative Study of Polymers Made from Isosorbide and 1,4-Butanediol

Romina Marín, Abdelilah Alla, Antxon Martínez de Ilarduya, Sebastián Muñoz-Guerra

Departament d'Enginyeria Química, Universitat Politècnica de Catalunya, ETSEIB, Diagonal 647, 08028 Barcelona, Spain

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ABSTRACT: A set of linear polyurethanes containing isosorbide units were synthesized by polymerization in solution from HDI and MDI diisocyanates and 1,4-butanediol (BD), isosorbide (Is) or diisosorbide diurethanes (Is₂HDI and Is₂MDI) as diols. The thermal transitions, thermal stability, and crystal structure of the polyurethane homopolymers and copolymers containing isosorbide were evaluated and compared with those displayed by their polyurethane analogues entirely made of BD. It was found that incorporation of Is units in the polyur-

ethane chain produced significant changes in T_g , T_m , and T_d but no significant differences were noticed between copolymers made from Is or Is₂ monomers. Degradation assays revealed that the presence of Is units increased slightly the hydrolysis rate of polyurethanes. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 986–994, 2012

Key words: polyurethanes; renewable resources; structure–property relations; copolymerization

INTRODUCTION

Monomers deriving from renewable resources are of increasing interest as convenient alternatives to oil-based chemicals used today in the production of well-established industrial polymers. Among the naturally-occurring sources, carbohydrates stand at a prominent position due to their huge abundance and because they are inexhaustible and readily available.^{1–5} Furthermore, carbohydrates are able to provide great functional diversity, and polymers containing carbohydrate-based units are in principle more prone to be biodegradable and biocompatible.^{6,7} A good number of remarkable examples of carbohydrate-based polymers have been reported in the recent literature.^{8–15}

Isosorbide (1,4 : 3,6-dianhydro D-glucitol), abbreviated as Is (Fig. 1), appears today as one of the most promising carbohydrate-based monomers suitable for the preparation of bio-based polymeric materials. This cyclic diol has been proved to be useful in the synthesis of a variety of polycondensates such as

polyesters, polyamides, and polycarbonates.¹⁶ The efficiency of Is as monomer is somewhat limited by the relative lower reactivity displayed by its secondary hydroxyl groups.^{17,18} Furthermore, since the two hydroxyl groups occupy dissimilar spatial positions relative to the puckered bicycle (*exo* and *endo*), they have therefore different reactivity. The influence exerted by Is on physical properties of polymers is well-known, i.e., T_g increases and crystallinity and crystallizability decrease with the content in Is units.^{19,20} It has been also proved that polyesters, poly(ester-amide)s, poly(ester-carbonate)s, and polycarbonates containing Is units are more or less biodegradable depending on their chemical structure, as judged from degradation tests carried out in activated sludge, in soil, and in the presence of enzymes.²¹

Polyurethanes (PUR) constitute a large family of high performance materials with a wide variety of properties that are tunable by a proper control of the molecular design.²² Dirlikov and Schneider patented the synthesis of linear PUR containing Is as early as 1984²³ and the first papers describing this type of polymers appeared short later²⁴ and in the beginning of the 90s.^{25,26} Nevertheless, the publishing work following such pioneering work has been relatively scarce²⁷ and therefore the knowledge on these PUR is still very limited. Recently the synthesis of a series of polyurethanes containing Is alone or in combination with a second cyclic diol has been reported and their thermal and mechanical properties studied

Correspondence to: S. Muñoz-Guerra (sebastian.munoz@upc.edu).

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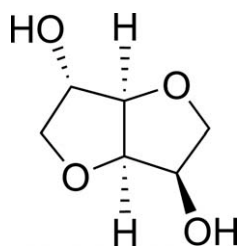


Figure 1 Chemical structure of 1,4 : 3,6-dianhydro-D-glucitol (isosorbide) indicating the *endo* (solid wedge) and *exo* (dashed wedge) position of the two secondary hydroxyl groups.

comparatively.²⁸ Conversely, the incorporation of Is in segmented PUR has drawn much more attention due to their much wider scope of applicability. In this regard poly(ester-urethane)s in which the familiar diol 1,4-butanediol (BD) was replaced by Is as chain extender have been recently reported.²⁹ It was shown there that the presence of isosorbide changed the physical properties of the polymer as expected, and enhanced its degradability by hydrolysis though the degradation process affected the ester counterpart almost exclusively. As a continuation of such work, the present work was conceived as a comparative study of nonsegmented polyurethanes with the purpose of evaluating the effect of the replacement of BD by the bicyclic diol Is on structure and thermal properties of these polymers. Both aliphatic and aromatic polyurethanes are explored, and hexamethylene diisocyanate (HDI) and 4,4'-methylenebis(phenyl isocyanate) (MDI) are the diisocyanates chosen for their synthesis. Incorporation of the Is units was accomplished by using either isosorbide itself or a diol-diurethane compound made from diisocyanate and isosorbide. The chemical structures of the PUR homopolymers and copolymers studied in this work are depicted in Figure 2. Thermal properties including thermal transitions and stability to

heating as well as some data relative to their crystalline structure are compared. The influence of the presence of Is units on the susceptibility to hydrolysis of the polyurethane chain is also assessed.

