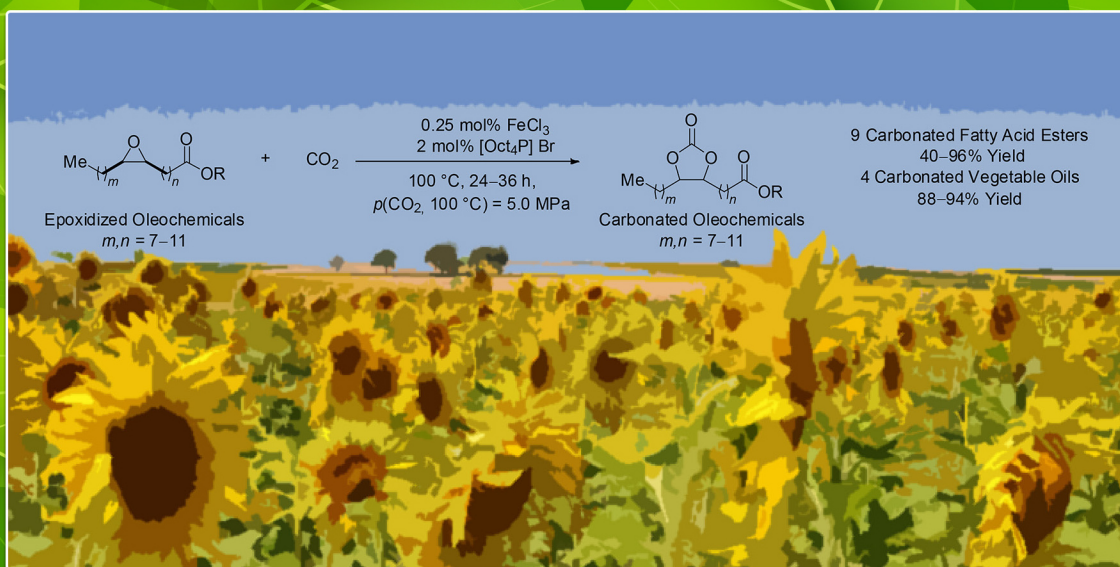
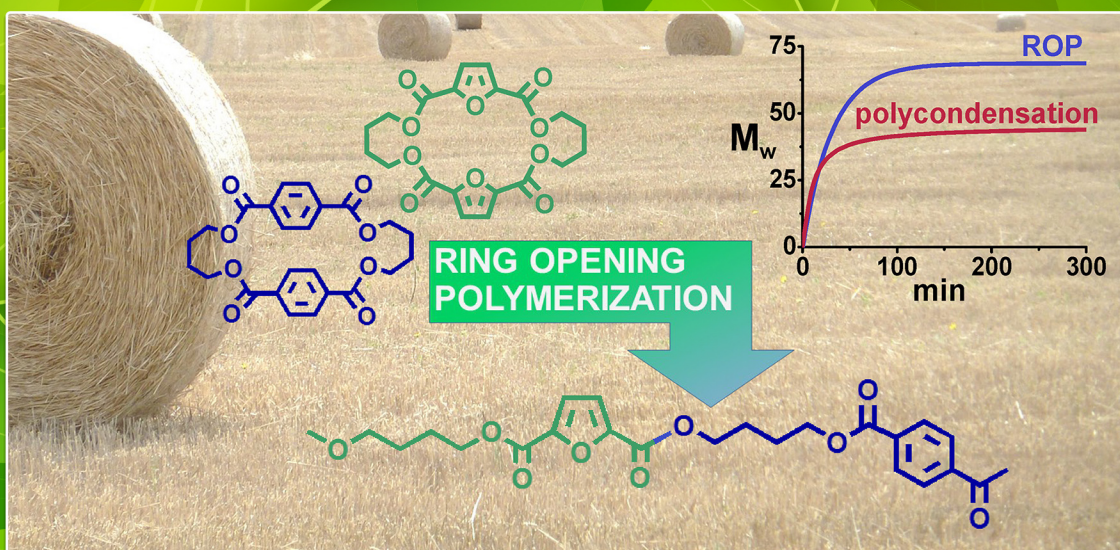


ACS Sustainable Chemistry & Engineering

September 2016 | Volume 4 Number 9

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Sustainable Aromatic Copolyesters via Ring Opening Polymerization: Poly(butylene 2,5-furandicarboxylate-co-terephthalate)s

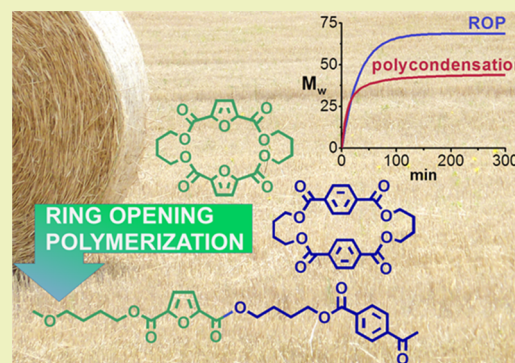
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Supporting Information

ABSTRACT: A series of poly(butylene 2,5-furandicarboxylate-co-terephthalate) copolyesters $coPBF_xT_y$, covering the whole range of compositions has been prepared via ring opening polymerization (ROP). Cyclic oligomers of butylene 2,5-furandicarboxylate $c(BF)_n$ and butylene terephthalate $c(BT)_n$, both mainly consisting of a mixture of dimer, trimer, and tetramer species, were synthesized by the high dilution condensation method. Random copolyesters with the targeted compositions and weight-average molecular weights within the 55 000–80 000 $g \cdot mol^{-1}$ range were obtained by ROP of $c(BF)_n/c(BT)_n$ mixtures in periods of time much shorter than those required by melt polycondensation. The thermal properties of these copolyesters were consistent with their compositions and comparable to their isocompositional analogs obtained by polycondensation. A comparative kinetics study of the isothermal crystallization of the homopolyesters and copolyesters differing in composition revealed that the presence of the 2,5-furandicarboxylate units decreased the crystallization rate of PBT. Nevertheless, $coPBF_xT_y$ copolyesters with moderate contents in BF units were still able to crystallize rapidly from the melt.

