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POLY(BUTYLENE 2,5-FURAN DICARBOXYLATE-*CO*-BUTYLENE SUCCINATE) *VIA* RING OPENING POLYMERIZATION

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Poly(butylene terephthalate) (PBT) is one of the most important polyesters used today as industrial thermoplastic. This aromatic polyester displays excellent thermal and mechanical properties but it is non-sustainable and practically insensitive to biodegradation. Furan-based polyesters, in particular poly(butylene 2,5-furandicarboxylate) (PBF), are new bio-based polymers that are considered appropriate to reduce these disadvantages. On the other hand, the aromatic copolyesters incorporating aliphatic and especially succinic units have been reported to be biodegradable materials of interest in packaging. Only two papers dealing with poly(butylene 2,5-furan dicarboxylate-*co*-butylene succinate) (PBF_xS_y) copolyesters have been found in the accessible literature [1,2]. In both cases the copolyesters were obtained by polycondensation in the melt using organometallic catalysts.

In this communication we wish to report on the synthesis of PBF_xS_y copolyesters by ring opening polymerization (ROP) using either organometallic catalysts or enzymes. The ROP of macrocyclic oligomers (MCOs) has been demonstrated to offer significant advantages over the traditional polycondensation method. The synthesis of MCOs of butylene succinate $c(BS)_n$ is known from long whereas MCOs of butylene 2,5-furandicarboxylate ($c(BF)_n$) have not been reported until very recently [3,4]. In this work, the synthesis of $c(BF)_n$ and $c(BS)_n$ has been performed using high dilution condensation (HDC) [3] and enzymatic cyclization [5], respectively. Mixtures of dimer to tetramer and dimer to nonamer were obtained for $c(BF)_n$ and $c(BS)_n$ respectively.

The PBF_xS_y copolyesters were prepared according to the scheme depicted in Fig.1. Mixtures of $c(BF)_n$ and $c(BS)_n$ with varying molar ratios were prepared and polymerized at 200 °C for 12 h using $Sn(Oct)_2$ or at 150 ºC for 24 h in the presence of CALB. The properties of the resulting polyesters are summarized in Table 1.

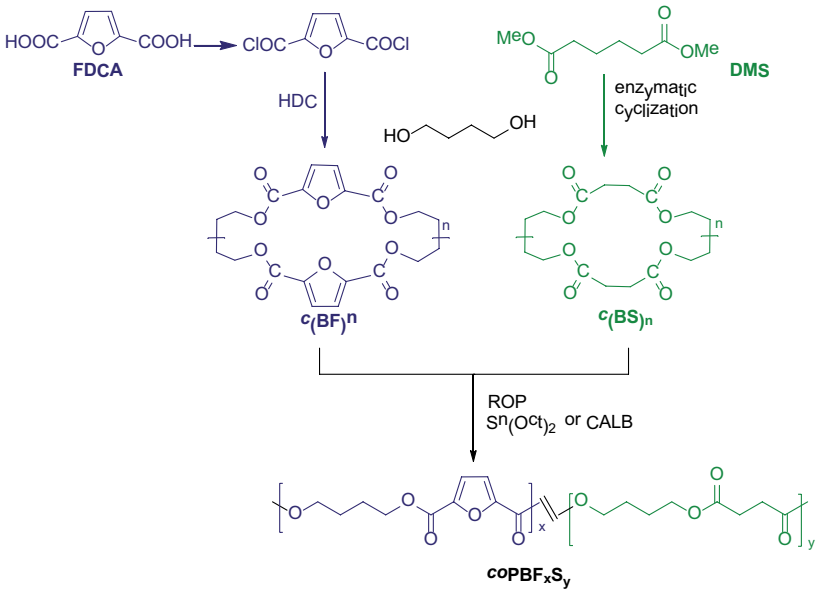

Fig. 1. Synthesis of *co*PBF_xS_y by ROP of $c(BF)_n$ and $c(BS)_n$

Table 1. Molecular weight and thermal properties of *co*PBF$_x$S$_y$ copolyesters obtained via ROP assisted by either organometallic or enzymatic catalysts.

Molecular weight			Thermal properties											
Copolyester	M_w [a] (kg·mol^{-1})		Đ[a]		T_g (°C)		T_m (°C)		H_m (J·mol^{-1})		$T_{d\ 5\%}$ (°C)		$T_{d\ max}$ (°C)	
	S[b]	C[c]	S[b]	C[c]	S[b]	C[c]	S[b]	C[c]	S[b]	C[c]	S[b]	C[c]	S[b]	C[c]
PBF	65	-	2.0	-	42	-	170	-	40	-	370	-	400	-
*co*PBF$_{90}$S$_{10}$	64	-	1.8	-	28	-	166	-	38	-	350	-	395	-
*co*PBF$_{80}$S$_{20}$	66	21	1.8	1.3	23	20	146	140	33	34	350	348	395	396
*co*PBF$_{60}$S$_{40}$	62	23	1.9	1.3	7	-5	114	126	12	15	343	342	397	397
*co*PBF$_{50}$S$_{50}$	50	45	1.8	1.6	-1	-6	95	86	11	21	349	341	400	399
*co*PBF$_{40}$S$_{60}$	56	46	2.0	1.7	-13	-20	60	72	5	20	347	344	399	399
*co*PBF$_{20}$S$_{80}$	43	46	1.9	1.5	-23	-23	90	93	55	61	343	338	399	400
*co*PBF$_{10}$S$_{90}$	53	40	1.9	1.5	-23	-25	100	102	71	80	340	337	401	400
PBS	49	46	2.0	1.4	-30	-30	112	112	106	112	350	348	399	398

[a] Measured by GPC.
[b] Polymers obtained using Sn(Oct)2 as catalyst.
c Polymers obtained using CALB as catalyst.

The M_w of the copolyesters obtained using Sn(Oct)$_2$ were in the range of 43 to 65 kg·mol^{-1} whereas those synthesized with the concourse of CALB oscillated between 21 and 46 kg·mol^{-1}. The differences observed in molecular weight should be related to the temperature of reaction used in each case, which must be 150 ºC as maximum in the case of the enzymatic ROP due to limitations in the stability of the enzyme [6]. ^{1}H and ^{13}C NMR analysis revealed that the copolymers had a composition in BF and BS units close to that of the mixtures used for feeding the polymerization reaction, and also that a random microstructure is present for whichever procedure is used for the synthesis.

The properties of the homopolyesters and copolyesters prepared by ROP were almost coincident to those reported in the literature for the same polymers prepared by melt polycondensation [1,2]. Melting and glass transition temperatures of the copolyesters are strongly depending on composition, the first one following approximately a parabolic trend with the maximum values corresponding to PBS and PBF. The minimum value for both melting point and enthalpy was displayed by the *co*PBF$_{40}$S$_{60}$ copolyester. The crystallinity in the copolyesters decreased with copolymerization up to values near 50%. On the other hand, the copolyesters with a content near to 90% in either furanic or succinic units displayed an increased crystallinity.

The conclusion is that the ROP methodology, and particularly when enzymatic catalysis is used, may be considered an eco-friendly alternative for the preparation of furan-aliphatic copolyesters.

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