EXPERIMENTAL

Materials and methods

Isosorbide was a gift from Roquette Freres S.A. This bicyclic diol is prepared from corn starch following a well-established procedure of the proprietary company. Common reagents and solvents, and BD were purchased from Aldrich and used as received. *N,N*-dimethylformamide (DMF) and tetrahydrofuran (THF) solvents were dried prior to use by distillation under inert atmosphere. Diols and reagents for polymerization were stored in desiccator under vacuum until used. HDI was vacuum distilled prior to use and, together with MDI, stored at 4°C. Both compounds were handled under inert atmosphere.

Viscosities were measured in dichloroacetic acid at 25.0°C ± 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 with Waters equipment provided with a refraction-index detector. The samples were chromatographed with 0.05M sodium trifluoroacetate-hexafluoroisopropanol (NaTFA-HFIP) at a flow rate of 0.5 mL min⁻¹ using a polystyrene-divinylbenzene packed linear column. Chromatograms were calibrated against monodisperse poly(methylmethacrylate) standards. ¹H and ¹³C{¹H} NMR spectra were recorded on a Bruker AMX-300 spectrometer operating at 300.1 and 75.5 MHz for ¹H and ¹³C, respectively, in deuterated DMSO and using TMS as internal reference. Sample concentrations of about 1–5% (w/v) were used for these analyses, and spectra were recorded either at 298.1 and 343.1 K. The spectra were acquired with 64 scans and 1000–10,000 scans for ¹H and ¹³C, respectively, and relaxation

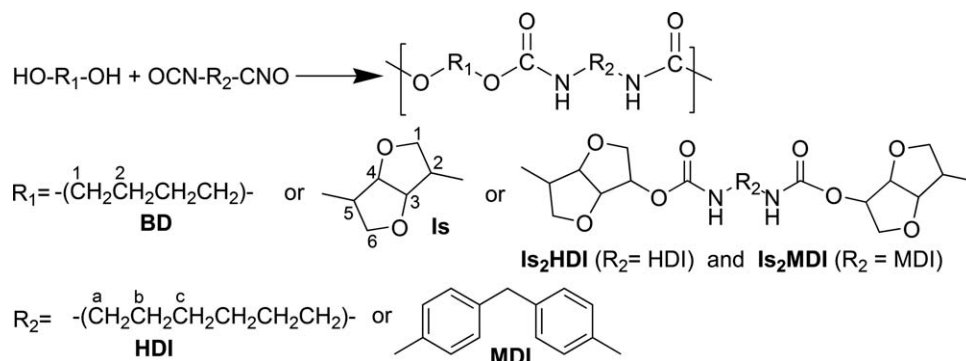


Figure 2 Chemical structures of polyurethanes studied in this work.

delays of 1 and 2 s. Differential scanning calorimetry (DSC) experiments were performed at heating/cooling rates of $10^{\circ}\text{C min}^{-1}$ on a Perkin-Elmer Pyris 1 instrument calibrated with indium. All the experiments were carried with samples of 3–4 mg within a range of temperatures from 0°C to 200 or 250°C , and under a nitrogen flow of 20 mL min^{-1} to minimize possible oxidative degradations. Thermogravimetry analysis (TGA) was carried out under inert atmosphere at a heating rate of $10^{\circ}\text{C min}^{-1}$ and within a temperature range of $30\text{--}600^{\circ}\text{C}$ using a Mettler TA4000 thermobalance. Sample weights of about 15 mg were used in these experiments. Wide angle X-ray scattering (WAXS) analysis was performed on a Philips automatic horizontal axis diffractometer using $\text{Cu K}\alpha\text{-Ni}$ filtered radiation. Spectra were taken at room temperature with the scattering angle 2θ varying from 3 to 50° . Additional WAXS experiments using synchrotron radiation of 0.154 nm wavelength were performed at the A2 beamline of the HASYLAB synchrotron facility (DESY, Hamburg). In this case, the scattering was detected with linear detectors and calibrated with semicrystalline PET standard.

Synthesis of monomers and polymers

Synthesis of monomers (urethane-diols Is_2HDI and Is_2MDI)

To a solution of 4 mmol of isosorbide in 10 mL of dry tetrahydrofuran containing 2% (w/w) of dibutyltin dilaurate catalyst, 1 mmol of either HDI or MDI was added dropwise. The mixture was stirred for 3 h at room temperature under inert atmosphere and then concentrated to oil from which a white solid precipitated. The two diols were dried under vacuum and stored in desiccator until needed. Is_2HDI : Yield 85%. Is_2MDI : Yield 83%.

Is_2HDI : $^1\text{H NMR}$ (DMSO, 300 MHz at 298.1 K): δ (ppm) 7.23, 7.18, (2 m, *N-H*), 5.08, 4.20 (2 m, 1H, H-5(Is)), 5.00, 4.15 (2 m, H-2(Is)), 4.82, 4.55 (2 m, H-4(Is)), 4.55, 4.30 (2 m, H-3(Is)), 3.91–3.30 (m, H-1(Is), H-6(Is)), 2.88 (m, H-a), 1.31 (m, H-b), and 1.18 (m, H-c). $^{13}\text{C NMR}$ (DMSO, 75.5 MHz at 298.1 K): δ (ppm) 155.54, 155.22, (C=O), 87.97, 85.31 (C-3(Is)), 81.59, 80.27 (C-4(Is)), 78.11, 75.15 (C-2(Is)), 73.66, 72.00 (C-5(Is)), 72.87, 75.26 (C-1(Is)), 71.31, 69.30 (C-6(Is)), 40.17 (C-a), 29.26 (C-b), and 25.89 (C-c).