KEYWORDS: Biobased aromatic copolyesters, FDCA-based aromatic copolyesters, FDCA cyclic oligomer, Furanic copolyesters by ROP, Thermal properties of furanic copolyesters



INTRODUCTION

The attention given to sustainability in polymer science is continuously growing, and the use of renewable resources in industrial polymer synthesis is rapidly increasing in parallel.^{1–4} This is mainly due to the fact that society is becoming more and more concerned with environmental problems associated with fossil fuel CO₂ emissions. Also the announced scarcity of petroleum in a not very far future and the difficulty for controlling the market prices of its derivatives are additional factors contributing to the increasing interest for sustainable polymers. As a consequence chemicals coming from naturally occurring compounds of very different natures are incessantly proposed to substitute petrochemicals in the production of industrial polymers.^{5–7}

Among the different renewable feedstocks that can be used for building suitable monomers, carbohydrates are distinguished by their easy availability and tremendous structure diversity. The potential of sugar resources in the manufacture of sustainable polymers, and in particular of polycondensation polymers, has been recently reviewed by Galbis et al.⁸ A wide variety of difunctionalized sugar derivatives has been explored in these last years for the synthesis of polycondensates that includes polyesters, polyamides, polyurethanes, and polycarbonates among others.^{9–14} In this context, aromatic polyesters deserve specific attention. Poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) are commercial well-known thermoplastics that are produced in huge amounts from

terephthalic acid (TPA), a compound of petrochemical origin for which several green alternative syntheses are currently under consideration.^{15–17} Nevertheless, partial or even full substitution of TPA by other diacids derived from carbohydrates has been also an extensively investigated approach. Among them, 2,5-furandicarboxylic acid (FDCA) has attained a privileged position due to its aromatic character and easy accessibility. The enormous potential of this compound in the production of aromatic polyesters able to replace PET and PBT has been rigorously reviewed by Sousa et al.¹⁸ To date a wide variety of poly(alkylene furanoate)s, both homopolyesters and copolyesters, have been reported, although polycondensation in the melt catalyzed by organometallics has been almost invariably the method used for their synthesis.^{19–23}

Ring opening polymerization (ROP) of lactones is an interesting technique for the synthesis of polyesters that is currently used for the production of several industrial aliphatic polyesters, i.e. polyglycolic and polylactic acids,²⁴ and that has been demonstrated to be also suitable for the synthesis of aromatic polyesters and copolyesters.^{25–28} This method offers as distinguishing advantages the possibility of using milder polymerization conditions and no generation of side-products in the polymerization reaction. Moreover the method would

Received: June 11, 2016

Revised: July 7, 2016

Published: July 11, 2016

attain particular interest regarding chemical recycling in the case that the feed lactones were accessible by thermal depolymerization of polyester wastes. The synthesis of both poly(ethylene 2,5-furandicarboxylate) (PEF)²⁹ and poly(butylene 2,5-furandicarboxylate) (PBF)^{29,30} by ROP of their respective cyclic oligomers has been recently reported. The polyfuranates thus obtained were perfectly comparable in molecular weights and thermal properties to those prepared by melt polycondensation but they were exempted of the chain defects commonly present in polycondensates.

In this paper we wish to report on the synthesis of poly(butylene 2,5-furandicarboxylate-co-terephthalate) copolyesters, abbreviated *coPBF_xT_y*, by ROP of mixtures of cyclic oligo(butylene 2,5-furandicarboxylate)s and oligo(butylene terephthalate)s, initiated by Sn(Oct)₂. A series of *coPBF_xT_y* covering the whole range of BF to BT ratios has been prepared and synthesis results are compared to those obtained by melt polycondensation. Zhou et al. published in 2015³¹ an extensive and systematic study of several series of aromatic copolyesters derived from FDCA and TPA and different linear alkanediols including 1,4-butanediol. The method of synthesis used therein was polycondensation in the melt with tetrabutyl titanate as catalyst. Data provided by these authors on the PBF/PBT copolyesters have been taken in this work as reference for evaluating the suitability of the ROP method for producing furan-based aromatic copolyesters.

EXPERIMENTAL SECTION

Materials. 2,5-Furandicarboxylic acid (FDCA, >98% purity) was purchased from Satachem. 1,4-Butanediol (BD, 99%), terephthaloyl chloride (TPA-Cl₂, 98%), dimethyl terephthalate (DMT, 99%), as well as catalysts, diazabicyclo[2.2.2] octane (DABCO, 99%) and tin(II) ethylhexanoate (Sn(Oct)₂, 99%), were purchased from Sigma-Aldrich Co. TPA-Cl₂ and DABCO were purified by sublimation before using. Antioxidants Irganox 1010 and Irgafos 126 were gifts from BASF. All solvents were of high-purity grade and used as received with the exception of dichloromethane (DCM) and tetrahydrofuran (THF) that were dried on 3 Å-molecular sieves.

Measurements. ¹H and ¹³C NMR spectra were recorded on a Bruker AMX-300 spectrometer at 25 °C, operating at 300.1 and 75.5 MHz, respectively. For NMR analysis, monomers and intermediate compounds were dissolved in deuterated chloroform (CDCl₃) and polymers in a mixture of CDCl₃ and trifluoroacetic acid (TFA) (8:1, v/v), and spectra were internally referenced to tetramethylsilane (TMS). About 10 and 50 mg of sample in 1 mL of solvent were used for ¹H and ¹³C NMR, respectively. Sixty-four scans were recorded for ¹H NMR and between 1000 and 10 000 scans for ¹³C NMR. High-performance liquid chromatography (HPLC) analysis was performed at 25 °C in a Waters apparatus equipped with a UV detector of Applied Biosystems operating at 254 nm wavelength, and a Scharlau Science column (Si60, 5 μm; 250 mm × 4.6 mm). Cyclic oligomers (1 mg) were dissolved in CHCl₃ (1 mL) and eluted with the mixture hexane/1,4-dioxane 70/30 (v/v) at a flow rate of 1.0 mL·min⁻¹. Molecular weight analysis was performed by GPC on a Waters equipment provided with RI and UV detectors. 100 μL of 0.1% (w/v) sample solution were injected and chromatographed with a flow of 0.5 mL·min⁻¹ using 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as solvent. HRSE and HR2 Waters linear Styragel columns (7.8 mm × 300 mm, pore size 10³–10⁴ Å) packed with cross-linked polystyrene and protected with a precolumn were used. Molar mass average and distributions were calculated against PMMA standards. Intrinsic viscosities of polyesters were measured in solution of dichloroacetic acid (DCA) using an Ubbelohde viscometer thermostated at 25 ± 0.1 °C.

The thermal behavior of cyclic compounds and polymers were examined by differential scanning calorimetry (DSC), using a Perking-

Elmer Pyris apparatus. The thermograms were obtained from 4 to 6 mg samples at heating and cooling rates of 10 °C·min⁻¹ from 0 to 250 °C under a nitrogen flow of 20 mL·min⁻¹. Indium and zinc were used as standards for temperature and enthalpy calibration. The glass transition temperature (*T_g*) was taken as the inflection point of the heating DSC traces recorded at 20 °C·min⁻¹ from melt-quenched samples, and the melting temperature (*T_m*) was taken as the maximum of the endothermic peak appearing on heating traces. Thermogravimetric analysis were performed on a Mettler-Toledo TGA/DSC 1 Star System under a nitrogen flow of 20 mL·min⁻¹ at a heating rate of 10 °C·min⁻¹ and within a temperature range of 30 to 600 °C. X-ray diffraction patterns were recorded on the PANalytical X'Pert PRO MPD θ/θ diffractometer using the Cu K α radiation of wavelength 0.1542 nm from powdered samples coming directly from synthesis. Micrographs were recorded using an Olimpus BX 51 polarizing optical microscope with a Linkam THMS 600 stage attached. For observation, 10 mg of each sample were dissolved in 1 mL of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) in a vial and aliquots of 0.2 mL were slowly evaporated on a glass slide.

