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**BIO-BASED AROMATIC POLYESTERS AND COPOLYESTERS BY RING
 OPENING POLYMERIZATION**

J. C. Morales-Huerta, A. Martínez-de-Illarduya, S. Muñoz-Guerra*

*Departament d'Enginyeria Química. Universitat Politècnica de Catalunya. 08028 Barcelona, Spain (34)934016680;
 sebastian.munoz@upc.edu*

In favour of a higher sustainability, bio-based polymers, in particular those derived from sugars, are currently receiving great attention as substitutes of the traditional polymers made from petrochemical monomers [1,2]. Poly(butylene terephthalate) (PBT) is an important industrial polyester that combines excellent thermal and mechanical properties with a high resistance to chemical attack. The synthesis of polyesters from renewable resources that are able to replace PBT is today a frontier topic in polymer field, and in this regards, poly(butylene 2,5-furandicarboxylate) (PBF) stands out as a firm candidate [3]. This polyester is usually prepared by melt polycondensation of 2,5-furandicarboxylic acid (FDCA) or its dimethyl ester with 1,4-butanediol, a process that requires reaction conditions so severe that occurrence of thermal degradation is difficult to prevent completely.

Polymerization of macrocyclic oligomers via entropically driven ring opening polymerization (ED-ROP) is widely considered as a suitable alternative to melt polycondensation. While the cyclic oligomers of butylene terephthalate, $c(BT)_n$, are well described in the literature, those made of butylene-2,5-furandicarboxylate, $c(BF)_n$ have not been studied until very recently [4,5]. In this work, the synthesis of both $c(BF)_n$ and $c(BT)_n$ has been performed using the high dilution cyclization technique and these cycles have been then used for the preparation of the homopolyesters PBF and PBT, as well as of a series of poly(butylene 2,5-furandicarboxylate-co-terephthalate) ($coPBF_xT_y$) with a wide range of compositions (Fig. 1). Results are compared with those obtained from similar copolyesters prepared by melt polycondensation, which have been recently reported [6].