Is_2MDI : $^1\text{H NMR}$ (DMSO, 300 MHz at 343.1 K): δ (ppm) 9.44, 9.39, (2 bs, *N-H*), 7.31–7.00 (2 d, Ar-H), 5.02, 4.10 (m, 1H, H-5(Is)), 5.00, 4.02 (m, H-2(Is)), 4.66, 4.38 (t, H-4(Is)), 4.45, 4.25 (s, d, H-3(Is)), 3.91–3.30 (m, H-1(Is), H-6(Is)). $^{13}\text{C NMR}$ (DMSO, 75.5 MHz at 343.1 K): δ (ppm) 152.57, 152.33, (C=O), 136.66, 135.22, 128.42, 118.34 (Ar), 87.96, 85.04 (C-3(Is)), 81.37, 79.93 (C-4(Is)), 78.35, 74.93 (C-2(Is)),

73.83, 71.62 (C-5(Is)), 72.42, 74.97 (C-1(Is)), 71.36, 69.04 (C-6(Is)).

Synthesis of polymers

The selected diol or combination of diols (1 mmol) (1,4-butanediol, isosorbide, Is_2HDI , or Is_2MDI) and DMF (4 mL) were placed in a round bottom flask saturated with inert gas. The mixture was stirred at room temperature up to homogenization and then 1 mmol of HDI or MDI followed by dibutyltin dilaurate (20 ppm) catalyst were added, and the mixture maintained under stirring for 24 h at room temperature. The reaction mixture was then added dropwise into cold diethyl ether (25 mL) to precipitate the polymer. Purification of the polyurethane was carried out by redissolution in the minimum volume of chloroform or chloroform/trifluoroacetic acid and reprecipitation into diethyl ether.

PUR-(BD-HDI): $^1\text{H NMR}$ (DMSO, 300 MHz at 298.1 K): δ (ppm) 6.56 (bs, 2H, *N-H*), 3.91 (m, 4H, H-1), 2.93 (m, 4H, H-a), 1.54 (m, 4H, H-2), 1.36 (m, 4H, H-b), and 1.21 (m, 4H, H-c). $^{13}\text{C NMR}$ (DMSO, 75.5 MHz at 298.1 K): δ (ppm) 161.47 (C=O), 68.40 (C-1), 45.59 (C-a), 34.59 (C-b), 31.14 (C-c), and 30.72 (C-2).

PUR-(Is-HDI): $^1\text{H NMR}$ (DMSO, 300 MHz, at 298.1 K): δ (ppm) 7.25, 7.20 (t, 2H, *N-H*), 4.90 (m, 1H, H-5), 4.85 (m, 1H, H-2), 4.60 (t, 1H, H-4), 4.30 (d, 1H, H-3), 3.85–3.45 (m, 4H, H-1, H-6), 2.94 (m, 4H, H-a), 1.36 (m, 4H, H-b), and 1.22 (m, 4H, H-c). $^{13}\text{C NMR}$ (DMSO, 75.5 MHz at 298.1 K): δ (ppm) 155.15 (C=O), 85.57 (C-3), 80.71 (C-4), 77.44 (C-2), 73.93 (C-5), 73.26 (C-1), 69.92 (C-6), 40.59 (C-a), 29.21 (C-b), and 25.81 (C-c).

PUR-(BDIs-HDI) and PUR-(BDIs₂-HDI): $^1\text{H NMR}$ (DMSO, 300 MHz at 343.1 K): δ (ppm) 6.95, 6.68 (2 bs, 2H, *N-H*), 4.92 (m, 1H, H-5(Is)), 4.89 (m, 1H, H-2(Is)), 4.61 (t, 1H, H-4(Is)), 4.34 (d, 1H, H-3(Is)), 3.90 (m, 4H, H-1(BD)), 3.86–3.20 (m, 4H, H-1(Is) and H-6(Is)), 2.91 (m, 4H, H-a), 1.53 (m, 4H, H-2(BD)), 1.34 (m, 4H, H-b), and 1.22 (m, 4H, H-c). $^{13}\text{C NMR}$ (DMSO, 75.5 MHz at 343.1 K): δ (ppm) 155.85, 155.04, 154.82 (C=O), 85.40 (C-3(Is)), 80.31 (C-4(Is)), 77.40 (C-2(Is)), 73.06 (C-5(Is)), 72.54 (C-1(Is)), 69.56 (C-6(Is)), 62.86 (C 1(BD)), 39.96 (C-a), 29.03 (C-b), 25.60 (C-c), and 25.11 (C-2(BD)).

PUR-(BD-MDI): $^1\text{H NMR}$ (DMSO, 300 MHz at 298.1 K): δ (ppm) 9.45 (bs, 2H, *N-H*), 7.31–7.02 (2 d, 8H, Ar), 4.05 (m, 4H, H-1), 3.72 (bs, 2H, Ph-CH₂-Ph from MDI), and 1.65 (m, 4H, H-2). $^{13}\text{C NMR}$ (DMSO, 75.5 MHz at 298.1 K): δ (ppm) 153.6 (C=O), 137.1, 135.47, 128.84, 118.39 (Ar), 63.70 (C-1), 39.79 (Ph-CH₂-Ph from MDI), and 25.26 (C-2).