Synthesis of Cyclic Oligomers. The synthesis of both *c*(BF)_{*n*} and *c*(BT)_{*n*} was carried out by applying the well-known high-dilution condensation method (HDC).³² *c*(BF)_{*n*} were prepared by reaction of 2,5-furandicarboxylic dichloride (FDCA-Cl₂) with BD following the procedure previously reported by us.²⁹ *c*(BT)_{*n*} were prepared from commercial TPA-Cl₂ and BD according to the work of Brunelle et al.³² Linear oligomers invariably present in the cycling reaction product were removed by chromatography on a short column of silica gel using a cold mixture of DCM/acetone 90/10 (v/v) as eluent. This fraction amounted around 10% of the total product according to both HPLC and ¹H NMR measurements. The purity of the cyclic fractions was assessed by NMR. *c*(BF)_{*n*}. Yield: 67%. ¹H NMR (δ ppm, CDCl₃, 300 MHz): 7.23, 7.24, 7.25 (3s, 2H, C=C-H), 4.40 (m, 4H, COOCH₂), 1.92, 1.99 (2m, 4H, COOCH₂CH₂), ¹³C NMR (δ ppm, CDCl₃, 75.5 MHz): 158.1, 157.9, 146.7, 146.5, 118.7, 118.6, 118.5, 65.0, 64.8, 25.4. *c*(BT)_{*n*}. Yield: 80%. ¹H NMR (δ ppm, CDCl₃, 300 MHz): 8.10, 8.07, 7.87 (3s, 4H, Ar-H), 4.42 (m, 4H, COOCH₂), 2.05, 1.96 (2m, 4H, COOCH₂CH₂), ¹³C NMR (δ ppm, CDCl₃, 75.5 MHz): 165.7, 165.6, 165.5, 134.0, 133.9, 129.5, 129.4, 65.0, 64.8, 64.6, 25.9, 25.6, 25.5. These spectra are available in the Supporting Information (SI; Figures S1 and S2).

Synthesis of Copolyesters. Polycondensation. For comparative purposes, the copolyester *coPBF₅₀T₅₀* was synthesized by polycondensation in the melt from an equimolar mixture of the dimethyl esters of FDCA and TPA following the two-step procedure reported in the literature.³³ Dimethyl 2,5-furandicarboxylate (DMFDCA) was obtained by Fischer esterification of FDCA with methanol in the presence of small amounts of HCl as reported by Gubbels et al.³⁴ For polymerization, a three-necked round-bottom flask provided with stirring was charged with 10.8 mmol of each diester, i.e., DMFDCA (2 g) and DMT (2.1 g), and 23.8 mol of BD (4.3 g). Antioxidants Irganox 1010 and Irgafos 126 (0.1% and 0.3% (w/w) respectively) and 0.5% (mol/mol) of Sn(Oct)₂ as catalyst were then added. The first step was carried out at 190 °C for 2 h and in the second step, the temperature was raised to 250 °C, and the reaction mass left under stirring for 5 h under reduced pressure (0.03–0.06 mbar). To follow the evolution of the molecular weight, aliquots were removed at scheduled periods of time from 20 to 300 min and analyzed by GPC. The final reaction product was analyzed by NMR. *coPBF₅₀T₅₀*. ¹H NMR (δ ppm, CDCl₃/TFA (8:1), 300 MHz): 8.12 (s, 2H, Ar-H), 7.35 (s, 1H, C=C-H), 4.50 (m, 4H, COOCH₂), 2.0 (m, 4H, COOCH₂CH₂), ¹³C NMR (δ ppm, CDCl₃/TFA (8:1), 75.5 MHz): 168.2, 158.1, 157.9, 146.7, 146.5, 134.0, 130.2, 120.7, 66.7, 66.6, 66.5, 66.4, 25.4, 25.2, 25.1, 25.0.

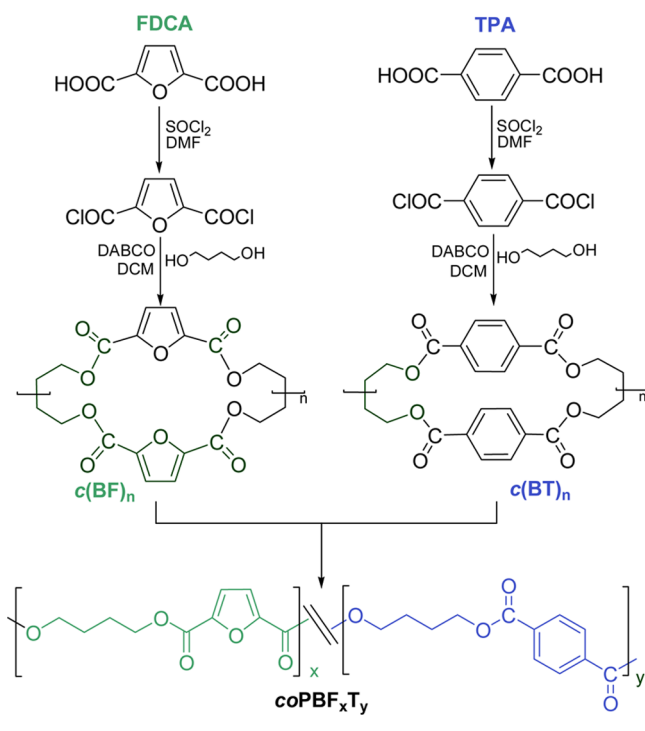
Ring Opening Polymerization (ROP). Mixtures of *c*(BF)_{*n*} and *c*(BT)_{*n*} with selected molar ratios were polymerized following the procedure described previously by us for the synthesis of PBF and PEF homopolyesters.²⁹ In brief, 25 mmol of the mixture of the two cyclic fractions at the chosen ratio along with 0.5 mol % of Sn(Oct)₂ were dissolved in 10 mL of DCM and slowly evaporated to dryness at room temperature in a three-necked round-bottom flask. The mixture was

then heated at temperatures between 200 and 250 °C depending on composition and left to react for 3 h under stirring and under a stream of nitrogen at atmospheric pressure. The reaction product was analyzed by GPC and NMR. For comparison purposes, the copolymerization reaction leading to $coPBF_{50}T_{50}$ was conducted at both 230 and 250 °C, and aliquots of the reaction mass were collected for periods of time similar to those scheduled for polycondensation, and analyzed by GPC.

RESULTS AND DISCUSSION

Synthesis. The route of synthesis followed in this work to produce the copolyesters $coPBF_xT_y$ is depicted in Scheme 1.

