A Comparative Study of Polymers Made from Isosorbide and 1,4-Butanediol

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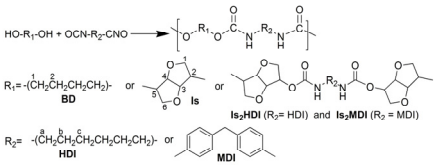
Introduction

Although some polyurethanes (PUR) containing isosorbide units (Is) were described at the beginning of the nineties, the knowledge on these compounds is very limited. The main purpose of this work was to make a comparative study of non-segmented Is containing polyurethanes with their analogues made from butanediol (BD). Hexamethylene diisocyanate (HDI) and 4,4'-methylene-bis(phenyl isocyanate) (MDI) are used for this synthesis.



Scheme I. Chemical structure of polyurethanes.

Materials and Methods

Isosorbide was a gift from Roquette Freres S.A. Molecular sizes of PUR were estimated by both viscosimetry in dichloroacetic acid and GPC. NMR spectra were recorded on a Bruker AMX-300 in DMSO-d_6. DSC experiments were performed at heating/cooling rates of 10 ºC•min^{-1} and TGA analysis was carried out under inert atmosphere. Wide angle X-ray scattering (WAXS) was performed on a lab diffractometer or at the A2 beamline of the HASYLAB synchrotron (DESY, Hamburg).

Results

The selected diol or combination of diols was made to react with the selected diisocyanate using dibutyltin dilaurate catalyst. The use of diol-urethane compounds as monomers ensured the incorporation of the Is units as dyads in the PUR chain and contributed to minimize the decomposition of Is.

Table 1. Polymerization results and some properties of polyurethanes.

PUR	Reaction			Molecular size[b]			Solubility[c]			
	%[a]	%[a]	Yield (%)	$[\eta]$ (dL·g^{-1})	M_w (g·mol^{-1})	M_w/M_n	H_2O	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] Molar percentage of Is or Is$_2$HDI/Is$_2$MDI of the total of diols in the feed and in the resulting polymer.
[b] Intrinsic viscosity measured in DCA and average molecular weights determined by GPC.
[c] Solubility at 20 ± 5 ºC at a sample concentration of 1 g L^{-1}; + soluble; +/- partially soluble; - insoluble.
[d] Precipitated from solution after 2 hours of reaction.

The ^{1}H and ^{13}C NMR spectra showed that PURs were enriched in BD units and all them displayed predominance of isosorbide end groups with excess of the unreacted hydroxyl in *exo* position. This result is contrary to the relative reactivity of the hydroxyl groups observed in the synthesis of polyesters.

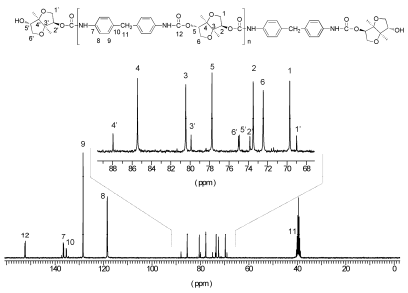


Figure 1. ^{13}C NMR of PUR-(Is-MDI) with assignment of all the signals and revealing the major presence of *exo* hydroxyl end groups.

The thermal properties and stability of PUR containing Is were evaluated and compared with those of PUR entirely made of BD.The TGA traces of aliphatic and aromatic PURs indicated that 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 ºC.

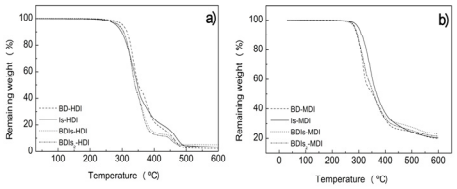


Figure 2. TGA traces of aliphatic (a), and aromatic (b) polyurethanes.

Incorporation of Is produced significant changes in T_g, T_m and T_d but no noteworthy differences were found between copolymers made from Is or Is$_2$ monomers. In general the insertion of the Is units in the PUR chain increased the T_g and depressed the crystallinity.
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 Tg values were observed for the latter (93-183 ºC) than for the former (15-77 ºC).

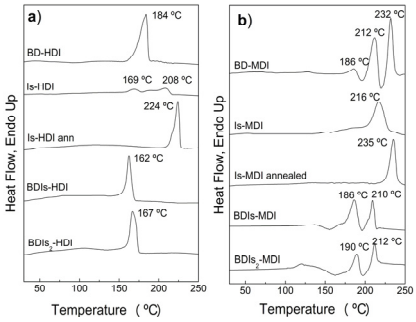


Figure 3. Comparative heating DSC traces of aliphatic (a) and aromatic (b) polyurethane samples coming directly from synthesis and annealed.

WAXS revealed that the triclinic structure of PUR-(BD-HDI) was essentially retained in PUR-(BDIs-HDI), whereas the aromatic PUR gave profiles typical of disordered material. Annealing of PUR-(Is-HDI) induced the split of the 0.43 nm peak indicating that a new crystal structure was adopted.

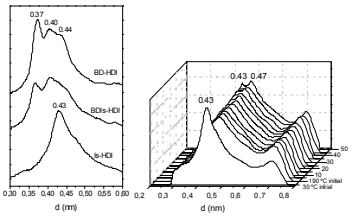


Figure 4. X-ray diffraction profiles of the HDI polyurethanes (left) and evolution of the profile of PUR-(Is-HDI) with time (in min) under annealing at 190 ºC (right).

Conclusions

The incorporation of Is in a polyurethane chain happens with asymmetrical reactivity of its two hydroxyl groups and without altering significantly the thermal stability and increasing notably the T_g. Both aliphatic and aromatic polyurethanes containing Is are semicrystalline polymers and maintain the crystal structure although the crystallinity is largely reduced.

Acknowledgements

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