PUR-(Is-MDI): $^1\text{H NMR}$ (DMSO, 300 MHz at 298.1 K): δ (ppm) 9.76 (2 s, 2H, *N-H*), 7.38–7.11 (2 d, 8H, Ar), 5.10 (m, 1H, H-5), 5.04 (m, 1H, H-2), 4.76 (m, 1H, H-4), 4.45 (m, 1H, H-3), and 3.91–3.73 (m, 4 H,

TABLE I
Polymerization Results and Some Properties of Polyurethanes

PUR	Reaction			Molecular size ^a			Solubility ^b			
	% ^c	% ^c	Yield (%)	[η] (dL g ⁻¹)	M_w (g mol ⁻¹)	M_w/M_n	H ₂ O	DMSO	CHCl ₃	THF
BD-HDI ^d	—	—	88	0.63	30,000	2.2	—	+	+/-	+/-
Is-HDI	—	—	85	0.32	18,000	2.0	—	+	—	—
BDIs-HDI	20	18.5	85	0.29	17,200	1.8	—	+	—	—
BDIs ₂ -HDI	11	12.2	86	0.30	17,600	1.9	—	+	—	—
BD-MDI	—	—	90	0.60	28,600	2.2	—	+	—	+/-
Is-MDI	—	—	86	0.38	18,500	2.1	—	+	—	—
BDIs-MDI	20	10.7	84	0.33	19,900	2.0	—	+	—	—
BDIs ₂ -MDI	11	15.9	85	0.35	21,000	2.1	—	+	—	—

^a Intrinsic viscosity measured in DCA and average molecular weights determined by GPC.

^b Solubility at 20 °C \pm 5°C at a sample concentration of 1 g L⁻¹: + soluble; +/- partially soluble; - insoluble.

^c Molar percentage of Is or Is₂HDI/Is₂MDI of the total of diols by in the feed (first column) and in the resulting polymer (second column).

^d Precipitated from solution after 2 h of reaction.

H-1, H-6), 3.74 (bs, 2H, Ph-CH₂-Ph from MDI). ¹³C NMR (DMSO, 75.5 MHz at 298.1 K): δ (ppm) 152.68, 152.45 (C=O), 136.93, 135.55, 128.83, 118.25 (Ar), 85.65 (C-3), 80.90 (C-4), 77.66 (C-2), 73.40 (C-5), 72.65 (C-1), 70.20 (C-6), and 39.5 (Ph-CH₂-Ph from MDI).

PUR-(BDIs-MDI) and PUR-(BDIs₂-MDI): ¹H NMR (DMSO, 300 MHz at 343.1 K): δ (ppm) 9.48, 9.45, 9.43 (3 bs, 2H, N-H), 7.31–7.00 (2 d, 8H, Ar), 5.10 (m, 1H, H-5(Is)), 5.0 (m, 1H, H-2(Is)), 4.76 (t, 1H, H-4(Is)), 4.48 (d, 1H, H-3(Is)), 4.07 (m, 4H, H-1(BD)), and 3.91–3.50 (m, 6H, H-1(Is), H-6(Is)), 3.74 (bs, 2H, Ph-CH₂-Ph from MDI), and 1.64 (m, 4H, H-2(BD)). ¹³C NMR (DMSO, 75.5 MHz at 343.1 K): δ (ppm) 153.3, 152.60, 152.53 (C=O), 137.38, 135.13, 128.40, 118.35 (Ar), 85.44 (C-3(Is)), 80.49 (C-4(Is)), 78.35 (C-2(Is)), 75.50 (C-5(Is)), 72.42 (C-1(Is)), 69.75 (C-6(Is)), 63.39 (C-1(BD)), 39.54 (Ph-CH₂-Ph from MDI), and 25.00 (C-2(BD)).

Hydrolytic degradation assays

For hydrolytic degradation studies, films of selected polyurethanes with a thickness of \sim 300 μ m were prepared by hot-press molding at a temperature of 250°C for 3 min. 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 discs into vials and 10 mL of buffered solutions were added at the selected pH. Parallel experiments were carried out 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 fixed period of time, the samples were rinsed thoroughly with water and dried to constant weight. Sample weighing and GPC measure-

ments were used to follow the evolution of the hydrodegradation.

RESULTS AND DISCUSSION

Synthesis

Polyurethanes were prepared by polymerization reaction in DMF solution at room temperature with dibutyltin dilaurate as catalyst and using HDI and MDI as diisocyanates. The 1,4-butanediol, isosorbide, and compounds Is₂HDI or Is₂MDI were the diols of choice for this study. The use of these diol-urethane compounds as monomers ensured the incorporation of the Is units as dyads in the formation of PUR chain and contributed to minimize decomposition of isosorbide during polymerization. Results from polymerizations and copolymerizations are compared in Table I. Copolymers were made from BD to Is or urethane-diol (Is₂HDI and Is₂MDI) at the molar ratios of 4 : 1 or 8 : 1, respectively, so that the BD to Is units ratio in the resulting copolymers were expected to be 4 : 1 in all cases. However, the content in Is of the resulting polymers was considerably lower than expected. The loss of isosorbide in polycondensation reactions carried out at high temperatures is a well known fact that is usually explained by the relative low reactivity and thermal instability of this compound.³⁰