Scheme 1. Synthetic Route via ROP Towards Aromatic Copolyesters Containing Butylene 2,5-Furandicarboxylate and Butylene Terephthalate Units



First the cyclic oligoesters $c(BF)_n$ and $c(BT)_n$ were prepared by cyclization of the mixture of 1,4-butanediol and the respective diacid dichloride following the high dilution method reported by Brunelle et al.³² The composition of the cyclic fractions were determined by HPLC-MALDI-Tof combined analysis and showed to be a mixture of dimer, trimer and tetramer in both cases (see Figure S3 in the SI). According to the original procedure, DCM was the solvent used in these cyclization reactions. In order to check if the sustainability of the process could be increased, the possibility of using a greener solvent as THF instead of DCM was explored. The synthesis of the BF cyclic oligomers following the same protocol but using THF as solvent produced a mixture also enriched in dimer to tetramer cycles but with a significantly different composition and a higher proportion in linear species (see Figure S4 in the SI). For polymerization, mixtures of the two cyclic fractions at molar ratios covering the whole range of proportions of furanoate to terephthalate units in the copolyester, in addition to the both isolated fractions leading to the parent PBF and PBT homopolyesters, were made to react at 200–250 °C in the presence of small amounts of $Sn(Oct)_2$.

The constitution and composition of the ensuing copolyesters were ascertained by 1H and ^{13}C NMR spectroscopy, which differentiated clearly the aromatic proton and carbon signals arising from the 2,5-furandicarboxylate and terephthalate units and did not display detectable signals arising from other structures than those expected for the constitution of the copolyester. For illustrative purposes, the spectra recorded from $coPBF_{50}T_{50}$ are reproduced in Figure 1, and the spectra of the remaining whole series are accessible in the SI (Figure S5). The results attained in the synthesis of $coPBF_xT_y$ copolyesters are collected in Table 1. Yields were over 90% in all cases and the compositions of the copolyesters were practically the same as those of the cyclic oligomers mixtures used for feeding with deviations rarely overpassing 5%.

The advance of the reaction in the polymerization of the equimolar mixture of $c(BF)_n$ and $c(BT)_n$ was followed by GPC, and the plots showing the evolution of molecular weight with time at two different reaction temperatures, i.e. 230 and 250 °C, are depicted in Figure 2. These plots reveal that no significant differences are appreciated in the reaction rate for the two chosen temperatures and that polymer growing ceased after 1 h of reaction. A clearly different profile was generated when the same study was carried out for the polycondensation reaction of BD with an equimolar mixture of the dimethyl esters of FDCA and TPA. In this case polymerization seems to slow down also after 1 h, but the molecular weight of the ensuing copolyester was now much lower with a value of \bar{M}_w around 40 000 $g \cdot mol^{-1}$ against the near 70 000 $g \cdot mol^{-1}$ attained by ROP. It is worthy to remark that these results prove not only the suitability of ROP for producing high molecular weight copolyesters containing furanoate units but also that they may be obtained by this method in shorter times than by polycondensation.

The microstructure of the copolymers was examined by ^{13}C NMR. As it is shown in Figure 3, the ^{13}C resonance signal appearing within the 65.5–67.5 ppm range and arising from the α -carbon of the butylene segment was sensitive to sequence effects at the level of dyads. Four peaks are therefore present in the spectra of the copolyesters which correspond to the four feasible dyad arrangements of the furanoate and terephthalate units (FBF, FBT, TBF, TBT) along the polymer chain. Integration of these peaks and application of equations reported for sequence determination,³⁵ which takes into account the copolyester composition, led to determine the number-average sequence lengths (n) and the degree of randomness (R) of $coPBF_xT_y$. Results are given in Table 1 and indicate that the arrangement of the two aromatic units in the copolyesters is near to random whichever is their composition. The homogeneous distribution of the BF and BT units attained in the copolyesters could be taken as indicative of the similar relative reactivity displayed by the two monomeric cyclic species when they are made to react via ROP. This interpretation is however questionable since the occurrence of transesterification reactions, which would lead to homogenization of the initially blocky copolyester, is very likely occurring at the temperatures applied for polymerization.

Thermal Properties. The data afforded by TGA and DSC analyses of $coPBF_xT_y$ are collected in Table 2. These data revealed that the basis thermal behavior of these copolyesters obtained by ROP is similar to that displayed by those prepared by polycondensation in the melt. The reference we have used for comparison is the paper recently published by Zhou et al.,³¹ which is the only one describing these copolyesters that may be

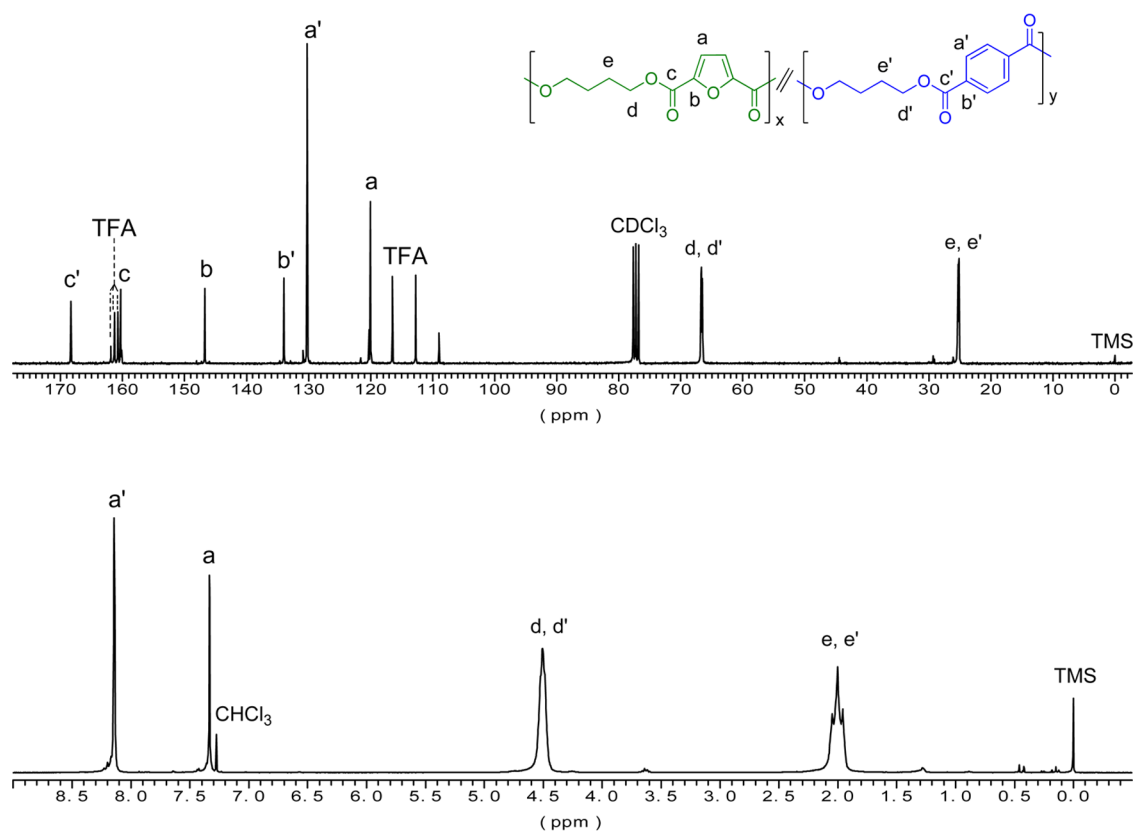


Figure 1. ^{13}C (top) and ^1H NMR (bottom) spectra of $\text{coPBF}_{50}\text{T}_{50}$.

