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Carbohydrate-based aromatic polyesters: New products and processes

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Carbohydrate-based building blocks are rapidly increasing their presence in polyesters due to their easy accessibility, full sustainability and high capacity to keep or even improve the properties of traditional polymers.1 Dianhydro-1,4:3,6-D-glucitol (isosorbide)2 and 2,5-furandicarboxylic acid (FDCA)3 are two paradigmatic examples of widely used carbohydrate derived monomers that have attained commercial realization. Nevertheless there are still severe drawbacks that prevent a fully satisfactory exploitation of these compounds such as a restricted reactivity, too high sensitivity to heating, and a considerable propensity to give secondary reactions with negative consequences as discoloration or limitation in achieving high molecular weights. Bicyclic acetalized alditols and aldaric acids (BBA), e.g. 2,4:3,5-di-O-methylene-D-mannitol (Manx-OH) or 2,4:3,5-di-O-methylene-D-glucaric acid (Glux-COOH), are a new family of carbohydrate-based monomers that have been shown to be very suitable for the preparation of aromatic copolyesters with high Tg and noticeable biodegradability4. These compounds exert an enhancing effect on structure and thermal properties of poly(phthalate)s similar to isosorbide while their reactivity is significantly higher because primary hydroxyl groups are now involved in polycondensation. Although BBA have come from common carbohydrates such as mannitol and glucose, their relatively rather complicated synthesis is the main hindrance for their development at industrial scale. Polycondensation in the melt is the usual process applied for the synthesis of aromatic polyesters. On the contrary, ring-opening polymerization (ROP) is scarcely applied in spite that it allows using milder conditions and generates lesser amounts of byproducts. The difficult accessibility of the lactones required for doing ROP is doubtlessly the main reason for the minor relevance of this method. Nevertheless, cyclic oligofuranoates derived from FDCA are now accessible by a simple synthesis so a diversity of FDCA-based polyesters and random copolyesters can be readily prepared by ROP. The method has proven to be very efficient when assisted by either organometallic5 or enzymatic catalysis.6 The results presented in this communication open new prospective for the progress of polyesters and copolyesters containing cyclic carbohydrate-based units.

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