Polymerization yields were of 85–90% and the resulting Is-containing PUR displayed molecular weights significantly lower than the reference polyurethanes PUR-(BD-HDI) and PUR-(BD-MDI), according to what should be expected from the lower reactivity of the secondary hydroxyl groups of Is compared to the primary ones of BD. The chemical structure of PUR was ascertained by ¹H and ¹³C NMR spectroscopy, all peak data and assignments being listed in the Experimental section. The ¹H NMR spectra

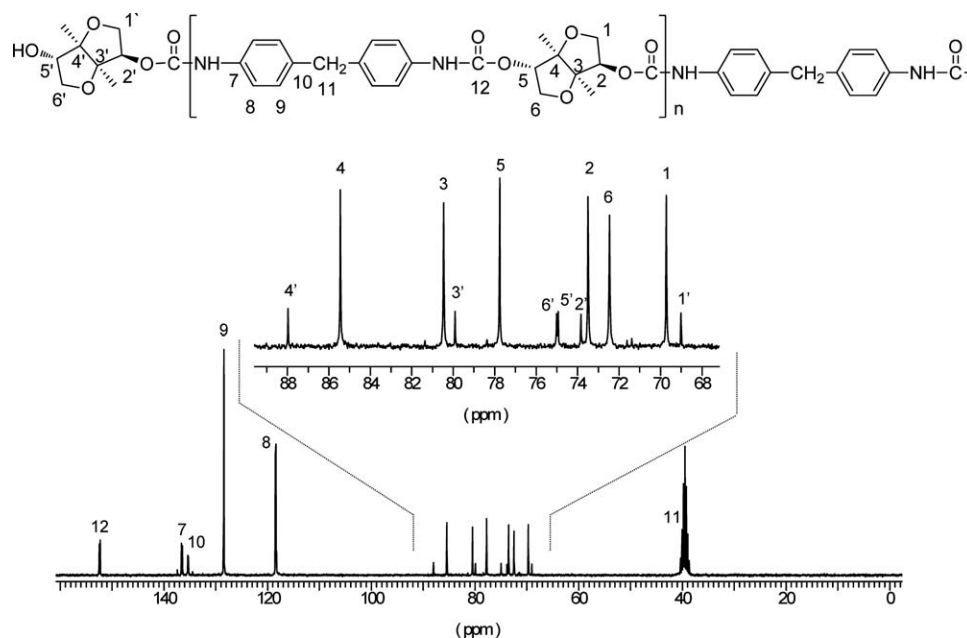


Figure 3 ^{13}C NMR of PUR-(Is-MDI) with assignment of all the signals and revealing the major presence of *exo* hydroxyl end groups.

showed that copolyurethanes were enriched in BD units and all of them show predominance of Is end groups, mostly with the unreacted hydroxyl in *exo* position. The ^{13}C NMR spectrum of PUR-(Is-MDI) is depicted in Figure 3 to illustrate these features.

These results not only indicate a lower reactivity for secondary hydroxyl groups of isosorbide compared to BD, but also that the hydroxyl in *exo* position is relatively disfavored to add to the isocyanate group. This result is in agreement with the work of Lemieux et al. on tosylation of isosorbide¹⁷ but contrary to the relative reactivity of the two isosorbide hydroxyl groups observed in the reaction with carboxylic diacids to give polyesters.¹⁸ Lastly it is worthy to mention that the low solubility characteristic of PUR not only is essentially maintained but even slightly more restricted in the Is containing PUR; specifically, the partial solubility in CHCl_3 and THF

displayed by PUR-(BD-HDI) and PUR-(BD-MDI) disappeared upon insertion of Is units.

Thermal properties and crystalline structure

The thermal stability of PUR under inert atmosphere was comparatively evaluated by TGA. The TGA traces of aliphatic and aromatic PUR are compared in Figure 4(a,b), respectively, and the decomposition parameters on such traces are listed in Table II. Results indicated that major differences are those between aliphatic and aromatic PUR whereas no significant changes in thermal stability were produced by replacing BD by Is. In all cases, polyurethanes made of HDI appeared to be more stable than the aromatic ones showing higher onset and maximum rate decomposition temperatures and leaving much lower amounts of residue after heating at 600°C.

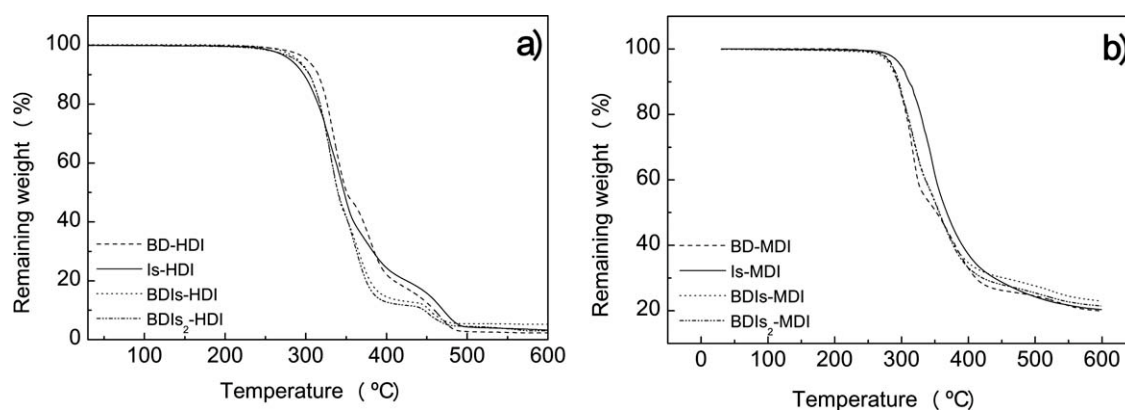


Figure 4 TGA traces of aliphatic (a), and aromatic (b) polyurethanes.