Table 1. Synthesis Results for coPBF_xT_y Copolymers Obtained via ROP

copolyester	yield (%)	$x_{\text{BF}}/y_{\text{BT}}^a$ (mol/mol)	molecular weight ^b		dyad content (mol %) ^c			sequence length ^d		R^d
			\bar{M}_w	D	FBF	FBT + TBF	TBT	n_{BF}	n_{BT}	
PBF	90	100/0	60000	1.65						
$\text{coPBF}_{90}\text{T}_{10}$	92	88/12	58000	1.90	74.1	25.8	1.2	6.90	1.09	1.05
$\text{coPBF}_{80}\text{T}_{20}$	91	77/23	55000	1.54	57.3	37.3	5.4	4.06	1.29	1.02
$\text{coPBF}_{60}\text{T}_{40}$	93	59/42	65000	1.40	34.9	47.3	17.8	2.47	1.75	0.97
$\text{coPBF}_{50}\text{T}_{50}$	93	52/48	70000	1.75	30.1	36.6	34.0	1.98	2.05	1.00
$\text{coPBF}_{40}\text{T}_{60}$	92	41/59	69000	1.80	24.3	49.7	26.0	1.65	2.44	1.02
$\text{coPBF}_{20}\text{T}_{80}$	94	21/79	71000	1.30	16.5	47.9	35.5	1.31	5.36	0.95
$\text{coPBF}_{10}\text{T}_{90}$	94	11/89	75000	1.43	5.5	29.8	64.7	1.17	11.1	0.95
PBT	95	0/100	79000	1.67						

^aMeasured by ^1H NMR. ^bWeight-average molecular weight in $\text{g}\cdot\text{mol}^{-1}$ and dispersity determined by GPC. ^cDetermined by deconvolution of the ^{13}C NMR peaks appearing in the 67.0–66.5 ppm region. ^dNumber-average sequence lengths and degree of randomness (R) calculated according to the literature.³⁵

found by now in the accessible literature. However, it must be noted that molecular weights up to $500\,000\ \text{g}\cdot\text{mol}^{-1}$ for furan containing polyesters were obtained by these authors, which are indeed astonishing values without precedent in the available literature of polyesters made by polycondensation.

The TGA traces recorded from the whole series together with their derivative curves are comparatively depicted in Figure 4. Both the onset ($^{\circ}\text{T}_d$) and maximum degradation rate ($^{\text{max}}\text{T}_d$) temperatures of PBT decreased with the incorporation of BF units but the decay is not so large as to impair the furanoate-terephthalate copolyesters for thermal processing. In fact, onset temperatures measured for 5% of mass loss were above $330\ ^{\circ}\text{C}$ and massive decompositions started around $400\ ^{\circ}\text{C}$ and proceeded along one main decomposition step. The residue left after heating at $600\ ^{\circ}\text{C}$ was about 4–7% for the

whole series. It should be noticed that variations in decomposition temperatures with composition do not follow a consistent trend but they oscillate up and down with some values overpassing those of PBT and PBF. $^{\circ}\text{T}_d$ display deviations from PBT up to near $40\ ^{\circ}\text{C}$ which must be attributed to the destabilizing effect of the furanic structure. On the contrary, differences in $^{\text{max}}\text{T}_d$ are hardly greater than $10\ ^{\circ}\text{C}$, a low deviation that cannot be discarded to be due to experimental error.

In order to evaluate the influence of composition on crystallinity and melting behavior of copolyesters, a comparative DSC study was carried out on the whole series including the two parent homopolyesters. The DSC traces registered at heating from pristine samples of coPBF_xT_y recovered from the reaction mass after cooling but without any further treatment

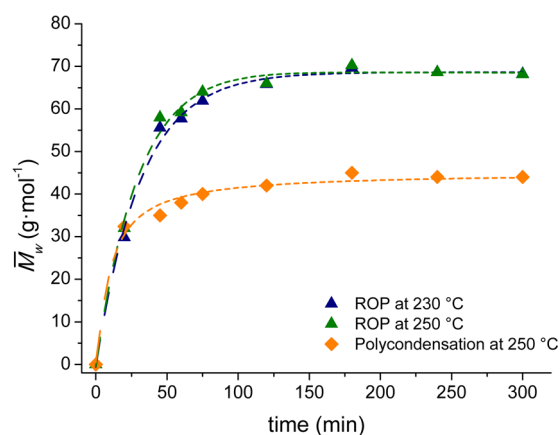


Figure 2. Evolution in \bar{M}_w of $\text{coPBF}_{50}\text{T}_{50}$ produced by ROP and by melt polycondensation.

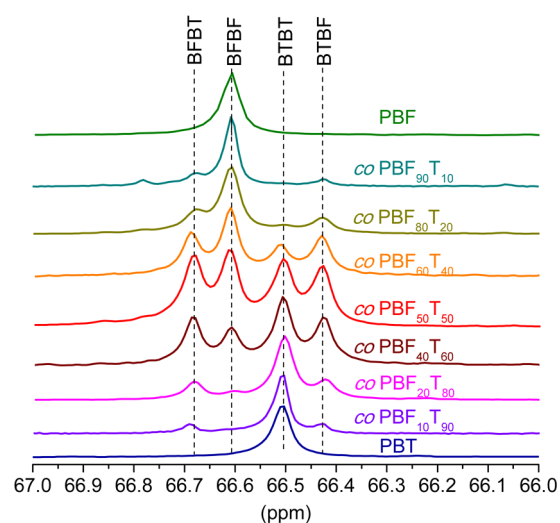


Figure 3. Enlarged ^{13}C NMR spectra (65.5–67.5 ppm region) of coPBF_xT_y obtained by ROP.

are depicted in Figure 5. The melting parameters measured on these thermograms are listed in Table 2. The trend followed by both T_m and ΔH_m along the coPBF_xT_y series becomes clearly apparent when these parameters are plotted against copolyester composition as it is shown in Figure 6a. All copolyesters gave traces displaying melting peaks at temperatures that are situated

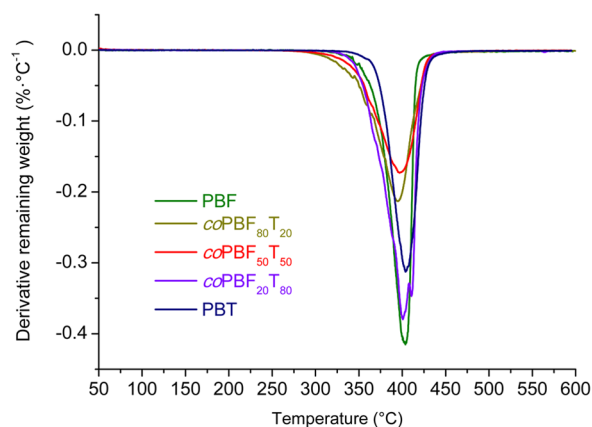
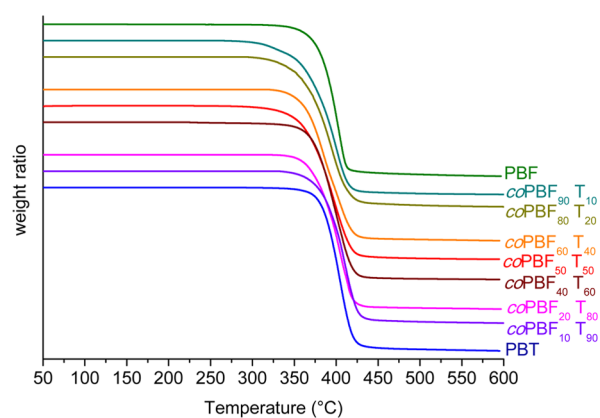