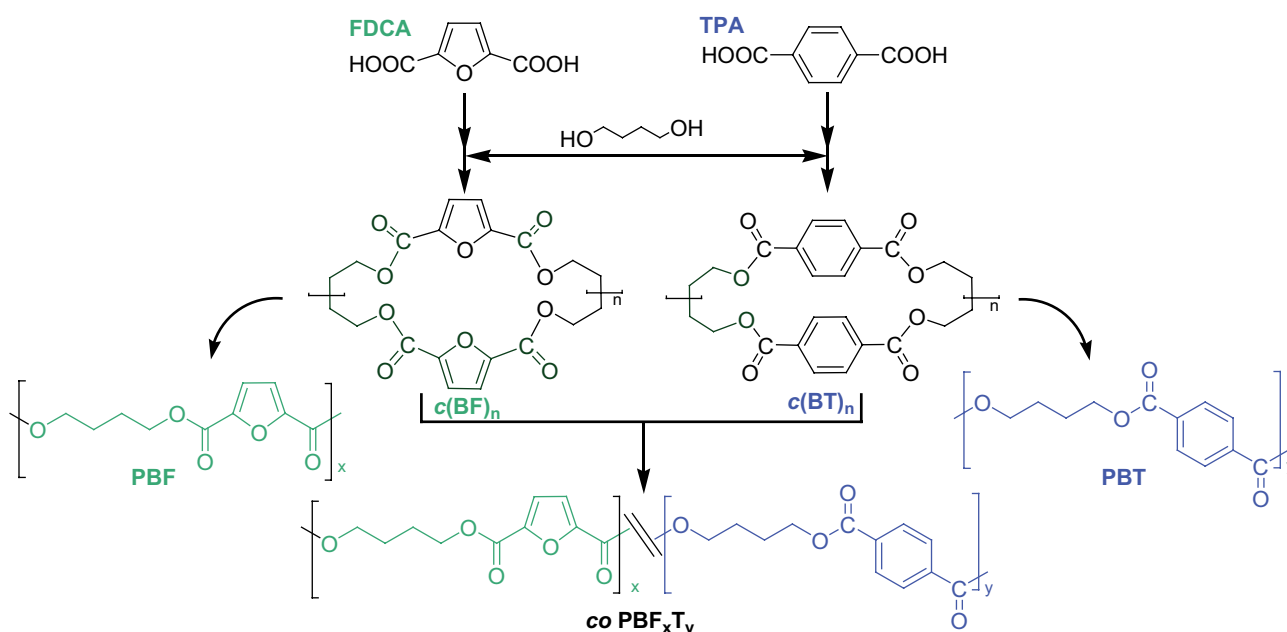


Fig.1. Synthetic route leading to aromatic homopolyesters and copolyesters via ROP of cyclic oligoesters.

Mixtures of cyclic oligomers containing from 2- to 4-mers, with the dimer as main product, were obtained from the respective dicarboxylic acid dichlorides by condensation with 1,4-butanediol in high diluted solutions. The oligomeric mixtures were polymerized in

the bulk by heating at temperatures around 240-250 °C for several hours in the presence of Sn(Oct)₂ as catalyst. The copolyesters were prepared by applying the same procedure to mixtures of c(BF)_n and c(BT)_n. The characteristics of the homopolyesters and copolyesters prepared by this method are collected in Table 1.

Table 1. Characteristics of PBF, PBT and co(PBF_xT_y) obtained via ROP.

Polyester	M_w^a (g·mol ⁻¹)	\bar{D}^a	T_g^b (°C)	T_m^c (°C)	ΔH_m^c (J·mol ⁻¹)	$^oT_d^d$ (°C)	$\max T_d^d$ (°C)
PBF	60,000	1.7	42	169	35	360	400
coPBF ₉₀ T ₁₀	58,000	1.9	35	157	33	337	400
coPBF ₈₀ T ₂₀	55,000	1.5	29	143	12	338	395
coPBF ₆₀ T ₄₀	65,000	1.4	32	135	1	348	394
coPBF ₅₀ T ₅₀	70,000	1.8	35	131	8	342	397
coPBF ₄₀ T ₆₀	69,000	1.8	39	155	11	357	398
coPBF ₂₀ T ₈₀	71,000	1.3	45	194	22	362	403
coPBF ₁₀ T ₉₀	75,000	1.4	50	207	31	367	410
PBT	79,000	1.7	66	227	52	375	408

^aWeight-average molecular weight and dispersity measured by GPC; ^bGlass-transition temperature measured by DSC; ^cMelting temperature and enthalpy measured by DSC; ^dOnset (5%) and maximum decomposition temperatures measured by TGA.

The homopolyester PBF was obtained with average molecular weights and properties comparable to that obtained by polycondensation as reported by different authors (see references 7-15 in [4]). The copolyesters coPBF_xT_y could be prepared with molecular weights within the 55,000-75,000 range and compositions very close to those used in their respective feeds. A detailed ¹³C NMR study revealed that all the copolyesters displayed a random microstructure and that such homogeneous distribution was adopted by the copolyesters since the early polycondensation stages.

The coPBF_xT_y copolyesters display properties ranging from those of PBF and PBT. All the copolyesters were semicrystalline with melting temperatures swinging between the two maxima corresponding to the parent PBT and PBF homopolyesters and falling to a minimum of 131 °C for the coPBF₅₀T₅₀ copolyester. A similar trend was observed for the glass transition temperature which reached the minimum value of 29 °C for the coPBF₈₀T₂₀ copolyester. This behaviour is similar to that reported in the literature for such copolyesters prepared by melt polycondensation. The application of the ROP methodology to the synthesis of copolyesters containing 2,5-furandicarboxylate units constitutes a valuable contribution to the inventory of aromatic copolyesters with increased sustainability.

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