TABLE II
Thermal Properties and Bragg Spacings of the Studied Polyurethanes

PUR	TGA ^a			DSC					WAXS ^b
	$^{\circ}T_d$ (°C)	$^{\max}T_d$ (°C)	W (%)	T_g^c (°C)	T_m^d (°C)	ΔH_m^d (J g ⁻¹)	T_c^e (°C)	ΔH_c^e (J g ⁻¹)	d_{hkl} (nm)
BD-HDI	300	340,371,464	1	15	183	77	157	76	0.44s,0.40s,0.37s
Is-HDI	296	342,384,471	3	77	169,189,208	27	147	9	0.47s,0.43s
BDIs-HDI	300	331,365,453	5	30	162	48	129	44	0.45s,0.43s,0.41s,0.37s
BDIs ₂ -HDI	302	330,363,452	3	24	167	62	136	50	n.d.
BD-MDI	282	315,366	20	93	212,233	20	–	–	0.49s,0.45s,0.38s
Is-MDI	297	346,375	20	183	217	20	–	–	0.47s
BDIs-MDI	281	318,355	23	120	186,209	18	–	–	0.47s,0.44s
BDIs ₂ -MDI	283	320,353	21	115	190,212	18	–	–	n.d.

^a Onset decomposition temperature ($^{\circ}T_d$), maximum rate decomposition temperatures ($^{\max}T_d$) and remaining weight at 600°C (W).

^b Powder X-ray diffraction. d -spacing with indication of visually estimated intensities denoted as: s, strong; m, medium; w, weak. n.d. = not determined.

^c Glass transition temperatures measured at heating on samples quickly cooled from the melt.

^d Melting temperature and enthalpy measured on the first heating traces of pristine samples.

^e Crystallization temperature and enthalpy measured at cooling from the melt at 10°C min⁻¹ rate.

The effect of Is units on the thermal transitions of PUR was evaluated by DSC and data collected from this study are compared in Table II. First, T_g was measured at heating from samples that had been rapidly quenched at -70°C from the melt. As it could be anticipated, the insertion of the rigid isosorbide ring hampered the molecular mobility of the polymer chain with the subsequent increase in T_g . In fact, T_g values of PUR increased with the content in Is, the highest values being displayed by PUR entirely made of the cyclic diol. The same trend was observed for both aliphatic and aromatic series and,

as it should be expected from the contribution of the aromatic ring to the stiffness of the chain; much higher T_g values were observed for the latter (93–183°C) than for the former (15–77°C).

All the studied aliphatic polyurethanes were semicrystalline polymers. The heating DSC traces of samples of PUR coming directly from synthesis are compared in Figure 5. They all contain more or less pronounced endothermic peaks characteristic of melting. Frequently, broad multiple melting peaks were observed, presumably indicating the occurrence of crystallite size heterogeneities; in

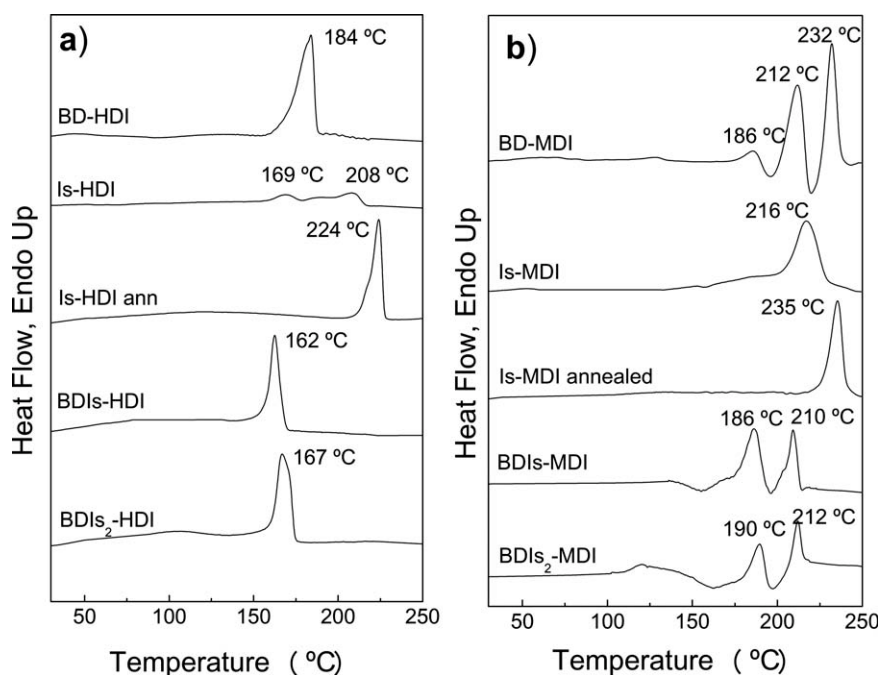


Figure 5 Comparative heating DSC traces of aliphatic (a) and aromatic (b) polyurethane samples coming directly from synthesis.