Figure 4. TGA analysis of coPBF_xT_y . (top) TGA traces registered under inert atmosphere. (bottom) Selected TGA derivative curves showing the main maximum rate degradation peaks.

between or below the T_m of the two parent homopolyesters (PBF 165 °C and PBT 227 °C). Exceptionally, the copolyester containing 90% of BF displays a cold crystallization peak in spite that the thermal history is the same for the whole series. A similar behavior was reported by Zhou et al.³¹ The melting enthalpy was also diminished by copolymerization to the point that copolyesters with nearly equilibrated compositions in the two aromatic counterparts, i.e. between 40 and 60%, displayed hardly perceivable crystallinities. Apparently the incorporation of BF units in the PBT chain gives rise to a decreasing in both stability and amount of crystal phase.

Table 2. Thermal Properties and Crystallizability of coPBF_xT_y Copolyesters Prepared via ROP

copolyester	DSC											
	TGA				first heating		second heating		crystallization kinetics			
	T_d^a (°C)	$\text{max}T_d$ (°C)	R_w (%)	T_g (°C)	T_m (°C)	ΔH (J·mol ⁻¹)	T_m (°C)	ΔH (J·mol ⁻¹)	T_c (°C)	n^b	$\ln K^b$	$t_{1/2}$ (min)
PBF	360	400	6	42	165	35	165	35	146	2.2	-4.42	6.91
$\text{coPBF}_{90}\text{T}_{10}$	337	400	7	35	157	33	155	5				
$\text{coPBF}_{80}\text{T}_{20}$	338	395	6	29	143	12	140	1				
$\text{coPBF}_{60}\text{T}_{40}$	348	394	7	32	135	1						
$\text{coPBF}_{50}\text{T}_{50}$	342	397	6	35	132	8	138	2				
$\text{coPBF}_{40}\text{T}_{60}$	357	398	4	39	155	11	155	11				
$\text{coPBF}_{20}\text{T}_{80}$	362	403	5	45	194	22	194	25	175	2.7	-4.46	5.12
$\text{coPBF}_{10}\text{T}_{90}$	367	410	6	50	207	31	205	32	186	2.7	-3.02	3.72
PBT	375	408	5	51	227	52	223	39	204	2.8	-2.42	2.72

^a T_d obtained at 5% of weight lost. ^bAvrami parameters.

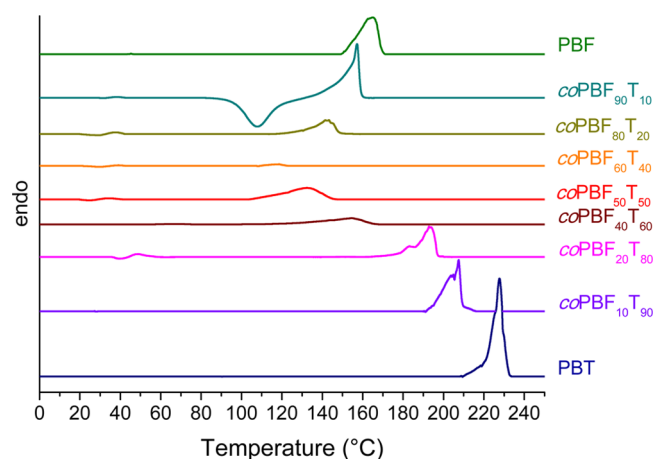


Figure 5. DSC traces of pristine samples of $coPBF_xT_y$ registered at heating in the 0–250 °C interval.

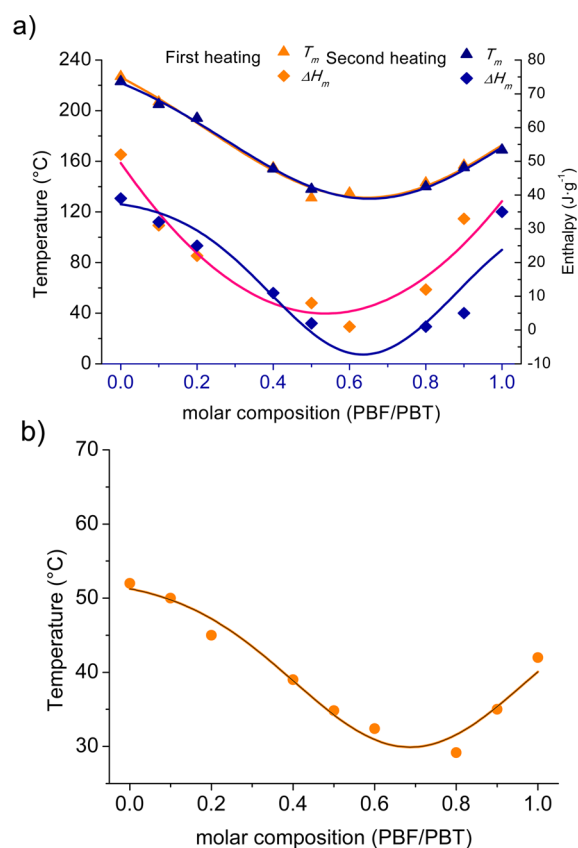


Figure 6. Variation of T_m (a) and T_g (b) in the $coPBF_xT_y$ copolyesters as a function of the molar composition.

The glass-transition temperatures were measured on samples that were previously quenched for fully repressing crystallinity. As it happens with T_m and according to expectations, T_g values were also found to decrease when BT units were replaced by the BF ones. The trend followed by T_g of $coPBF_xT_y$ copolyesters along the whole range of compositions is clearly evidenced in the plot depicted in Figure 6b. Although the decrease observed in T_g respect to PBT is considerable, the values displayed are still high enough as to allow the copolyester to retain satisfactory mechanical properties. It should be noted in this regard that replacement of terephthalate units in poly(alkylene terephthalates) by biobased units is

certainly a big challenge provided that their basic properties have to be retained. To our knowledge only a couple of cases, both of them based on the use of bicyclic glucose-based diacids, have been reported as able to render biobased polyesters with properties comparable to those displayed by the parent terephthalates.^{36,37}

Crystallinity and Crystallizability. Polymer crystallizability, understood as the ability of a polymer to adopt the crystalline state upon cooling from the melt, is a prime property of the material regarding its suitability to be used as thermoplastic for thermal processing. This property becomes particularly important in the case of PBT given its extensive utilization in injection molding. In fact, the capacity of PBT to develop a considerable degree of crystallinity in a very short cooling time is a distinguishing feature of PBT that makes it the material of choice in a good number of applications. The effect that the total or partial replacement of terephthalate by furanoate units exerts on the crystallizability of PBT is therefore an issue that deserves detailed attention. Accordingly, a preliminary crystallization study of $coPBF_xT_y$ copolyesters has been carried out in this work.

