A Comparative Study of Polymers Made from Isosorbide and 1,4-Butanediol
R. Marín, A. Alla, A. Martinez de Iillarduya and S. Muñoz-Guerra
Departament d’Enginyeria Química, ETSEIB
Universitat Politècnica de Catalunya, Barcelona, Spain

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.

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-d6. DSC experiments were performed at heating/cooling rates of 10 °C/min 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.

The H and 13C 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.

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 °C.

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 Tg. Both aliphatic and aromatic polyurethanes containing Is are semicrystalline polymers and maintain the crystal structure although the crystallinity is largely reduced.

Acknowledgements

Financial support given by MICINN with grant MAT-2009-14053-C02-01. The X-ray experiments have been performed at HASYLAB-DESY and have received funding from the European Community’s Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 226716.