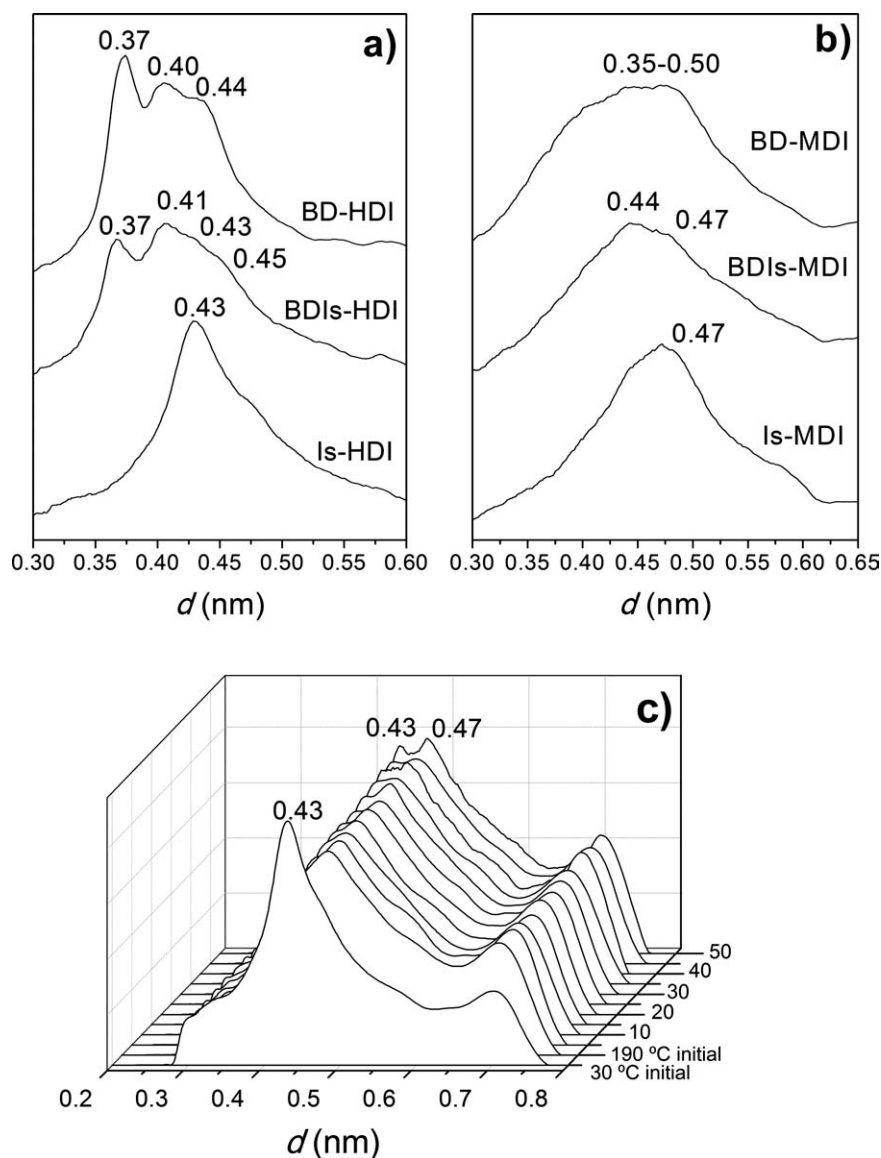


Figure 6 X-ray diffraction profiles of the HDI (a) and MDI (b) polyurethanes and evolution of the profile of PUR-(Is-HDI) homopolymer with time (in min) under annealing at a temperature of 190°C (c).

some cases the complex endotherm could be merged in only one peak by annealing at temperatures close to the highest temperature melting peak for several hours. For both aliphatic and aromatic PUR, the Is homopolymer displayed T_m similar to the BD homopolymer whereas copolymers showed lower values. A significant decrease in the melting enthalpy was noticed when BD was replaced by Is in the aliphatic PUR whereas almost no difference was perceived for the aromatic ones. Furthermore no remarkable differences in the melting behavior were observed between copolymers with the Is units distributed in either monads or dyads.

The X-ray diffraction profiles of aliphatic and aromatic PUR are compared in Figure 6(a,b) respectively, and the Bragg's spacings measured on such profiles are listed in Table II. The profile recorded from

homopolymer PUR-(BD-HDI) displays the three spacings at 0.44, 0.37, and 0.40 nm, which have been reported to be characteristic of linear aliphatic polyurethanes, and respectively, indexed as the 100 and 010 of a triclinic structure, and as the 100 of an accompanying second hexagonal form.³¹ The copolymer PUR-(BDIs-HDI) gave a profile containing again the characteristic peaks at 0.43, 0.37, and 0.41 nm with a broad shoulder at ~ 0.45 nm attributed to the presence of amorphous material. It can be concluded therefore that the crystalline structure of the parent homopolymer PUR-(BD-HDI) is mostly retained in the copolymer although some disorder is introduced by the presence of the Is units. This is a plausible interpretation given the minor content in Is and the preferred location of these units at the chain ends, i.e., the amount of inner Is units in the PUR chain is