First the copolyesters were subjected to X-ray diffraction in order to ascertain their crystallinities and to get an idea of what crystal structure is adopted in each case. The powder WAXS profiles obtained from a representative assortment of polyesters are depicted in Figure 7. The profile produced by PBT is the

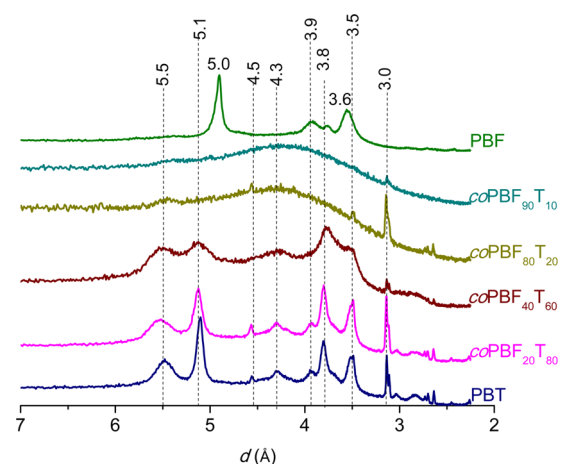


Figure 7. Powder X-ray diffraction profiles of PBF, PBT, and $coPBF_xT_y$. Main spacings indicated in angstroms.

familiar one displaying the well-defined peaks with spacings and intensities characteristic of the monoclinic structure adopted by the α -phase of this polyester when crystallized from the melt under unstrained conditions.³⁸ As expected, a clearly different profile arose from PBF with three main reflections at approximately 5.0, 3.9, and 3.5 Å indicates that a different crystal structure is adopted in this case. To our knowledge the crystal structure of PBF has not been determined yet. The scattering produced by the copolyesters was clearly depending on composition with the pattern of PBT remaining clearly perceivable up to 40% contents in BF units but vanishing at higher contents. Conversely no sign revealing the presence of the PBF structure could be detected in the profiles obtained from copolyester enriched in BF units. It seems therefore that the PBF structure is highly sensitive to copolymerization and unable to persist in the presence of small amounts of BT units.

As it is shown in Table 2, all coPBF_xT_y , except that containing 60% of BF units, were able to crystallize upon cooling from the melt with a crystallinity degree highly depending on composition. Melting temperatures and enthalpies of the crystallized material are represented against composition in Figure 6a where they can be compared with values registered for the pristine samples. Whereas differences in T_m for the first and second heating are not high, the enthalpies of the copolyesters decreased considerably after recrystallization. Larger differences were observed for copolyesters containing similar amounts of BF and BT units in which the melting enthalpy of the recrystallized material became very small or even unperceivable. Conversely the two parent homopolyesters PBT and PBF were able to recover almost completely their initial crystallinity after melting and cooling, which is indicative that copolymer heterogeneity must be responsible for the decay observed in crystallizability.

The copolyesters $\text{coPBF}_{10}\text{T}_{90}$ and $\text{coPBF}_{20}\text{T}_{80}$ were selected for the isothermal crystallization kinetics study because they were unique in crystallizing from the melt in an extent large enough as to allow following the evolution of crystallization by DSC. The study included the homopolyesters PBT and PBF for reference. The cooling and second heating traces of the four polyesters subjected to study are depicted in Figure 8a showing both the crystallization and melting peaks produced by each of them.

Noticeably two melting peaks are seen for PBT and for the two copolyesters whereas PBF was unique in displaying a single peak. As it is usually interpreted in polymer crystallization, the two peaks should arise from two crystal populations differing in size that were generated at two different crystallization stages.³⁹ The presence of the secondary peak does not affect the kinetics results since the used data were restricted to short crystallization times when only primary crystallization takes place. The popular Avrami approach was applied here for interpreting isothermal crystallization data. The increase in relative crystallinity with crystallization time measured by DSC for the four polyesters examined in this work is plotted in Figure 8b. The double logarithmic plots (see SI Figure S6) ascertained the validity of the time ranges fixed for this study and they were therefore used for determining the Avrami parameters which are collected in Table 2. The polymer morphologies generated upon crystallization were observed by polarizing optical microscopy and a representative selection of them are shown in Figure 9. Although no well-developed spherulites could be seen at any case, the three-dimensional morphology became much easier recognizable in the crystallized copolymers. According to the values found for the Avrami exponent (n), which are around 2.7–2.8, it can be inferred that isothermal crystallization could be a heterogeneously nucleated spherulitic process.

Unfortunately, the large differences in melting temperatures among homopolyesters and copolyesters prevented to fix a common crystallization temperature for the whole set under study, as it would have been desirable for a more straightforward comparison of crystallizability. A useful approximation is however to crystallize the polymers at the same undercooling degree, i.e. at the same $\Delta T = T_m - T_c$. Thus, the four selected polyesters were isothermally crystallized at 19 °C below their respective melting temperatures and the kinetic parameters obtained from such essays are listed in Table 2. Valuable conclusions drawn from these results are the following: (a) Crystallization half times increased steadily with

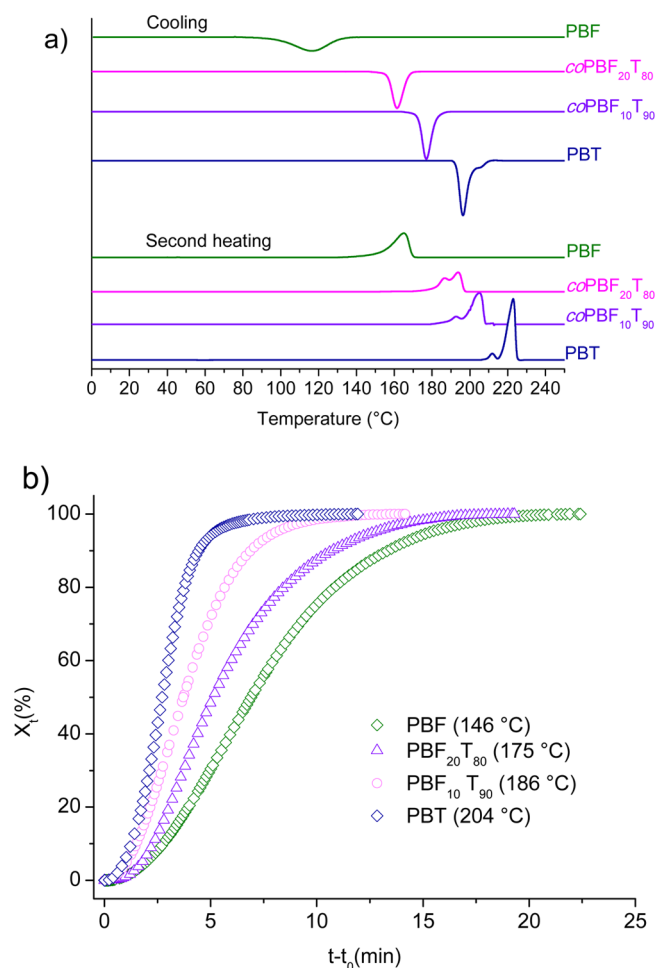


Figure 8. Cooling and second heating DSC traces (a) and evolution of the relative crystallinity as a function of time in the isothermal crystallization (b) of PBF, PBT, and the copolyesters $\text{coPBF}_{10}\text{T}_{90}$ and $\text{coPBF}_{20}\text{T}_{80}$.