TABLE III
Hydrolytic Degradation of PUR-(BD-HDI) and PUR-(Is-HDI)^a

		pH 2		pH 7.4		pH 10	
		37°C	60°C	37°C	60°C	37°C	60°C
BD-HDI							
Days							
0	W (%)	–	100	–	100	–	100
	M_w (g mol ⁻¹)	–	30,000	–	30,000	–	30,000
20	W (%)	–	99	–	99	–	98
	M_w (g mol ⁻¹)	–	30,000	–	30,000	–	29,700
40	W (%)	–	99	–	98	–	97
	M_w (g mol ⁻¹)	–	30,000	–	29,900	–	29,700
Is-HDI							
0	W (%)	100	100	100	100	100	100
	M_w (g mol ⁻¹)	18,000	18,000	18,000	18,000	18,000	18,000
20	W (%)	99	94	99	95	99	94
	M_w (g mol ⁻¹)	18,000	17,200	18,000	17,300	17,900	17,200
40	W (%)	97	93	98	94	97	93
	M_w (g mol ⁻¹)	17,500	17,100	17,900	17,300	17,400	17,000

^a Percentage of remaining weight (W) and weight-average molecular weight (M_w).

low enough as to allow the copolymer to adopt the same crystal structure as the homopolymer PUR-(BD-HDI), most probably by excluding the Is units from the crystal lattice. It is highly interesting fact that the homopolymer PUR entirely made of Is (PUR-(Is-HDI)) displays a quite different behavior. The WAXS profile recorded from this PUR consists of a single broad peak at ~ 0.43 nm, which is indicative of a structure made of poorer-formed crystallites. The evolution of this profile upon annealing the polymer at 190°C for 1 h was followed by synchrotron radiation. The collection of profiles obtained every 5 min of treatment is depicted in Figure 6(c). Upon heating, the peak at 0.43 nm indicative of a hexagonal packing split in the two well resolved peaks at 0.43 and 0.47 nm revealing that a new crystal structure is adopted in this case. The melting temperature and enthalpy of the annealed sample increased up to 225°C and 50 J g⁻¹, respectively.

On the other hand, all the aromatic PUR gave WAXS profiles consisting of broad peaks centered at 0.44–0.47 nm which did not change appreciably upon annealing. Taking into account the DSC results (Fig. 3 and Table II), these PUR are semicrystalline and such broad peaks should be interpreted therefore as involving multiple nonresolved discrete scattering. Because of the poor resolution of the profiles obtained in this case, no relevant differences could be appreciated between the copolymer and its parent homopolymers. It cannot be inferred from these results therefore whether the insertion of Is units in the aromatic PUR chain modifies their crystal structure.

Hydrolytic degradation

The reluctance to hydrolysis of nonsegmented PUR made from alkanediols and diisocyanates is a well known fact. It was interesting to explore the effect of

the insertion of a carbohydrate-based diol such as Is in a polyurethane chain. With this aim, the hydrolytic degradation of the pair PUR-(BD-HDI) and PUR-(Is-HDI) was comparatively evaluated by incubation in aqueous buffers at pH 2, 7.4, and 10, and at temperatures of 37 and 60°C for a period of 40 days. The evolution of the process was followed by weighing and GPC running of the samples after regular periods of time and results are given in Table III. The general observation is that PUR containing Is show a slightly greater weight loss than PUR made of BD, the weight loss being more perceivable at neutral or basic pH. The fact that the decay in molecular weight is so meager could be due to the rapid solubilization of the generated PUR fragments. These data indicate that the replacement of BD by isosorbide weakens the resistance of the polyurethane to be attacked by water. This result is in agreement with previously reported work on polycondensates as polyamides, and polyesters in which the hydrodegradability of these polymers was enhanced by the presence of different carbohydrate-based units in the polymer chain.^{32,33}

CONCLUSIONS

The comparative study carried out in this work on nonsegmented linear polyurethanes in which 1,4-butanediol is partially or totally replaced by isosorbide provides the following conclusions:

- The incorporation of Is in a polyurethane chain happens with asymmetrical reactivity of its two hydroxyl groups, the one located at the *exo* position being less reactive and appearing therefore as the major chain end group.
- The replacement of BD by Is in both aliphatic and aromatic polyurethanes does not alter

significantly the thermal stability of the polymers but notably reduces their solubility in the common organic solvents.

- c. The replacement of BD by Is in both aliphatic and aromatic polyurethanes renders semicrystalline polymers but the crystallinity is largely reduced, mainly in the former case. Also the crystallizability is repressed to the point that aromatic PUR containing Is are unable to crystallize from the melt. These compositional effects on thermal properties are not much affected by changes in the microstructure, at least within the range of substitution explored in this study.
- d. The partial replacement of BD by Is in aliphatic PUR does not alter substantially the crystal structure of the polymer. Conversely, a new crystal form different to the typical of linear PUR seems to be adopted by the homopolymer entirely based on Is.
- e. The increasing T_g effect of Is is apparent in both aliphatic and aromatic polyurethanes; such an effect becomes very strong when BD is fully replaced by Is and also quite noticeable in the copolymers.

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