the amount of furan units present in the polyester indicating that crystallizability is disfavored by the presence of these units. (b) PBF crystallized at a considerable lower rate than PBT in spite that crystallization was conducted at 60 °C lower. (c) From a practical point of view, PBF and PBT containing moderate amounts of BF units are able to crystallize from the melt at reasonable crystallization rates.

The crystallizability of a random copolymer composed of crystallizable comonomeric units is usually dictated by composition. The nucleating effect and the relative mobility of the units are the factors determining the crystallinity and the crystallization rate of the copolymer. The X-ray diffraction data recorded from coPBF_xT_y (Figure 7) reveal that the crystal structure of PBF vanished with the presence of small amounts of BT units whereas vestiges of the PBT crystalline scattering remain still detectable in the profiles recorded from copolymers containing large amounts of BF units. Since crystallization of coPBF_xT_y seems to be nucleated by exogenous species, it can be inferred that the straight linear shape of the BT sequences is more favorable to attain the chain packing than the weaving segments made of BF units. Nevertheless a more detailed study taking into account the influence of temperature on crystallization rate should be made to ascertain with higher accuracy the influence of BF units on crystallizability.

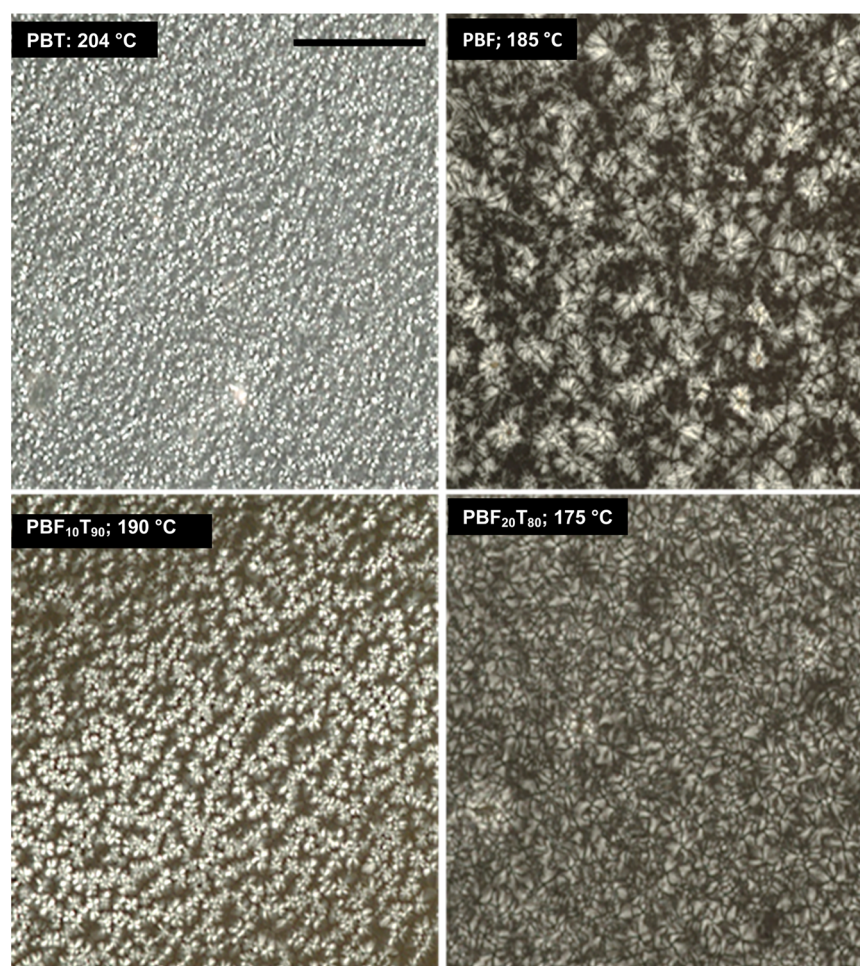


Figure 9. POM of polyesters isothermally crystallized at the indicated temperatures. The scale bar corresponds to 200 μm , and all the pictures are at the same magnification.

CONCLUSIONS

The application of the ROP technique frequently used for the preparation of sustainable aliphatic polyesters has been extended here to biobased aromatic copolyesters containing 2,5-furandicarboxylate units. Mixtures of cyclic butylene 2,5-furandicarboxylate and butylene terephthalate oligomers were able to react in the melt to produce a series of poly(butylene 2,5-furandicarboxylate-*co*-terephthalate) copolyesters with a random microstructure and weight-average molecular weights above 55 000 $\text{g}\cdot\text{mol}^{-1}$. It is remarkable that times required for polymerization of the cyclic oligoesters were considerable shorter than those needed for polycondensation of the diols and diesters mixtures provided that similar molecular weights are reached. The ensuing copolyesters displayed a good thermal stability and were semicrystalline for the almost whole range of compositions. Crystallinity was largely repressed by the presence of furanoate units in spite that the homopolymer PBF was highly crystalline. Both T_m and T_g of the copolyesters varied steadily according to the furanoate/terephthalate ratio and the values observed for these temperatures were comparable to those reported for similar copolyesters prepared by melt polycondensation by other authors. Copolyesters containing moderate amounts of furanoate units were able to crystallize from the melt by developing a nearly spherulitic texture. It was evidenced however that the replacement of the terephthalate units by the furanoate ones implied a decrease in

the crystallizability of PBT. The poly(butylene 2,5-furandicarboxylate) homopolymer is also able to crystallize from the melt but at a much lower rate than PBT, in part due the lower temperature at which it was crystallized.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.6b01302.

^1H and ^{13}C NMR spectra of cyclic BF and BT oligomers; HPLC of cyclic BF and BT oligomers; ^1H and ^{13}C NMR spectra of the whole series of coPBF_xT_y copolyesters; double logarithmic plot of isothermal crystallization data of PBT, PBF, $\text{coPBF}_{10}\text{T}_{90}$, and $\text{coPBF}_{20}\text{T}_{80}$ (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support for this research was given by MINECO with grant MAT-2012-38044-CO3-03. J.C.M.-H. thanks CONA-

CYT (Mexico) for the Ph.D. grant awarded. The authors are indebted to Abdelilah Alla for his assistance with XRD experiments and data processing.

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